

# IB Chemistry DP

YOUR NOTES



## 10. Organic Chemistry

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## 10.1 Fundamentals of Organic Chemistry

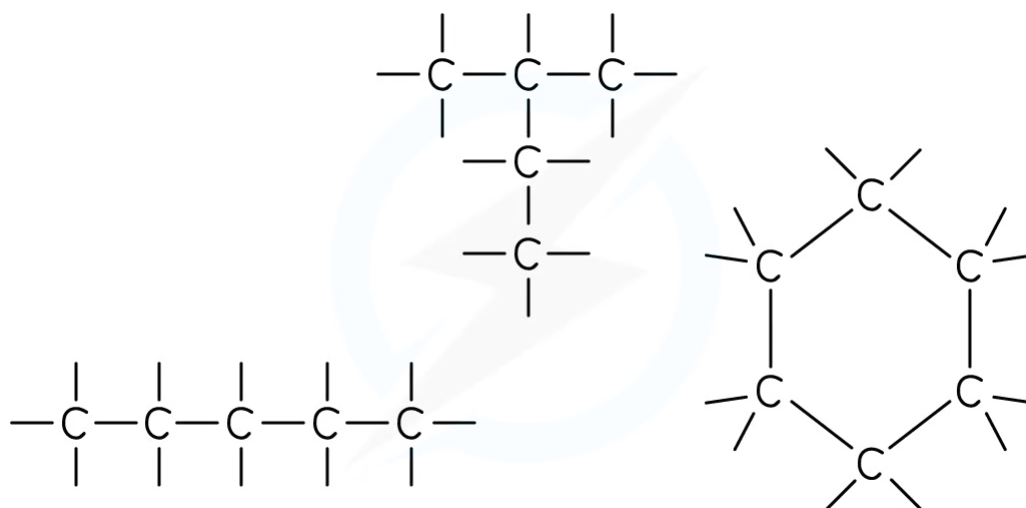
### 10.1.1 Homologous Series

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### Homologous Series

- **Organic chemistry** is the chemistry of carbon compounds
- Carbon forms a vast number of compounds because it can form strong covalent bonds with itself
- This enables it to form long chains of carbon atoms, and hence an almost infinite variety of carbon compounds are known
- The tendency of identical atoms to form covalent bonds with each other and hence form chains is known as **catenation**



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**Catenation in carbon allows an almost infinite variety of chains, branches and rings**

- Carbon always forms four covalent bonds which can be single, double or triple bonds
- A **functional group** is a specific atom or group of atoms which confer certain physical and chemical properties onto the molecule
- Organic molecules are classified by the dominant **functional group** on the molecule
- Organic compounds with the same functional group, but a different number of carbon atoms, are said to belong to the same **homologous series**
- Every time a carbon atom is added to the chain, two hydrogen atoms are also added

#### Homologous Series of Alkanes Table

Name of alkane	Number of carbons	Chemical formula	Boiling point in °C	State at room temperature	Melting point in °C
Methane	1	CH <sub>4</sub>	-162	gas	-182
Ethane	2	C <sub>2</sub> H <sub>6</sub>	-89	gas	-183
Propane	3	C <sub>3</sub> H <sub>8</sub>	-42	gas	-188
Butane	4	C <sub>4</sub> H <sub>10</sub>	-1	gas	-138
Pentane	5	C <sub>5</sub> H <sub>12</sub>	36	liquid	-130

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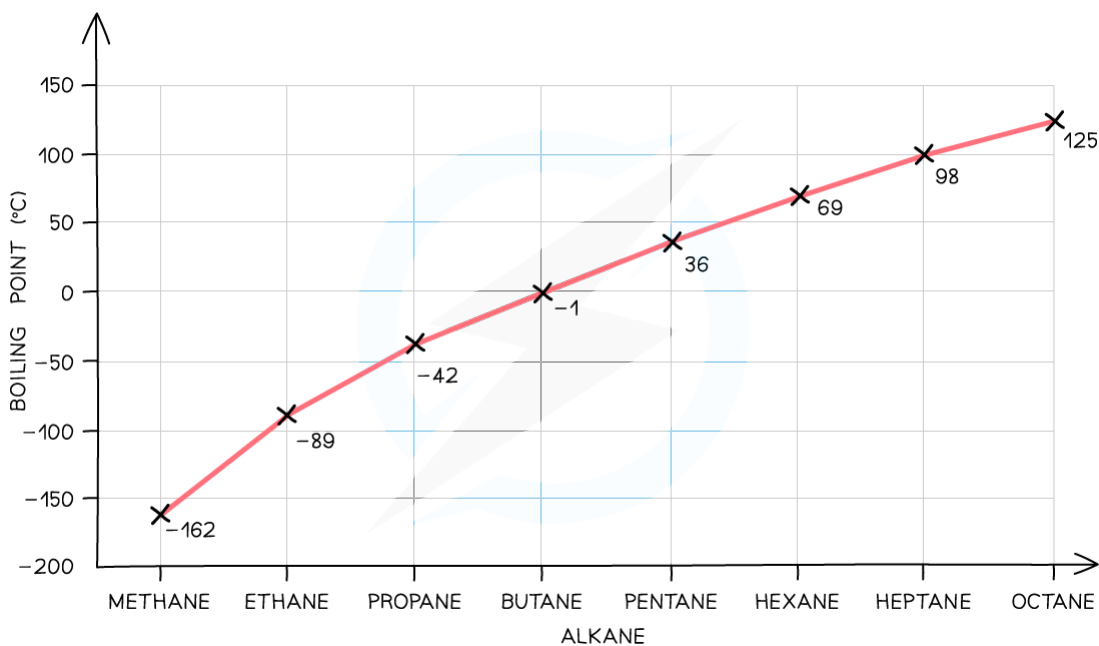
- Things we can say about a **homologous series**:
  - each member has the same **functional group**
  - each member has the same **general formula**
  - each member has similar chemical properties
  - each member differs by -CH<sub>2</sub>-
  - members have gradually changing physical properties, for example, boiling point, melting point and density
- As a homologous series is ascended, the size of the molecule increases
- This has an effect on the physical properties, such as boiling point and density

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## Boiling Point Trends

- A graph of boiling point for the first eight alkanes looks like this:



- The broad trend is that **boiling point increases** with increased molecular size
- Each additional  $\text{-CH}_2\text{-}$  (called the **homologous increment**) adds 8 more electrons to the molecule
- This increases the strength of the **London Dispersion Forces**
- Stronger **LDF** leads to a higher boiling point
- These trends are followed in other **homologous series**

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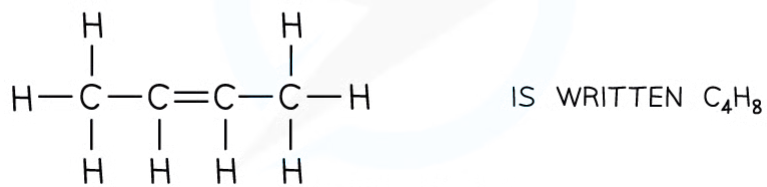
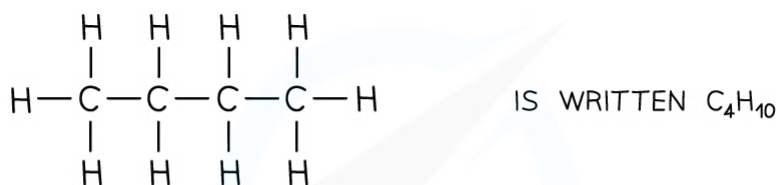


## 10.1.2 Understanding Organic Molecules

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**Representing Formulae**

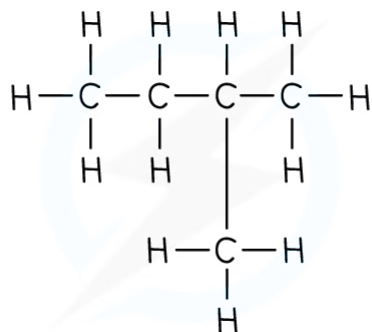
- Organic compounds can be represented in a number of ways:
  - Empirical Formulae**
  - Molecular Formulae**
  - Structural Formulae**
  - Condensed Structural Formulae**
- The **empirical formula** shows the **simplest possible ratio** of the atoms in a molecule
- For example:
  - Hydrogen peroxide is  $\text{H}_2\text{O}_2$  but the empirical formula is HO
- The **molecular formula** shows the **actual number** of atoms in a molecule
- For example:



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**The molecular formulae of butane and butene**

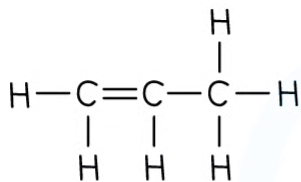
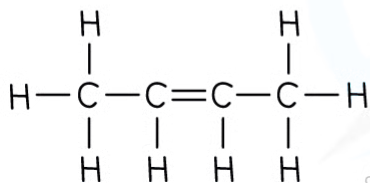
- The **structural formula** shows the spatial arrangement of all the atoms and bonds in a molecule
- This is also known as the **displayed formula** or **graphical formula**.
- For example:



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**The structural formula of 2-methylbutane**



IS REPRESENTED AS  $\text{CH}_2=\text{CHCH}_3$ IS REPRESENTED AS  $\text{CH}_3\text{CH}=\text{CHCH}_3$ 

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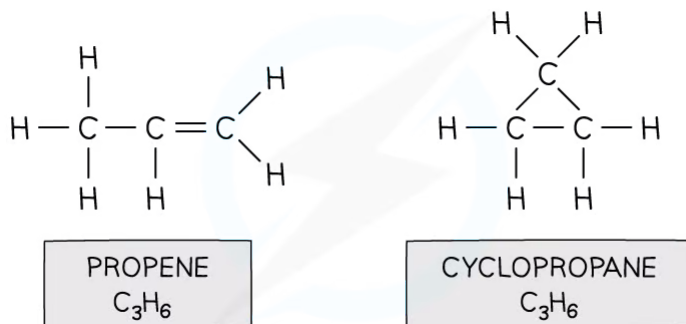
**Representing condensed structural formulae of alkenes**

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## Isomers

- **Structural isomers** are compounds that have the same **molecular** formula but different **structural** formulae
  - Eg. propene and cyclopropane



**Both propene and cyclopropane are made up of 3 carbon and 6 hydrogen atoms but the structure of the two molecules differs**

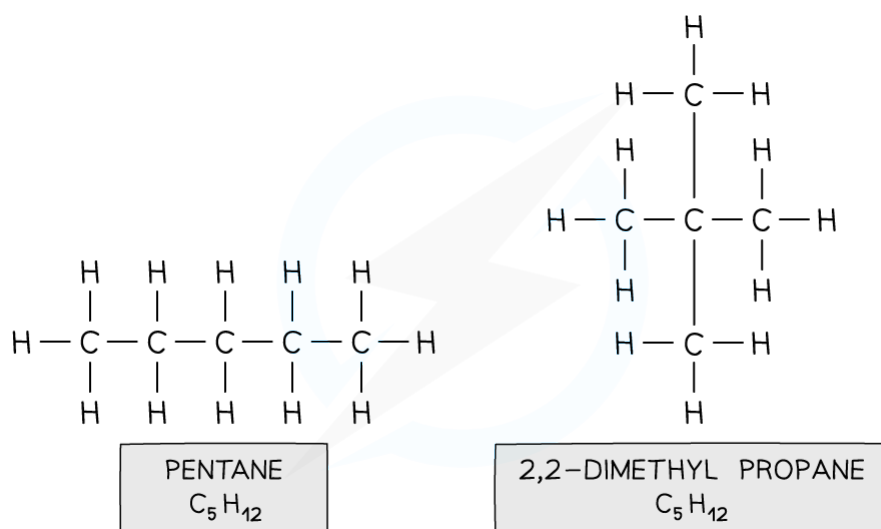
- There are three different types of structural isomerism:
  - **Branch-Chain** isomerism
  - **Positional** isomerism
  - **Functional** group isomerism

### Branch-Chain isomerism

- **Branch-Chain isomerism** is when compounds have the same molecular formula, but their longest hydrocarbon chain is not the same
- This is caused by branching
  - Eg. pentane and 2,2-dimethylpropane

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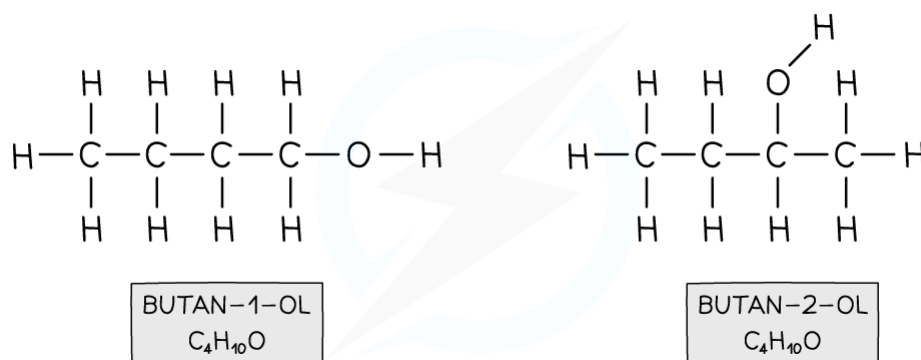


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**Both compounds are made up of the same atoms however the longest carbon chain in pentane is 5 and in 2,2-dimethylpropane it is 3 (with two methyl branches)**

## Positional isomerism

- **Positional isomers** arise from differences in the position of a functional group in each isomer
  - The functional group can be located on different carbons
  - For example, butan-1-ol and butan-2-ol



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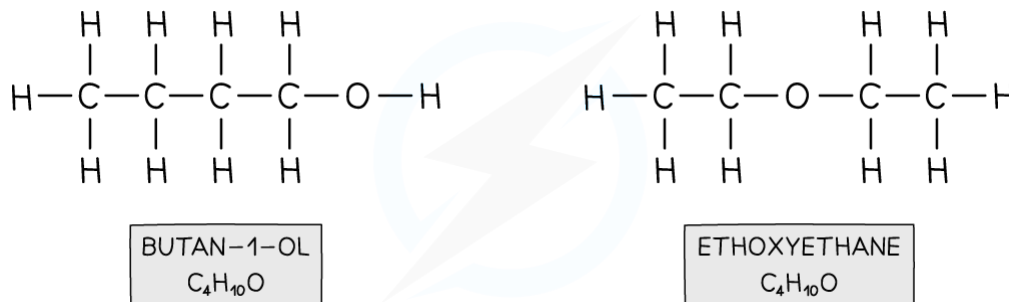
**Both compounds have an alcohol group and are made up of 4 carbon, 10 hydrogen and one oxygen atom however in butan-1-ol the functional group is located on the first carbon and in butan-2-ol on the second carbon**

## Functional group isomerism

- When different functional groups result in the same molecular formula, **functional group isomers** arise

- The isomers have very different chemical properties as they have different functional groups
  - For example, butanol and ethoxyethane

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**Both compounds have the same molecular formula however butan-1-ol contains an alcohol functional group and ethoxyethane an ether functional group**

- You should be able to deduce all possible isomers for organic compounds knowing their molecular formula

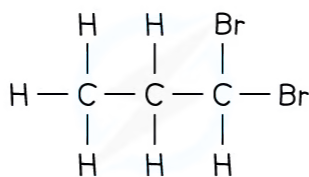


### Worked Example

How many isomers are there of,  $\text{C}_3\text{H}_6\text{Br}_2$ ?

