

A Level Chemistry AQA

YOUR NOTES



3. Organic Chemistry

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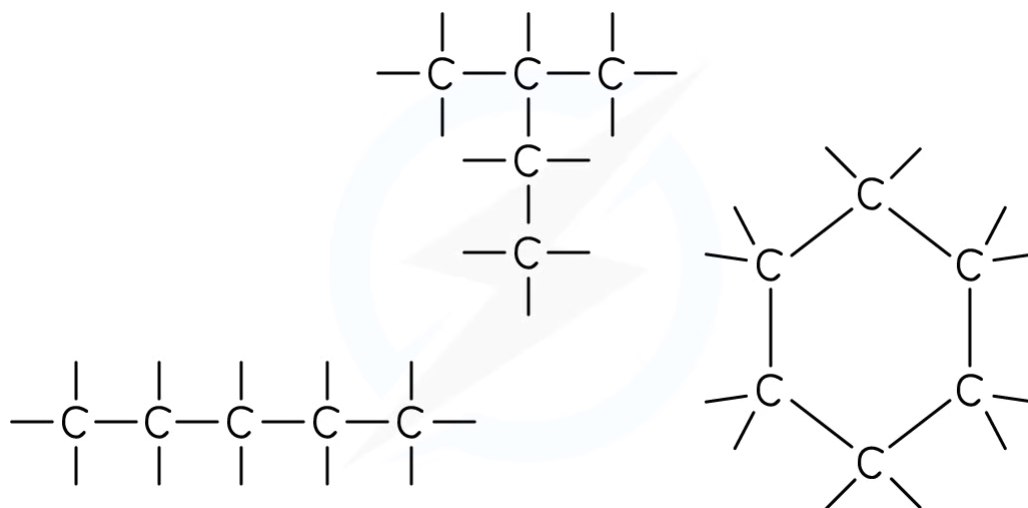


3.1 Introduction to Organic Chemistry

3.1.1 Functional Groups

Organic Definitions & Terminology

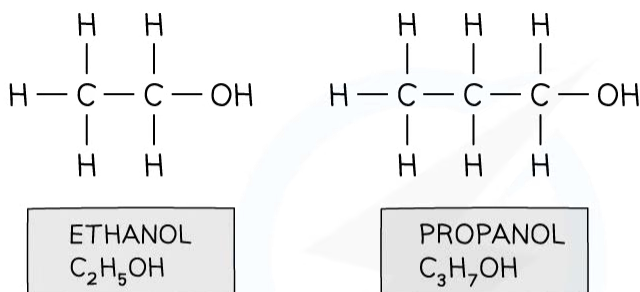
- **Organic chemistry** is the chemistry of carbon compounds
- Carbon forms a vast number of compounds because it can form strong covalent bonds with itself
- This enables it to form long chains of carbon atoms, and hence an almost infinite variety of carbon compounds are known



An almost infinite variety of chains, branches and rings is possible

Homologous series

- A homologous series is a group of organic compounds that have the same functional group, but each successive member differs by CH_2



- BOTH HAVE AN ALCOHOL FUNCTIONAL GROUP ($-\text{OH}$)
- BOTH HAVE THE SAME GENERAL FORMULA ($\text{C}_n\text{H}_{2n+1}\text{OH}$)
- BOTH HAVE SIMILAR CHEMICAL REACTIVITY

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Ethanol and propanol belong to the same homologous series

Homologous Series of Alkanes

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Name of alkane	Number of carbons	Chemical formula	Boiling point in °C	State at room temperature	Melting point in °C
Methane	1	CH ₄	-162	gas	-182
Ethane	2	C ₂ H ₆	-89	gas	-183
Propane	3	C ₃ H ₈	-42	gas	-188
Butane	4	C ₄ H ₁₀	-1	gas	-138
Pentane	5	C ₅ H ₁₂	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 successive member differs by -CH₂ -
 - 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

Functional Groups

- Functional groups determine the physical and chemical properties of molecules
- The table below shows a summary of common functional groups found in compounds
- R is any other atom or group of atoms (except for hydrogen)

