

## 6: Organic Chemistry I

### 6A. Introduction to Organic Chemistry

#### Basic definitions to know

**Hydrocarbon** is a compound consisting of hydrogen and carbon **only**

**Saturated:** Contain single carbon-carbon bonds only

**Unsaturated :** Contains a C=C double bond

**Molecular formula:** The formula which shows the actual **number of each type of atom**

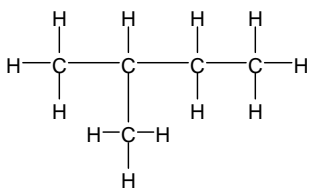
**Empirical formula:** shows the simplest whole number ratio of atoms of each element in the compound

**General formula:** algebraic formula for a homologous series e.g.  $C_nH_{2n}$

**Structural formula** shows the minimal detail that shows the arrangement of atoms in a molecule, eg for butane:  $CH_3CH_2CH_2CH_3$  or  $CH_3(CH_2)_2CH_3$ ,

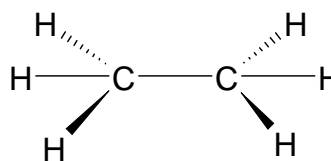
**Displayed formula:** show all the covalent bonds present in a molecule

#### Drawing Displayed formulae

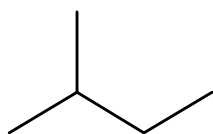


When drawing organic compounds add the hydrogen atoms so that each carbon has 4 bonds

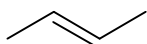
Remember that the shape around the carbon atom in saturated hydrocarbons is tetrahedral and the bond angle is  $109.5^\circ$



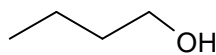
**Skeletal formula** shows the simplified organic formula, shown by removing hydrogen atoms from alkyl chains, leaving just a carbon skeleton and associated functional Groups.



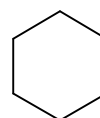
2-methylbutane



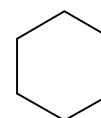
But-2-ene



Butan-1-ol



cyclohexane

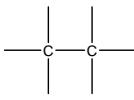
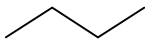

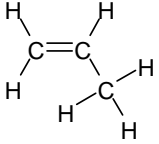
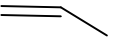
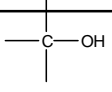
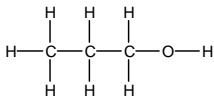
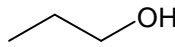
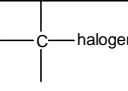
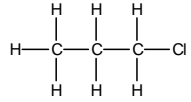
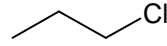

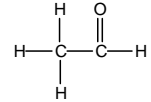
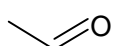

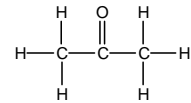
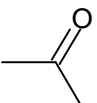
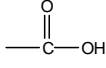
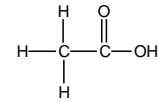
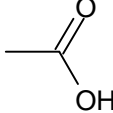
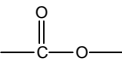
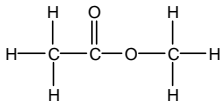
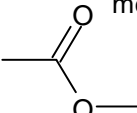


cyclohexene

**Homologous series** are families of organic compounds with the **same functional group** and **same general formula**.

- They show a gradual change in physical properties (e.g. boiling point).
- Each member differs by  $\text{CH}_2$  from the last.
- same chemical properties.

**Functional group** is an atom or group of atoms which when present in different molecules causes them to have similar chemical properties

homologous series	functional group	prefix / suffix (* = usual use)	example
Alkane		-ane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$  Butane
Alkenes		suffix <b>-ene</b>	  propene
Alcohols		suffix* <b>-ol</b> prefix <b>hydroxy-</b>	 Propan-1-ol 
Halogenoalkanes		prefix <b>chloro-</b> <b>bromo-</b> <b>iodo-</b>	 1-chloropropane 
Aldehydes		suffix <b>-al</b> prefix <b>formyl-</b>	  ethanal
Ketones		suffix* <b>-one</b> prefix <b>oxo-</b>	 Propanone 
carboxylic acids		suffix <b>-oic acid</b>	 Ethanoic acid 
Esters		-yl -oate	 methylethanoate 

When compounds contain more than one functional group, the order of precedence determines which groups are named with prefix or suffix forms. The highest precedence group takes the suffix (and the lowest number on the carbon chain), with all others taking the prefix form. However, double and triple C-C bonds only take suffix form.

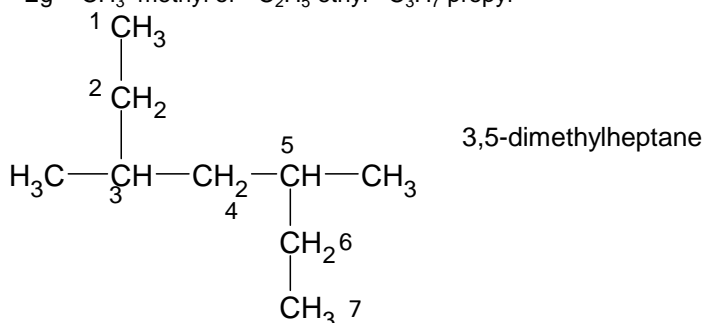
**Order of priority highest first:**

Carboxylic acids > aldehydes > ketones > alcohols > alkenes > halogenoalkanes

### General rules for naming carbon chains

- Count the longest carbon chain and name appropriately
- Find any branched chains and count how many carbons they contain
- Add the appropriate prefix for each branch chain

Eg -CH<sub>3</sub> methyl or -C<sub>2</sub>H<sub>5</sub> ethyl -C<sub>3</sub>H<sub>7</sub> propyl



code	no of carbons
meth	1
eth	2
prop	3
but	4
pent	5
hex	6
hept	7
oct	8
non	9
dec	10

### Basic rules for naming functional groups

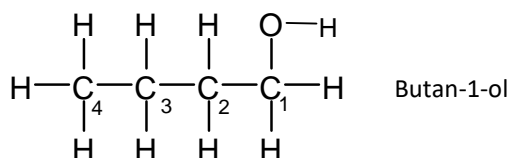
The functional group is named by a prefix or suffix. e.g. **bromoethane**, **ethanol**, **propene**

- When using a suffix, add in the following way :

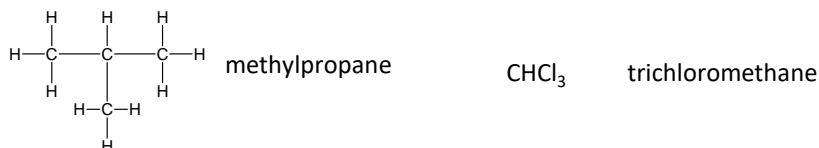
If the suffix starts with a vowel- remove the -e from the stem alkane name  
e.g. Propan-1-ol, butan-1-amine, ethanoic acid, ethanoylchloride, butanamide

If the suffix starts with a consonant or there are two or more of a functional group meaning di, or tri needs to be used then **do not remove the -e** from the stem alkane name  
e.g. Propanenitrile, ethane-1,2-diol, propanedioic acid, propane-1,2,3-triol, Pentane-2,4-dione.

- The position of the functional group on the carbon chain is given by a number – counting from the end of the molecule that gives the functional group the lowest number. For aldehydes, carboxylic acids & nitriles, the functional group is always on carbon 1.



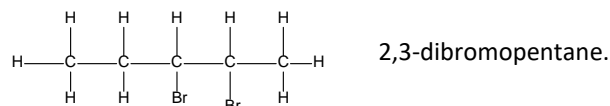
- We only include numbers, however, if they are needed to avoid ambiguity.



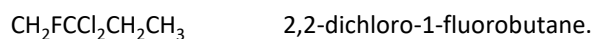
- The functional groups take precedence over branched chains in giving the lowest number

3-methylbut-1-ene is correct and not 2-methylbut-3-ene

- Where there are two or more of the same groups, **di-**, **tri-**, **tetra-**, **penta-** or **hexa-** are used. Note the point made above about the addition of 'e' to the stem



- Words are separated by numbers with dashes



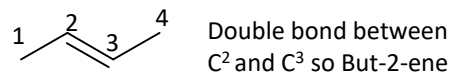
- numbers are separated by commas



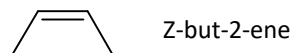
- If there is more than one functional group or side chain, the groups are listed in alphabetical order (ignoring any *di*, *tri*).

## Alkenes

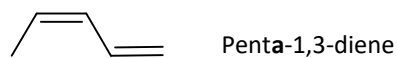
The double bond will be between two carbons. Use the lower number of the two to show the position of the double bond



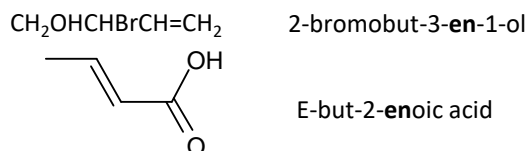
The name for alkenes may include E or Z at start to show the type of stereoisomer



If more than one double bond is present then suffix ends **diene** or **triene**. The stem ends in **a**

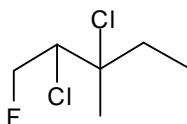
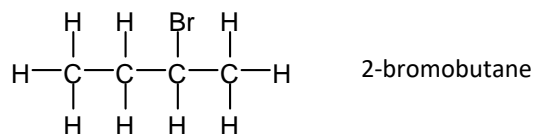


The suffix **-en** for alkenes can go in front of other suffixes. The alcohol and carboxylic acid groups have higher priority than the alkene group so take precedence with numbering

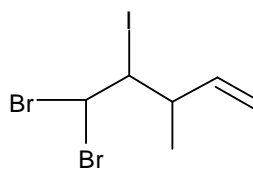


## Halogenoalkanes

Class the halogen as a substituent on the C chain and use the suffix **-fluoro**, **-chloro**, **-bromo**, or **-iodo**. (Give the position number if necessary)



2,3-dichloro-1-fluoro-3-methylhexane



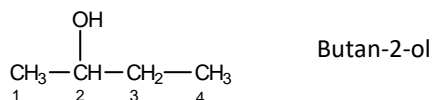
5,5-dibromo-4-iodo-3-methylpent-1-ene

Multiple functional group and side chains are listed in alphabetical order (ignoring any *di*, *tri*).

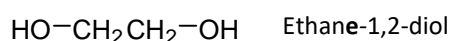
The alkene group has higher priority than the halogenoalkane group so it takes the lowest number on the carbon chain

## Alcohols

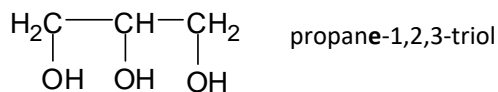
These have the ending **-ol** and if necessary the position number for the OH group is added between the name stem and the **-ol**



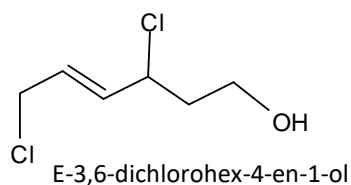
If there are two or more -OH groups then *di*, *tri* are used.



