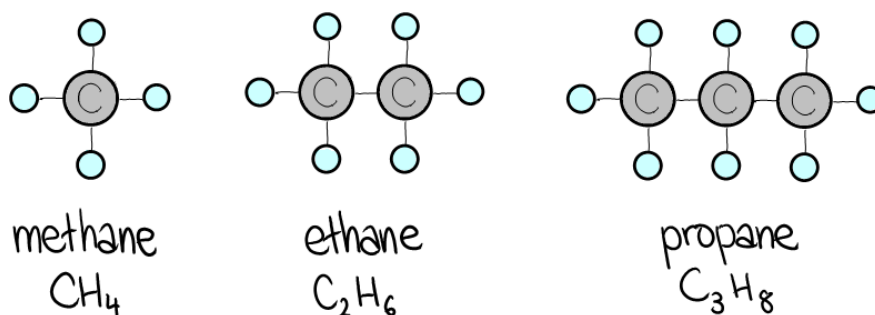


## 10.1 – Introduction to Organic Chemistry

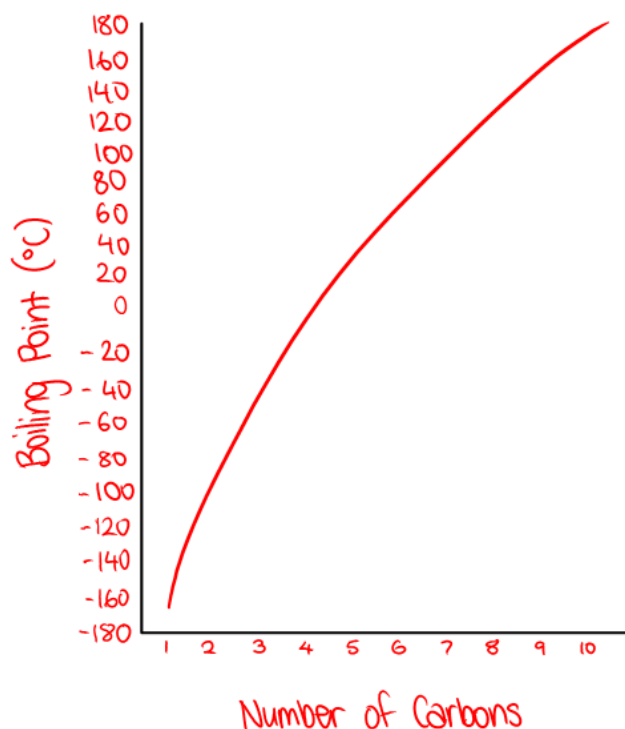
### 10.1.1 - Describe the features of a homologous series

Compounds of carbon that are in a homologous series have **common characteristics**. One of these is that they are all hydrocarbons, meaning that they are made up of carbon and hydrogen atoms only. They also have the same general formula, differing from each other by only a  $\text{CH}_2$  group. They will also demonstrate gradation in physical properties as more carbons are added, and similar chemical properties.



### 10.1.2 - Predict and explain the trends in boiling point of members of a homologous series

In a homologous series, the boiling point of members gradually **increases** as more carbon atoms are added, as do many other physical properties. This is because, as the molecule gets longer, the strength of the intermolecular forces also changes as there are increasing Van der Waals' forces between the molecules.

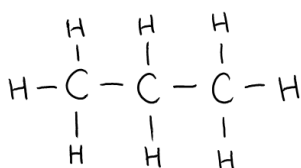


### 10.1.3 - Distinguish between empirical, molecular and structural formulas

The **molecular formula** of a compound tells us how many atoms of each element there are in the compound, while giving no information about the shape and arrangement of the compound.

i.e.  $C_3H_8$

The **structural formula** shows how the atoms are bonded and the shape of the molecule. This is more useful for visualising the molecule



The **empirical formula** is the lowest whole-number ratio of the atoms of each element in a compound. This also does little to help us with determining the structure and bonding of the molecule.

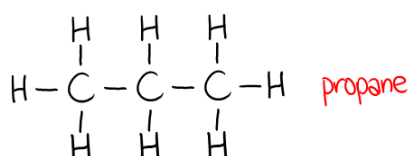
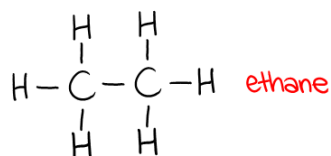
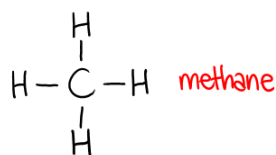
### 10.1.4 - Describe structural isomers as compounds with the same molecular formula but different arrangements of atoms

For different molecules, there are a variety of possible arrangements. Any molecule with the same molecular formula but different structural formula is called a **structural isomer**

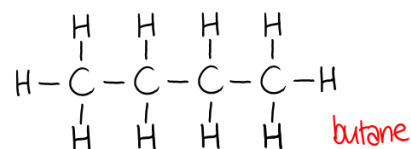
When these molecules become larger and more complex, the condensed structural formulas are drawn, with the carbon and its attached hydrogen atoms written together (i.e.  $CH_2$ )



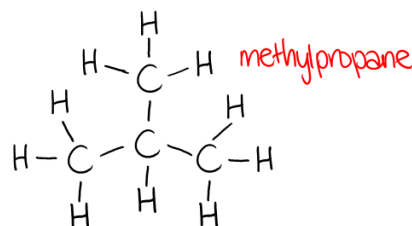
### 10.1.5 - Deduce structural formulas for the isomers of the non-cyclic alkanes up to C<sub>6</sub>



**Structural formulae** give an idea of the arrangement of the atoms in the molecule. Although it is not the most accurate representation, it is useful for the naming of compounds and identification of physical properties.



Butane is the first alkane that can have isomers: butane or methylpropane.



### 10.1.6 - Apply IUPAC rules for naming the isomers of the non-cyclic alkanes up to C<sub>6</sub>

The larger molecules become, the more isomers they can form. Each isomer has different physical and chemical properties, and it is for this reason that they must be named differently. Many compounds are still known by their common names, which were used before the IUPAC system was introduced. For example, methylbutane is often called isobutane.

The method of naming alkanes is through identifying them as straight-chain alkanes with side groups attached. These side groups are named using the **organic prefixes**, then adding the suffix '-yl.' Hence, CH<sub>3</sub>- is a methyl group.

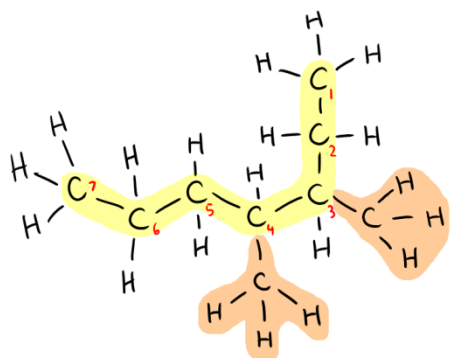
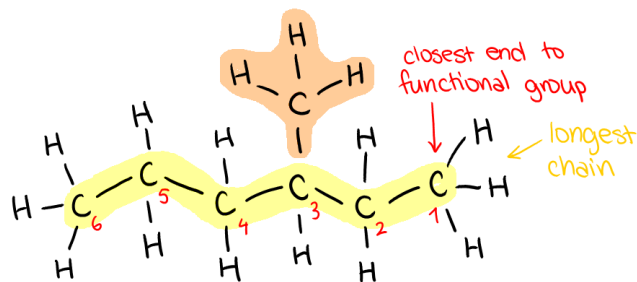
**IUPAC** stands for International Union of Pure Applied Chemistry, and they developed the system of naming compounds. These names are more informative than the common names. The standard way of naming compounds is called **nomenclature**.