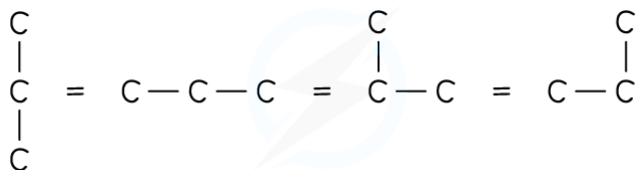
**Answer:**

**Step 1:** Draw the structural formula of the compound

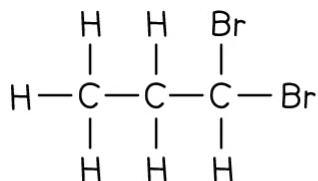


**Step 2:** Determine whether there is functional group, branch-chain or positional isomerism

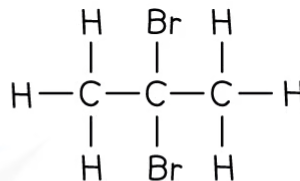
- Functional group? No, as Br is the only functional group possible
- Branch-chain? No, as the longest chain can only be 3
- Positional? Yes, as the two bromine atoms can be bonded to different carbon atoms



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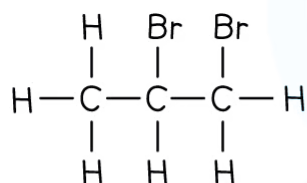


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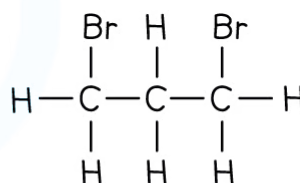


1,1-DIBROMOPROPANE

2,2-DIBROMOPROPANE



AND



1,2-DIBROMOPROPANE

1,3-DIBROMOPROPANE

$\text{C}_3\text{H}_6\text{Br}_2$  THEREFORE HAS 4 STRUCTURAL ISOMERS

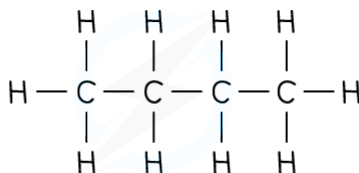
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### ? Worked Example

How many isomers are there of the compound with molecular formula  $\text{C}_4\text{H}_{10}$ ?

**Answer:**

**Step 1:** Draw the structural formula of the compound



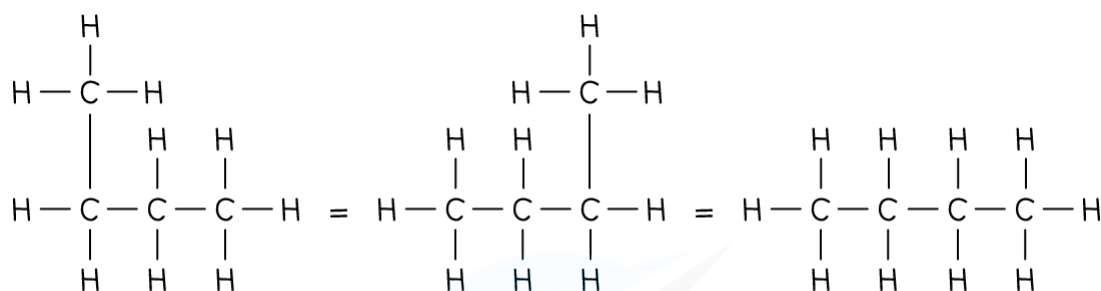
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**Step 2:** Determine whether it is a functional group, chain or positional isomerism

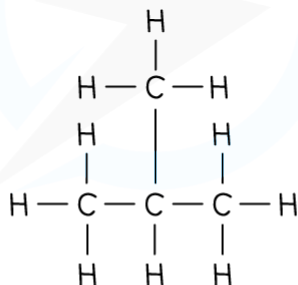
- Functional group? No, as there are no functional groups
- Positional? No, as there are no functional groups which can be positioned on different carbon atoms

- Chain? yes!

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BUTANE



2-METHYLPROPANE

$\text{C}_4\text{H}_{10}$  THEREFORE HAS 2 STRUCTURAL ISOMERS

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### Exam Tip

Don't be fooled by molecules by bending and turning through 90 degrees - that does not make them isomers. The best test is to try and name them - isomers will have a different name.





## 10.1.3 Nomenclature

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**Nomenclature**

- **Systematic nomenclature** can be used to name organic compounds and therefore make it easier to refer to them
- The **alkanes** provide the basis of the naming system and the **stem** of each name indicates how many carbon atoms are in the **longest chain** in one molecule of the compound

**Nomenclature of Organic Compounds Table**

Number of C atoms	Molecular formula of straight-chain alkane	Name of alkane	Stem used in naming
1	CH <sub>4</sub>	methane	meth-
2	C <sub>2</sub> H <sub>6</sub>	ethane	eth-
3	C <sub>3</sub> H <sub>8</sub>	propane	prop-
4	C <sub>4</sub> H <sub>10</sub>	butane	but-
5	C <sub>5</sub> H <sub>12</sub>	pentane	pent-
6	C <sub>6</sub> H <sub>14</sub>	hexane	hex-
7	C <sub>7</sub> H <sub>16</sub>	heptane	hept-
8	C <sub>8</sub> H <sub>18</sub>	octane	oct-
9	C <sub>9</sub> H <sub>20</sub>	nonane	non-
10	C <sub>10</sub> H <sub>22</sub>	decane	dec-

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**Exam Tip**

Although the table shows up to 10 carbons for reference, in your IB Chemistry exam you are only required to name molecules with up to 6 carbons

## Chains & Branches

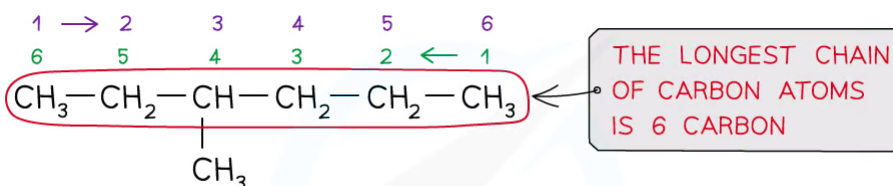
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- If there are any side-chains or functional groups present, then the position of these groups are indicated by numbering the carbon atoms in the longest chain starting at the end that gives the lowest possible numbers in the name
- The hydrocarbon **side-chain** is shown in **brackets** in the structural formula



- The side-chain is named by adding '-yl' to the normal alkane **stem**
- This type of group is called an **alkyl** group



COUNTING FROM RIGHT TO LEFT GIVES: 4-METHYL HEXANE

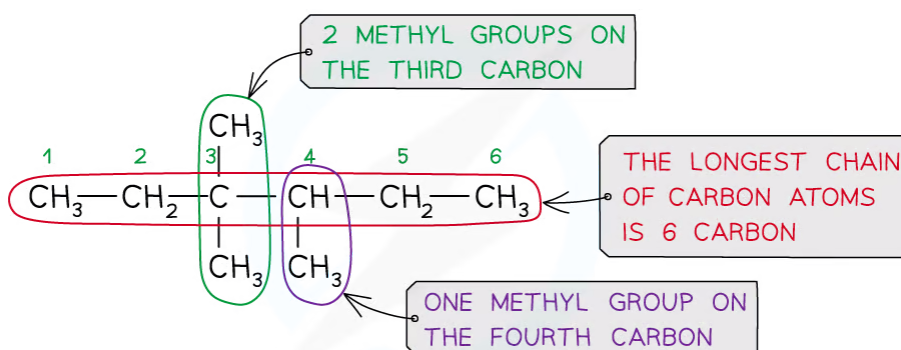
COUNTING FROM LEFT TO RIGHT GIVES: 3-METHYL HEXANE

THE NOMENCLATURE GIVES THE LOWEST POSSIBLE NUMBER IN THE NAME

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### Naming Side Chains

- If there are more than one of the same alkyl side-chain or functional groups, **di-** (for two), **tri-** (for three) or **tetra-** (for four) is added in front of its name
- The adjacent **numbers** have a comma between them
- Numbers** are separated from **words** by a hyphen

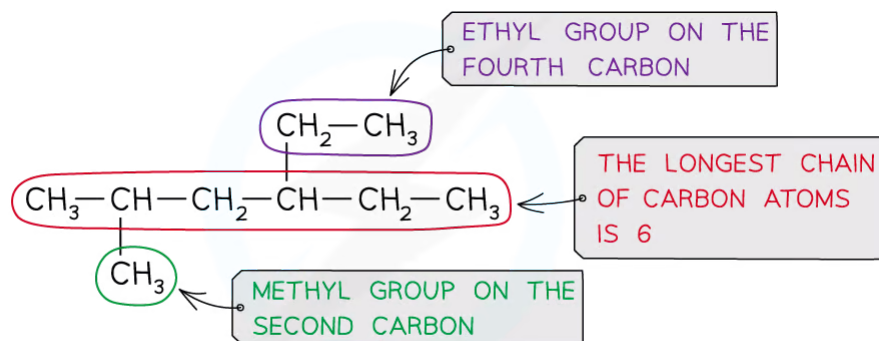


3, 3, 4 - TRIMETHYL HEXANE

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### Naming Multiple Side Chains

- If there is more than one type of alkyl side-chain, they are listed in alphabetic order



4-ETHYL-2-METHYL HEXANE

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### Naming Side Chains in Alphabetical Order



#### Exam Tip

An **aliphatic** compound is **straight** or **branched-chain** and also includes **cyclic** organic compounds that do not contain a **benzene** ring

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## 10.1.4 Organic Families - Hydrocarbons

### Alkanes

- **Hydrocarbons** are compounds containing hydrogen and carbon only
- There are four families of hydrocarbons you should know: **alkanes**, **alkenes**, **alkynes** and **arenes**
- **Alkanes** have the general molecular formula  $C_nH_{2n+2}$ . They contain only single bonds and are said to be saturated
- **Alkanes** are named using the nomenclature rule **alk + ane**
- The **alk** depends on the number of carbons as outlined in the previous Section 10.1.2

YOUR NOTES



YOUR NOTES



Structural Formula	Name	Molecular Formula
$  \begin{array}{c}  \text{H} \\    \\  \text{H}-\text{C}-\text{H} \\    \\  \text{H}  \end{array}  $	methane	$\text{CH}_4$
$  \begin{array}{c}  \text{H} \quad \text{H} \\    \quad   \\  \text{H}-\text{C}-\text{C}-\text{H} \\    \quad   \\  \text{H} \quad \text{H}  \end{array}  $	ethane	$\text{C}_2\text{H}_6$
$  \begin{array}{c}  \text{H} \quad \text{H} \quad \text{H} \\    \quad   \quad   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\    \quad   \quad   \\  \text{H} \quad \text{H} \quad \text{H}  \end{array}  $	propane	$\text{C}_3\text{H}_8$
$  \begin{array}{c}  \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\    \quad   \quad   \quad   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\    \quad   \quad   \quad   \\  \text{H} \quad \text{H} \quad \text{H} \quad \text{H}  \end{array}  $	butane	$\text{C}_4\text{H}_{10}$
$  \begin{array}{c}  \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\    \quad   \quad   \quad   \quad   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\    \quad   \quad   \quad   \quad   \\  \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H}  \end{array}  $	pentane	$\text{C}_5\text{H}_{12}$
$  \begin{array}{c}  \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\    \quad   \quad   \quad   \quad   \quad   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\    \quad   \quad   \quad   \quad   \quad   \\  \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H}  \end{array}  $	hexane	$\text{C}_6\text{H}_{14}$

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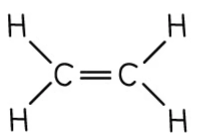
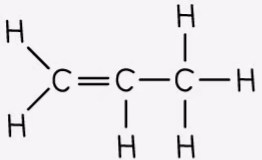
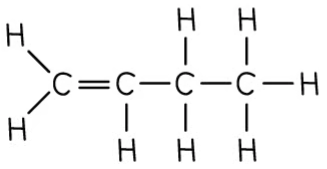
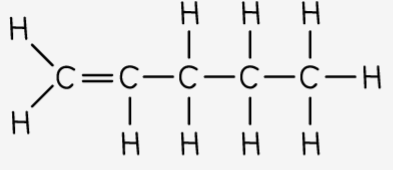
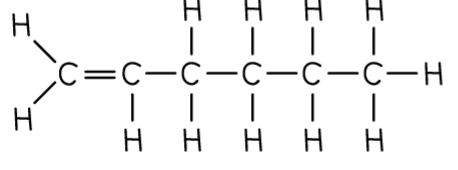
***The first six members of the alkane family***

## Alkenes

- **Alkenes** have the general molecular formula  $C_nH_{2n}$
- They are said to be **unsaturated**
- Alkenes are named using the nomenclature rule **alk + ene**
- In molecules with a straight chain of 4 or more carbon atoms, the position of the  $C=C$  double bond must be specified
- The carbon atoms on the straight chain must be numbered, starting with the end closest to the double bond
- The lowest-numbered carbon atom participating in the double bond is indicated just before the -ene:

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Structural Formula	Name	Molecular Formula
	ethene	$C_2H_4$
	propene	$C_3H_6$
	but-1-ene	$C_4H_8$
	pent-1-ene	$C_5H_{10}$
	hex-1-ene	$C_6H_{12}$

*The first five members of the alkene family*

- There is a distinction to be made between the name of the **functional group** and the name of the **family**
- The name of the family is **alkene**, but the name of the functional group is **alkenyl**

YOUR NOTES





## Alkynes

- **Alkynes** have the general molecular formula  $C_nH_{2n-2}$
- The triple bond makes them **unsaturated** molecules
- **Alkynes** are named using the nomenclature rule **alk + yne**
- As with alkenes, in molecules with a straight chain of 4 or more carbon atoms, the position of the triple bond must be specified
- The carbon atoms on the straight chain must be numbered, starting with the end closest to the triple bond
- The lowest-numbered carbon atom participating in the triple bond is indicated just before the -yne:

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Structural Formula	Name	Molecular Formula
$H-C \equiv C-H$	ethyne	$C_2H_2$
$  \begin{array}{c}  H \\    \\  H-C \equiv C-C-H \\    \\  H  \end{array}  $	propyne	$C_3H_4$
$  \begin{array}{c}  H \quad H \\    \quad   \\  H-C \equiv C-C-C-H \\    \quad   \\  H \quad H  \end{array}  $ <small>Copyright © Save My Exams. All Rights Reserved</small>	but-1-yne	$C_4H_6$
$  \begin{array}{c}  H \quad H \quad H \\    \quad   \quad   \\  H-C \equiv C-C-C-C-H \\    \quad   \quad   \\  H \quad H \quad H  \end{array}  $	pent-1-yne	$C_5H_8$
$  \begin{array}{c}  H \quad H \quad H \quad H \\    \quad   \quad   \quad   \\  H-C \equiv C-C-C-C-C-H \\    \quad   \quad   \quad   \\  H \quad H \quad H \quad H  \end{array}  $ <small>Copyright © Save My Exams. All Rights Reserved</small>	hex-1-yne	$C_6H_{10}$

*The first five members of the alkyne family*

- The name of the functional group is **alkynyl**

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## Arenes

- Arene** is the collective name given to compounds with one or more rings with **pi electrons** that are **delocalised** throughout the ring(s)
- Compounds with this feature are said to be **aromatic**
- This doesn't mean they are necessarily smelly, although a lot of naturally occurring arenes do have distinctive smells!