Functional Groups found in Compounds Table

Family	Functional Group
Alkene	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{R} - \text{C} = \text{C} - \text{R} \end{array}$
Halogenoalkane	$\text{R} - \text{X}$ <p>Where X = F, Cl Br and I</p>
Alcohol	$\begin{array}{c} \text{H} \\ \\ \text{R} - \text{C} - \text{OH} \\ \\ \text{H} \end{array}$ Primary alcohol $\begin{array}{c} \text{R} \\ \\ \text{R} - \text{C} - \text{OH} \\ \\ \text{H} \end{array}$ Secondary alcohol $\begin{array}{c} \text{R} \\ \\ \text{R} - \text{C} - \text{OH} \\ \\ \text{R} \end{array}$ Tertiary alcohol
Aldehydes	$\begin{array}{c} \text{O} \\ // \\ \text{R} - \text{C} \\ \backslash \\ \text{H} \end{array}$
Ketone	$\begin{array}{c} \text{R} \\ \backslash \\ \text{C} = \text{O} \\ / \\ \text{R} \end{array}$
Carboxylic Acid	$\begin{array}{c} \text{O} \\ // \\ \text{R} - \text{C} \\ \backslash \\ \text{OH} \end{array}$
Ester	$\begin{array}{c} \text{O} \\ \\ \text{R} - \text{C} - \text{O} - \text{R} \end{array}$
Primary Amine	$\text{R} - \text{NH}_2$
Nitrile	$\text{R} - \text{C} \equiv \text{N}$

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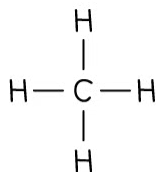
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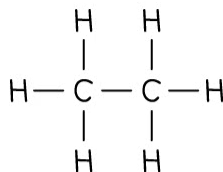
Hydrocarbons

- Hydrocarbons are compounds that are made up of carbon and hydrogen atoms **ONLY**

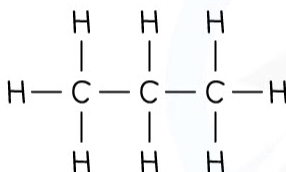
HYDROCARBONS



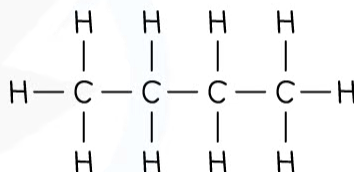
METHANE



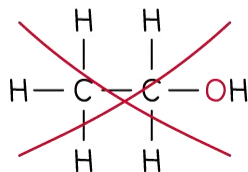
ETHANE



PROPANE



BUTANE



ETHANOL

NOT A HYDROCARBON AS
 THE COMPOUND ALSO
 CONTAINS AN OXYGEN

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The diagram shows examples of hydrocarbons

Ethanol is NOT a hydrocarbon as the molecule also contains an oxygen atom and is not solely made up of carbon and hydrogen

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3.1.2 Types of Formulae

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Types of Formulae

- The **general formula** is a formula that represents a **homologous series** of compounds using letters and numbers
 - Eg. the general formula of alkanes is C_nH_{2n+2}
 - A homologous series is a group of organic compounds that have the same functional group, the same general formula and the same chemical properties
- The **structural formula** is a formula that shows how the atoms are bonded to each carbon atom in a molecule
- The **displayed formula** is a 2D representation of an organic molecule showing **all** its atoms (by their **symbols**) and their bonds (by single, double or triple bonds)
- The **skeletal formula** is a simplified displayed formula with all the carbon and hydrogen (C-H) bonds removed

Overview of the Formulae of Organic Compounds Table

Homologous Series	General Formula	Structural Formula	Displayed Formula	Skeletal Formula	Name
Alkene	C_nH_{2n}	$\begin{array}{c} R & & R \\ & \backslash & / \\ & C = C \\ & / & \backslash \\ R & & R \end{array}$	$\begin{array}{c} H & H & H \\ & & \\ H - C - C = C - H \\ & & \\ H & & H \end{array}$		propene
Halogenoalkane	$C_nH_{2n+1}X$	$R - X$	$\begin{array}{c} H & H & X \\ & & \\ H - C - C - C - H \\ & & \\ H & H & H \end{array}$		halogenopropane
Alcohol	$C_nH_{2n+1}OH$	$R - OH$	$\begin{array}{c} H & H & H \\ & & \\ H - C - C - C - OH \\ & & \\ H & H & H \end{array}$		propan-1-ol
Aldehydes	$C_nH_{2n+1}CHO$	$\begin{array}{c} R & & \\ & \backslash & / \\ & C = O \\ & / & \\ H & & \end{array}$	$\begin{array}{c} H & H & O \\ & & \\ H - C - C - C - H \\ & & \\ H & H & \end{array}$		propanal
Ketone	$C_nH_{2n}O$	$\begin{array}{c} R & & \\ & \backslash & / \\ & C = O \\ & / & \\ R & & \end{array}$	$\begin{array}{c} H & O & H \\ & & \\ H - C - C - C - H \\ & & \\ H & & H \end{array}$		propanone
Carboxylic Acid	$C_nH_{2n+1}COOH$	$\begin{array}{c} O \\ \\ R - C \\ \\ OH \end{array}$	$\begin{array}{c} H & H & O \\ & & \\ H - C - C - C - O - H \\ & & \\ H & H & \end{array}$		propanoic acid
Ester	$C_nH_{2n}O_2$	$\begin{array}{c} O \\ \\ R - O - C - R \end{array}$	$\begin{array}{c} H & O & H & H \\ & & & \\ H - C - O - C - C - C - H \\ & & & \\ H & & H & H \end{array}$		methyl propanoate
Amine	$C_nH_{2n+1}NH_2$	$R - NH_2$	$\begin{array}{c} H & H & H & H \\ & & & \\ H - C - C - C - N - H \\ & & & \\ H & H & H & H \end{array}$		propylamine
Nitrile	$C_nH_{2n+1}CN$	$R - C \equiv N$	$\begin{array}{c} H & H \\ & \\ H - C - C - C \equiv N \\ & \\ H & \end{array}$		propanitrile