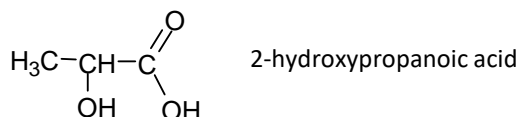
Add the **'e'** on to the stem name though.



The OH group has a higher priority than the halogenoalkane group and alkene so takes precedence in numbering. The OH is on carbon 1



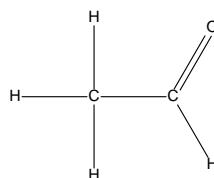
If the compound has an -OH group in addition to another functional group with a higher priority. The priority group gets the suffix ending and the OH can be named with the prefix **hydroxy-**:



### Aldehydes

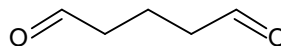
An aldehyde's name ends in **-al**

It always has the C=O bond on the first carbon of the chain so it does not need an extra number. It is by default number one on the chain.



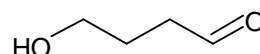
Ethanal

If two aldehyde groups then **di** is put before **-al** and an **e** is added to the stem.



pentanedial

Aldehydes have a higher priority than alcohol so the **-OH** group uses the hydroxy prefix.



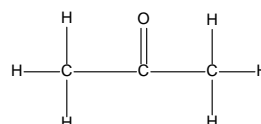
4-hydroxybutanal

### Ketones

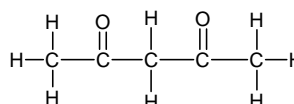
Ketones end in **-one**

When ketones have 5C's or more in a chain then it needs a number to show the position of the double bond. E.g. pentan-2-one

If two ketone groups then **di** is put before **-one** and an **e** is added to the stem.



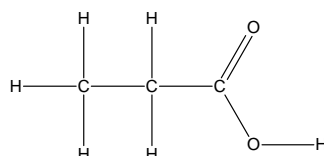
Propanone



Pentane-2,4-dione

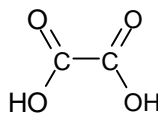
### Carboxylic acids

These have the ending **-oic acid** but no number is necessary for the acid group as it must always be at the end of the chain. The numbering always starts from the carboxylic acid end.



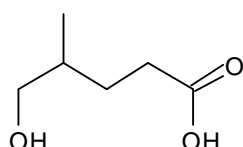
Propanoic acid

If there are carboxylic acid groups on both ends of the chain then it is called a -dioic acid



Ethanedioic acid

Note the **e** in this name



5-hydroxy-4-methylpentanoic acid

## Isomers

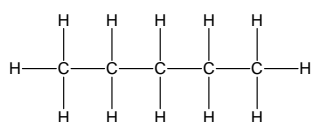
**Structural isomers:** same molecular formula different structures (or structural formulae)

Structural isomerism can arise from

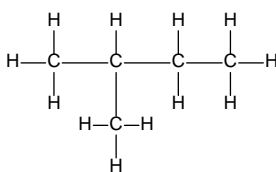
- Chain isomerism
- Position isomerism
- Functional group isomerism

EDEXCEL does not split structural isomers into the different categories. They are all classed as structural isomers.

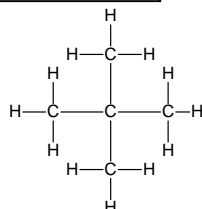
**Chain isomers:** Compounds with the same molecular formula but different structures of the carbon skeleton



pentane

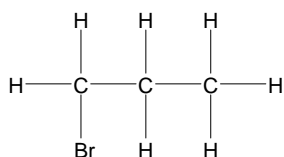


2-methylbutane

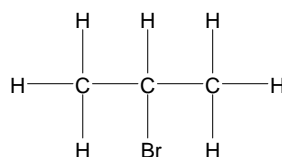


2,2-dimethylpropane

**Position isomers:** Compounds with the same molecular formula but different structures due to different positions of the same functional group on the same carbon skeleton

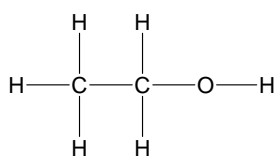


1-bromopropane

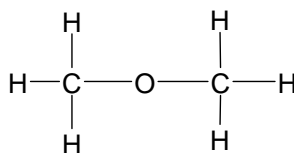


2-bromopropane

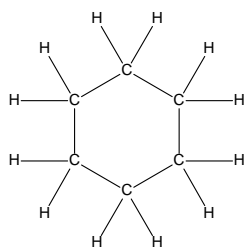
**Functional group isomers:** Compounds with the same molecular formula but with atoms arranged to give different functional groups



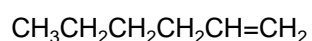
ethanol: an alcohol



Methoxymethane: an ether



Cyclohexane- cyclo alkane



hexene- alkene

Note: alkene and cyclo alkanes have the same general formula. Hexene and cyclohexane have the same molecular formula but have a different functional group

## Stereoisomerism

Stereoisomers have the same structural formulae but have a different spatial arrangement of atoms.

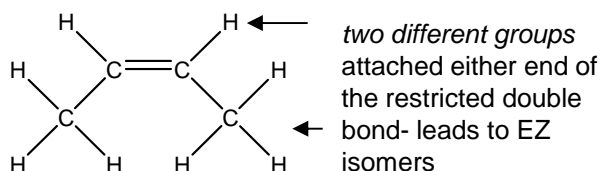
Alkenes can exhibit a type of isomerism called **E-Z stereoisomerism**

E-Z isomers exist due to restricted rotation about the C=C bond

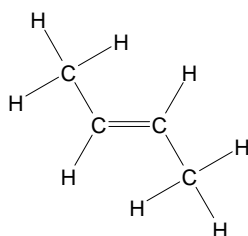
E-Z stereoisomers arise when:

- There is **restricted rotation** around the C=C double bond.
- There are **two different groups/atoms** attached both ends of the double bond

Single carbon-carbon covalent bonds can easily rotate

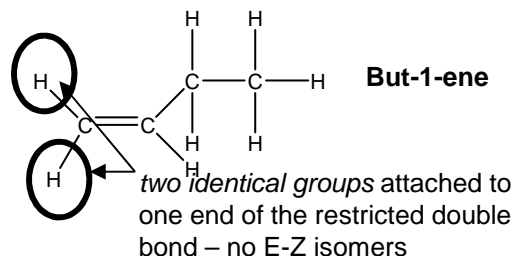


**Z-but-2-ene**



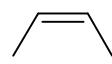
**E-but-2-ene**

These are two isomers as the lack of rotation around the double bonds means one cannot be switched to the other

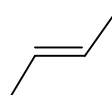


But-1-ene is a structural isomer of But-2-ene but does not show E-Z isomerism

Skeletal formulae can also represent E-Z isomerism



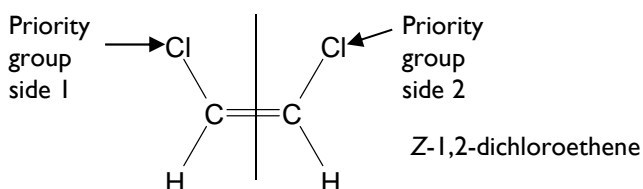
Z-but-2-ene



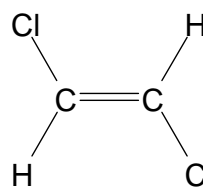
E-but-2-ene

### Naming E-Z stereoisomers

First determine the priority groups on both sides of the double bond



If the priority atom is on the same side of the double bond it is labelled Z from the german zusammen (The Zame Zide!)

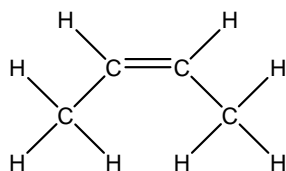


E-1,2-dichloroethene

**Priority Group:** The atom with the bigger atomic number is classed as the priority atom

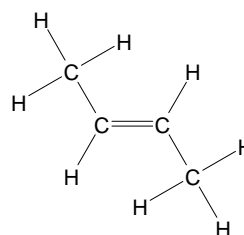
If the priority atom is on the opposite side of the double bond it is labelled E from the german entgegen (The Epposite side!)

*cis-trans isomerism* is a special case of *EIZ* isomerism in which two of the substituent groups are the same.



**Z-but-2-ene**

Can also be called  
**Cis-but-2-ene**



**E-but-2-ene**

Can also be called  
**trans-but-2-ene**

## 6A Alkanes

Alkanes are saturated hydrocarbons

**General formula** alkane  $C_nH_{2n+2}$

**Saturated:** Contain single carbon-carbon bonds only

**Hydrocarbon** is a compound consisting of hydrogen and carbon **only**

### Fuels from crude oil

They are obtained from the crude oil in the order of fractional distillation, cracking and reformation of crude oil

Alkanes are used as fuels

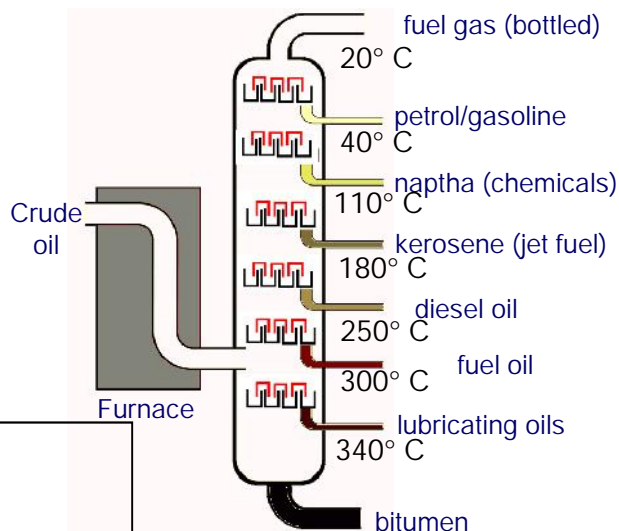
### Refining crude oil

#### Fractional Distillation:

Petroleum is a mixture consisting mainly of alkane hydrocarbons

**Petroleum fraction:** mixture of hydrocarbons with a similar chain length and boiling point range

- Oil is pre-heated
- then passed into column.
- The fractions condense at different heights
- The temperature of column decreases upwards
- The separation depends on boiling point.
- Boiling point depends on size of molecules.
- The larger the molecule the larger the London forces
- Similar molecules (size, bp, mass) condense together
- Small molecules condense at the top at lower temperatures
- and big molecules condense at the bottom at higher temperatures.