*Arenes are present in many everyday chemicals and pharmaceuticals*

- Benzene, C<sub>6</sub>H<sub>6</sub>**, is the only **aromatic hydrocarbon** that is covered in IB Chemistry and is dealt with in Section 10.1.12
- The functional group in **benzene** is known as a **phenyl group** when attached to other molecules

## 10.1.5 Organic Families - Halogenoalkanes

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### Halogenoalkanes

- **Halogenoalkanes** or **Haloalkanes** have the general molecular formula,  $C_nH_{2n+1}X$ , where X represents a halogen
- **Haloalkanes** are named using the prefix **chloro-**, **bromo-** or **iodo-**, with the ending **-ane**
- In molecules with a straight chain of three or more carbon atoms, the position of the halogen atom must also be specified
- The carbon atoms on the straight chain must be numbered, starting with the end closest to the halogen atom
- The number of the carbon atom attached to the halogen is indicated before the prefix:

Haloalkanes Examples Table

Structural Formula	Name	Molecular Formula
$  \begin{array}{c}  \text{H} \quad \text{H} \\    \quad   \\  \text{H}-\text{C}-\text{C}-\text{Cl} \\    \quad   \\  \text{H} \quad \text{H}  \end{array}  $	chloroethane	$C_2H_5Cl$
$  \begin{array}{c}  \text{H} \quad \text{Br} \quad \text{H} \\    \quad   \quad   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\    \quad   \quad   \\  \text{H} \quad \text{H} \quad \text{H}  \end{array}  $	2-bromopropane	$C_3H_7Br$
$  \begin{array}{c}  \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\    \quad   \quad   \quad   \quad   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{I} \\    \quad   \quad   \quad   \quad   \\  \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H}  \end{array}  $	1-iodopentane	$C_5H_{11}I$
$  \begin{array}{c}  \text{H} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad \text{H} \\    \quad   \quad   \quad   \quad   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\    \quad   \quad   \quad   \quad   \\  \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H}  \end{array}  $	3-chloropentane	$C_5H_{11}Cl$

- The position of all halogens in dihaloalkanes except those with one carbon atom must be specified.
- If there is more than one of the same type of halogen atom on the molecule, the di (two), tri (three) or tetra (four) prefixes must also be used

## Dihaloalkanes Examples Table

YOUR NOTES



Structural Formula	Name	Molecular Formula
$  \begin{array}{c}  \text{H} \quad \text{H} \\    \quad   \\  \text{H}-\text{C}-\text{C}-\text{Cl} \\    \quad   \\  \text{H} \quad \text{Cl}  \end{array}  $	1,1-dichloroethane	$\text{C}_2\text{H}_4\text{Cl}_2$
$  \begin{array}{c}  \text{H} \quad \text{H} \\    \quad   \\  \text{H}-\text{C}-\text{C}-\text{Cl} \\    \quad   \\  \text{Cl} \quad \text{H}  \end{array}  $	1,2-dichloroethane	$\text{C}_2\text{H}_4\text{Cl}_2$
$  \begin{array}{c}  \text{H} \quad \text{H} \quad \text{H} \\    \quad   \quad   \\  \text{Br}-\text{C}-\text{C}-\text{C}-\text{H} \\    \quad   \quad   \\  \text{H} \quad \text{Cl} \quad \text{H}  \end{array}  $	1-bromo-2-chloropropane	$\text{C}_3\text{H}_6\text{BrCl}$

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## 10.1.6 Organic Families – Alcohols &amp; Ethers

YOUR NOTES


**Alcohols & Ethers**
**Alcohols**

- **Alcohols** are a family of molecules that contain the **hydroxyl functional group**, **-OH**
- Their general formula is  **$C_nH_{2n+1}OH$**
- The nomenclature of alcohols follows the pattern **alkan + ol**
- If there are two **-OH** groups present the molecule is called a **diol**

**The first four Alcohols and their Structures Table**

ALCOHOL	STRUCTURAL FORMULA	DISPLAYED FORMULA
METHANOL	$CH_3OH$	$  \begin{array}{c}  H \\    \\  H-C-O-H \\    \\  H  \end{array}  $
ETHANOL	$CH_3CH_2OH$	$  \begin{array}{c}  H \quad H \\    \quad   \\  H-C-C-O-H \\    \quad   \\  H \quad H  \end{array}  $
PROPANOL	$CH_3CH_2CH_2OH$	$  \begin{array}{c}  H \quad H \quad H \\    \quad   \quad   \\  H-C-C-C-O-H \\    \quad   \quad   \\  H \quad H \quad H  \end{array}  $
BUTANOL	$CH_3CH_2CH_2CH_2OH$	$  \begin{array}{c}  H \quad H \quad H \quad H \\    \quad   \quad   \quad   \\  H-C-C-C-C-O-H \\    \quad   \quad   \quad   \\  H \quad H \quad H \quad H  \end{array}  $

**Classification of alcohols**

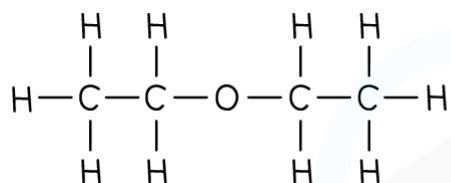
- Alcohols are classified as **primary**, **secondary** or **tertiary** depending on the number of carbons attached to the **functional group** carbon
- This is covered in detail in Section 10.1.11

**Ethers**

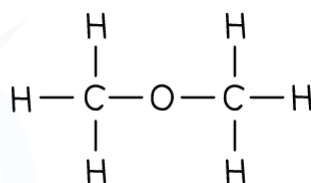
- **Ethers** are a family of molecules that contain the **ether functional group**, **R-O-R**, where **R** is an **alkyl group**
- Their general formula is  **$C_nH_{2n+2}O$**
- The nomenclature of ether follows the pattern **alkoxy + alkane**
- Sometimes you will see an older nomenclature for **ethers** where each **R** group is given an **alkyl** name

◦ For Example:  $\text{CH}_3\text{OCH}_3$  is dimethyl ether and  $\text{C}_2\text{H}_5\text{OCH}_3$  is ethyl methyl ether

- Ethers are functional group isomers of alcohols



ETHOXYETHANE IS COMMON ETHER AND IS A COLOURLESS, SWEET-SMELLING HIGHLY FLAMMABLE LIQUID



METHOXYMETHANE IS A COLOURLESS GAS AND IS USED AS AN AEROSOL PROPELLANT

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**Ethers are useful substances**

YOUR NOTES



## 10.1.7 Organic Families - Carbonyls

### Carbonyls

- **Carbonyl** is the collective name for compounds containing the functional group **C=O**
- The general formula of a carbonyl is **C<sub>n</sub>H<sub>2n</sub>O**
- The two sub-families of **carbonyls** are **aldehyde** and **ketone** (known in some countries as alkanals and alkanones)

### Aldehydes

- If the carbonyl group is on the end of a chain then it is an **aldehyde** and has the functional group formula, **RCHO**
  - the H is written before the O so as not to confuse it with an alcohol
- The nomenclature of **carbonyls** follows the pattern **alkan + al**
- There is no need to use numbers in the name as aldehyde will always be on the number 1 carbon atom

### Ketones

- **Ketones** have a minimum of three carbons and have the general functional group formula, **RCOR**
- The nomenclature of **ketones** follows the pattern **alkan + one**
- After butanone, the **carbonyl** group can have **positional isomers**, so numbering must be used
  - For example pentan-2-one and pentan-3-one

### Aldehyde and Ketone Examples Table

YOUR NOTES



YOUR NOTES



Structural Formula	Name	Molecular Formula
$\begin{array}{c} \text{O} \\    \\ \text{H}-\text{C}-\text{H} \end{array}$	methanal (also known as formaldehyde)	$\text{CH}_2\text{O}$
$\begin{array}{c} \text{H} \quad \text{O} \\   \quad    \\ \text{H}-\text{C}-\text{C}-\text{H} \\   \\ \text{H} \end{array}$	ethanal	$\text{C}_2\text{H}_4\text{O}$
$\begin{array}{c} \text{H} \quad \text{H} \quad \text{O} \\   \quad   \quad    \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$	propanal	$\text{C}_3\text{H}_6\text{O}$
$\begin{array}{c} \text{H} \quad \text{O} \quad \text{H} \\   \quad    \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\   \quad \quad   \\ \text{H} \quad \quad \text{H} \end{array}$	propanone (also known as acetone)	$\text{C}_3\text{H}_6\text{O}$
$\begin{array}{c} \text{H} \quad \text{O} \quad \text{H} \quad \text{H} \quad \text{H} \\   \quad    \quad   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	pentan-2-one	$\text{C}_5\text{H}_{10}\text{O}$

- As they have a very similar functional group arrangement, **aldehydes** and **ketones** show similar chemical reactions
- Differences in their chemistry are due to the reactions that involve the H on the **aldehyde** or the nature of the R group
- The difference in **electronegativity** between oxygen and carbon means the  $\text{C}=\text{O}$  is polar, leading to dipole-dipole attractions between the molecules which results in:
  - higher than expected boiling points for small molecules
  - solubility in water for the lower members of the families
- Aldehydes** and **ketones** with the same number of carbons are **functional group isomers**



## 10.1.8 Organic Families - Carboxylic Acids &amp; Esters

YOUR NOTES


**Carboxylic Acids & Esters**
**Carboxylic acids**

- **Carboxylic acids** is the name given to compounds containing the functional group **carboxyl, -COOH**
- The general formula of a carboxylic acid is  $C_nH_{2n+1}COOH$  which can be shortened to just **RCOOH**
  - (In some countries the family is called alkanonic acid)
- The nomenclature of **carboxylic acid** follows the pattern **alkan + oic acid**
- There is no need to use numbers in the name as the carboxyl group will always be on the number 1 carbon atom

**Carboxylic Acids Examples Table**

Structural Formula	Name	Molecular Formula
$\begin{array}{c} \text{O} \\    \\ \text{H}-\text{C}-\text{O}-\text{H} \end{array}$	methanoic acid (also known as formic acid)	$\text{HCO}_2\text{H}$
$\begin{array}{c} \text{H} \quad \text{O} \\   \quad    \\ \text{H}-\text{C}-\text{C}-\text{O}-\text{H} \\   \\ \text{H} \end{array}$	ethanoic acid (also known as acetic acid)	$\text{CH}_3\text{CO}_2\text{H}$
$\begin{array}{c} \text{H} \quad \text{H} \quad \text{O} \\   \quad   \quad    \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{O}-\text{H} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$	propanoic acid	$\text{C}_2\text{H}_5\text{CO}_2\text{H}$

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**Esters**

- **Esters** are **functional group isomers** of **carboxylic acids** and contain the functional group, **carboxylate, -COOR**
- The general formula of an ester is usually represented as **RCOOR** where **R** can be the same or different on either side of the carboxylate group
- The nomenclature of **esters** follows the pattern **alkyl + alkanoate**
- The alkyl group in the name is the **R** group attached to the oxygen

**Esters Examples Table**

YOUR NOTES



Structural Formula	Name	Molecular Formula
$  \begin{array}{c}  \text{O} \\  \parallel \\  \text{H}-\text{C}-\text{O}-\text{C}-\text{H} \\    \\  \text{H}  \end{array}  $	methyl methanoate	$\text{HCO}_2\text{CH}_3$
$  \begin{array}{c}  \text{H} \quad \text{O} \quad \text{H} \\    \quad \parallel \quad   \\  \text{H}-\text{C}-\text{C}-\text{O}-\text{C}-\text{H} \\    \quad \quad   \\  \text{H} \quad \quad \text{H}  \end{array}  $	methyl ethanoate	$\text{CH}_3\text{CO}_2\text{CH}_3$
$  \begin{array}{c}  \text{H} \quad \text{O} \quad \text{H} \quad \text{H} \\    \quad \parallel \quad   \quad   \\  \text{H}-\text{C}-\text{C}-\text{O}-\text{C}-\text{C}-\text{H} \\    \quad \quad   \quad   \\  \text{H} \quad \quad \text{H} \quad \text{H}  \end{array}  $	ethyl ethanoate	$\text{C}_2\text{H}_5\text{CO}_2\text{C}_2\text{H}_5$

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- **Carboxylic acids** and **esters** contain few similarities in their chemical and physical properties
- **H-bonds** are present between **carboxylic acid** molecules and not between **esters**, so this affects the melting point, boiling point and solubility:
  - Smaller chain **carboxylic acids** are soluble in water and have higher boiling points than expected (e.g. ethanoic acid is  $117^\circ\text{C}$ )
  - **Esters** are insoluble in water and have lower boiling points than their isomeric carboxylic acids (e.g. methyl methanoate is  $31^\circ\text{C}$ )



### Exam Tip

The C in RCOOR is included in the name of the first R group, so  $\text{C}_3\text{H}_7\text{COOCH}_3$  is methyl butanoate not methyl propanoate. Don't be fooled by the order of the atoms in the linear formula:  $\text{CH}_3\text{OC(O)C}_3\text{H}_7$  is also an acceptable way to write the formula of methyl butanoate!

## 10.1.9 Organic Families – Organic Nitrogen Compounds

YOUR NOTES


**Organic Nitrogen Compounds**
**Amines**

- There are three organic nitrogen families that you need to know: **amines**, **amides** and **nitriles**
- **Amine** is the name given to compounds containing the functional group **amino**,  $-\text{NH}_2$
- **Amines** are derived from ammonia where one H in ammonia ( $\text{NH}_3$ ) has been replaced by an R (alkyl) group
- The general formula of an amine is  $\text{C}_n\text{H}_{2n+1}\text{NH}_2$  which can be shortened to just  $\text{RNH}_2$

**Amides**

- **Amide** is the name given to compounds containing the functional group **carboxamide**,  $-\text{CONH}_2$
- **Amides** are a combination of **amino** and **carbonyl** groups
- The general formula of an **amide** is  $\text{C}_n\text{H}_{2n+1}\text{CONH}_2$  which can be shortened to just  $\text{RCONH}_2$

**Nitriles**

- **Nitriles** are compounds containing the functional group **nitrile**,  $-\text{CN}$
- This is the same **CN** group that is called a **cyanide** group as an ion, just as hydroxyl group, **OH** is called **hydroxide** in inorganic chemistry
- The general formula of an **nitrile** is  $\text{C}_n\text{H}_{2n+1}\text{CN}$  which can be shortened to just  $\text{RCN}$

**Organic Nitrogen Compounds Examples**

Structural Formula	Name	Molecular Formula
$  \begin{array}{c}  \text{H} \\    \\  \text{H}-\text{C}-\ddot{\text{N}}-\text{H} \\    \quad   \\  \text{H} \quad \text{H}  \end{array}  $	methylamine or aminomethane	$\text{CH}_3\text{NH}_2$
$  \begin{array}{c}  \text{H} \quad \text{O} \\    \quad    \\  \text{H}-\text{C}-\text{C}-\ddot{\text{N}}-\text{H} \\    \quad   \\  \text{H} \quad \text{H}  \end{array}  $	ethanamide	$\text{CH}_3\text{CONH}_2$
$  \begin{array}{c}  \text{H} \\    \\  \text{H}-\text{C}-\text{C}\equiv\ddot{\text{N}} \\    \\  \text{H}  \end{array}  $	ethanenitrile	$\text{CH}_3\text{CN}$

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### Exam Tip

Be careful about counting all the carbons when naming a nitrile. For example  $\text{C}_3\text{H}_7\text{CN}$  is butanenitrile not propanenitrile as the longest chain is 4 carbons.

You are not required to know the nomenclature of these nitrogen compounds, but you are expected to identify the functional groups in molecules.