Steps for naming compounds:

1. Identify the longest carbon chain
2. Number the carbons, starting from the end closest to the branch
3. Name the **side branches** and **main chain**
4. Combine to give the complete name



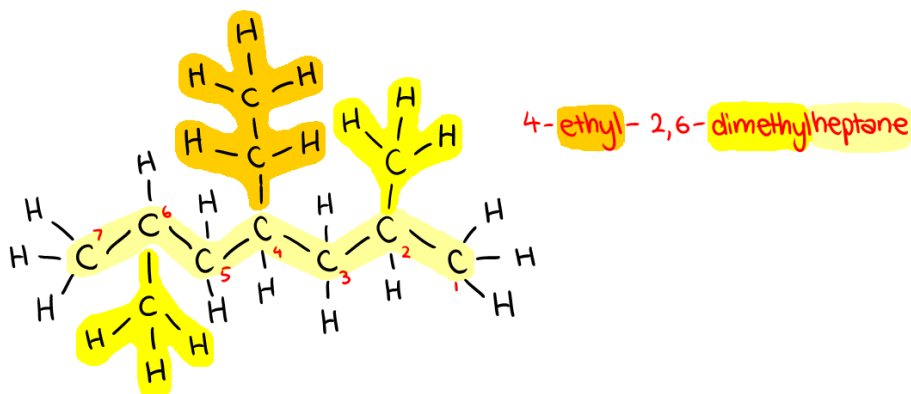
We number the carbon chain in the order so that the side groups have the lowest numbers possible. This is why the molecule below is called 3-methylhexane, not 4-methylhexane.



It is important to inspect a formula to ensure that you do not just pick the most obvious carbon chain, but the **longest chain**.

When more than one of a type of side group appears on a hydrocarbon stem, the prefixes **di-**, **tri-**, etc are placed before the name of the group on the hydrocarbon name.

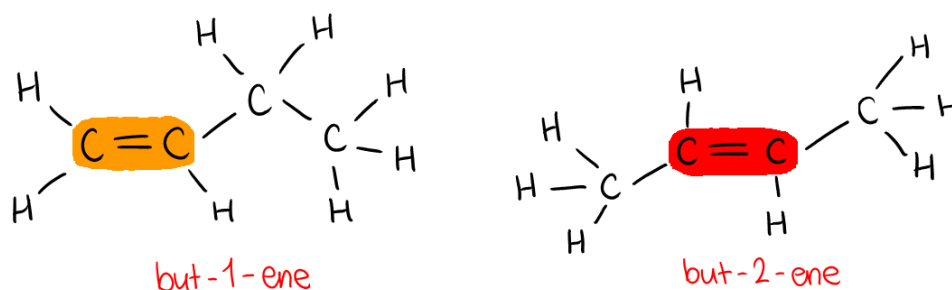
Names of hydrocarbon names are written as single words, with hyphens separating the different prefixes and numbers. When there are two or more substituents, they are placed in **alphabetical order**, disregarding the prefixes.



### 10.1.7 - Deduce structural formulas for the isomers of the straight-chain alkenes up to C<sub>6</sub>

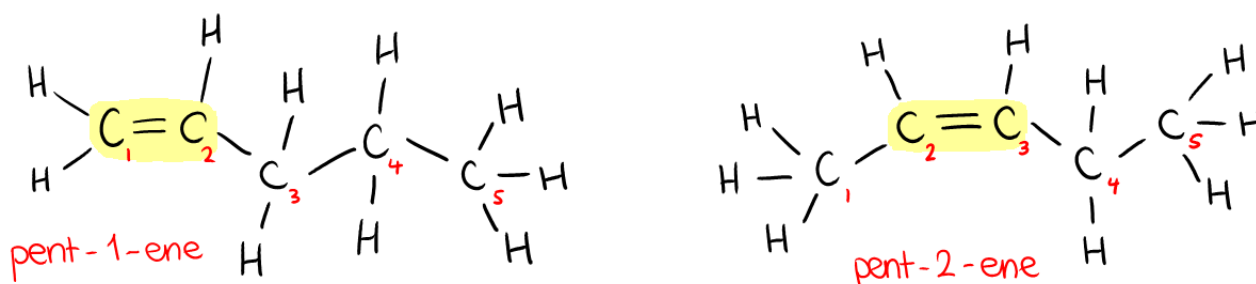
All molecules can be represented **by molecular, empirical or structural formulas**. Molecular formulas tell us the number of atoms of each element in the molecule, whilst giving no information about the structure. For this reason, structural formulas are used to give a better idea of how it looks in real life. Empirical formulas can also be used, which show the lowest possible whole number ratio for the molecule, however these tell us very little about the structure and bonding.

Alkenes also exhibit **structural isomerism**, as the double bond may occur at different places along the chain as well as branches.



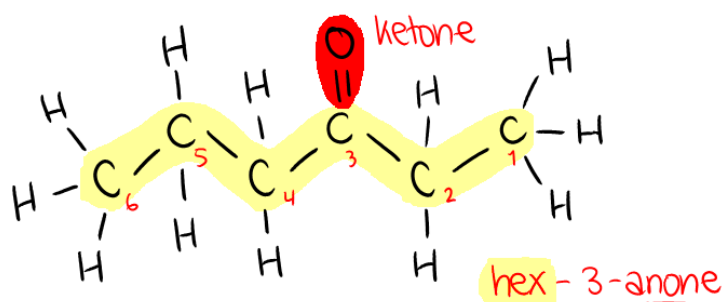
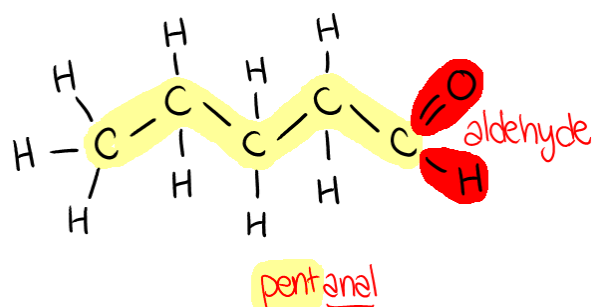
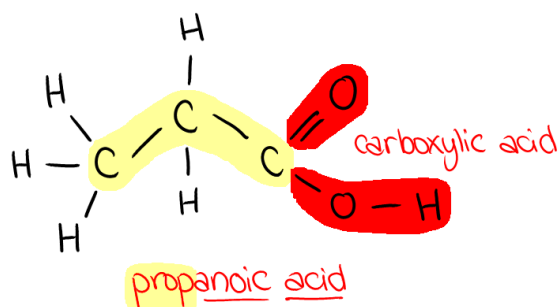
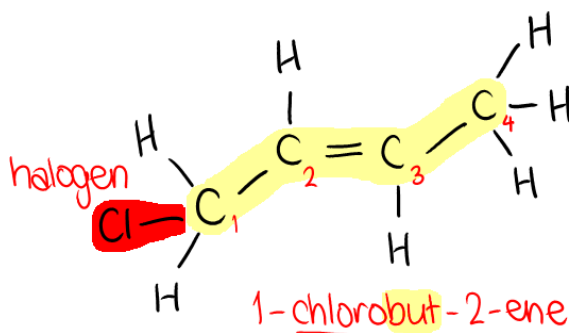
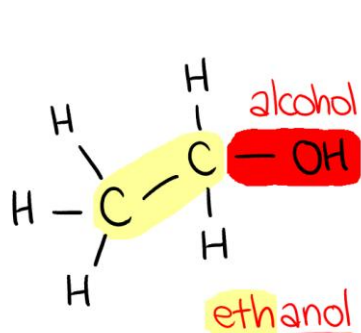
### 10.1.8 - Apply IUPAC rules for naming the isomers of the straight chain alkenes up to C<sub>6</sub>