This is a physical process involving the splitting of weak London forces between molecules

### Cracking

**Cracking:** conversion of large hydrocarbons to smaller molecules by breakage of C-C bonds

High Mr alkanes  $\rightarrow$  smaller Mr alkanes + alkenes + (hydrogen)

#### Economic reasons for catalytic cracking

- The petroleum fractions with shorter C chains (e.g. petrol and naphtha) are in **more demand** than larger fractions.
- To make use of excess larger hydrocarbons and to supply demand for shorter ones, longer hydrocarbons are cracked.
- The products of cracking are **more useful and valuable** than the starting materials (e.g. ethene used to make poly(ethene) and ethane-1,2-diol, and ethanol) The smaller alkanes are used for motor fuels which burn more efficiently.

This is a chemical process involving the splitting of strong covalent bonds so requires high temperatures.

### Reforming

**Turns straight chain alkanes into branched and cyclic alkanes and Aromatic hydrocarbons**

Branched and cyclic hydrocarbons burn more cleanly and are used to give fuels a higher octane number.

Used for making motor fuels



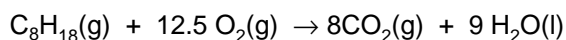
## Alkanes as Fuels

**Fuel** : releases heat energy when burnt

### Complete Combustion

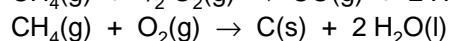
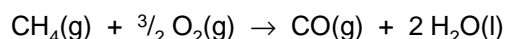
In excess oxygen alkanes will burn with complete combustion

The products of *complete* combustion are CO<sub>2</sub> and H<sub>2</sub>O.



### Incomplete Combustion

If there is a **limited amount of oxygen** then *incomplete* combustion occurs, producing CO (which is very toxic) and/or C (producing a sooty flame)



**Alkanes** readily burn in the presence of oxygen. This combustion of alkanes is highly exothermic, explaining their use as **fuels**.

Incomplete combustion produces less energy per mole than complete combustion.

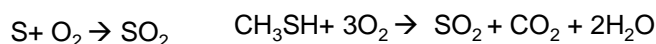
Carbon (soot)/particulates can cause global dimming- reflection of the sun's light

Carbon monoxide is an highly toxic but odourless gas. It can cause death if it builds up in a enclosed space due to faulty heating appliances.

CO is toxic to humans as CO can form a strong bond with haemoglobin in red blood cells. This is a stronger bond than that made with oxygen and so it prevents the oxygen attaching to the haemoglobin.

## Pollution from Combustion

Sulfur containing impurities are found in petroleum fractions which produce SO<sub>2</sub> when they are burned.



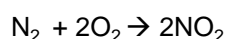
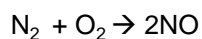
Coal is high in sulfur content, and large amounts of sulfur oxides are emitted from power stations.

SO<sub>2</sub> is acidic and will dissolve in atmospheric water and can produce **acid rain**.

## Nitrogen Oxides NO<sub>x</sub>

Nitrogen oxides form from the reaction between N<sub>2</sub> and O<sub>2</sub> inside the car engine.

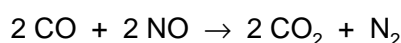
The **high temperature** and **spark** in the engine provides sufficient energy to break strong N<sub>2</sub> bond



Pollutant	Environmental consequence
Nitrogen oxides (formed when N <sub>2</sub> in the air reacts at the <b>high temperatures and spark</b> in the engine)	NO is toxic and can form smog NO <sub>2</sub> is toxic and acidic and forms acid rain
Carbon monoxide	toxic
Carbon dioxide	Contributes towards global warming
Unburnt hydrocarbons (not all fuel burns in the engine)	Contributes towards formation of smog
Soot/particulates	Global dimming and respiratory problems

## Catalytic converters

These remove CO, NO<sub>x</sub> and unburned hydrocarbons (e.g. octane, C<sub>8</sub>H<sub>18</sub>) from the exhaust gases, turning them into 'harmless' CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>O.



Converters have a ceramic honeycomb coated with a thin layer of catalyst metals **platinum, palladium, rhodium** – to give a large surface area.

## Biofuels

Most fossil fuels come from crude oil, which is a non-renewable resource. Fossil fuel reserves will eventually run out

Alternative fuels have been developed from renewable resources. Alcohols and biodiesel, which can both be made from plants, are two examples of renewable plant-based fuels

Alcohols such as ethanol can be produced from the fermentation of sugars from plants.

Biodiesel is produced by reacting vegetable oils with a mixture of alkali and methanol

### **Advantages of using Biofuels**

Reduction of use of fossil fuels which are finite resources  
biofuels are renewable

Use of biodiesel is more carbon-neutral

Allows fossil fuels to be used as a feedstock for organic compounds

No risk of large scale pollution from exploitation of fossil fuels

### **Disadvantages of Biofuels**

Less food crops may be grown

Land not used to grow food crops

Rain forests have to be cut down to provide land

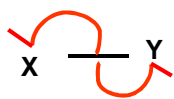
Shortage of fertile soils

## Introduction to Mechanisms

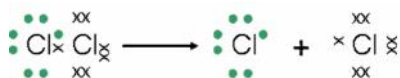
To understand how the reaction proceeds we must first understand how bonds are broken in organic mechanisms  
There are two ways to break a covalent bond:

### 1. HOMOLYTIC FISSION:

*each atom gets one electron from the covalent bond*



one headed arrow shows movement of one electron



The bond has broken in a process called **homolytic** fission.

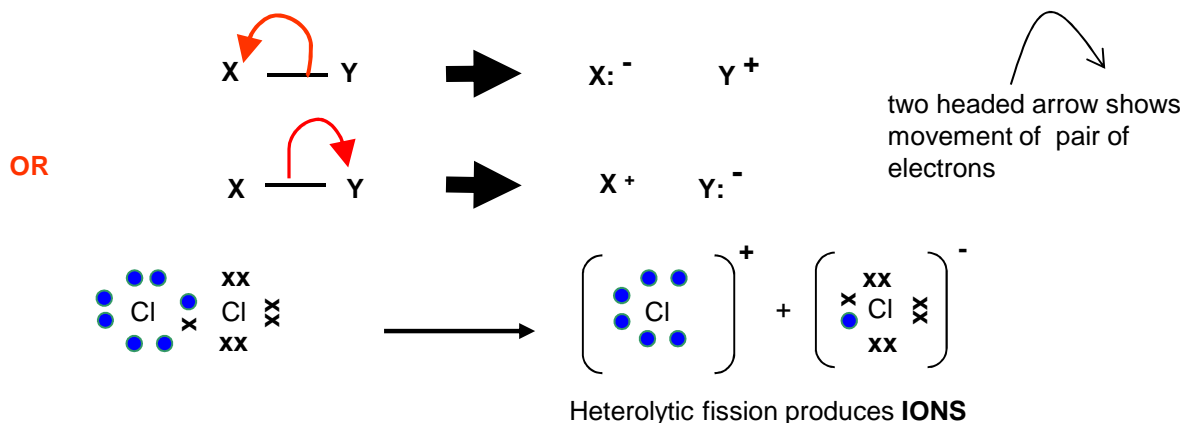
When a bond breaks by homolytic fission it forms two **Free Radicals**.

**Free Radicals** do not have a charge and are represented by a  $\cdot$

#### DEFINITION

A **Free Radical** is a reactive species which possess an **unpaired electron**

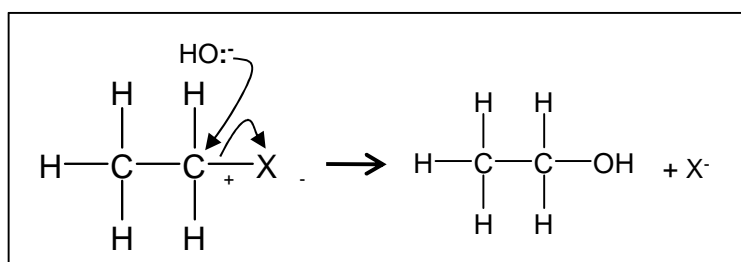
### 2. HETEROLYTIC FISSION: (*one atom gets both electrons*)



Most organic reactions occur via heterolytic fission, producing ions

### The Mechanism:

To understand a reaction fully we must look in detail at how it proceeds step by step. This is called its **mechanism**



The carbon has a small positive charge because of the electronegativity difference between the carbon and the halogen

We use curly arrows in mechanisms to show the movement of an electron pair showing either breaking or formation of a covalent bond;

A curly arrow will always **start** from a **lone pair** of electrons or the **centre of a bond**

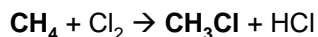
## Free Radical Substitution Reactions of Alkanes

### Reaction of alkanes with bromine / chlorine in UV light

In the presence of **UV light** alkanes react with chlorine to form a mixture of products with the halogens substituting hydrogen atoms.

In general, alkanes do not react with many reagents. This is because the C-C bond and the C-H bond are relatively strong.

#### Overall Reaction



methane      chloromethane

*This is the overall reaction, but a more complex mixture of products is actually formed*

The **mechanism** for this reaction is called a **free radical substitution**

It proceeds via a series of steps:

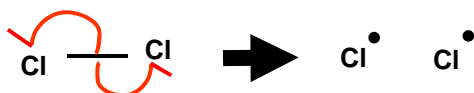
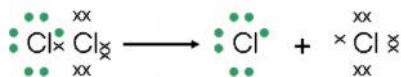
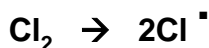
Step one: **Initiation**

Step two: **Propagation**

Step three: **Termination**

#### Step one Initiation

Essential condition: UV light



The UV light supplies the energy to break the Cl-Cl bond. It is broken in preference to the others as it is the weakest.

UV light does not have enough energy to break the C-H bond

The bond has broken in a process called **homolytic fission**.

*each atom gets **one** electron from the covalent bond*

When a bond breaks by homolytic fission it forms **Free Radicals**.

**Free Radicals** do not have a charge and are represented by a  $\cdot$

#### DEFINITION

A **Free Radical** is a reactive species which possess an **unpaired electron**

#### Step two Propagation



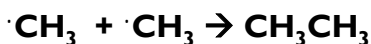
The chlorine free radicals are very reactive and remove an H from the methane leaving a methyl free radical

The methyl free radical reacts with a  $\text{Cl}_2$  molecule to produce the main product and another Cl free radical

All propagation steps have a **free radical** in the **reactants** and in the **products**.

As the Cl free radical is regenerated, it can react with several more alkane molecules in a **chain reaction**

#### Step three Termination



Collision of two free radicals *does not generate* further free radicals: the chain is **terminated**.