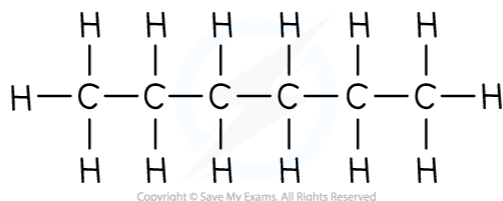
YOUR NOTES





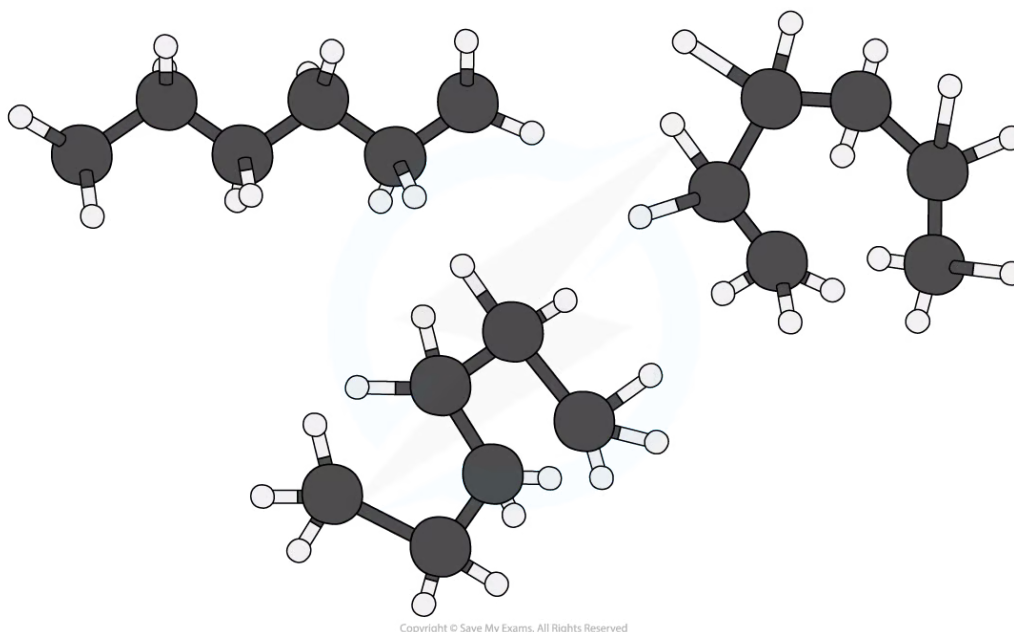
### 3-D Modelling

- Representing **3-D** molecules on a **2D** surface is not easy and the best way to understand **3-D** structures is to use modelling kits or **3-D** modelling software, such as ACD Labs ChemSketch
- For simplification, complex organic molecules are shown with  $90^\circ$  bond angles that give the minimum information of which atoms are connected together as in this representation of hexane,  $C_6H_{14}$



#### *A simplified displayed structure for hexane*

- The true structure of hexane looks very different when viewed in 3-D modelling software
- Free rotation of the single bonds gives rise to structures that look different on paper:

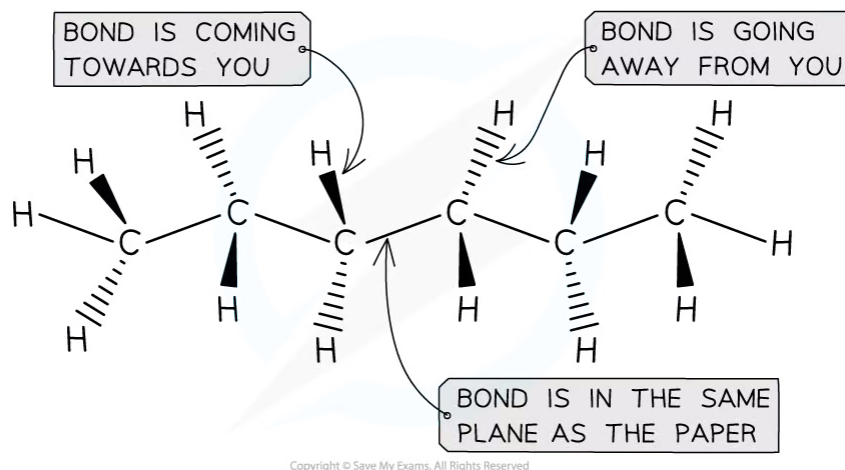


#### *Different 3-D structures for hexane*

- By convention, when showing using 3-D models or drawings, carbon is black, hydrogen is white and oxygen is red
- These structures may not contain accurate **atomic radii**, **bond angles** or **bond lengths** (modelling software usually allows you to manipulate these), but they convey information about the orientation of atoms that is very important in **stereochemistry**
- **Stereochemistry** is the study of the relative spatial arrangements of atoms in molecules

## Stereochemical drawings

- To simplify 3-D drawings, chemists use a convention of drawing 'wedge' bonds to show bonds coming out of the plane of the paper or receding away from the plane
  - A single solid line indicates the bond is in the same plane as the paper
  - The solid wedge shows the bond is coming towards you and the hatched or partial wedge bond is going away from you
- The stereochemical drawing for hexane is shown below:



### A stereochemical drawing for hexane

- Stereochemical drawings are particularly useful for representing isomers and complex biomolecules such as carbohydrates and proteins



#### Exam Tip

You are not expected to be able to draw 3-D molecules, but in an exam you may be presented with 3-D drawings from which you have to extract information such as the molecular formula or functional group

YOUR NOTES



## 10.1.11 Primary, Secondary &amp; Tertiary atoms

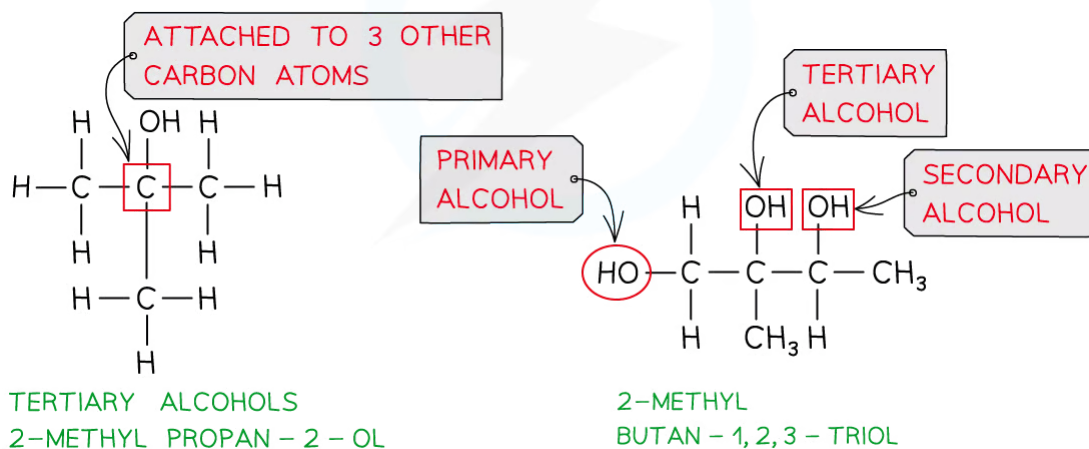
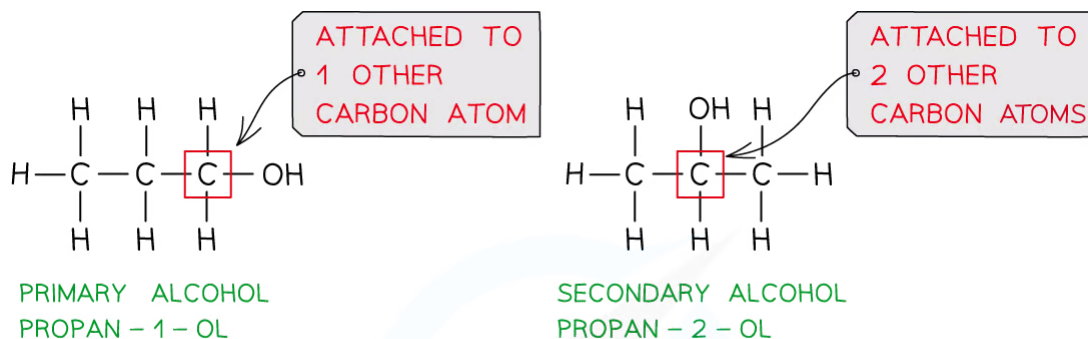
YOUR NOTES



## Primary, Secondary & Tertiary Atoms

### Alcohols and halogenoalkanes

- **Primary alcohols** and **halogenoalkanes** are those in which the carbon atom bonded to the functional group is attached to **one** other carbon atom (or alkyl group)
- In **secondary alcohols** and **halogenoalkanes** the functional group carbon atom is attached to **two** other carbon atoms (or alkyl groups)
- In **tertiary alcohols** and **halogenoalkanes** the functional group carbon atom is attached to **three** other carbon atoms (or alkyl groups)



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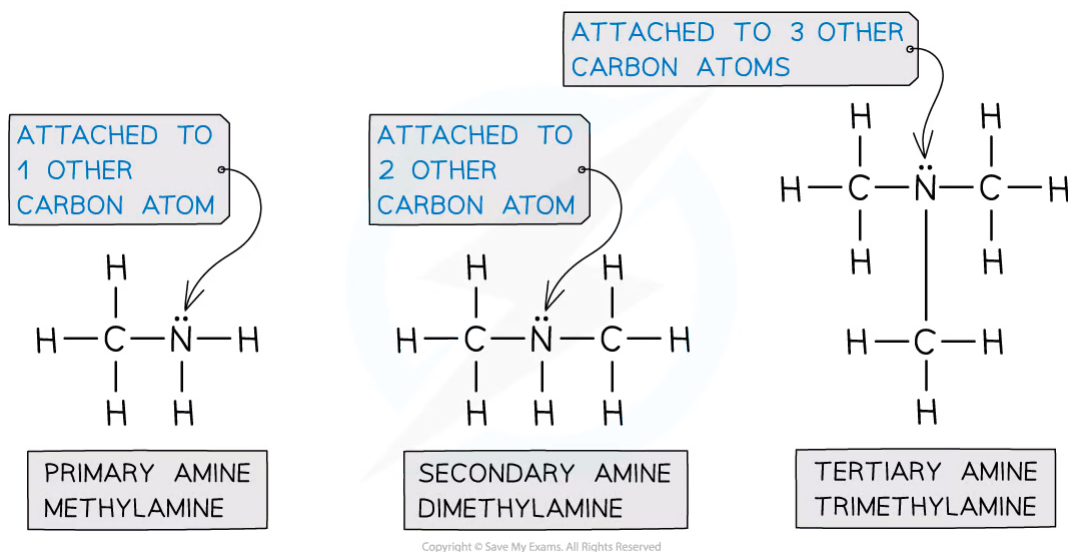
### Classifying primary, secondary and tertiary alcohols and alcohols with more than one alcohol group

### Amines

- **Amines** follow a slightly different classification system, although the terms **primary**, **secondary** and **tertiary** are still used
- The classification is based on the number of alkyl groups attached to the nitrogen in the **amine**
- **Primary amines** are those in which the nitrogen is attached to **one** other carbon atom (or alkyl group)

- In **secondary amines** the nitrogen atom is attached to **two** other carbon atoms (or alkyl groups)
- In **tertiary amines** the nitrogen is attached to **three** other carbon atoms (or alkyl groups)

YOUR NOTES



**Primary, secondary and tertiary Amines**





## Benzene

### Kekulé structure for benzene

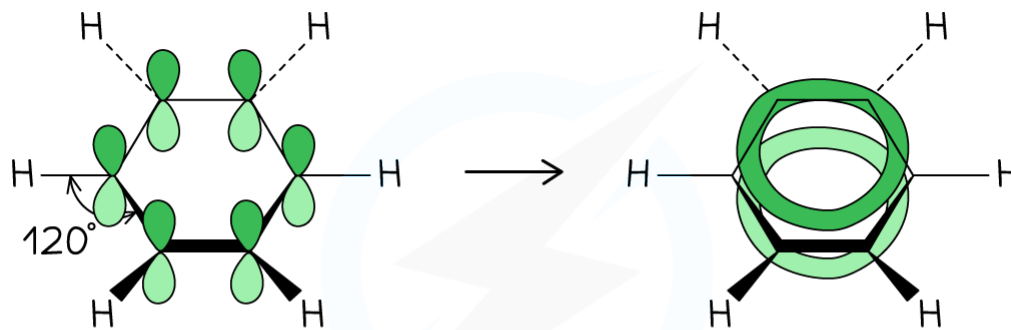
- Kekulé suggested that benzene was a **hexagon** with three double bonds
- It was therefore equivalent to three **ethene molecules**

### Problems with Kekulé's structure for benzene

- Since benzene has three double bonds, it should have similar reactivity to **ethene**
- However, this turned out not to be the case
  - Ethene undergoes **addition reactions** whereas **benzene** rarely does (only under very harsh conditions) and instead undergoes **substitution reactions**
- The presence of three double bonds also suggested that benzene had **shorter double** and **longer single** bonds
  - In fact, the bond lengths in benzene were **exactly** the same
  - They were found to be an **intermediate** between single and double bonds
- The benzene is also much more **stable** than Kekulé's suggested structure for benzene
  - Less energy was required to **hydrogenate** a benzene molecule compared to the hydrogenation of **three ethene** molecules
  - This means that the bonds broken in benzene are stronger than the double bonds in ethene
- The increase in stability of benzene is known as the **delocalisation energy** and is caused by the **delocalised electrons** in the benzene structure
- The C-C in benzene are an intermediate between single and double bonds which is a result of these **delocalised electrons**

### Shape of benzene

- Benzene is a **planar regular hexagon** with bond angles of **120°**
  - All the bonds are identical due to the delocalization of electrons
- Each  $sp^2$  hybridised carbon atom in benzene forms:
  - A  $\sigma$  bond with two other carbons
  - A  $\sigma$  bond with one hydrogen atom
- The remaining p orbital is **overlapping** with the p orbitals on both sides of it
  - To achieve maximum overlap, the benzene ring must be planar
- This results in the formation of a system of  $\pi$  bonds spread out over the whole ring
- Due to this, the electrons are not bound to specific atoms but can instead freely move around the structure and are said to be **delocalised**



OVERLAP OF P ORBITALS PRODUCES A RING OF DELOCALISED ELECTRONS ABOVE AND BELOW THE PLANE OF BENZENE'S CARBON ATOMS

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**Benzene has a  $\pi$  system of delocalised electrons with carbon atoms that have bond angles of  $120^\circ$**

## 10.2 Functional Group Chemistry

### 10.2.1 Alkanes - Combustion

YOUR NOTES



## Unreactive Alkanes

### Strength of C-H bonds

- Alkanes consist of carbon and hydrogen atoms which are bonded together by **single bonds**
- Unless a lot of heat is supplied, it is difficult to break these **strong** C-C and C-H covalent bonds
- This decreases the reactivity of alkanes in chemical reactions

### Lack of polarity

- The **electronegativities** of the carbon and hydrogen atoms in alkanes are almost the same
- This means that both atoms share the electrons in the covalent bond almost equally

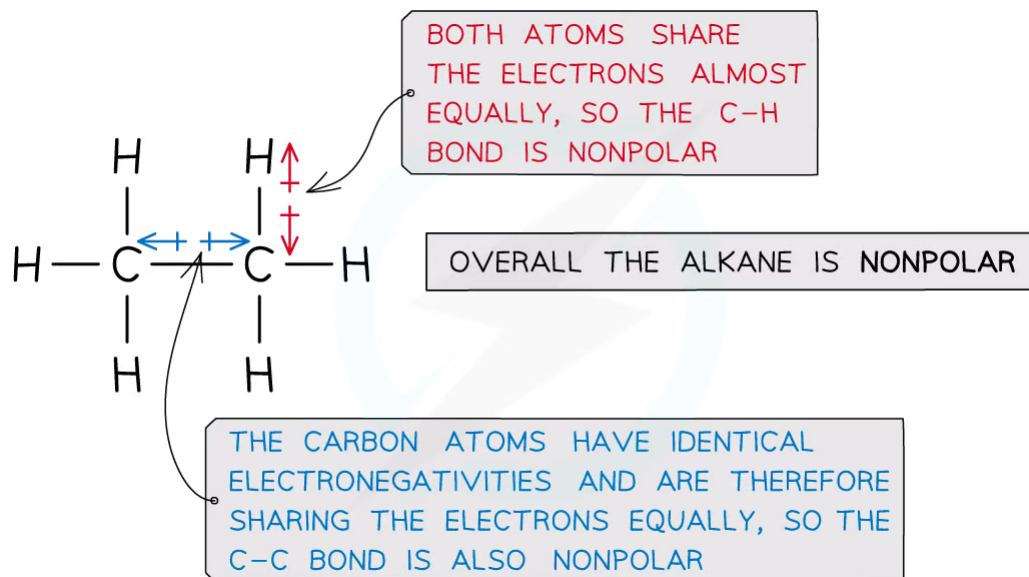
#### PAULING ELECTRONEGATIVITY VALUES FOR THE ELEMENTS

H 2.1																			He -
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0		Ne -	
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.2	S 2.5	Cl 3.0		Ar -	
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 3.0		
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe 2.6		
Cs 0.7	Ba 0.9	La-Lu 1.1-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn -		
Fr 0.7	Ra 0.9	Ac-No 1.1-1.7																	

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**The Pauling Scale shows that the difference in electronegativity between carbon and hydrogen is only 0.4**

- As a result of this, alkanes are **nonpolar** molecules and have no partial positive or negative charges ( $\delta^+$  and  $\delta^-$  respectively)
- Alkanes therefore do not react with **polar reagents**
  - They have no electron-deficient areas to attract **nucleophiles**
  - And also lack electron-rich areas to attract **electrophiles**



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**Ethane is an example of an alkane that lacks polarity due to almost similar electronegativities of the carbon and hydrogen atoms**

- Due to the unreactivity of alkanes, they only react in combustion reactions and undergo substitution by halogens



### Exam Tip

Remember: nucleophiles are negatively charged and are attracted to electron-deficient regions. Electrophiles are positively charged and attracted to electron-rich regions.