For straight chain butene, there are two isomers. These are but-1-ene and but-2-ene. These numbers tell us the position of the double bond on the chain. The number in the name indicates that the bond is located between that carbon and the following one. All other isomers follow this pattern.



**10.1.9 - Deduce the structural formula for compounds containing up to six carbon atoms with one of the following functional groups: alcohol, aldehyde, ketone, carboxylic acid and halide**

Atoms or groups of atoms that are attached to a hydrocarbon change the properties of that molecule, such as a higher chemical reactivity. These are called functional groups. When we look at their presence, we write the general formula. R is the symbol for the alkyl group, R' for two and R'' for three.

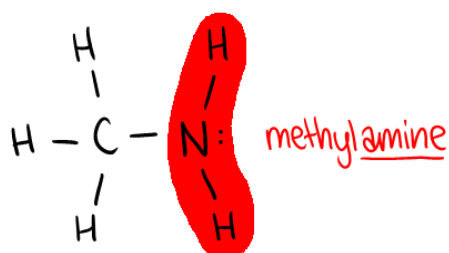


### 10.1.10 - Apply IUPAC rules for naming compounds containing up to six carbon atoms with one of the following functional groups: alcohol, aldehyde, ketone, carboxylic acid and halide

The alcohol functional group is an oxygen atom bonded to a hydrogen atoms. It is also known as the hydroxyl group, and can replace one hydrogen on the alkanes. The same prefixes are used for naming, but the ending -ol is added instead. The general formula for an alcohol is  $C_nH_{2n+1}OH$ , though this may be written as R-OH

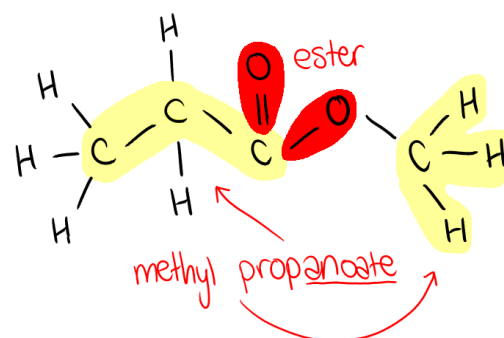
Number of carbons	Prefix	Functional group	Suffix
1	meth-	alcohol	-anol
2	eth-	aldehyde	-anal
3	prop-	ketone	-anone
4	but-	carboxylic acid	-anoic acid
5	pent-		
6	hex-	halide (prefix)	chloro- bromo- iodo-

### 10.1.11 - Identify the following functional groups when present in a structural formulas: amino ( $NH_2$ ), benzene ring (⦿) and esters ( $RCOOR$ )



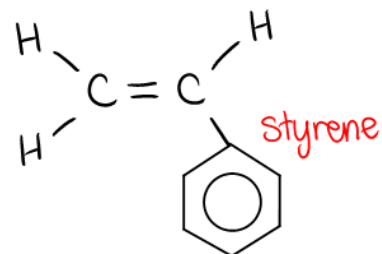
The amino group,  $-NH_2$ , is a functional group present in organic bases called amines. It is **basic** because of its non-bonding pair of electrons, which can be donated.

**Esters** are compounds that have a characteristic sweet, fruity odour. They will often occur in fruit and flowers. This functional group is found in the middle of the molecule. It is made up of a carbonyl group with a second oxygen attached.



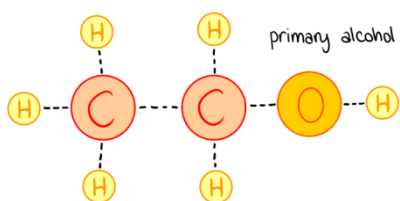
All the compounds considered so far have been **aliphatic**, being made up of straight or branched carbon chains. However, they may also occur as a closed carbon ring, described as **alicyclic**. A third group of the hydrocarbons is the aromatic molecules, all being related to benzene,  $C_6H_6$

Benzene can exist as an independent molecule or in compounds.



### 10.1.12 - Identify primary, secondary and tertiary carbon atoms in alcohols and halogenoalkanes

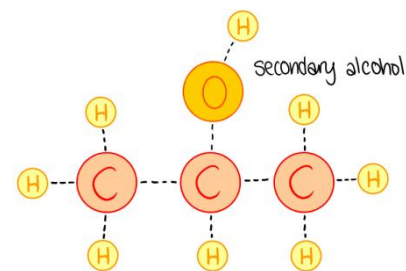
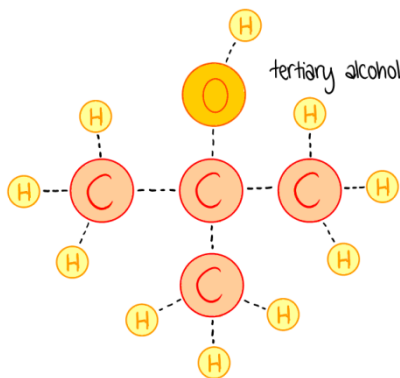
The boiling point decreases as the strength of the intermolecular forces decrease, and the branching of the hydrocarbon chain increases.



Alcohols are classified by where the hydroxyl group occurs on the molecule. Primary carbon atoms are only bonded to one other carbon atom, making the molecule a **primary alcohol**. Likewise, when the hydroxyl group is bonded to a carbon that is bonded to

two other carbon atoms, it is a secondary carbon, and the molecule is a **secondary alcohol**. Carbon atoms bonded to three other carbon

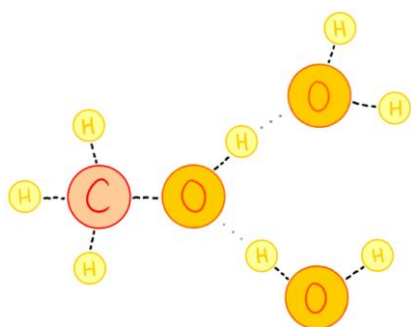
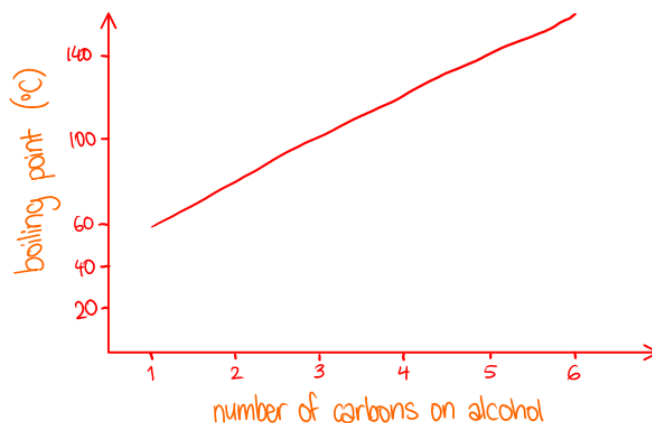
atoms are tertiary carbons, making molecules a **tertiary alcohol**.