Minor step leading to impurities of ethane in product. **Write this step using structural formulae** and don't use molecular formulae

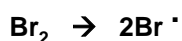
### Applying the mechanism to other alkanes

Example: Write mechanism of Br<sub>2</sub> and Propane

The same mechanism is used: Learn the patterns in the mechanism

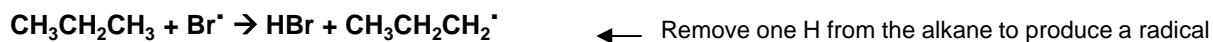
#### STEP ONE Initiation

Essential condition: UV light

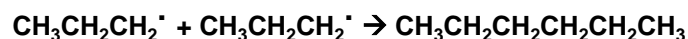


Br<sub>2</sub> splits in the same way as Cl<sub>2</sub>

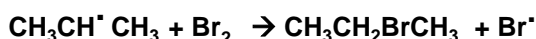
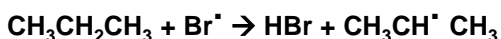
#### STEP TWO Propagation



#### STEP THREE Termination



### Propagation steps for substituting a halogen on a 'middle' carbon

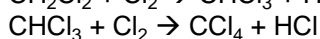
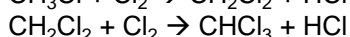
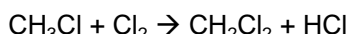


If the question asks for the halogen to be substituted onto a middle carbon in the chain, it is important to put the free radical 'dot' on the correct carbon in the propagation stages.

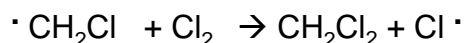
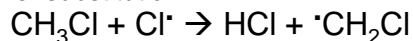
### Further substitution

Excess Cl<sub>2</sub> present will promote further substitution and could produce **CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> and CCl<sub>4</sub>**

These reactions could occur



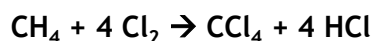
Example propagation steps that would lead to further substitution



### Overall reaction equations

You should be able to write overall reaction equations for various reactions

Example 1. Write the overall reaction equation for the formation of CCl<sub>4</sub> from CH<sub>4</sub> + Cl<sub>2</sub>



Example 2. Write the overall reaction equation for the formation of CFCI<sub>3</sub> from CH<sub>3</sub>F + Cl<sub>2</sub>



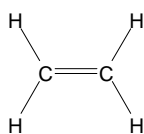
Note HCl is always the side product – never H<sub>2</sub>

## 6C Alkenes

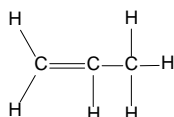
Alkenes are unsaturated hydrocarbons

General formula is  $C_nH_{2n}$

Alkenes contain a carbon-carbon double bond somewhere in their structure

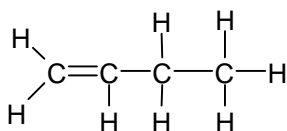


**Ethene**

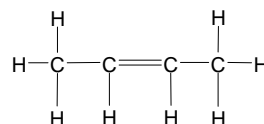


**Propene**

Numbers need to be added to the name when positional isomers can occur

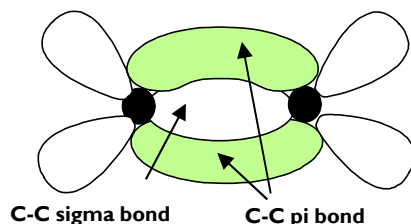


**But-1-ene**



**But-2-ene**

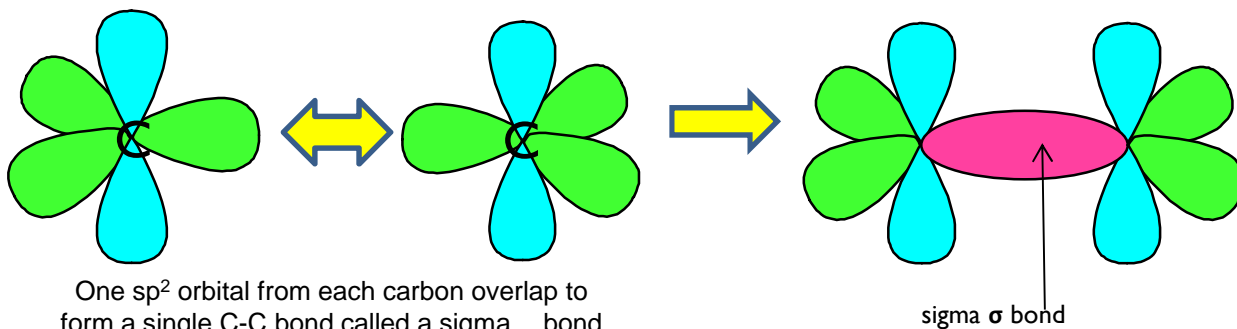
$C=C$  double covalent bond consists of **one sigma (  $\sigma$  ) bond and one pi (  $\pi$  ) bond.**



bonds are **exposed** and have **high electron density**.

They are therefore vulnerable to attack by species which 'like' electrons: these species are called **electrophiles**.

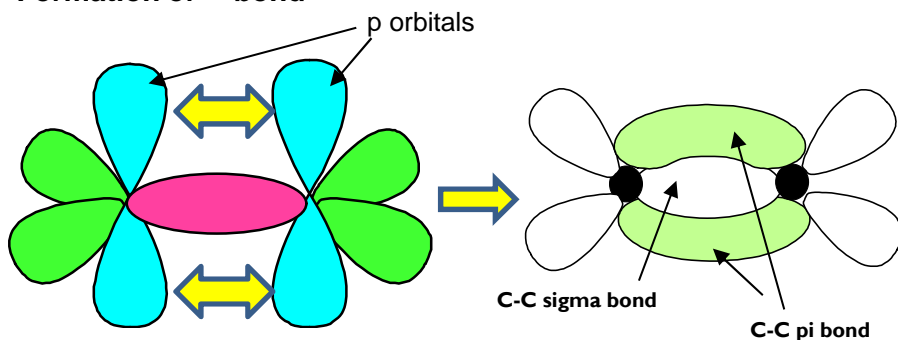
### Formation of $\sigma$ bond



One  $sp^2$  orbital from each carbon overlap to form a single C-C bond called a sigma bond

Rotation can occur around a sigma bond

### Formation of $\pi$ bond



**The  $\pi$  bond** is formed by sideways overlap of two p orbitals on each carbon atom forming a  $\pi$ -bond above and below the plane of molecule.

The  $\pi$  bond is weaker than the  $\sigma$  bond.

There is Restricted rotation about a pi bond

The pi bond leads to resultant high electron density above and below the line between the two nuclei

## Addition Reactions of Alkenes

Addition reaction: a reaction where two molecules react together to produce one

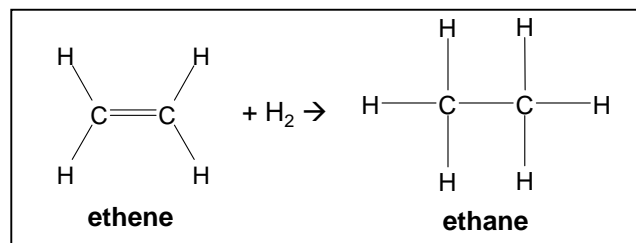
### 1. Reaction of Alkenes with Hydrogen

**Change in functional group:** alkene → alkane

**Reagent:** hydrogen

**Conditions:** Nickel Catalyst

**Type of reaction:** Addition/Reduction



### Electrophilic Addition: Reactions of Alkenes

A  $\pi$  bond is weaker than a  $\sigma$  bond so less energy is needed to break  $\pi$  bond  
The  $\pi$  bonds in alkenes are areas with high electron density. This is more accessible to electrophilic attack by electrophiles. Alkenes undergo addition reactions.

**Definition Electrophile:** an electron pair acceptor

### 2. Reaction of Alkenes with bromine/chlorine

**Change in functional group:**

alkene → dihalogenoalkane

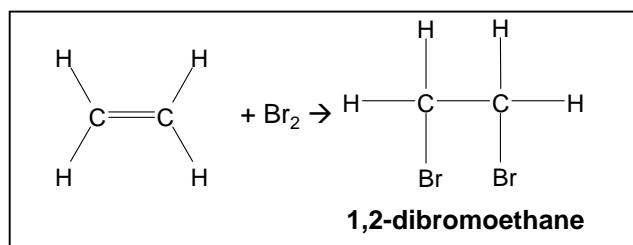
**Reagent:** Bromine (dissolved in organic solvent)

**Conditions:** Room temperature (not in UV light)

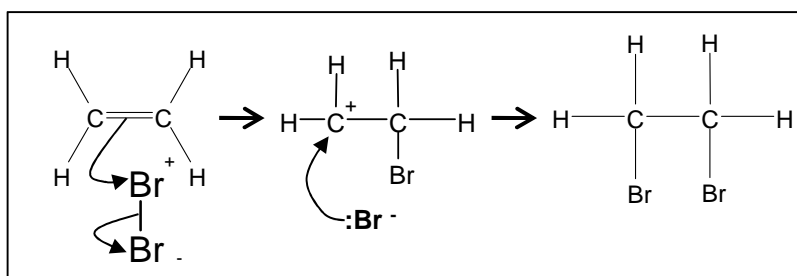
**Mechanism:** Electrophilic Addition

**Type of reagent:** Electrophile, Br $\delta^+$

**Type of Bond Fission:** Heterolytic



As the Br<sub>2</sub> molecule approaches the alkene, the pi bond electrons repel the electron pair in the Br-Br bond. This **INDUCES** a **DIPOLE**. Br<sub>2</sub> becomes **polar** and **ELECTROPHILIC** (Br $\delta^+$ ).