YOUR NOTES





## Combustion of Alkanes

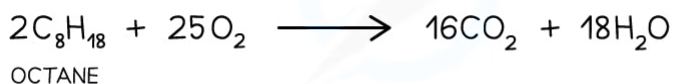
- Alkanes are **combusted** (burnt) on a large scale for their use as fuels
- They also react in **free-radical substitution** reactions to form more reactive halogenoalkanes

### Complete combustion

- When alkanes are burnt in **excess** (plenty of) oxygen, **complete combustion** will take place and all carbon and hydrogen will be oxidised to **carbon dioxide** and **water** respectively
  - For example, the complete combustion of octane to carbon dioxide and water

COMPLETE COMBUSTION

ALKANE + OXYGEN  $\xrightarrow{\hspace{2cm}}$  CARBON DIOXIDE + WATER



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#### *The complete combustion of alkanes*

### Incomplete combustion

- When alkanes are burnt in only a **limited supply** of oxygen, **incomplete combustion** will take place and not all the carbon is fully oxidised
- Some carbon is only **partially** oxidised to form **carbon monoxide**
  - For example, the incomplete combustion of octane to form carbon monoxide

INCOMPLETE COMBUSTION

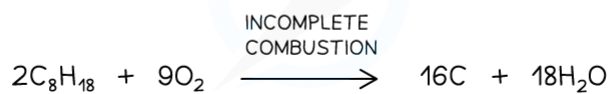
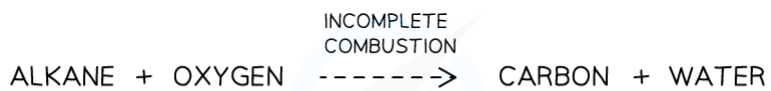
ALKANE + OXYGEN  $\xrightarrow{\hspace{2cm}}$  CARBON MONOXIDE + WATER



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#### *The incomplete combustion of alkanes*

- Carbon monoxide is a **toxic** gas as it will bind to haemoglobin in blood which can then no longer bind **oxygen**
- As no oxygen can be transported around the body, victims will feel **dizzy**, **lose consciousness** and if not removed from the carbon monoxide, they can **die**
- Carbon monoxide is extremely dangerous as it is **odourless** (it doesn't smell) and will not be noticed
- Incomplete combustion often takes place inside a **car engine** due to a limited amount of oxygen present
- With a reduced supply of oxygen, **carbon** will be produced in the form of soot:



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### ***The incomplete combustion of alkanes (2)***



#### **Exam Tip**

Incomplete combustion of alkanes never produces hydrogen as it is always preferentially oxidised in any available oxygen, rather than carbon

YOUR NOTES



10.2.2 Alkanes - Halogenation

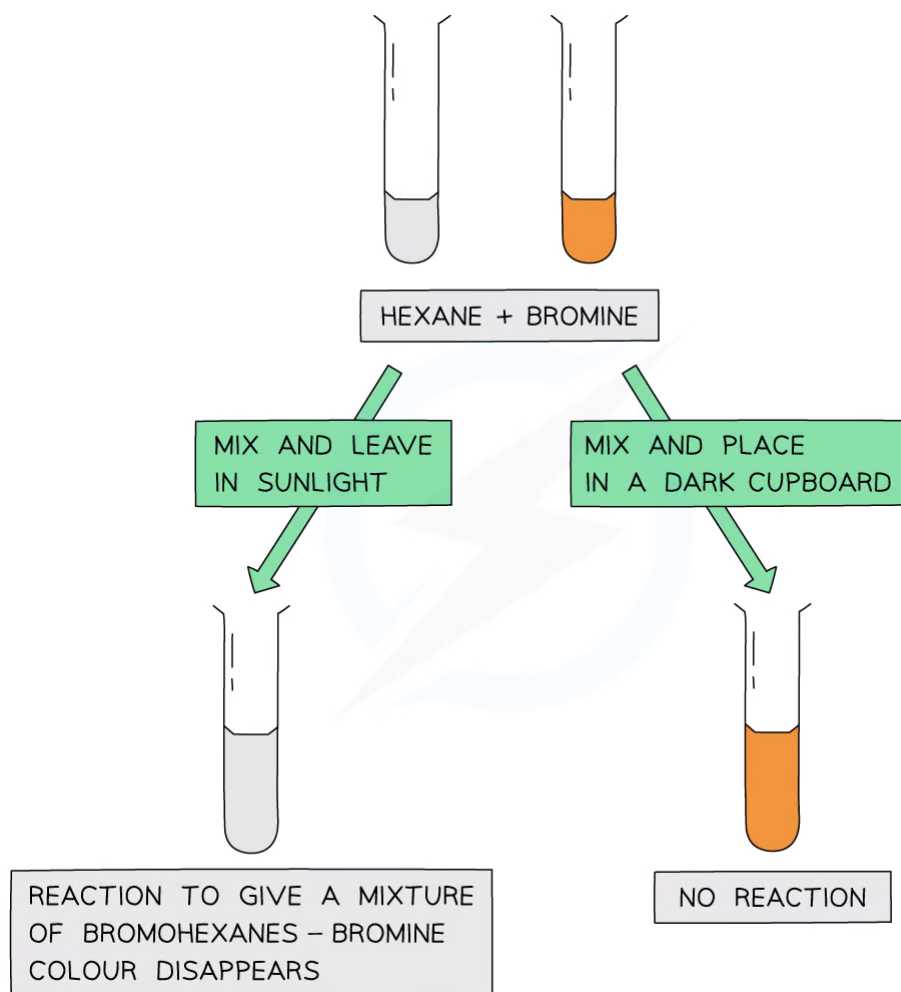
YOUR NOTES



### Halogenation of Alkanes

#### Free-radical substitution of alkanes

- Alkanes can undergo **free-radical substitution** in which a hydrogen atom gets **substituted** by a halogen (chlorine/bromine)
- Since alkanes are very unreactive, **ultraviolet light (sunlight)** is needed for this substitution reaction to occur
- The free-radical substitution reaction consists of three steps:
  - In the **initiation step**, the halogen bond (Cl-Cl or Br-Br) is broken by UV energy to form two radicals
  - These radicals create further radicals in a chain type reaction called the **propagation step**
  - The reaction is terminated when two radicals collide with each other in a **termination step**



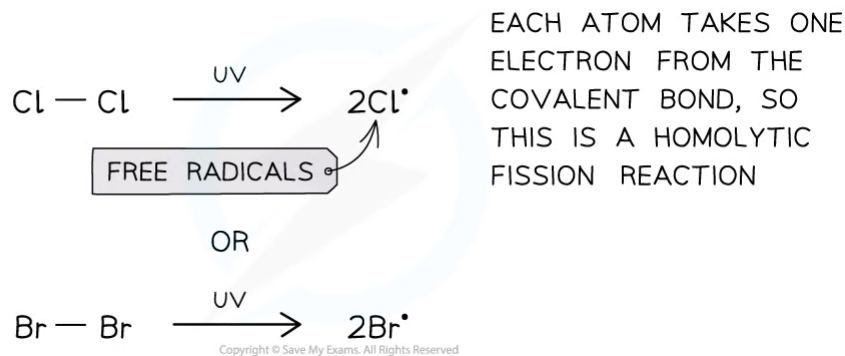
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**The fact that the bromine colour has disappeared only when mixed with an alkane and placed in sunlight suggests that the ultraviolet light is essential for the free radical substitution reaction to take place**

### Initiation step

- In the **initiation step** the Cl-Cl or Br-Br is broken by energy from the UV light
- This produces two radicals in a **homolytic fission** reaction

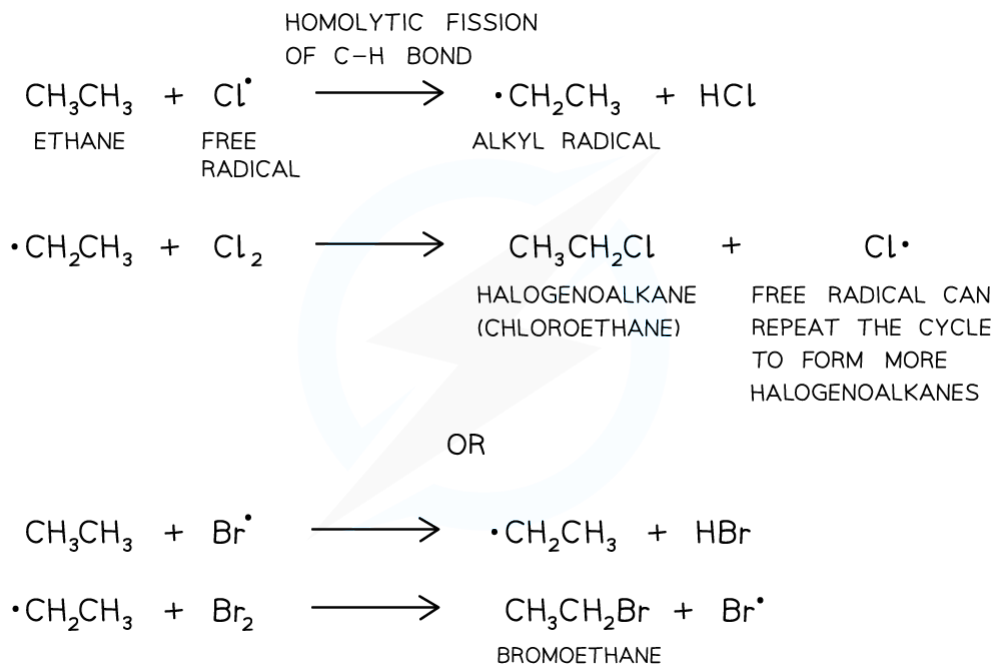


**The first step of the free-radical substitution reaction is the initiation step in which two free radicals are formed by sunlight**

### Propagation step

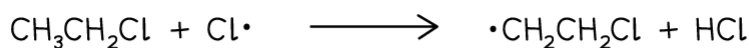
- The **propagation step** refers to the **progression** (growing) of the substitution reaction in a **chain type reaction**
  - **Free radicals** are very reactive and will attack the unreactive alkanes
  - A C-H bond breaks **homolytically** (each atom gets an electron from the covalent bond)
  - An **alkyl** free radical is produced
  - This can attack another chlorine/bromine molecule to form the **halogenoalkane** and **regenerate** the chlorine/bromine free radical
  - This free radical can then **repeat** the cycle



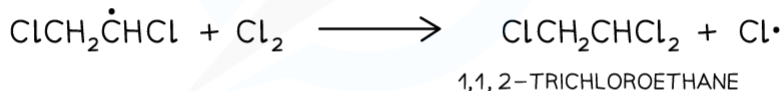
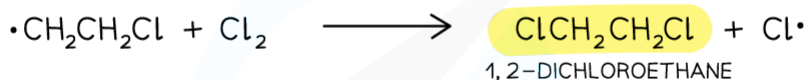


**The second step of the free-radical substitution reaction is the propagation step in which the reaction grows in a chain type reaction**

- This reaction is not very suitable for preparing specific halogenoalkanes as a **mixture** of substitution products are formed
- If there is enough chlorine/bromine present, all the hydrogens in the alkane will eventually get substituted (eg. ethane will become C<sub>2</sub>Cl<sub>6</sub>/C<sub>2</sub>Br<sub>6</sub>)



THIS CAN BE FOLLOWED BY:



THE SAME PROCESS CAN TAKE PLACE WITH BROMINE INSTEAD OF CHLORINE. THE REACTION WILL CARRY ON TO EVENTUALLY FORM C<sub>2</sub>Cl<sub>6</sub>

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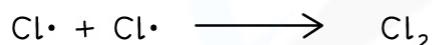
**The free-radical substitution reaction gives a variety of products and not a pure halogenoalkane**

YOUR NOTES



### Termination step

- The **termination step** is when the chain reaction **terminates** (stops) due to two free radicals reacting together and forming a single unreactive molecule
  - Multiple products are possible



THE SAME PROCESS CAN TAKE PLACE WITH BROMINE INSTEAD OF CHLORINE

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**The final step in the substitution reaction to form a single unreactive molecule**



#### Exam Tip

Make sure you practice and are able to write out these equations, especially the **propagation** steps which students frequently get wrong. It is quite common for students to incorrectly show a hydrogen radical produced in propagation, which does not happen:



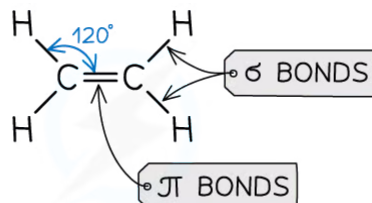
Do not fall into this trap!