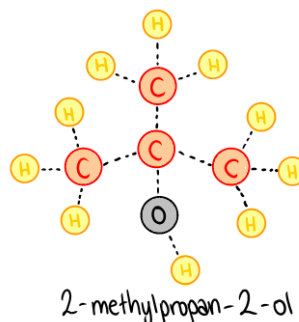
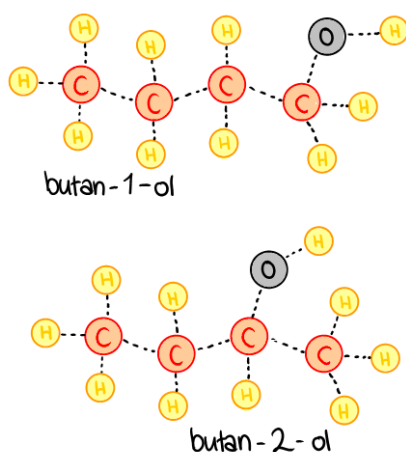
### 10.1.13 - Discuss the volatility and solubility in water of compounds containing the functional groups listed in 10.1.9

With all alkanes, the **boiling point of the alcohols increase as the size of the molecule increases**. The boiling points of alcohols are all higher than those of alkanes of a similar size. Also, alcohols are liquids at room temperature, due to the presence of the -OH group, which strengthens the intermolecular bonding. Alcohols also have a lower volatility than alkanes, as they have a higher boiling point, making it harder for them to evaporate.



The bonding also influences the solubility of the alcohols. Because of the -OH group, **hydrogen bonds** are able to form with the water. However, as the size of the carbon chain increases, the solubility decreases. This is because the influence of the -OH group diminishes compared to that of the rest of the molecule. Most of the molecule is non-polar, having a low attraction to water. Alcohols with more than three carbons are insoluble. Propanol is slightly soluble.

As with all isomers, the carbon atoms in an alcohol are counted from the end closest to the -OH group. This position influences the ability for the molecule to form intermolecular bonds. This can be seen in the boiling point of the isomers of butanol.



## 10.2 – Alkanes

### 10.2.1 - Explain the low reactivity of alkanes in terms of bond enthalpies and bond polarity

Alkanes are saturated hydrocarbons. They are non-polar molecules, so they are **insoluble** in water, along with being less dense than water. In their pure form, alkanes are colourless.

The C-C and C-H bonds are quite strong and stable, making alkanes fairly unreactive. In addition, they are non-polar, so they do not attract polar or ionic compounds. This makes them valuable lubricants.

Since they are so unreactive, reactions with alkanes have a high activation energy to break the bonds. Once this has been overcome, the reaction is able to proceed rapidly.

### 10.2.2 - Describe, using equations, the complete and incomplete combustion of alkanes

Alkanes react exothermically with oxygen when the temperature is high enough. This makes them useful as fuel. The main products of this reaction are water and carbon dioxide.

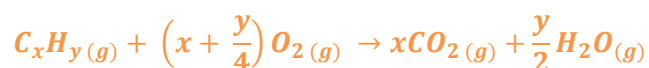
*Butane and Oxygen:-*



*Methane and Oxygen:-*



The general formula for the combustion of a hydrocarbon is:



If there is not enough oxygen available, **incomplete combustion** will occur, causing carbon and poisonous carbon monoxide to form. This can cause health problems and pollution.

The incomplete combustion in a car can be represented:



The supply of oxygen can be limited in a Bunsen burner by closing the air holes. This means that any test tube heated on it will blacken from the carbon:

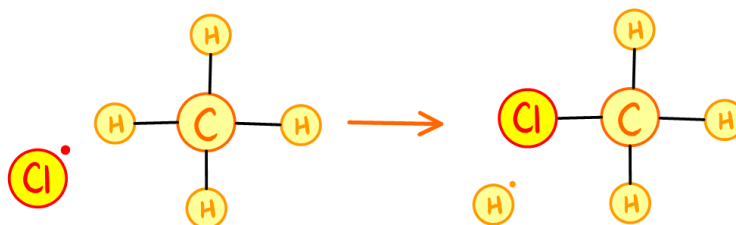


### 10.2.3 - Describe, using equations, the reaction of methane and ethane with chlorine and bromine

Halogens can be added to an alkane by a **substitution reaction**, where the halogen replaces a hydrogen atom. For this to happen, the bond between the hydrogen and carbon atoms must break. The bond between the halogen atoms will also need to break in a process called **homolytic fission** to form free radicals. Radicals do not have a charge, but have an unpaired electron in their outer shell, making them very reactive.



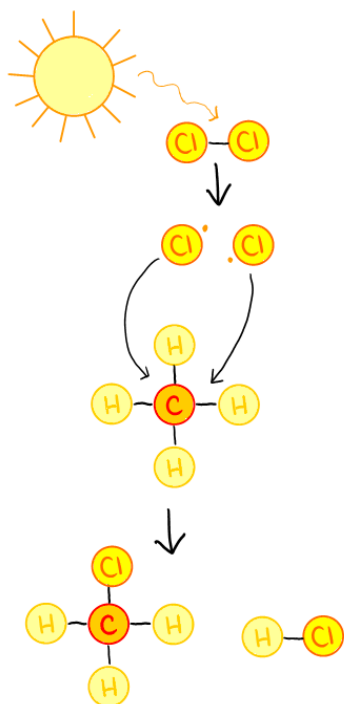
When the halogen radical reacts with the alkane, the hydrogen will then form a radical.



### 10.2.4 - Explain the reactions of methane and ethane with chlorine and bromine in terms of free-radical mechanism

UV light provides sufficient energy to break the Br-Br bond to form radicals, a process called **initiation**.





These bromine radicals then react with the methane molecules, called the **propagation** step:



Then there is another propagation step:



The final stage is called the **termination** stage, in which three reactions may take place:



Depending on the supply of bromine, other reactions may occur. If there is ample supply, the molecules may continue to react according to the equation:



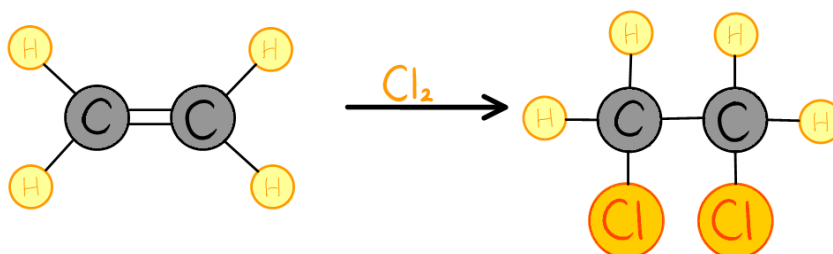
The same type of reactions can take place with chlorine. With ethane, there are more steps because the molecule is larger.