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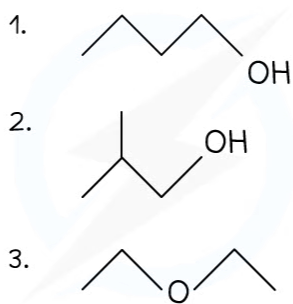
Worked Example

Drawing skeletal formulae of molecules

Draw the skeletal formula of the following molecules:

1. $\text{CH}_3(\text{CH}_2)_3\text{OH}$
2. $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$
3. $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$

Answer:



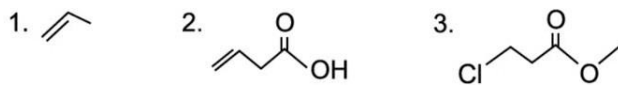
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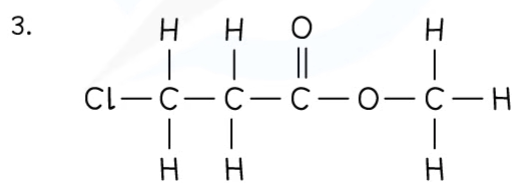
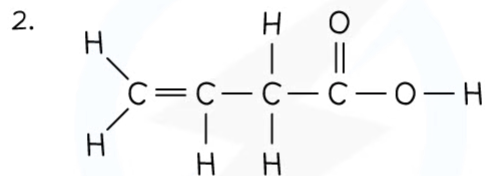
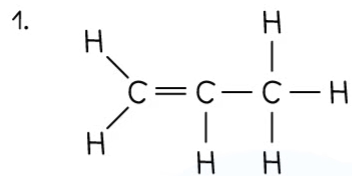
Worked Example

Drawing displayed formulae of molecules

Draw the displayed formula of the following molecules:



Answer



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Molecular & Empirical Formulae

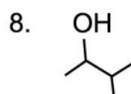
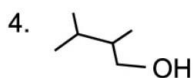
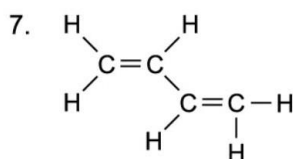
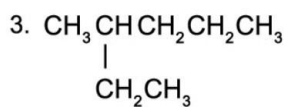
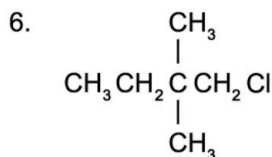
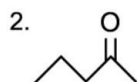
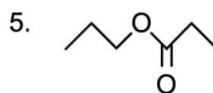
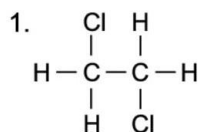
- The **molecular formula** shows the number and type of each atom in a molecule
 - Eg. the molecular formula of ethanoic acid is $C_2H_4O_2$
- The **empirical formula** shows the simplest whole number ratio of the elements present in one molecule of the compound
 - Eg. the empirical formula of ethanoic acid is CH_2O

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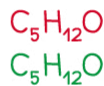
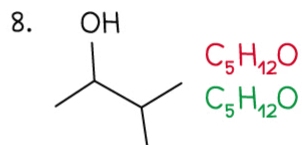
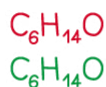
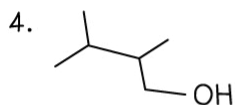
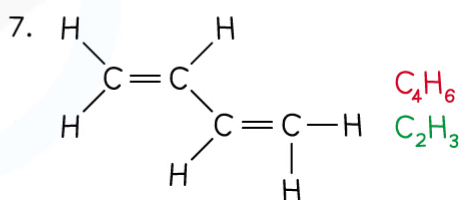
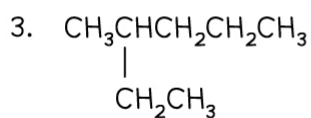
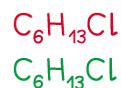
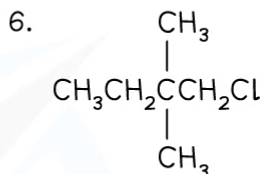
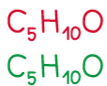
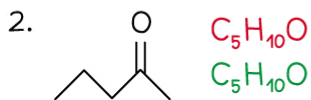
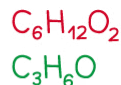
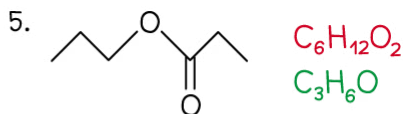
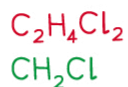
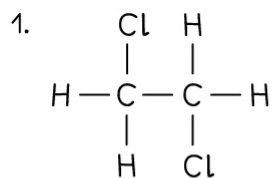