## 10.2.3 Alkenes - Reactivity

YOUR NOTES


**Reactivity of Alkenes**

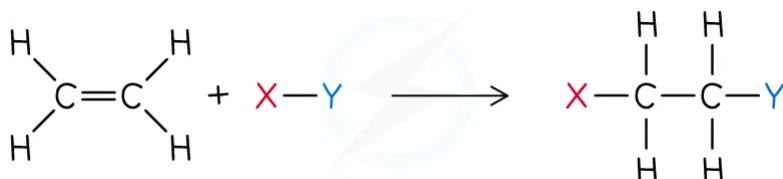
- **Alkenes** are **hydrocarbons** containing a carbon-carbon double bond
- The atoms around the carbon-carbon double bond adopt a **planar arrangement** and the bond angle is  $120^\circ$



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**The bonding arrangement around a carbon-carbon double bond**

- The presence of the **C=C** bond gives **alkenes** a number of chemical properties that are not seen in **alkanes**
- Since the **alkene** contains **π-bonds**, it is possible to break the weaker **π-bond** and form stronger **σ-bonds** with other species without forcing any atoms on the molecule to break off
- As a result **alkenes** (unlike **alkanes**) are capable of undergoing **addition reactions**



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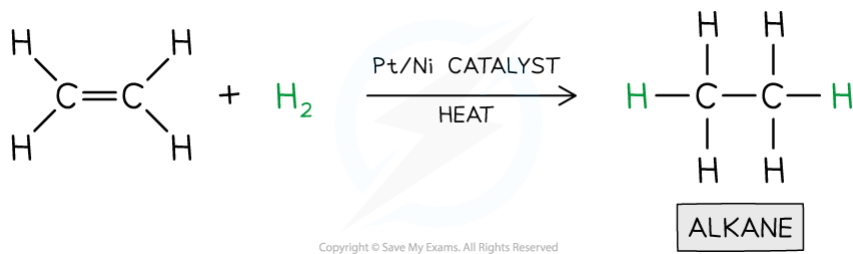
**Addition reactions in alkenes**

- Molecules which contain **π-bonds** and which can hence undergo **addition** are said to be **unsaturated**
- Molecules which do not contain **π-bonds** and which hence cannot undergo **addition** are said to be **saturated**.
- **Alkenes** are **unsaturated** and can hence undergo **addition**
- **Addition** is the combination of two or more molecules to form a single molecule
- **Addition reactions** are generally faster than **substitution reactions** since only weak **π-bonds** are broken, rather than stronger **σ-bonds**
- The ability of **alkenes** to undergo **addition** means that they are much **more reactive** than **alkanes**

## 10.2.4 Alkenes - Hydrogenation

### Hydrogenation of Alkenes

- **Alkenes** are very useful compounds as they can undergo many types of reactions
- They can therefore be used as starting molecules when making new compounds
- The reaction between an **alkene** and hydrogen is known as **hydrogenation** or **reduction**
- As well as a **nickel catalyst**, this requires a temperature of 200 °C and a pressure of 1000 kPa



**Catalytic hydrogenation converts alkenes into useful alkanes**

- One important application of this reaction is in the production of margarine from vegetable oils
- Vegetable oils are **unsaturated** and may be **hydrogenated** to make margarine, which has a higher melting point due to stronger **London Dispersion Forces**
- By controlling the conditions it is possible to restrict how many of the C=C bonds are broken and produce **partially hydrogenated vegetable oils** which have which have the desired properties and textures for margarine manufacture

YOUR NOTES



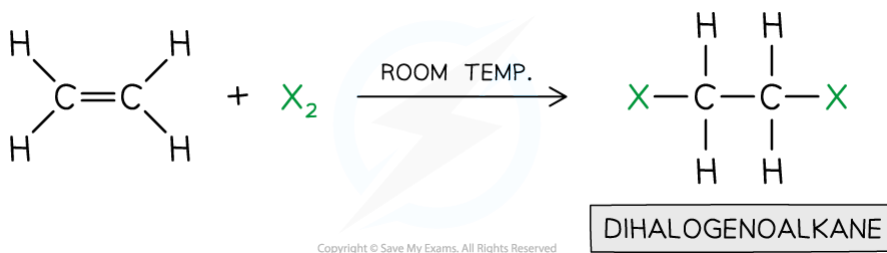
## 10.2.5 Alkenes - Halogenation

YOUR NOTES



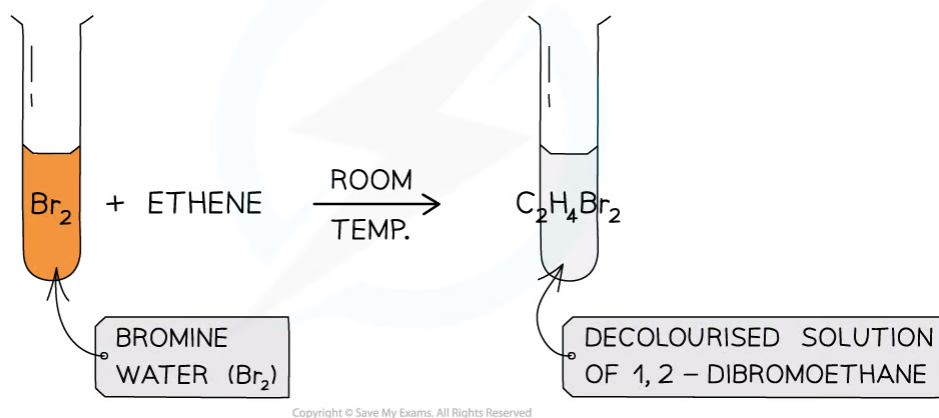
### Halogenation of Alkenes

- The reaction between **alkenes** and halogens is known as **halogenation**
- It is an example of an **electrophilic addition** where an electrophile ('electron seeker') joins onto to a double bond
- The C=C double bond is broken, and a new single bond is formed from each of the two carbon atoms
- The result of this reaction is a **dihaloalkane**
- The reaction occurs readily at room temperature and is the basis for the test for **unsaturation** in molecules



#### Halogenation in alkenes

- Halogens can be used to test if a molecule is **unsaturated** (i.e. contain a double bond)
- Br<sub>2</sub> is an orange or yellow solution, called **bromine water**
- The unknown compound is **shaken** with the bromine water
- If the compound is unsaturated, an addition reaction will take place and the coloured solution will decolourise



**The bromine water test is the standard test for unsaturation in alkenes**

**Exam Tip**

The mechanism of this reaction is part of Higher Level Chemistry and is covered in Section 20

YOUR NOTES



## 10.2.6 Alkenes - Hydrohalogenation

YOUR NOTES



### Hydrohalogenation of Alkenes

- Alkenes will react readily with **hydrogen halides** such as **HCl** and **HBr** to produce **halogenoalkanes**
- This reaction is known as **hydrohalogenation**
- It is also an **electrophilic addition** reaction that occurs quickly at room temperature



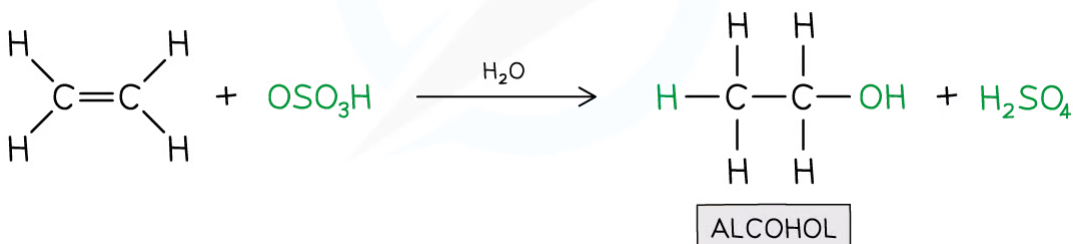
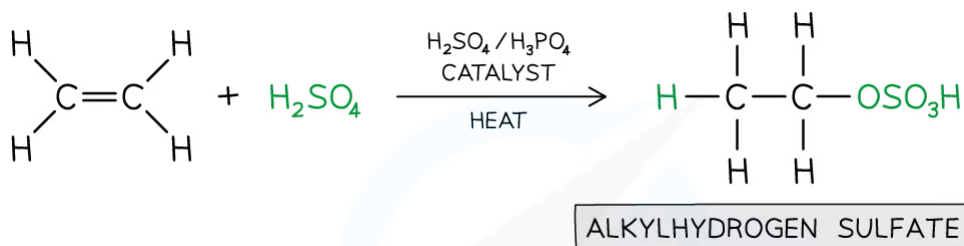
#### Hydrohalogenation reactions in alkenes

- All the **hydrogen halides** react in this way, but the **fastest reaction** occurs in the order **HI > HBr > HCl** due to the increasing bond strength of the hydrogen-halogen bond, so the weakest bond reacts most easily
- The mechanism of this reaction is part of Higher Level Chemistry and is covered in Section 20

## 10.2.7 Alkenes - Hydration

### Hydration of Alkenes

- When alkenes are treated with steam at **300 °C**, a pressure of **60 atmospheres** and **sulfuric acid (H<sub>2</sub>SO<sub>4</sub>)** or **phosphoric acid (H<sub>3</sub>PO<sub>4</sub>)** catalyst, the water is added across the double bond in a reaction known as **hydration**
- An **alkene** is converted into an **alcohol**
- The reaction processes via an intermediate in which H<sup>+</sup> and HSO<sub>4</sub><sup>-</sup> ions are added across the **double bond**
- The intermediate is quickly hydrolysed by water, reforming the sulfuric acid



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#### Hydration in Alkenes

- This is a very important industrial reaction for producing large quantities of ethanol, a widely used solvent and fuel
- The process is much faster and higher yielding than producing ethanol by **fermentation**

YOUR NOTES





10.2.8 Addition Polymers

YOUR NOTES

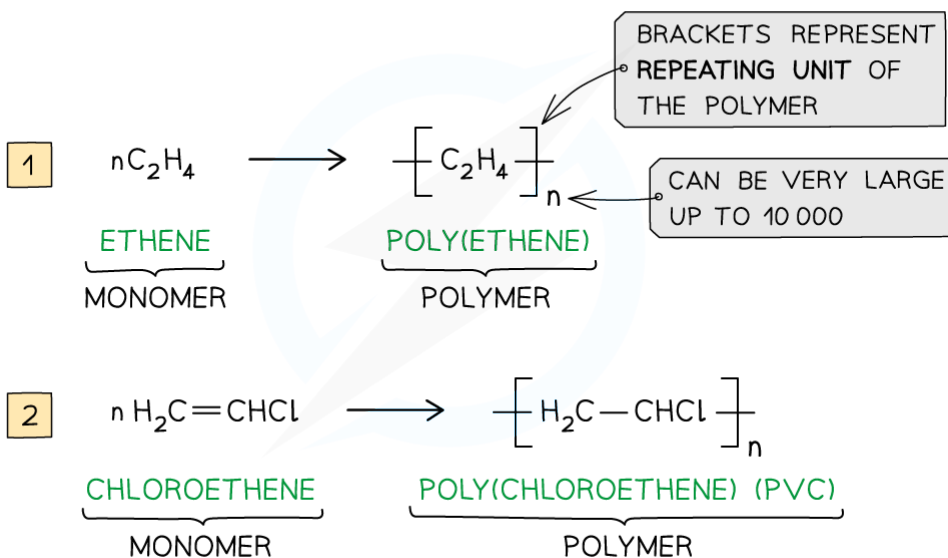


Polymers

Addition polymerisation

- **Addition polymerisation** is one of the most important addition reactions of alkenes which form the basis of the plastic industry
- Addition polymerisation is the reaction in which many **monomers** containing at least one C=C double bond form long chains of **polymers** as the only product
  - Just like in other addition reactions of alkenes, the π-bond in each C=C bond breaks and then the monomers link together to form new C-C single bonds
- A **polymer** is a long-chain molecule that is made up of many repeating units
- The small, reactive molecules that react together to form the polymer are called **monomers**
- A polymerisation reaction can be represented by a **general formula** or by using **displayed formulae**
  - E.g. poly(ethene) and poly(chloroethene) (also known as **PVC**) are polymers made up of the ethene and chloroethene monomers respectively and are commonly used in making plastics

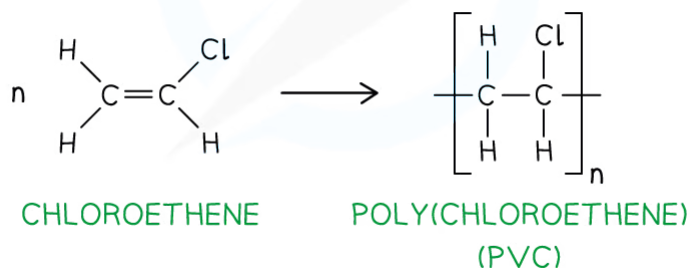
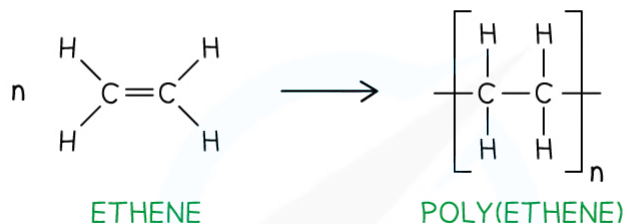
GENERAL FORMULA ADDITION POLYMERISATION



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The general formulae of the addition polymerisation of ethene (1) and chloroethene (2)

## DISPLAYED FORMULAE ADDITION POLYMERISATION



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**The addition polymerisation of ethene (1) and chloroethene (2)**

- Just like any other **addition** reaction of alkenes, addition polymerisation gives only **one** product

**Deducing repeat units**

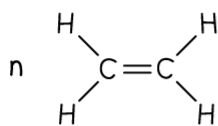
- A **repeat unit** is the smallest group of atoms that when connected one after the other make up the polymer chain
  - It is represented by **square brackets** in the displayed and general formula
- In **poly(alkenes)** (such as poly(ethene)) and **substituted poly(alkenes)** (such as PVC) made of **one type of monomer** the repeating unit is the same as the monomer except that the C=C double bond is changed to a C-C single bond

YOUR NOTES

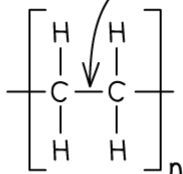




1



ETHENE  
MONOMER

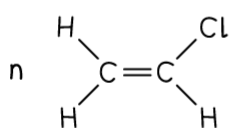


POLY(ETHENE)  
REPEATING UNIT  
OF POLYMER

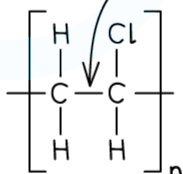
DOUBLE BOND HAS  
CHANGED INTO A  
SINGLE BOND

MONOMER AND REPEATING  
UNIT ARE THE SAME

2



CHLOROETHENE  
MONOMER



POLY(CHLOROETHENE)  
REPEATING UNIT  
OF POLYMER

DOUBLE BOND HAS  
CHANGED INTO A  
SINGLE BOND

MONOMER AND REPEATING  
UNIT ARE THE SAME

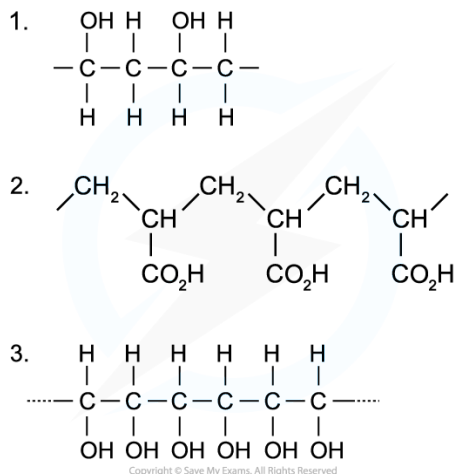
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**The repeating units of poly(ethene) and poly(chloroethene) are similar to their monomer except that the C=C bond has changed into a C-C bond**



## ? Worked Example

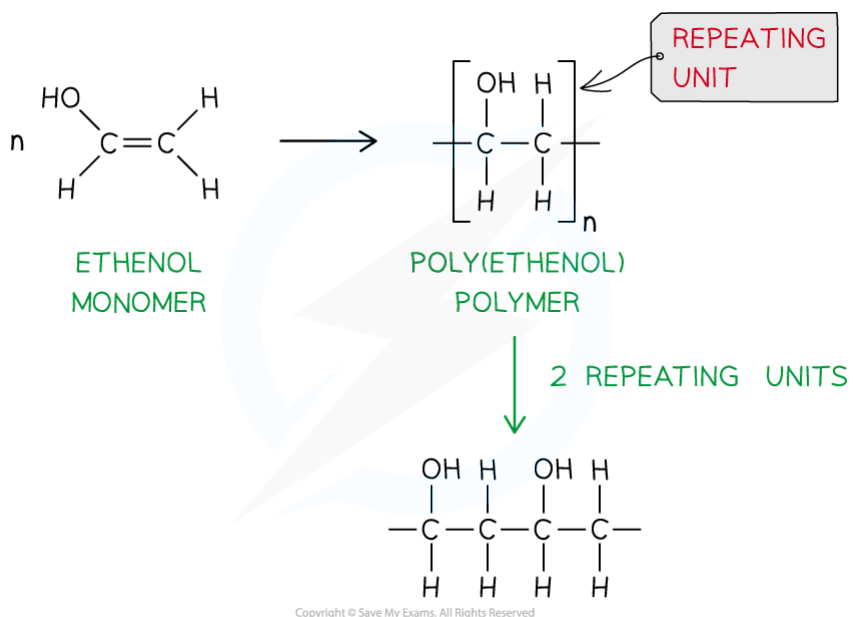
Identify the monomers present in the given sections of addition polymer molecules:



Answers:

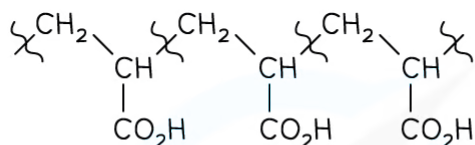
Answer 1:

When ethenol ( $\text{CH}(\text{OH})=\text{CH}_2$ ) is polymerised, the C-C double bond opens to produce a repeating unit of  $\text{CH}(\text{OH})-\text{CH}_2$ . This gives the polymer poly(ethenol)

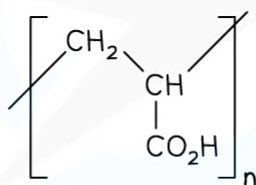


Answer 2:

- To find the monomer, first the repeating unit should be deduced. Repeating units have only 2 carbons in the polymer main chain



ONE REPEATING UNIT

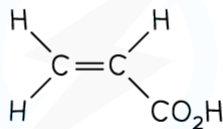


POLY(PROP-2-ENOIC ACID)

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- Since the repeating unit is now found, it can be concluded that the monomer is prop-2-enoic acid

MONOMER



PROP-2-ENOIC ACID

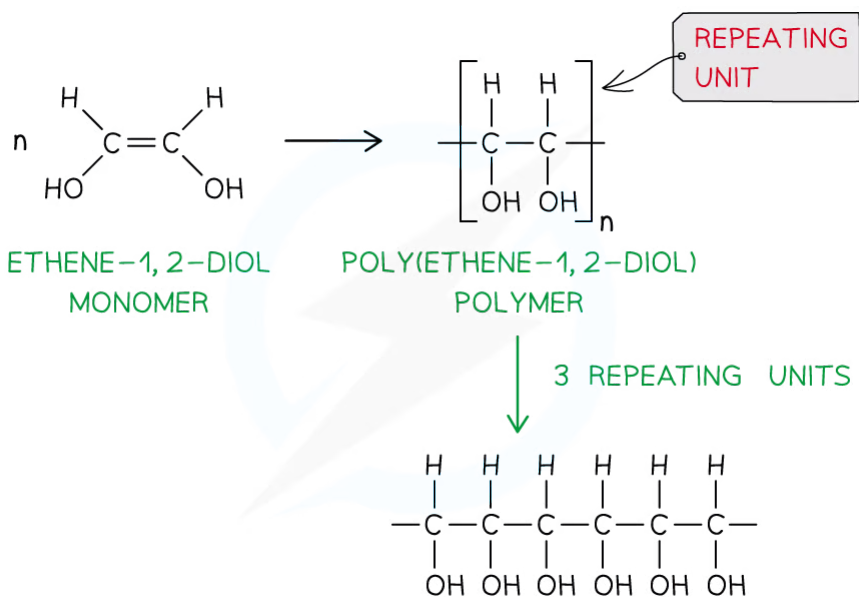
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YOUR NOTES



### Answer 3:

- Again, the repeating unit only has 2 carbons in the polymer chain which in this case are two carbon atoms that each contain one OH group
- Thus, when ethene-1,2-diol ( $\text{CH}(\text{OH})=\text{CH}(\text{OH})$ ) is polymerised, the  $\text{C}=\text{C}$  double bond opens to produce a repeating unit of  $\text{CH}(\text{OH})-\text{CH}(\text{OH})$  which gives the polymer poly(ethene-1,2-diol)



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### Exam Tip

The section of the polymer chain shown inside the square brackets by the structural or displayed formula is the **repeat unit** and **not** the monomer. The monomer is the same as the repeat unit except for that it has C=C bonds instead of C-C bonds.

YOUR NOTES



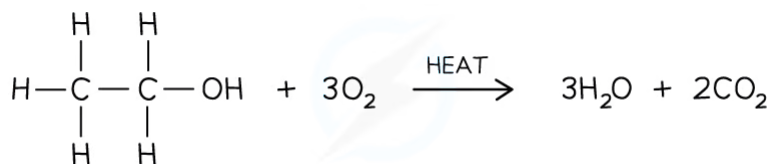
## 10.2.9 Alcohols - Combustion

YOUR NOTES


**Combustion of Alcohols**

- Alcohols react with oxygen in the air when ignited and undergo **complete combustion** to form carbon dioxide and water

**Alcohol + oxygen → carbon dioxide + water**



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**Complete combustion of alcohols to produce carbon dioxide and water**

- Lower alcohols burn with an almost invisible flame and make good fuels
- Ethanol** can be produced sustainably as a fuel by the **fermentation** of sugars
- However, the **energy density** (the amount of energy in kJ per kg of fuel) is lower than gasoline so cars that run on ethanol must either have a larger fuel tank or fill up more often
- Blending **ethanol** with gasoline or diesel increases the **energy density** and makes it safer in case of fires as it is easier to see the flames compared to pure **ethanol** burning
- However, there are socio-economic concerns about using large quantities of farm land to produce crops for fermentation, which could be better used for food production


**Exam Tip**

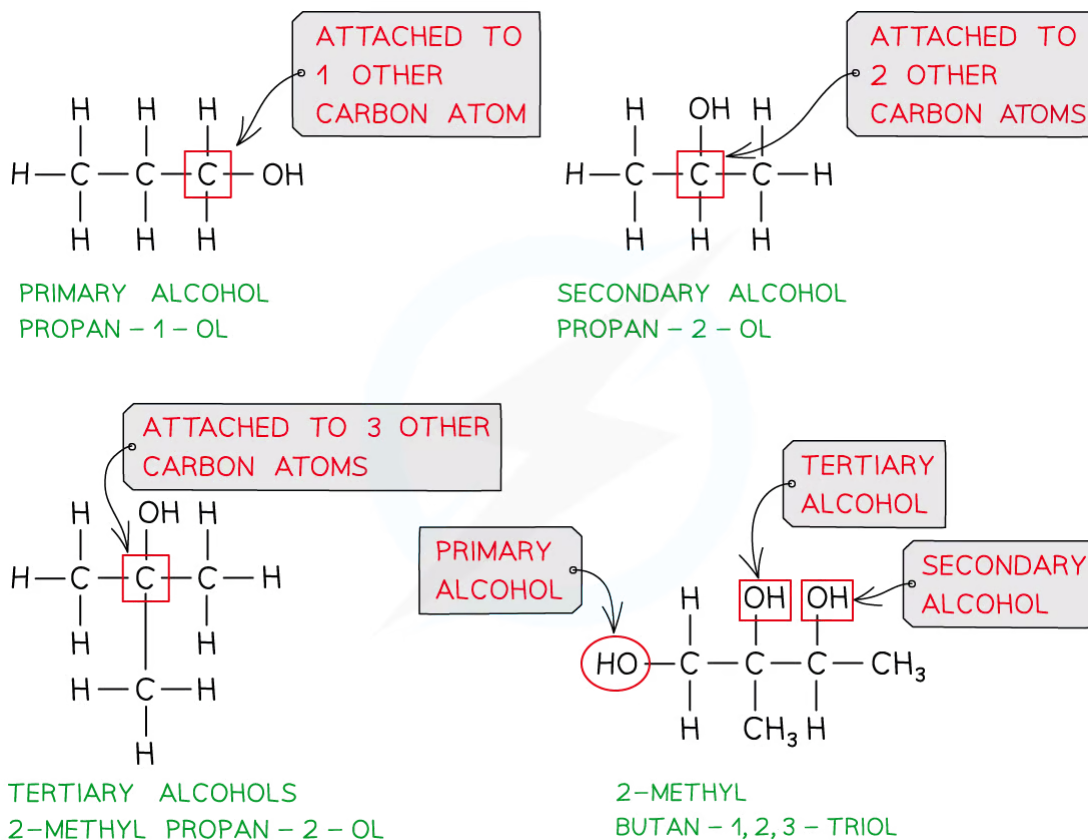
Be careful when balancing equations for the combustion of alcohols as students often forget to count the oxygen in the alcohol

## 10.2.10 Alcohols - Oxidation

YOUR NOTES


**Oxidation of Primary Alcohols**

- The products of oxidation of **alcohols** depends on the class of **alcohols**
- Here is a reminder of the three classes of alcohols:



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**The three classes of alcohols**
**Primary alcohols**

- Primary alcohols** can be oxidised to form **aldehydes** which can undergo further oxidation to form **carboxylic acids**
- The oxidising agents of alcohols include **acidified  $K_2Cr_2O_7$**  or **acidified  $KMnO_4$**
- Acidified potassium dichromate(VI)**,  $K_2Cr_2O_7$ , is an orange oxidising agent
  - Acidified means that that the potassium dichromate(VI) is in a solution of **dilute acid** (such as dilute sulfuric acid)
  - For potassium dichromate(VI) to act as an oxidising agent, it itself needs to be reduced
    - When alcohols are **oxidised** the orange dichromate ions ( $Cr_2O_7^{2-}$ ) are reduced to green  $Cr^{3+}$  ions
- Acidified potassium manganate(VII)**,  $KMnO_4$ , is a purple oxidising agent
  - As with acidified  $KMnO_4$  the potassium manganate(VII) is in an acidic medium to allow reduction of potassium manganate(VII) to take place

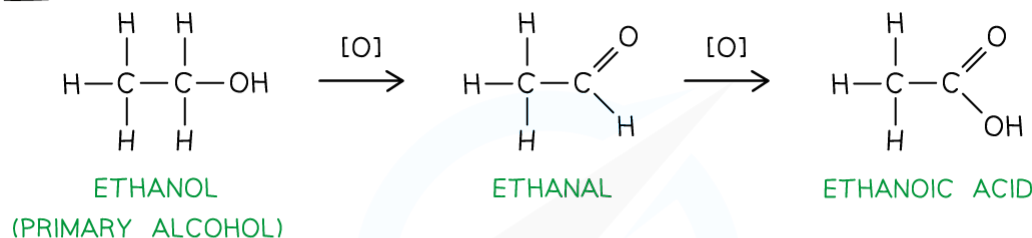


- When alcohols are **oxidised**, the purple manganate ions ( $\text{MnO}_4^-$ ) are reduced to colourless  $\text{Mn}^{2+}$  ions

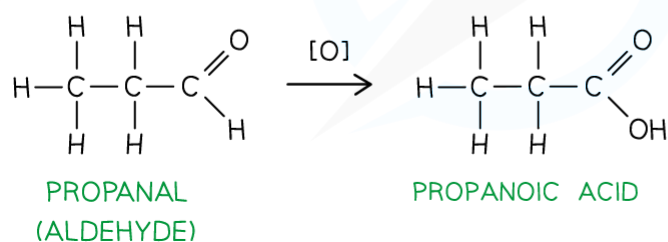
YOUR NOTES



1



2



[O] = ACIDIFIED  $\text{K}_2\text{Cr}_2\text{O}_7$   
OR  
ACIDIFIED  $\text{KMnO}_4$

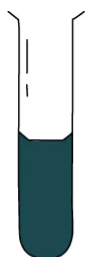
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## Further Oxidation

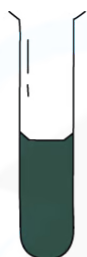
- If the **aldehyde** is not distilled off, further oxidation with **excess** oxidising agent will oxidise it to a **carboxylic acid**
- The reaction takes some time to complete and requires sustained heating

## Test for alcohols

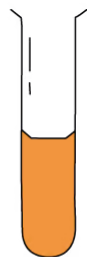
- The oxidation using **acidified dichromate** provides the basis for the test for **alcohols** as the reaction gives a strong colour change from **orange to green**
- Unfortunately, it does not work for tertiary alcohols, which cannot be oxidised



PROPAN-1-OL  
(PRIMARY ALCOHOL)



PROPAN-2-OL  
(SECONDARY ALCOHOL)



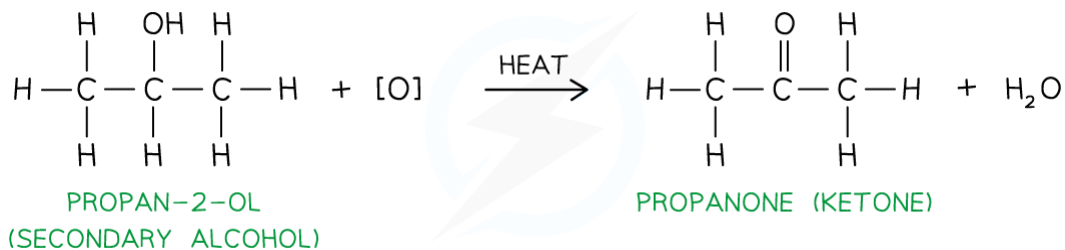
2-METHYL-PROPAN-2-OL  
(TERTIARY ALCOHOL)

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### The test for primary and secondary alcohols

## Oxidation of Secondary Alcohols

- **Secondary alcohols** can be oxidised to form **ketones** only
- To get a good yield of the **ketone** the reaction requires some sustained heating



### Oxidation of Secondary Alcohols

- **Tertiary alcohols** do not undergo oxidation
  - This is because there must be a hydrogen on the functional group carbon, which breaks off to form water
  - There are only **C-C** bonds on the functional group carbon in a **tertiary alcohol**

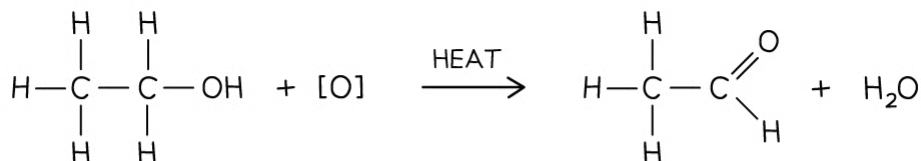
YOUR NOTES



## Distillation & Reflux

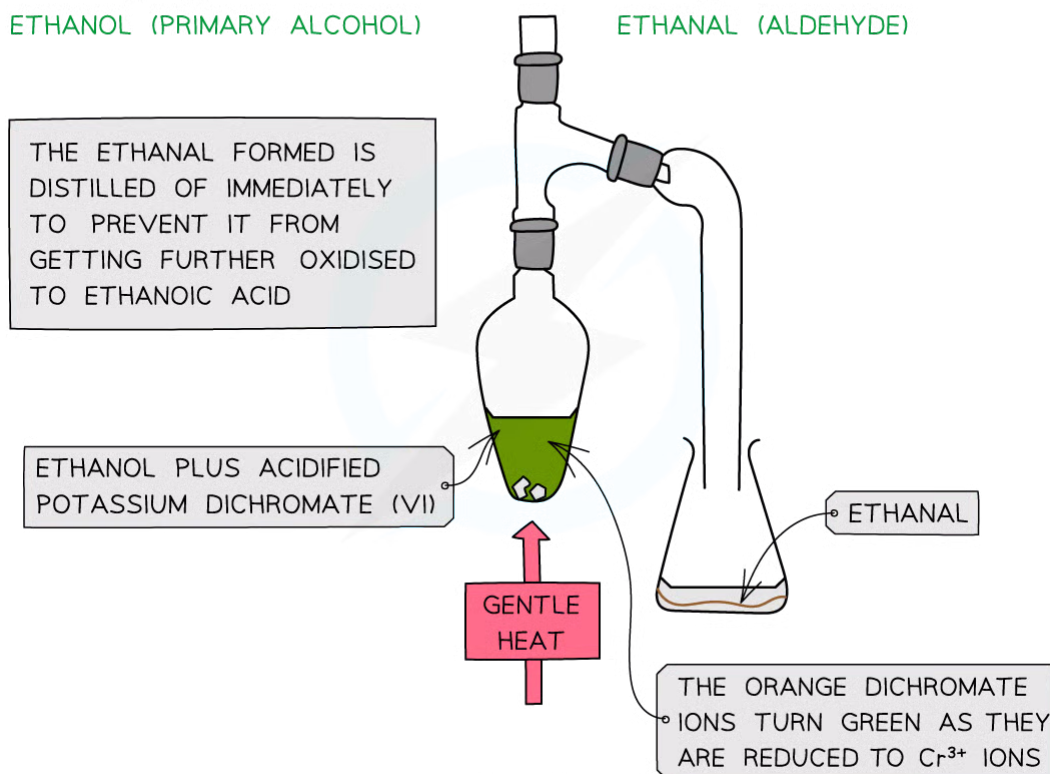
### The difference between using distillation and heating under reflux