## 10.3 – Alkenes

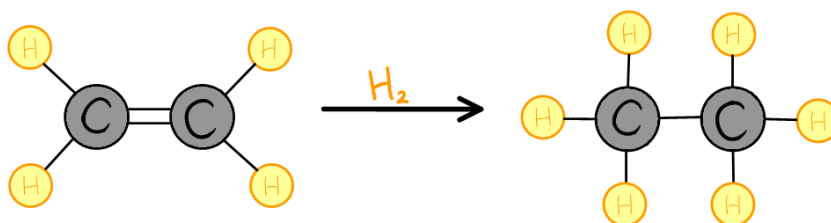
### 10.3.1 - Describe, using equations, the reactions of alkenes with hydrogen and halogens

Alkenes undergo **addition reactions**. This is when two substances react to form a single substance. Alkenes are more reactive than alkanes, as the double bond can be more easily converted into a single bond. Extra atoms or groups of atoms can be added to the molecule.



Chlorine and ethene will react at room temperature. The addition of chlorine happens across the double bond, with each chlorine atom attaching to the carbons. This happens with bromine and iodine as well, all the halogens.

Alkenes will also react with hydrogen, called **hydrogenation**. A catalyst is used, such as Nickel, and the product is a saturated molecule.

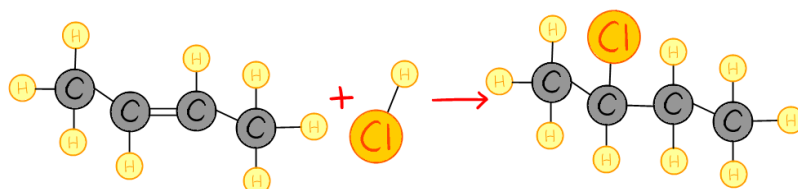


Platinum and palladium can also act as catalysts in this reaction.



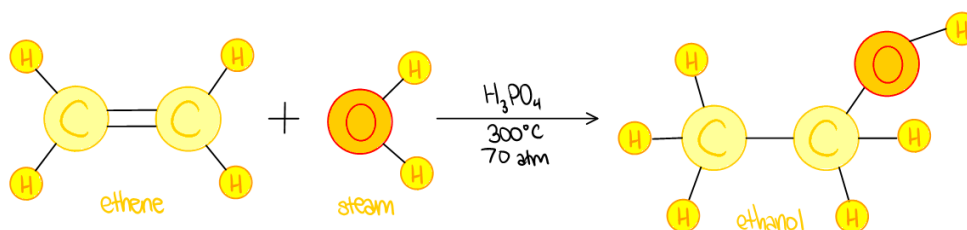
### 10.3.2 - Describe, using equations, the reactions of symmetrical alkenes with hydrogen halides and water

The alkenes may react with hydrogen halides and water to produce a halogenoalkane, an **addition reaction**. The halogen will bond to the carbon atoms that formed the double bond.

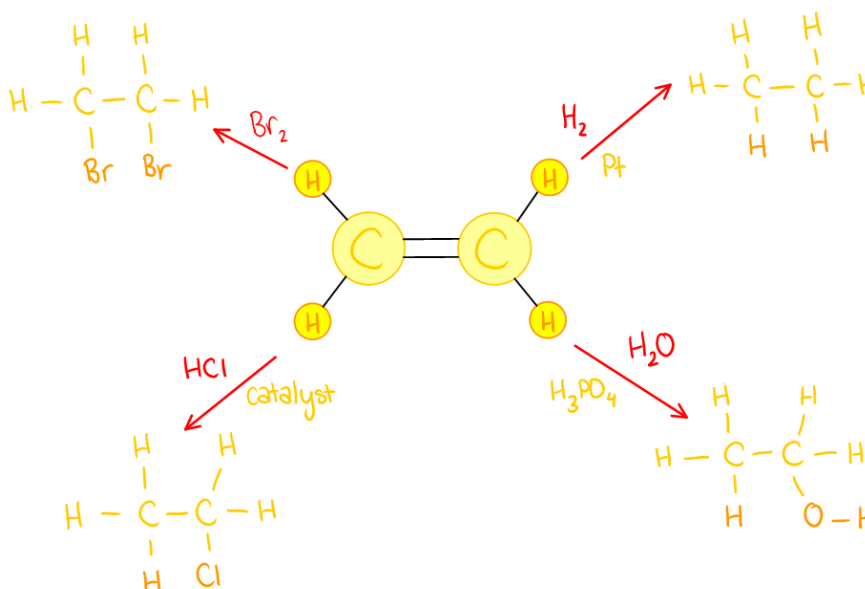


If the double bond was located elsewhere on the molecule, then the hydrogen and chlorine atoms would bond to those carbon atoms instead.

Another addition reaction is the reaction of alkenes with water, called **hydration**. This is used to convert ethene and steam into ethanol. A catalyst, phosphoric acid, is used to provide hydrogen ions for the reaction. It is performed at 300°C and 70atm.



The reaction is exothermic, but is conducted at moderately high temperatures and pressures with a catalyst to maximise reaction rate and yield.



### 10.3.3 - Distinguish between alkanes and alkenes using bromine water

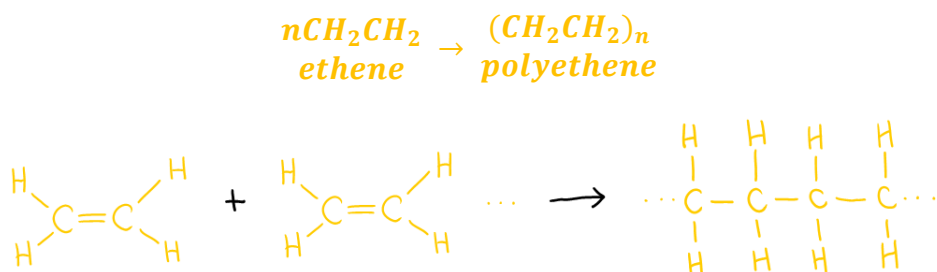
Both alkanes and alkenes are colourless. In an alkene, adding bromine will not change the colour - the bromine water undergoes **decolourisation**. Therefore, the test for an alkene is to add bromine water and look for a clear solution.

On the other hand, when bromine water to an alkane, there is a colour change - the solution will become yellow/orange. The two substances will not react unless there is strong **UV light** present.

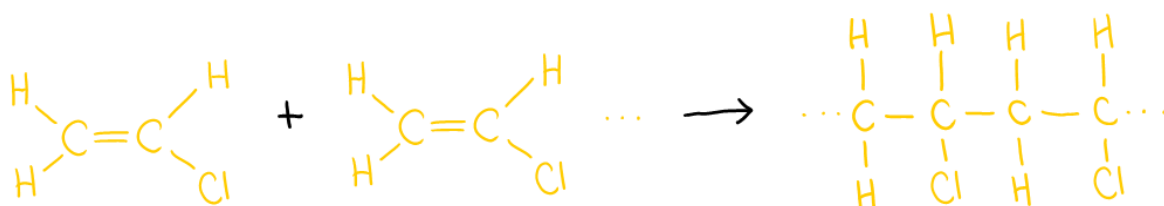
### 10.3.4 - Outline the polymerisation of alkenes

Polymers of alkenes are long, chain-like molecules that consist of many monomers joined together.