The **INTERMEDIATE** formed, which has a positive charge on a carbon atom is called a **CARBICATION**

### 3. Reaction of Hydrogen Bromide with alkenes

**Change in functional group:**

alkene → halogenoalkane

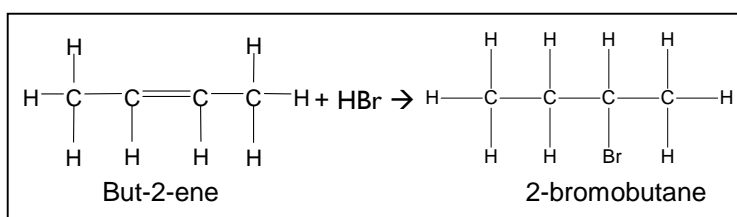
**Reagent:** HCl or HBr

**Conditions:** Room temperature

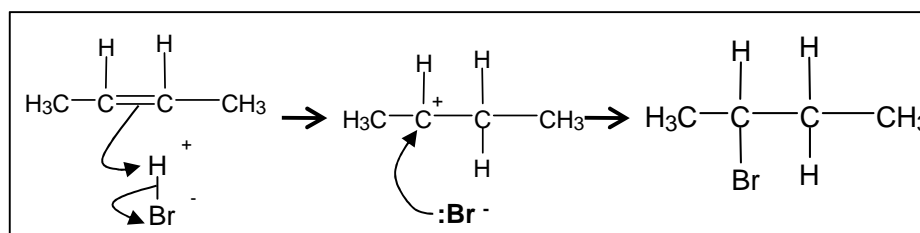
**Mechanism:** Electrophilic Addition

**Type of reagent:** Electrophile, H $\delta^+$

**Type of Bond Fission:** Heterolytic

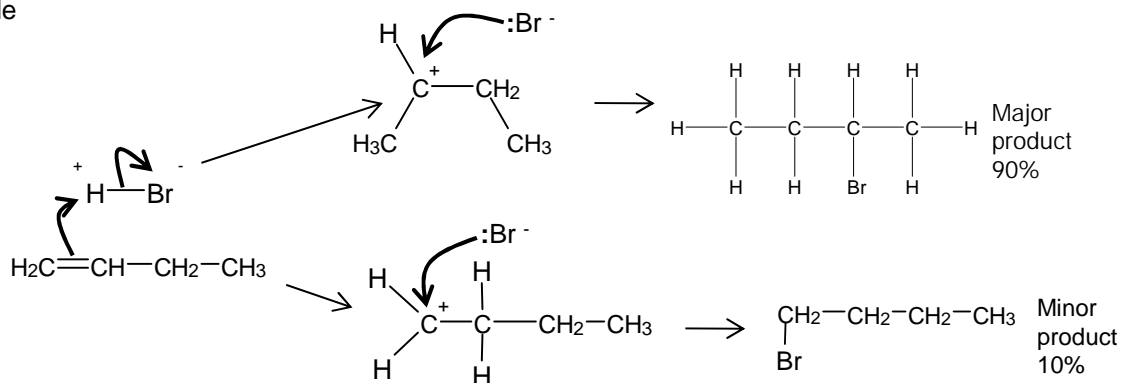


HBr is a polar molecule because Br is more electronegative than H. The H $\delta^+$  is attracted to the electron-rich pi bond.



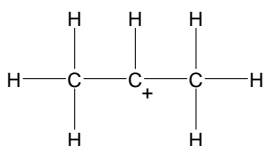
If the alkene is unsymmetrical, addition of hydrogen bromide can lead to two isomeric products.

But-1-ene will form a mixture of 1-bromobutane and 2-bromobutane on reaction with hydrogen bromide



#### WHY?

This carbocation intermediate is more stable because the methyl groups on either side of the positive carbon are electron releasing and reduce the charge on the ion which stabilises it.



The order of stability for carbocations is tertiary > secondary > primary

In **electrophilic addition** to alkenes, the **major product** is formed **via the more stable carbocation** intermediate.

In exam answers

- Draw out both carbocations and identify as primary, secondary and tertiary
- State which is the more stable carbocation e.g. secondary more stable than primary
- State that the more stable carbocation is stabilised because the methyl groups on either (or one) side of the positive carbon are electron releasing and reduce the charge on the ion.
- (If both carbocations are secondary then both will be equally stable and a 50/50 split will be achieved)

#### 4. Reaction of Potassium Manganate(VII) with Alkenes

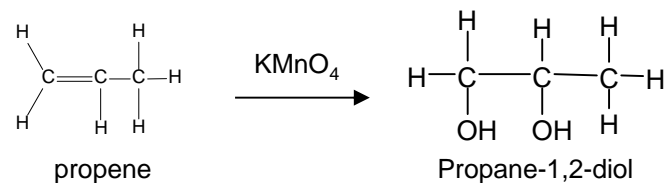
**Change in functional group:** alkene → diol

**Reagent:**  $\text{KMnO}_4$  in an acidified solution

**Conditions:** Room temperature

**Type of reaction:** Oxidation

**Observation:** purple colour of  $\text{MnO}_4^-$  ion will decolourise to colourless



This reaction with its colour change can be used as a test for the alkene functional group. It would not change colour with alkanes

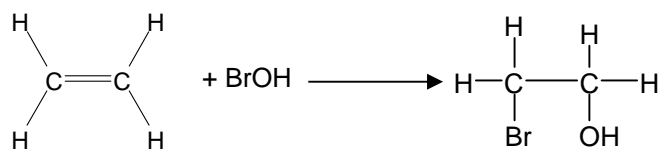
#### 5. Reaction of Bromine Water with Alkenes

**Reagent:** Bromine dissolved in water

**Conditions:** Room temperature

**Type of reaction:** Addition

**Observation:** Orange colour of bromine water will decolourise to colourless



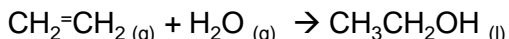
This reaction with its colour change is used as a test for the alkene functional group.



## Hydration of alkenes to form alcohols

Industrially alkenes are converted to alcohols in one step rather than the two in the above sulfuric acid reaction. They are reacted with water in the presence of an acid catalyst.

This reaction can be called **hydration**: a reaction where water is **added** to a molecule



### Essential Conditions

High temperature 300 to 600°C

High pressure 70 atm

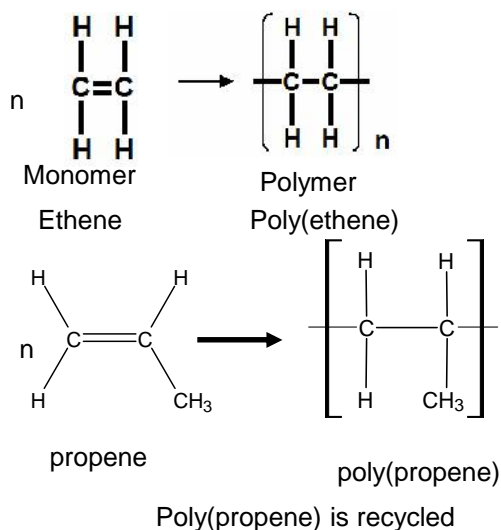
Catalyst of **concentrated H<sub>3</sub>PO<sub>4</sub>**

The high pressures needed mean this cannot be done in the laboratory. It is preferred industrially, however, as there are no waste products and so has a high atom economy. It would also mean separation of products is easier (and cheaper) to carry out. See equilibrium chapter for more on the industrial conditions for this reaction.

## Addition Polymers

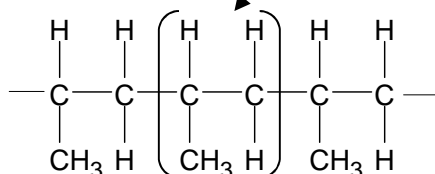
Addition polymers are formed from alkenes

This is called **addition polymerisation**



Poly(alkenes) like alkanes are unreactive due to the strong C-C and C-H bonds.

be able to recognise the repeating unit in a poly(alkene)

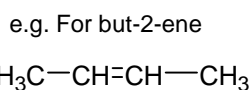


← Add the **n**'s if writing an equation showing the reaction where 'n' monomers become 'n' repeating units

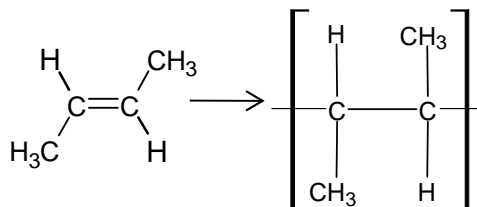
Poly(ethene): is used to make plastics bags, buckets, bottles. It is a flexible, easily moulded, waterproof, chemical proof, and low density plastic.

Poly(propene) is a stiffer polymer, used in utensils and containers and fibres in rope and carpets.

You should be able to draw the polymer repeating unit for any alkene



It is best to first draw out the monomer with groups of atoms arranged around the double bond



## Methods of disposal of waste Polymers

### Incineration

Rubbish is burnt and energy produced is used to generate electricity.

Some toxins can be released on incineration. (e.g. Combustion of halogenated plastics (ie PVC) can lead to the formation of toxic, acidic waste products such as HCl.) Modern incinerators can burn more efficiently and most toxins and pollutants can be removed. Greenhouse gases will still be emitted though.

Volume of rubbish is greatly reduced.

### Recycling

Saves raw materials- nearly all polymers are formed from compounds sourced/produced from crude oil. Saves precious resources.

Polymers need collecting/ sorting- expensive process in terms of energy and manpower.

Polymers can only be recycled into the same type – so careful separation needs to be done.

Thermoplastic polymers can be melted down and reshaped.

### feedstock for cracking

Polymers can be cracked into small molecules which can be used to make other chemicals and new polymers- Saves raw materials-

Chemists have designed ways to remove toxic waste products like HCl before they are emitted into the atmosphere. The waste gases from the incinerator are scrubbed/reacted with a base or carbonate. The base reacts with the acidic HCl gas, neutralising it (eg  $\text{CaO} + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O}$ )

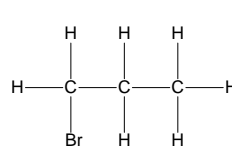
Chemists have also develop biodegradable and compostable polymers. Biodegradable polymers can be made from substances such as maize and starch

## 6D Halogenoalkanes

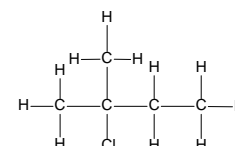
### Naming Halogenoalkanes

Based on original alkane, with a *prefix* indicating halogen atom:  
**Fluoro** for F; **Chloro** for Cl; **Bromo** for Br; **Iodo** for I.

Substituents are listed **alphabetically**



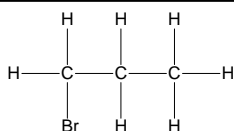
1-bromopropane



2-chloro-2-methylbutane

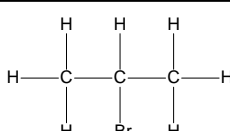
### Classifying Halogenoalkanes

Halogenoalkanes can be classified as primary, secondary or tertiary depending on the number of carbon atoms attached to the C-X functional group.



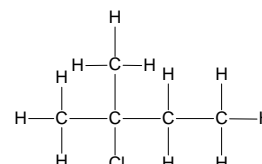
#### Primary halogenoalkane

One carbon attached to the carbon atom adjoining the halogen



#### Secondary halogenoalkane

Two carbons attached to the carbon atom adjoining the halogen



#### Tertiary halogenoalkane

Three carbons attached to the carbon atom adjoining the halogen

### Reactions of Halogenoalkanes

Halogenoalkanes undergo either **substitution** or **elimination** reactions

#### Nucleophilic substitution reactions

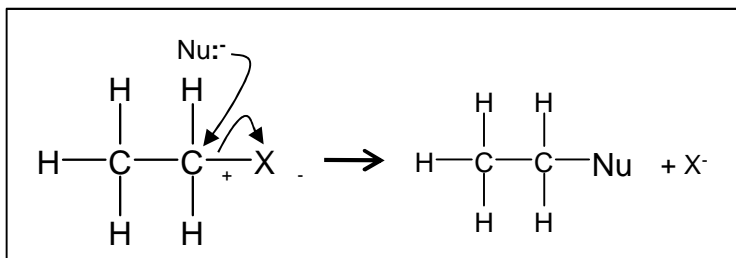
Substitution: swapping a halogen atom for another atom or groups of atoms

Nucleophile: electron pair donator e.g.  $\text{:OH}^-$ ,  $\text{:NH}_3$ ,  $\text{CN}^-$

**The Mechanism:** We draw (or **outline**) mechanisms to show in detail how a reaction proceeds

$\text{:Nu}$  represents any nucleophile – they always have a **lone pair** and act as **electron pair donors**

The nucleophiles attack the positive carbon atom



The carbon has a small positive charge because of the electronegativity difference between the carbon and the halogen



We use curly arrows in mechanisms (with two line heads) to show the movement of two electrons

A curly arrow will always **start** from a **lone pair** of electrons or the **centre of a bond**

**The rate of these substitution reactions depends on the strength of the C-X bond**

The weaker the bond, the easier it is to break and the faster the reaction.