- To produce an aldehyde from a primary alcohol the reaction mixture must be heated
- The **aldehyde** product has a lower boiling point than the **alcohol** (since it has lost the **H-bonding**) so it can be **distilled off** as soon as it forms
- Distillation** can be carried out using a simple side arm arrangement which acts as an air condenser or the vapours can be made to pass through a condenser



ETHANOL (PRIMARY ALCOHOL)

ETHANAL (ALDEHYDE)



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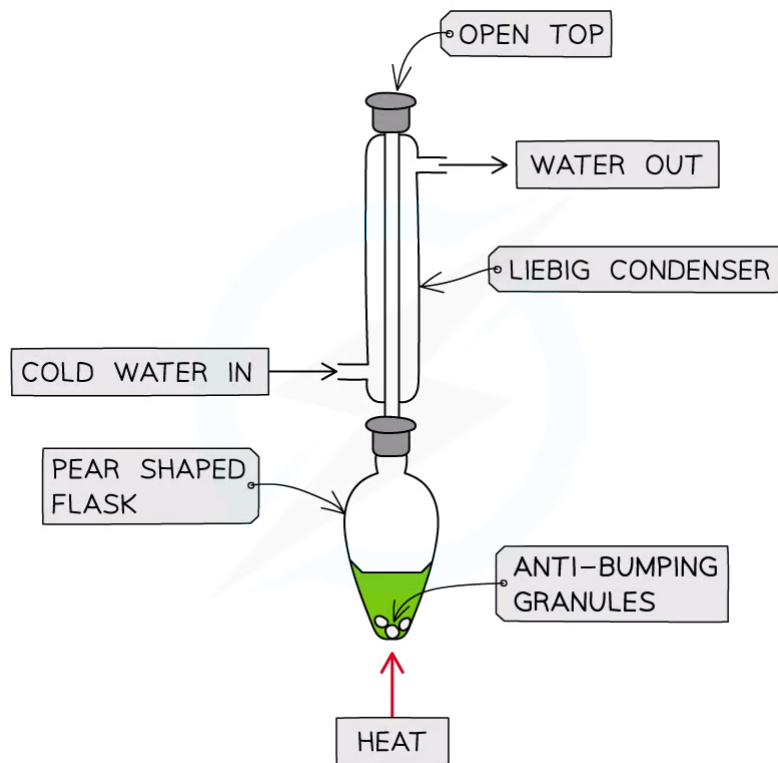
### Oxidation of ethanol by acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> to form an aldehyde by distillation

### Heating under reflux

- For reactions that require sustained heating the apparatus has to be modified
- To prevent loss of volatile reactants the apparatus includes a condenser in the vertical position which returns components back into the reaction flask
- This is known as **heating under reflux** (reflux means re-boiling)

YOUR NOTES





**Heating under Reflux Apparatus**

YOUR NOTES

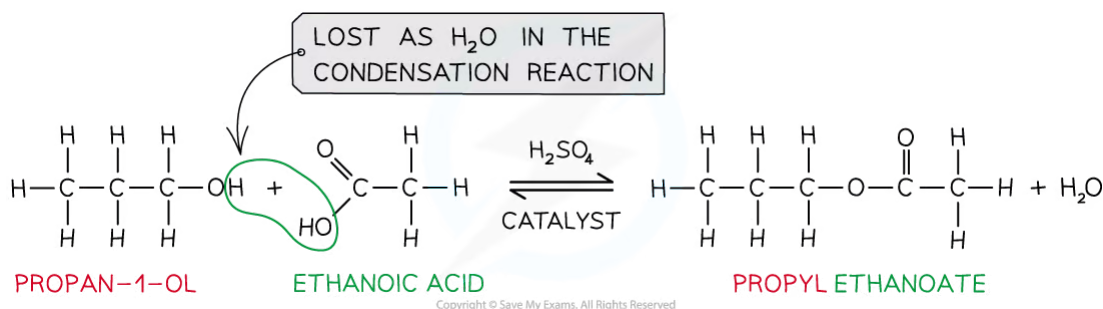


## 10.2.11 Alcohols - Esterification

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**Esterification**

- **Esters** are compounds with an  $-COOR$  functional group and are characterised by their **sweet** and **fruity** smells
- They are prepared from the **condensation** reaction between a **carboxylic acid** and **alcohol** with **concentrated  $H_2SO_4$**  as **catalyst**
  - This is also called **esterification**
- The first part of the ester's name comes from the alcohol and the second part of the name comes from the carboxylic acid
  - E.g. Propanol and ethanoic acid will give the ester propyl ethanoate



**Esters are formed from the condensation reaction between carboxylic acids and alcohols**

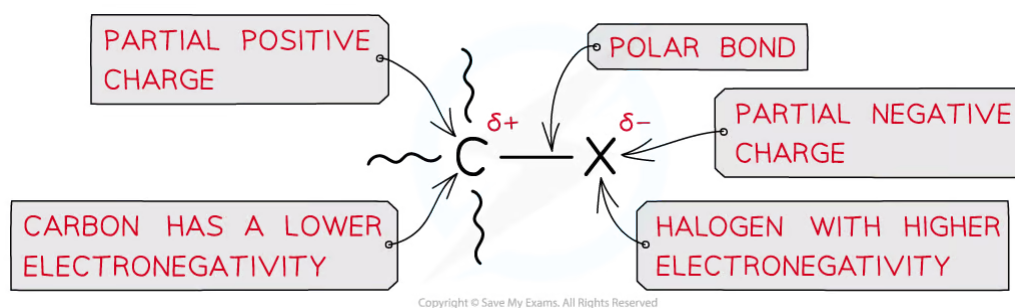

**Exam Tip**

The reaction is also classified as a **nucleophilic substitution** reaction



## Reactions of Halogenoalkanes

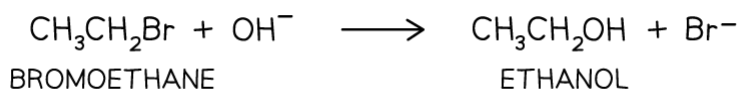
- **Halogenoalkanes** are much more reactive than alkanes due to the presence of the **electronegative** halogens
  - The halogen-carbon bond is polar causing the carbon to carry a partial positive and the halogen a partial negative charge
- A **nucleophilic substitution** reaction is one in which a **nucleophile** attacks a carbon atom which carries a **partial positive charge**
- An atom that has a **partial negative charge** is replaced by the nucleophile



**Due to large differences in electronegativity between the carbon and halogen atom, the C-X bond is polar**

### Reaction with NaOH

- The reaction of a halogenoalkane with **aqueous alkali** results in the formation of an alcohol
- The halogen is **replaced** by the OH<sup>-</sup>
- The **aqueous hydroxide** (OH<sup>-</sup> ion) behaves as a **nucleophile** by donating a pair of electrons to the carbon atom bonded to the halogen
- Hence, this reaction is a **nucleophilic substitution**
  - For example, bromoethane reacts with aqueous alkali when heated to form ethanol



**The halogen is replaced by a nucleophile, OH<sup>-</sup>**

- The reaction is slow at room temperature so to ensure a high yield it is **heated under reflux**
- Since haloalkanes are not usually soluble in water, a polar solvent such as ethanol is often used as it will dissolve haloalkanes as well as sodium hydroxide

## 10.2.13 Reactions of Benzene

YOUR NOTES

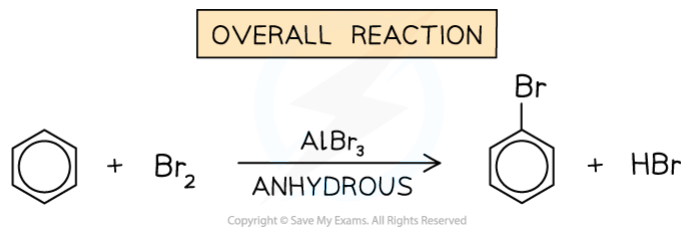


### Reactions of Benzene

- **Arenes** are very stable compounds due to the **delocalisation of  $\pi$  electrons** in the ring
  - This is because the electron density is spread out over the molecule instead of being confined to a small area
- During chemical reactions such as **substitution reactions**, this delocalised ring is maintained
- **Addition reactions** however, **disrupt** the **aromatic stabilisation** so they are not favoured

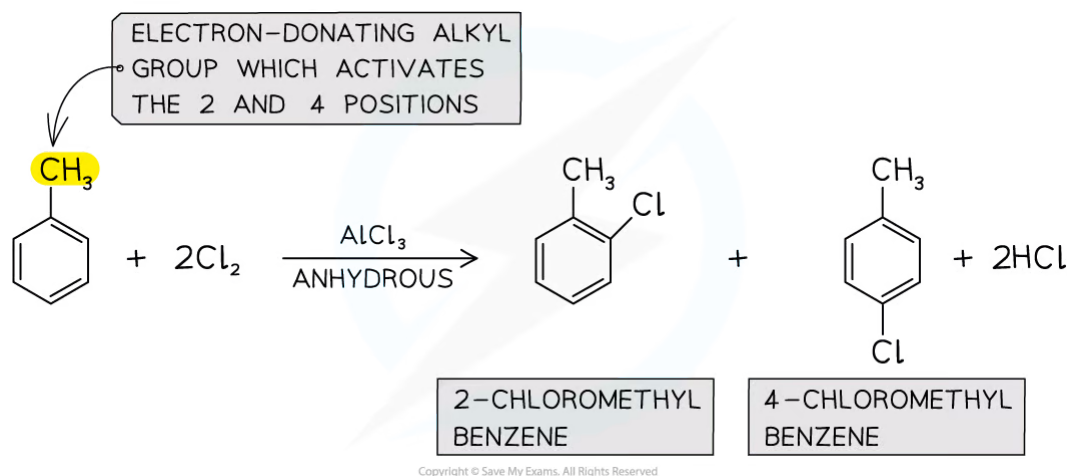
### Substitution

- **Halogenation** reactions are examples of **electrophilic substitution** reactions
- Arenes undergo **substitution** reactions with chlorine ( $\text{Cl}_2$ ) and bromine ( $\text{Br}_2$ ) in the presence of anhydrous  $\text{AlCl}_3$  or  $\text{AlBr}_3$  **catalyst** respectively to form **halogenoarenes (aryl halides)**
  - The chlorine or bromine act as an **electrophile** and replaces a hydrogen atom on the benzene ring
  - The catalyst is required for the reaction to take place, due to the stability of the benzene structure



**Arenes undergo substitution reactions with halogens to form aryl halides**

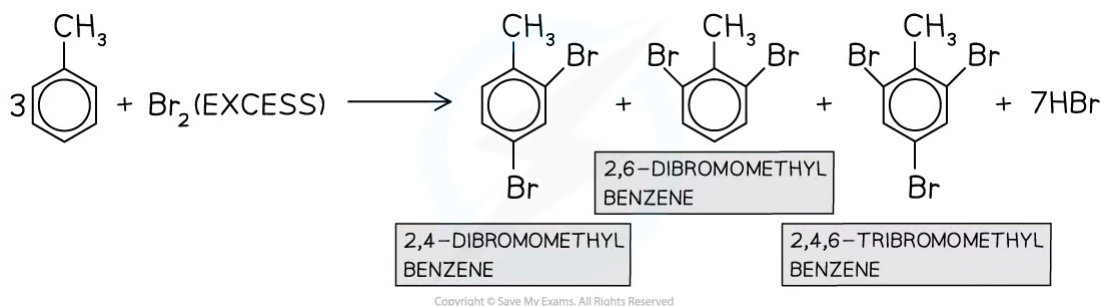
- **Alkylarenes** such as methylbenzene undergo halogenation on the 2 or 4 positions
- This is due to the **electron-donating** alkyl groups which activate these positions
- The halogenation of alkylarenes therefore result in the formation of **two products**



**Alkylarenes are substituted on the 2 or 4 position**

- **Multiple substitutions** occur when **excess** halogen is used

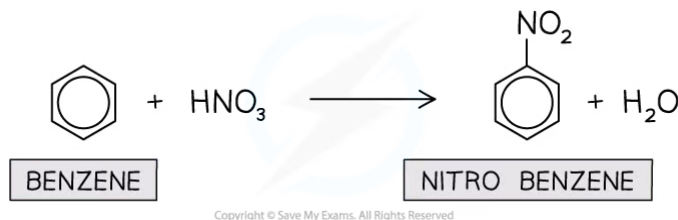
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*In the presence of excess halogen, multiple substitutions occur*

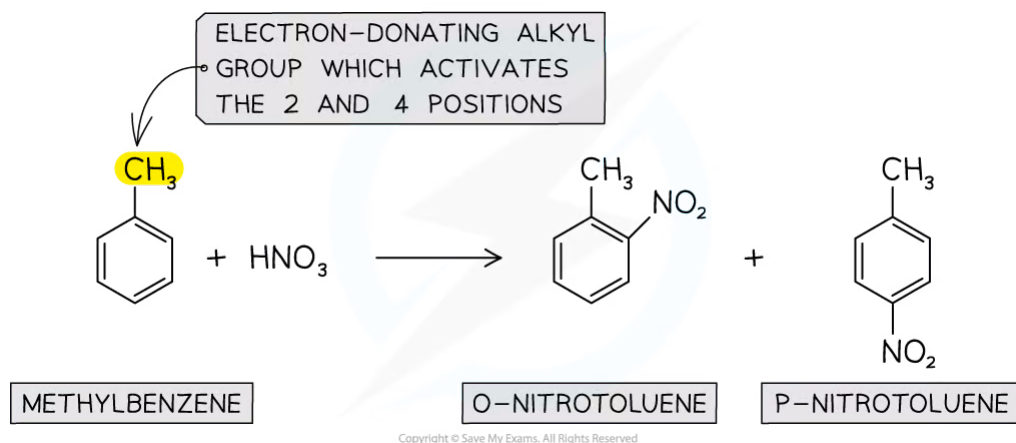
## Nitration

- Another example of a substitution reaction is the **nitration** of arenes
- In these reactions, a nitro ( $-\text{NO}_2$ ) group replaces a hydrogen atom on the arene
- The benzene is reacted with a mixture of concentrated nitric acid ( $\text{HNO}_3$ ) and concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) at a temperature between 25 and 60 °C



### Nitration of benzene

- Again, due to the **electron-donating** alkyl groups in alkylarenes, nitration of methylbenzene will occur on the 2 and 4 position



### Nitration of alkylarenes