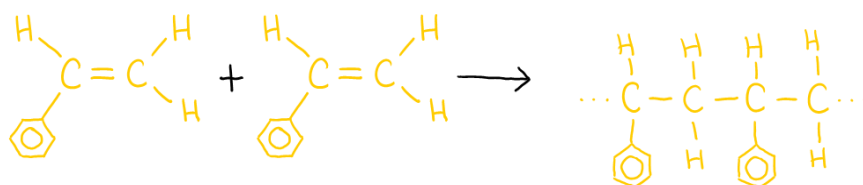
Polyethene is formed in an **addition polymerisation reaction**. Each repeating unit, or monomer, in the chain contains has a double bond that is converted to a single bond when they join.



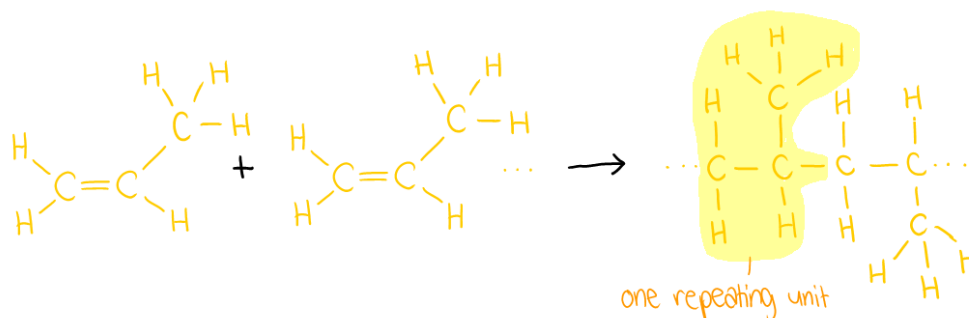
Since ethene is non-polar, there are only weak Van der Waals forces between the polymers. However, by adding other elements to the molecule, the properties of the polymers can be changed. For example, adding a chlorine atom makes **PVC (polyvinyl chloride)**, which has a dipole and leads to a higher melting point and lower flammability. It is used as insulation on electrical wiring, soft drink bottles, fabric coatings and water pipes.



Polystyrene formation:



Polypropene is used in carpeting, bottles and luggage.



### 10.3.5 - Outline the economic importance of the reactions of alkenes

Large amounts of alkenes can be produced by cracking **crude oil** into smaller molecules.

Alkenes form the starting materials for synthetic polymers that are useful to society. Ethene can be converted into ethanol or can be converted into plastics. Vegetable oils can form margarine. Polyethene is used to make plastic bags, bottles and toys. Polystyrene is used in Styrofoam insulation, cups and packing materials. Polychloroethene is used in plastic wrap, plumbing and garden hoses.





## 10.4 - Alcohols

Alcohols have the general formula:



### 10.4.1 - Describe, using equations, the complete combustion of alcohols

Alcohols will not affect the pH of a solution as they do not behave as bases and are weaker acids than water.

Alcohols are useful fuels because they have high enthalpies of combustion, create little pollution because there is **no sulfur** and can be **obtained from renewable resources**

They will undergo complete combustion:



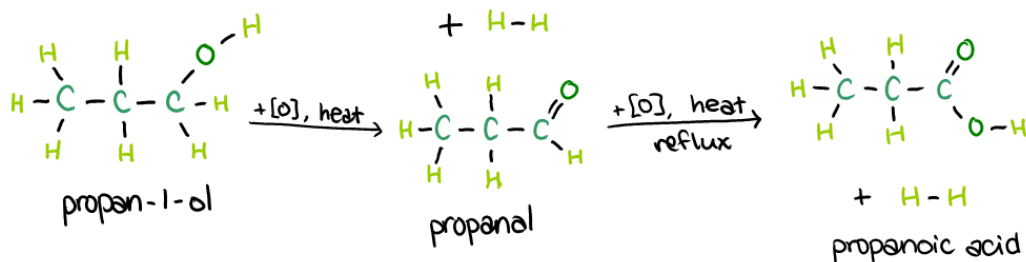
However, if there is limited supply of oxygen, they will produce carbon monoxide.

### 10.4.2 - Describe, using equations, the oxidation reactions of alcohols

If the oxidation of alcohols is controlled by the reagents used, then the skeleton can be kept intact and a variety of products can be formed. In most cases, **acidified potassium dichromate(VI)** -  $K_2Cr_2O_7$  can be used. However, **acidified potassium permanganate** -  $KMnO_4$  - can also be used. The oxidising agent can be written as  $+ [O]$

#### Primary Alcohols

The oxidation of alcohols must take place in two steps - first going to an **aldehyde**, then to a **carboxylic acid**.

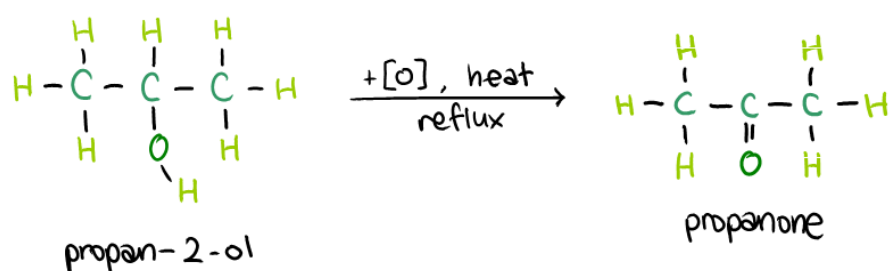


To obtain the aldehyde before it reacts further, distillation can be used to remove it due to its lower boiling point. It will go into the gaseous state and enter condensing tube. It will no longer be in contact with the oxidising agent and will not be converted to carboxylic acid.

To obtain the carboxylic acid as it is formed, heating in a reflux condenser is used instead.

### Secondary Alcohols

When secondary alcohols are oxidised, they form **ketones**.



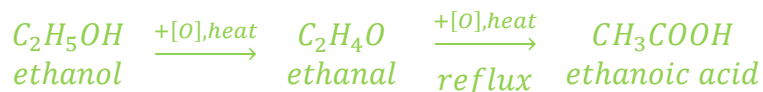
### Tertiary Alcohols

These **do not react** readily under normal conditions as a very large amount of energy is needed to break the bonds.

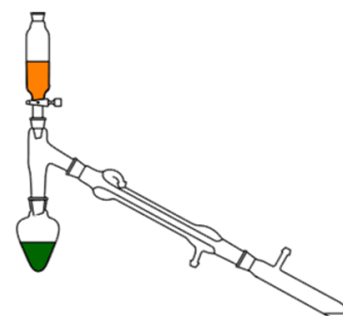
## 10.4.3 - Determine the products formed by the oxidation of primary and secondary alcohols

### Primary Alcohols (1°)

These are easily oxidised to aldehydes and then to carboxylic acids.



It is essential to distil off the aldehyde before it is oxidised to the carboxylic acid. Aldehydes do not have hydrogen bonding, and so have lower boiling points than alcohols and acids. The alcohol is dripped into a warm solution of acidified  $\text{K}_2\text{Cr}_2\text{O}_7$ .