The iodoalkanes are the fastest to substitute and the fluoroalkanes are the slowest. The strength of the C-F bond is such that fluoroalkanes are very unreactive

	Bond enthalpy / $\text{kJmol}^{-1}$
C-I	238
C-Br	276
C-Cl	338
C-F	484

## Comparing the rate of hydrolysis reactions

**Hydrolysis** is defined as the splitting of a molecule ( in this case a halogenoalkane) by a reaction with water



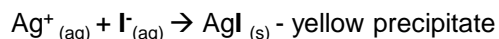
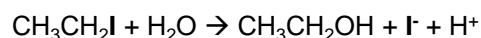
**Aqueous silver nitrate** is added to a halogenoalkane and the halide leaving group combines with a silver ion to form a **silver halide precipitate**.

The precipitate only forms when the halide ion has left the halogenoalkane and so the rate of formation of the precipitate can be used to compare the reactivity of the different halogenoalkanes.

The **quicker** the **precipitate** is formed, the **faster** the **substitution** reaction and the **more reactive** the haloalkane

The rate of these substitution reactions depends on the strength of the C-X bond . The weaker the bond, the easier it is to break and the faster the reaction.

**Water** is a **poor nucleophile** but it can react **slowly** with halogenoalkanes in a substitution reaction



The iodoalkane forms a precipitate with the silver nitrate first as the C-I bond is weakest and so it hydrolyses the quickest

$\text{AgI}_{(\text{s})}$  - yellow precipitate  
 $\text{AgBr}_{(\text{s})}$  - cream precipitate  
 $\text{AgCl}_{(\text{s})}$  - white precipitate

↑ forms faster

## Nucleophilic substitution with aqueous hydroxide ions

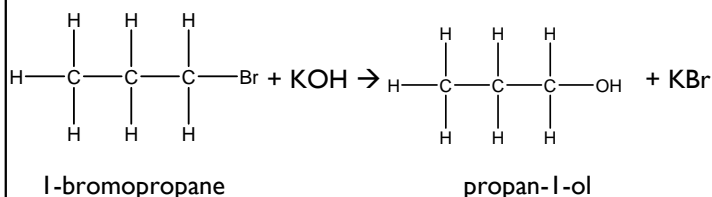
**Change in functional group:** halogenoalkane → alcohol

**Reagent:** potassium (or sodium) hydroxide

**Conditions:** In aqueous solution; Heat under reflux

**Mechanism:** Nucleophilic Substitution

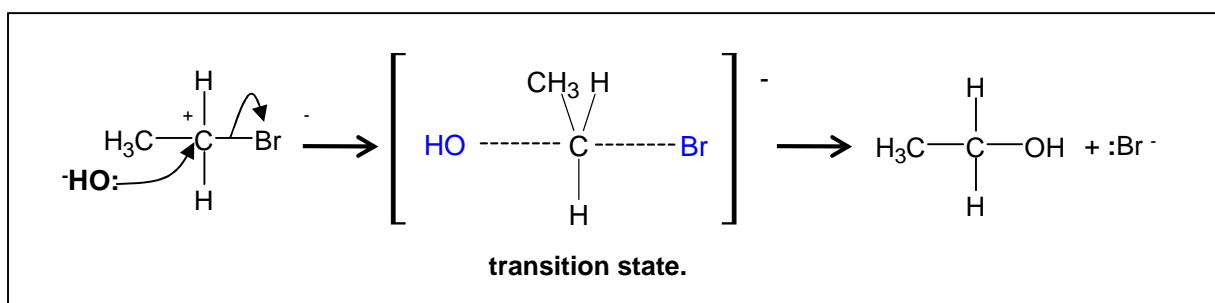
**Role of reagent:** Nucleophile,  $\text{OH}^-$



The  $\text{OH}^-$  is a stronger nucleophile than water as it has a full negative charge and so is more strongly attracted to the  $\text{C}^+$

The **aqueous** conditions needed is an important point. If the solvent is changed to **ethanol** an elimination reaction occurs

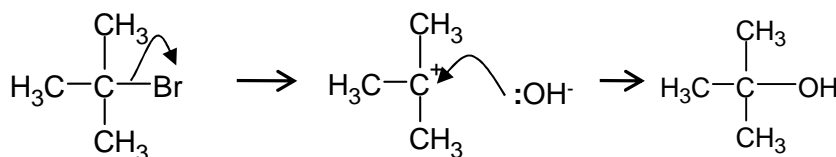
## $\text{S}_{\text{N}}2$ nucleophilic substitution mechanism for halogenoalkanes



This mechanism occurs with primary halogenoalkanes

## SN<sub>1</sub> nucleophilic substitution mechanism for tertiary halogenoalkanes

Tertiary haloalkanes undergo nucleophilic substitution in a different way



The Br first breaks away from the halogenoalkane to form a carbocation intermediate

The hydroxide nucleophile then attacks the positive carbon

Tertiary halogenoalkanes undergo this mechanism as the tertiary carbocation is stabilised by the electron releasing methyl groups around it. (see alkenes topic for another example of this). Also the bulky methyl groups prevent the hydroxide ion from attacking the halogenoalkane in the same way as the mechanism above

Primary halogenoalkanes do not do the SN<sub>1</sub> mechanism because they would only form an unstable primary carbocation.

## Nucleophilic substitution with ammonia

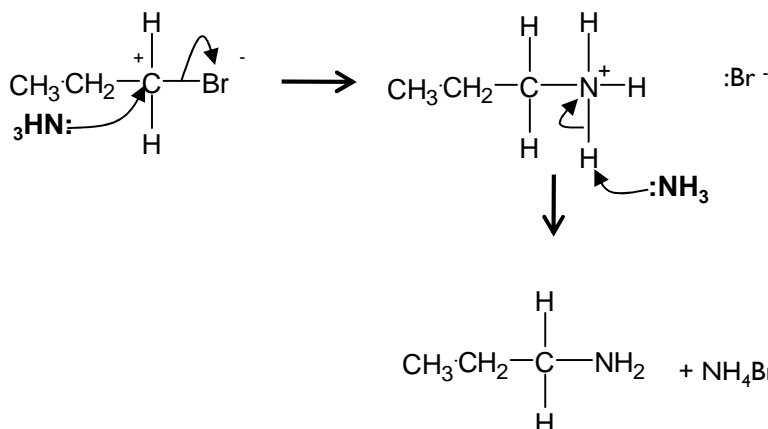
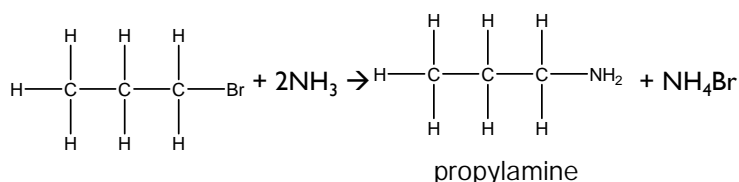
**Change in functional group:** halogenoalkane → amine

**Reagent:** NH<sub>3</sub> dissolved in ethanol

**Conditions:** Heating under pressure in a sealed tube

**Mechanism:** Nucleophilic Substitution

**Type of reagent:** Nucleophile, :NH<sub>3</sub>



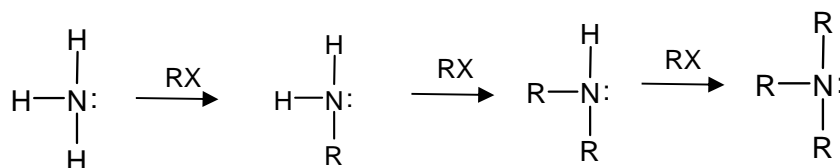
Naming amines:

In the above example propylamine, the propyl shows the 3 C's of the carbon chain.

Sometimes it is easier to use the IUPAC naming for amines e.g. Propan-1-amine

Further substitution reactions can occur between the halogenoalkane and the amines formed leading to a lower yield of the amine. Using excess ammonia helps minimise this.

Further reactions



## Elimination reaction of halogenoalkanes

Elimination: removal of small molecule (often water) from the organic molecule

### Elimination with alcoholic hydroxide ions

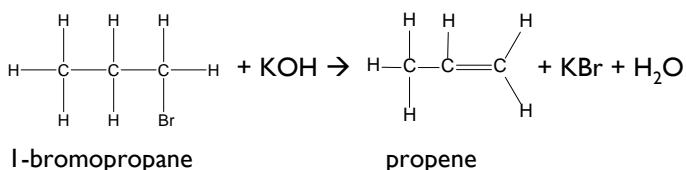
**Change in functional group:** halogenoalkane → alkene

**Reagents:** Potassium (or sodium) hydroxide

**Conditions:** In *ethanol*; Heat

**Mechanism:** Elimination

**Role of reagent:** Base, OH<sup>-</sup>



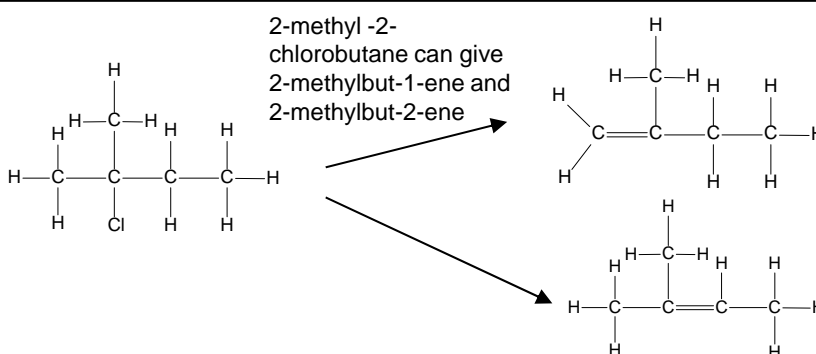
Note the importance of the solvent to the type of reaction here.

**Aqueous: substitution**

**Alcoholic: elimination**

Often a mixture of products from both elimination and substitution occurs

With unsymmetrical secondary and tertiary halogenoalkanes two (or sometimes three) different structural isomers can be formed



The structure of the halogenoalkane also has an effect on the degree to which substitution or elimination occurs in this reaction.

Primary tends towards substitution

Tertiary tends towards elimination

## Uses of halogenoalkanes

Halogenoalkanes have been used as **refrigerants**, **fire retardants**, pesticides and **aerosol propellants**.

Chloroalkanes and chlorofluoroalkanes can be used as solvents.

CH<sub>2</sub>Cl<sub>2</sub> was used as the solvent in dry cleaning

Some halogenoalkanes have low flammability.

Many of these uses have now been stopped due to the toxicity of halogenoalkanes and also their detrimental effect on the ozone layer.

## 6E Alcohols

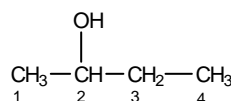
General formula alcohols  $C_nH_{2n+1}OH$

### Naming Alcohols

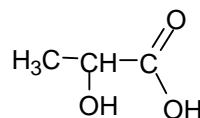
These have the ending **-ol** and if necessary the position number for the OH group is added between the name stem and the **-ol**

If the compound has an **-OH** group in addition to other functional groups that need a suffix ending then the OH can be named with the prefix **hydroxy-**:

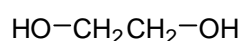
If there are two or more **-OH** groups then di, tri are used. Add the 'e' on to the stem name though



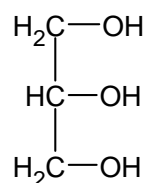
Butan-2-ol



2-hydroxypropanoic acid



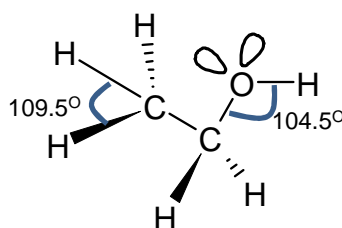
Ethane-1,2-diol



propane-1,2,3-triol

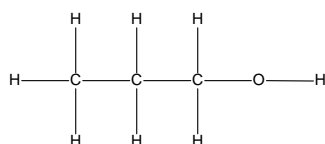
### Bond angles in Alcohols

All the H-C-H bonds and C-C-O are  $109.5^\circ$  (tetrahedral shape), because there are 4 bond pairs of electrons repelling to a position of minimum repulsion.



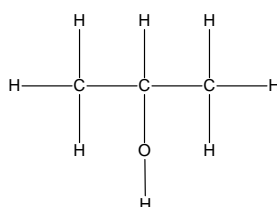
The H-O-C bond is  $104.5^\circ$  (bent line shape), because there are 2 bond pairs of electrons and 2 lone pairs repelling to a position of minimum repulsion. Lone pairs repel more than bond pairs so the bond angle is reduced.

### Different types of alcohols



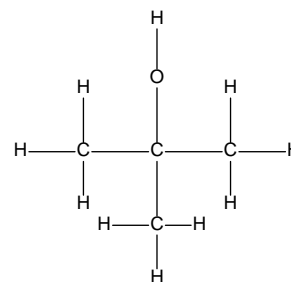
Propan-1-ol  
Primary

Primary alcohols are alcohols where 1 carbon is attached to the carbon adjoining the oxygen



Propan-2-ol  
Secondary

Secondary alcohols are alcohols where 2 carbon are attached to the carbon adjoining the oxygen

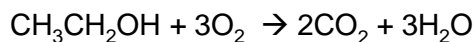


methylpropan-2-ol  
Tertiary

Tertiary alcohols are alcohols where 3 carbon are attached to the carbon adjoining the oxygen

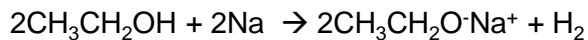
## 1. Combustion of Alcohols

Alcohols combust with a clean flame



## 2. Reaction of Alcohols with Sodium

Sodium reacts with alcohols



This reaction can be used as a test for alcohols

### Observations:

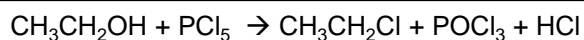
- effervescence,
- the mixture gets hot,
- sodium dissolves,
- a white solid is produced.

## 3. Substitution reactions of Alcohols to form Halogenoalkanes

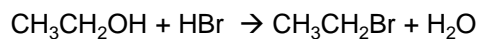
Various halogenating compounds can be used to substitute the -OH group for a halogen

$\text{PCl}_5$  /  $\text{PCl}_3$  / conc HCl /  $\text{SOCl}_2$  / mixture of NaCl +  $\text{H}_2\text{SO}_4$  can all be used for substituting a Cl

### Reaction with phosphorous (V) halide

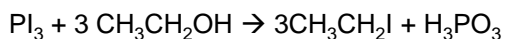


This reaction with  $\text{PCl}_5$  (phosphorous(V)chloride) can be used as a test for alcohols. You would observe misty fumes of HCl produced.



For Br use KBr, 50% concentrated  $\text{H}_2\text{SO}_4$  to produce HBr

### Reaction with phosphorous (III) iodide



The **phosphorous (III) iodide** is produced in situ by reacting red phosphorus and iodine.

The reaction of KI and conc  $\text{H}_2\text{SO}_4$  can't be used to produce HI because the sulfuric acid will oxidise the hydrogen halides to other products.

## 4. Oxidation reactions of the alcohols

Potassium dichromate  $\text{K}_2\text{Cr}_2\text{O}_7$  is an oxidising agent that causes alcohols to oxidise.

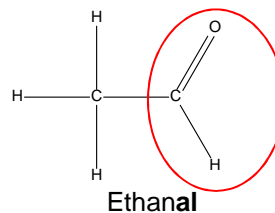
The exact reaction, however, depends on the type of alcohol, i.e. whether it is primary, secondary, or tertiary, and on the conditions.

### Partial Oxidation of Primary Alcohols

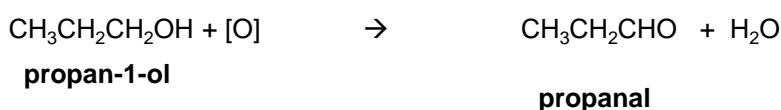
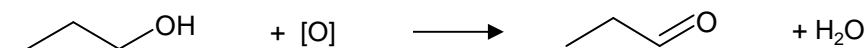
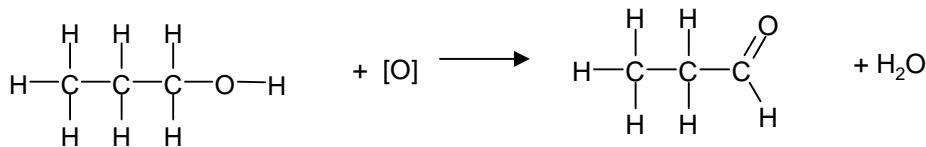
**Reaction:** primary alcohol  $\rightarrow$  aldehyde

**Reagent:** potassium dichromate (VI) solution and dilute sulfuric acid.

**Conditions:** (use a limited amount of dichromate) warm gently and **distil** out the aldehyde as it forms:



An aldehyde's name ends in **-al**  
It always has the C=O bond on the first carbon of the chain so it does not need an extra number



Observation: the orange dichromate ion ( $\text{Cr}_2\text{O}_7^{2-}$ ) reduces to the green  $\text{Cr}^{3+}$  ion

Write the oxidation equations in a simplified form using [O] which represents O from the oxidising agent

When writing the formulae of aldehydes in a condensed way write **CHO** and not COH e.g.  $\text{CH}_3\text{CH}_2\text{CHO}$

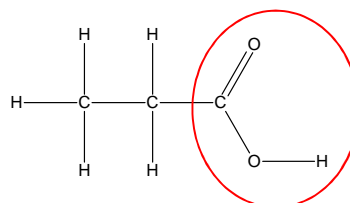


## Full Oxidation of Primary Alcohols

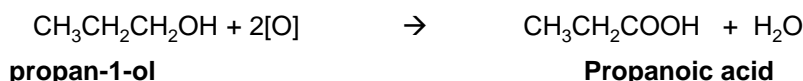
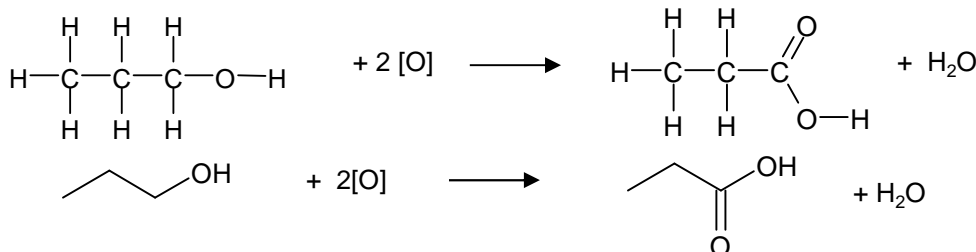
**Reaction:** primary alcohol → carboxylic acid

**Reagent:** potassium dichromate(VI) solution and dilute sulfuric acid

**Conditions:** use an excess of dichromate, and **heat under reflux**: (distil off product after the reaction has finished)



Propanoic acid



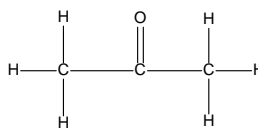
Observation: the orange dichromate ion ( $\text{Cr}_2\text{O}_7^{2-}$ ) reduces to the green  $\text{Cr}^{3+}$  ion

## Oxidation of Secondary Alcohols

**Reaction:** secondary alcohol → ketone

**Reagent:** potassium dichromate(VI) solution and dilute sulfuric acid.

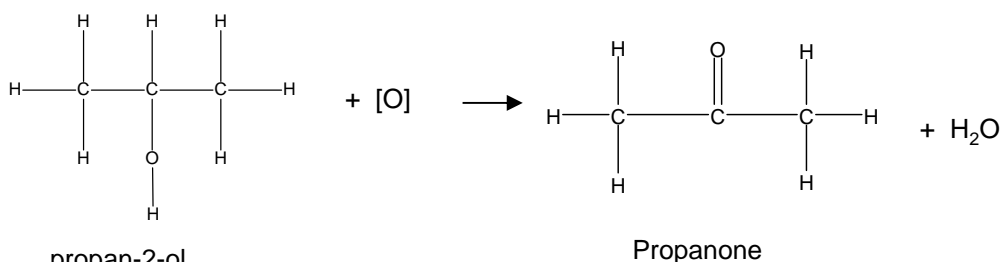
**Conditions:** heat under reflux



Propanone

Ketones end in **-one**

When ketones have 5C's or more in a chain then it needs a number to show the position of the double bond. E.g. pentan-2-one



propan-2-ol

Propanone

Observation: the orange dichromate ion ( $\text{Cr}_2\text{O}_7^{2-}$ ) reduces to the green  $\text{Cr}^{3+}$  ion

There is no further oxidation of the ketone under these conditions.