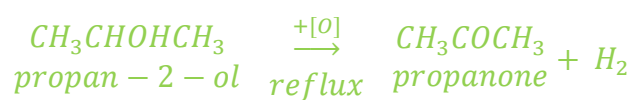




To oxidise an alcohol straight to the acid, reflux the mixture. **Reflux** is when the mixture is heated in a flask with a condenser in it. This way, the aldehyde will be put back into the liquid state so that it will remain in contact with the oxidising agent.

### Secondary Alcohols (2°)

These are easily oxidised to ketones.



The alcohol is refluxed with acidified  $\text{K}_2\text{Cr}_2\text{O}_7$

*Note that tertiary alcohols are not oxidised by potassium dichromate(VI) under normal conditions.*



## 10.5 - Halogenoalkanes

The halogens are the seventh group on the periodic table, including elements such as fluorine, chlorine, bromine and iodine.

Halogenoalkanes have a halogen bonded to the skeleton of the alkane. They have the general formula:



Where X is the halogen.

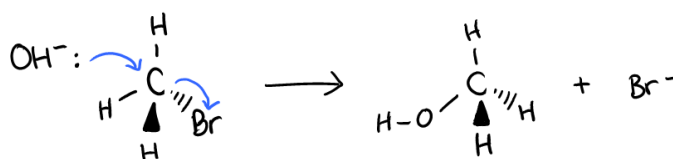
7	0
	2 <b>He</b> 4.00
9 <b>F</b> 19.00	10 <b>Ne</b> 20.18
17 <b>Cl</b> 35.45	18 <b>Ar</b> 39.95
35 <b>Br</b> 79.90	36 <b>Kr</b> 83.80
53 <b>I</b> 126.90	54 <b>Xe</b> 131.30
85 <b>At</b> (210)	86 <b>Rn</b> (222)

### 10.5.1 - Describe, using equations, the substitution of halogenoalkanes with sodium hydroxide

Halogens have greater electronegativity than carbon, causing halogenoalkanes to have a **polar bond**. This causes nucleophiles (species with a non-bonding pair of electrons such as  $\text{OH}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  and  $\text{CN}^-$ ) to be attracted to the carbon atom, allowing for substitution reaction to occur.



The curly arrows in the diagram below show the movement of electron pairs. The halogen is also called the **leaving group**.



The product of a substitution reaction with hydroxide is an **alcohol**. For example, the reaction between bromoethane (a primary halogenoalkane) and warm dilute sodium hydroxide:



On the other hand, the reaction between 2-bromo-2-methylpropane (a tertiary halogenoalkane) and warm dilute sodium hydroxide solution takes place according to the equation:



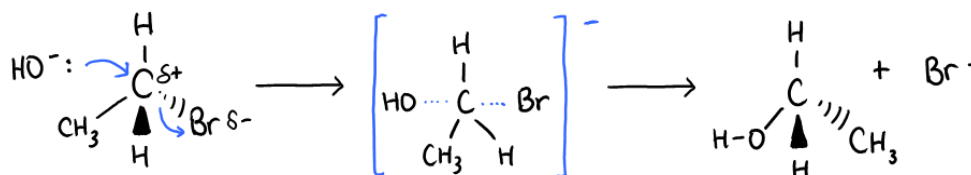
## 10.5.2 - Explain the substitution reactions of halogenoalkanes with sodium hydroxium in terms of $S_N1$ and $S_N2$ mechanisms

**Heterolytic fission** is when one of the species takes the shared electron pair, creating two oppositely charged ions.



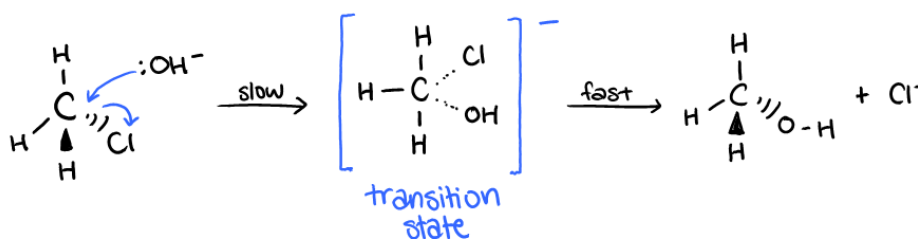
### Primary Halogenoalkanes

These have one alkyl group attached to the carbon bonded to the halogen, and **undergo  $S_N2$  reactions**. The hydrogen atoms that are also attached to the carbon are small and do not provide much protection for the halogen. This leaves it open to attack from a nucleophile.



The rate expression for this is:  $rate = k[C_2H_5Br][OH^-]$

The **transition state** formed during the reaction means that the rate is determined by both reactants. The slowest step involves both the halogenoalkane and the hydroxide ion, making it a bimolecular reaction. The transition state is when the carbon is weakly bonded to the halogen and the hydroxide.



### Secondary Halogenoalkanes

These have two alkyl groups attached to the carbon bonded to the halogen, and can undergo **both  $S_N1$  and  $S_N2$  reactions**, and there is no way of determining which will happen - they may use one or the other, or a combination of the two.



### Tertiary Halogenoalkanes

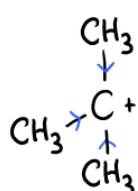
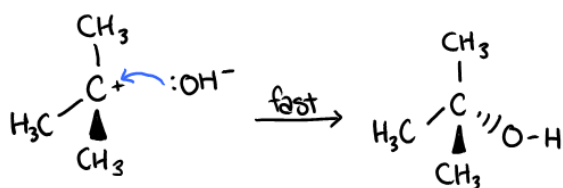
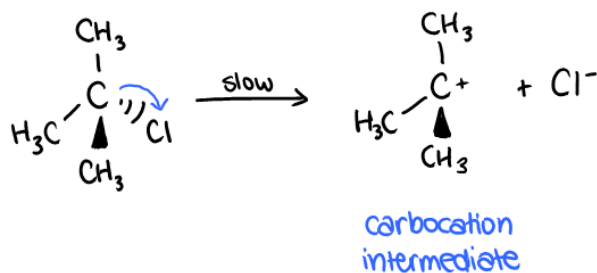
These have three alkyl groups attached to the carbon bonded to the halogen and **undergo S<sub>N</sub>1 reactions**. The alkyl groups are larger and protect the halogen from attack by nucleophiles, called steric hindrance.

This is a two-step reaction, happening according to the equations:



Since the first step is the slowest, it is the **rate-determining step**. There is only one molecule involved in this step; hence the overall reaction is S<sub>N</sub>1. The halogenoalkane splits heterolytically, with the halogen taking the bonding electron pair and forming a halide ion. The alkane now has a positive charge, called a **carbocation**. This means that the rate expression is:

$$\text{rate} = k[C(CH_3)_3Br]$$



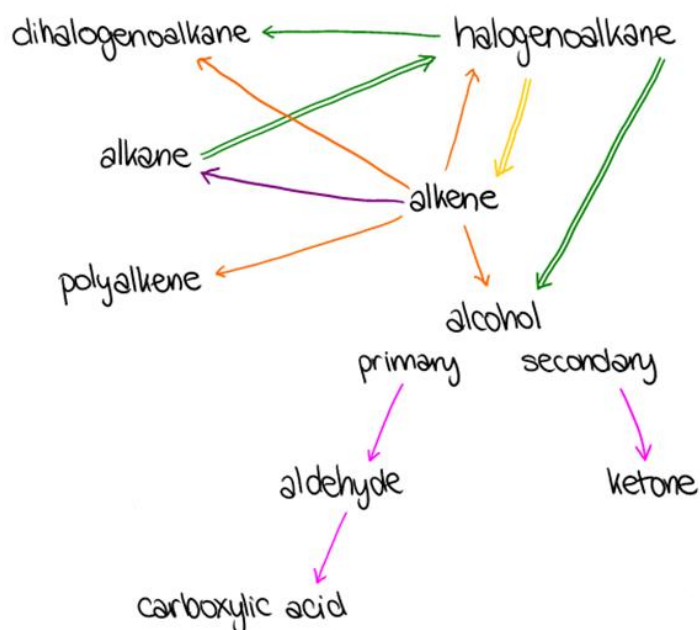
Once the carbocation is formed, it is available to bond with the nucleophile. The surrounding alkyl groups keep the carbocation stable long enough for the second step to occur by donating electrons, or a **positive inductive effect**.