**Tertiary alcohols** cannot be oxidised at all by potassium dichromate: This is because there is no hydrogen atom bonded to the carbon with the OH group

## Distinguishing between Aldehydes and Ketones

The fact that aldehydes can be further oxidised to carboxylic acids whereas ketones cannot be further oxidised is the chemical basis for tests that are commonly used to distinguish between aldehydes and ketones

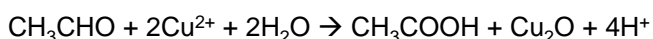
### Fehling's (Benedict's) solution

**Reagent:** Fehling's solution containing blue  $\text{Cu}^{2+}$  ions.

**Conditions:** heat gently

**Reaction:** **aldehydes only** are oxidised by Fehling's solution into a carboxylic acid and the copper (II) ions are reduced to copper(I) oxide

**Observation:** **Aldehydes** :Blue  $\text{Cu}^{2+}$  ions in solution change to a red precipitate of  $\text{Cu}_2\text{O}$ . **Ketones do not react**



The presence of a carboxylic acid can be tested by addition of sodium carbonate. It will fizz and produce carbon dioxide

## Reaction of Alcohols with Dehydrating Agents

**Reaction:** Alcohol  $\rightarrow$  Alkene

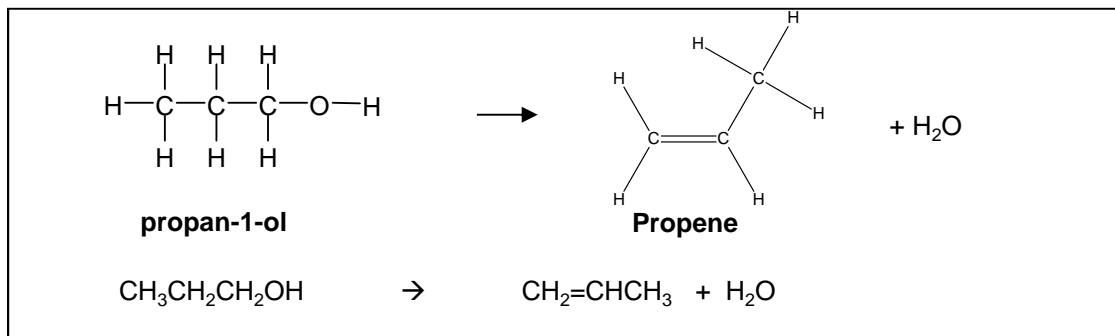
**Reagents:** Concentrated phosphoric acid

**Conditions:** warm (under reflux)

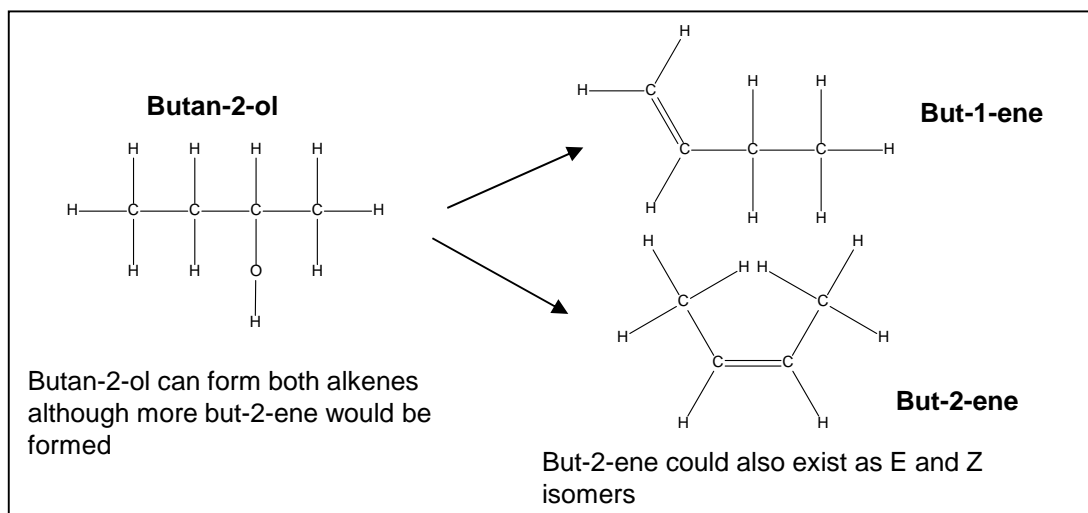
**Role of reagent:** dehydrating agent/catalyst

**Type of reaction:** acid catalysed elimination

Dehydration Reaction: removal of a water molecule from a molecule



Some 2° and 3° alcohols can give more than one product, when the double bond forms between different carbon atoms



Producing alkenes from alcohols provides a possible route to polymers without using monomers derived from oil

## Organic techniques

### Distillation

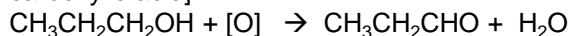
In general used as separation technique to separate an organic product from its reacting mixture. Need to collect the distillate of the approximate boiling point range of the desired liquid.

#### Classic AS reaction using distillation

**Reaction:** primary alcohol  $\rightarrow$  aldehyde

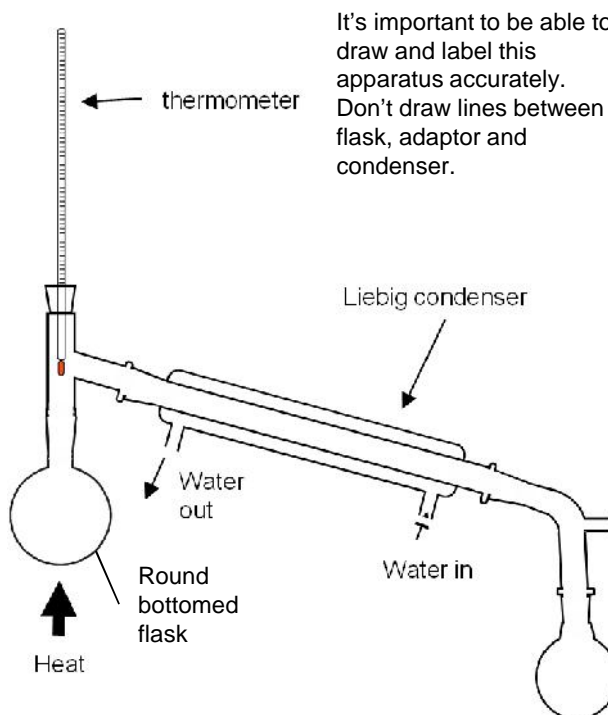
**Reagent:** potassium dichromate (VI) solution and dilute sulfuric acid.

**Conditions:** use a limited amount of dichromate and **warm gently and distil** out the aldehyde as it forms [This prevents further oxidation to the carboxylic acid]



#### Observation

Orange dichromate solution changes to green colour of  $\text{Cr}^{3+}$  ions



It's important to be able to draw and label this apparatus accurately. Don't draw lines between flask, adaptor and condenser.

### Reflux

Reflux is used when heating organic reaction mixtures for long periods. The condenser prevents organic vapours from escaping by condensing them back to liquids.

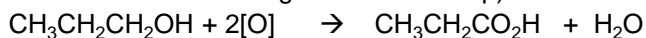
**Never seal the end of the condenser** as the build up of gas pressure could cause the apparatus to explode. This is true of any apparatus where volatile liquids are heated

#### Classic AS reaction using reflux

**Reaction:** primary alcohol  $\rightarrow$  carboxylic acid

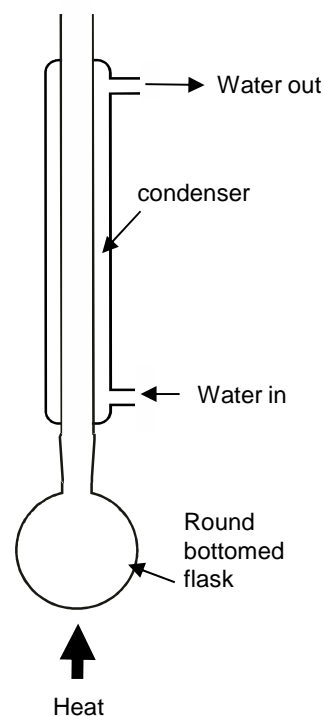
**Reagent:** potassium dichromate(VI) solution and dilute sulfuric acid

**Conditions:** use an excess of dichromate, and **heat under reflux:** (distil off product after the reaction has finished using distillation set up)



#### Observation

Orange dichromate solution changes to green colour of  $\text{Cr}^{3+}$  ions



Anti-bumping granules are added to the flask in both distillation and reflux to prevent vigorous, uneven boiling by **making small bubbles** form instead of large bubbles

It's important to be able to draw and label this apparatus accurately.

- Don't draw lines between flask and condenser.
- Don't have top of condenser sealed
- Condenser must have outer tube for water that is sealed at top and bottom
- Condenser must have two openings for water in and out that are open

Electric heaters are often used to heat organic chemicals. This is because organic chemicals are normally highly flammable and could set on fire with a naked flame.

## Purifying an organic liquid

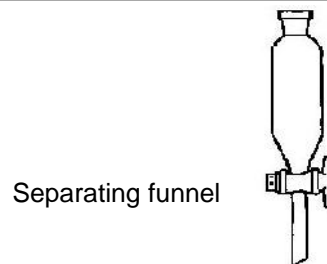
- Put the distillate of impure product into a separating funnel
- wash product by adding either
  - sodium hydrogencarbonate solution, shaking and releasing the pressure from CO<sub>2</sub> produced.
  - Saturated sodium chloride solution
- Allow the layers to separate in the funnel, and then run and discard the aqueous layer.
- Run the organic layer into a clean, dry conical flask and add three spatula loads of drying agent (anhydrous sodium sulfate) to dry the organic liquid.
- Carefully decant the liquid into the distillation flask
- Distil to collect pure product

Sodium hydrogencarbonate will neutralise any remaining reactant acid.

Sodium chloride will help separate the organic layer from the aqueous layer

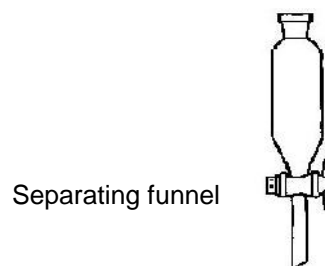
The drying agent should

- be insoluble in the organic liquid
- not react with the organic liquid



## Solvent extraction

Mix organic solvent and oil-water mixture in a separating funnel then separate the oil layer.  
Distil to separate oil from organic solvent  
Add anhydrous CaCl<sub>2</sub> to clove oil to dry oil  
Decant to remove CaCl<sub>2</sub>



## Measuring boiling point

Purity of liquid can be determined by measuring a boiling point. This can be done in a distillation set up or by simply boiling a tube of the sample in an heating oil bath.

Pressure should be noted as changing pressure can change the boiling point of a liquid

Measuring boiling point is not the most accurate method of identifying a substance as several substances may have the same boiling point.

To get a correct measure of boiling point the thermometer should be above the level of the surface of the boiling liquid and be measuring the temperature of the saturated vapour.