## 10.6 - Reaction Pathways

The different reactions that are possible for organic compounds are explained in more detail in previous sections. Some are outlined in this section too. It is important to be able to manipulate the reactions and create combinations that will produce the desired product. Remember that the IB will never ask you to deduce a reaction pathway that involves more than two steps.

### 10.6.1 - Deduce reaction pathways given the starting materials and the product



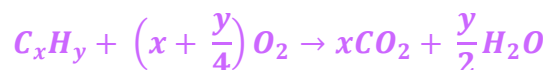
⇒ mechanism required

- oxidation
- reduction
- substitution
- addition
- elimination
- condensation

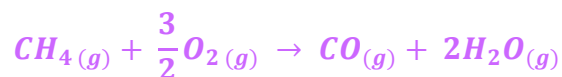
### Reactions of Alkanes

#### Combustion

The general equation for the complete combustion of alkanes is:



However, if there is insufficient oxygen available, the alkanes undergo incomplete combustion to produce a mixture of  $CO_2$ ,  $CO$  and  $C$ . For example:



## Substitution

Alkanes will undergo substitution reactions with halogens if there is a mechanism present (such as UV light or heat). During these reactions, the halogens will form **free radicals** - these have no charge, but have an unpaired electron, making them highly reactive. During the reaction, the halogen will undergo **homolytic fission** to make the radicals.



This reaction takes place in a few steps:

### Initiation

This is when the radicals are formed.



This step happens first because the bonds between the halogen molecules are weaker and have a lower enthalpy than the C-H or C-C bonds.

### Propagation

In this step, the radicals are used, and new radicals are formed.



In the second stage of propagation, the  $\text{CH}_3$  radical reacts with the chlorine molecule to make  $\text{CH}_3\text{Cl}$



### Termination

The free radicals are removed by reacting together



The methane and chlorine radicals can also be removed:



The methane radicals may react together:



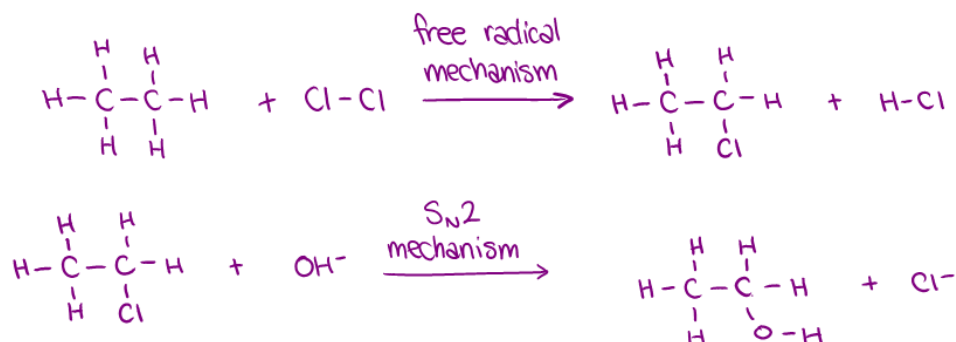
In reality, there will be a mixture of products, depending on the concentration of the reactants. These products can then be separated using distillation processes.





### Alkane to Alcohol

This reaction must take place in two steps. In the first step, UV light is used to create chlorine radicals, and the reaction continues to form a halogenoalkane.



The second step is an S<sub>N</sub>2 reaction, with the OH<sup>-</sup> ion attacking the carbon-chlorine bond. A reactive intermediate is formed, which then loses the Cl<sup>-</sup>.

### Formation of a Halogenoalkane

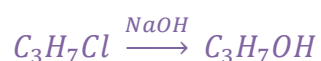
This is a substitution reaction using a free radical mechanism



### Reactions of Halogenoalkanes

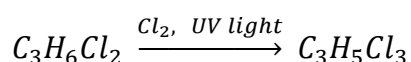
#### Formation of an Alcohol

This is an S<sub>N</sub>2 substitution reaction



#### Formation of a Trihalogenoalkane from a Dihalogenoalkane

This is a substitution reaction using a free radical mechanism



## Reactions of Alkenes

### Formation of an Alkane

This is an addition reaction



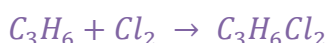
### Formation of a Halogenoalkane

This is an addition reaction



### Formation of a Dihalogenoalkane

This is an addition reaction



### Formation of an Alcohol

This is an addition reaction



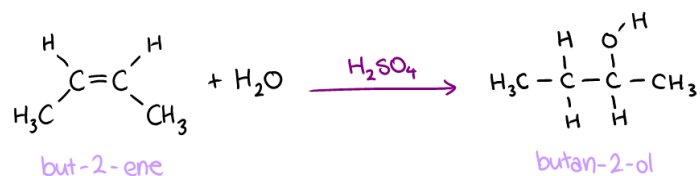
### Formation of a poly(alkene)

This is an addition polymerisation reaction

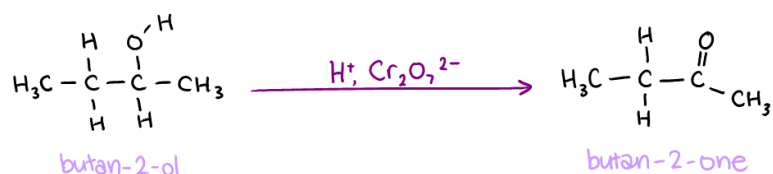


### Formation of a Ketone

**Step 1** - The but-2-ene is heated with steam and a catalyst to form butan-2-ol. Sulfuric acid ( $H_2SO_4$ ) can act as a catalyst here:



**Step 2** - Butan-2-ol is oxidised when heated with potassium dichromate(VI) solution to butan-2-one.

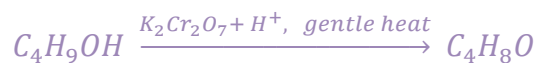


## Reactions of Alcohols

### Primary Alcohols

#### *Formation of an Aldehyde*

This is an oxidation reaction



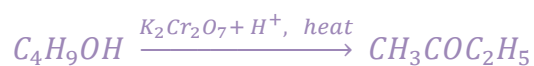
#### *Formation of a Carboxylic Acid*

This is an oxidation reaction



### Secondary Alcohols

#### *Formation of a Ketone*



Tertiary alcohols are not easily oxidised and are not considered in the IB Chemistry course.