Worked Example

Deducing molecular & empirical formulae Deduce the molecular and empirical formula of the following compounds:



Answer



MOLECULAR FORMULA
EMPIRICAL FORMULA

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3.1.3 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

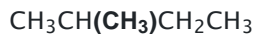
Nomenclature of Organic Compounds Table

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

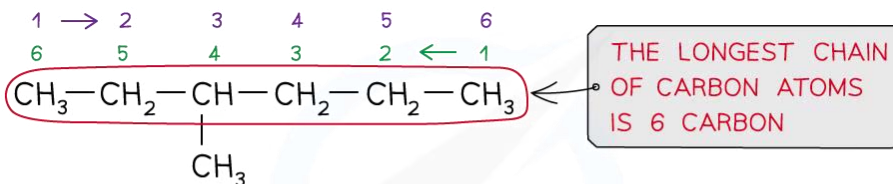
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- If there are any side-chains or functional groups present, then the position of these groups is indicated by numbering the carbon atoms in the longest chain starting at the end that gives the lowest possible numbers in the name
- The hydrocarbon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

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- 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

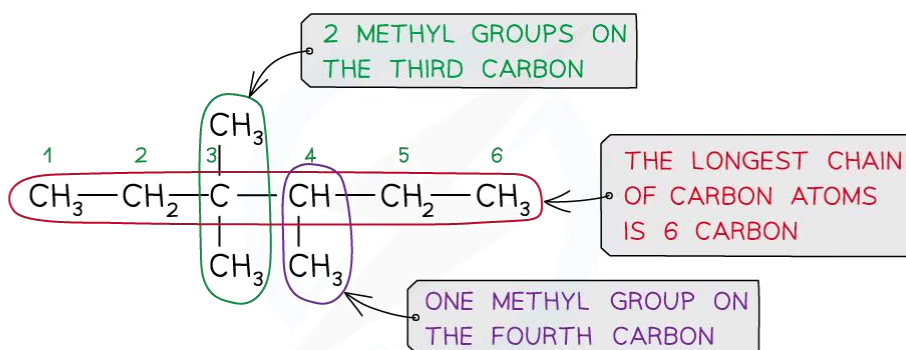
COUNTING FROM LEFT TO RIGHT GIVES: 3-METHYL HEXANE

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

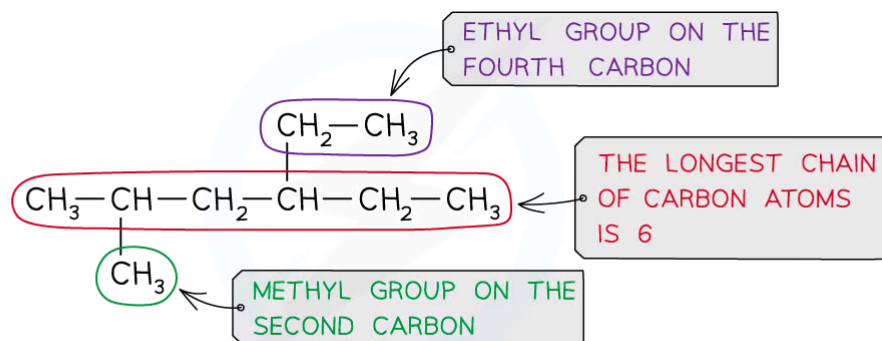


3, 3, 4 - TRIMETHYL HEXANE

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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.

Functional Groups & their Nomenclature Table

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Functional Group	Nomenclature	Example	Name
Alkenes	-ene	$\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{H} & & \text{H} \end{array}$	Ethene
Halogenoalkane	chloro- fluoro- iodo- bromo-	$\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C}- & \text{C}-\text{Cl} \\ & \\ \text{H} & \text{H} \end{array}$	Chloroethane
Alcohol	-ol	$\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C}- & \text{C}-\text{OH} \\ & \\ \text{H} & \text{H} \end{array}$	Ethanol
Aldehyde	-al	$\begin{array}{c} \text{H} & & \text{O} \\ & & // \\ \text{H}-\text{C}- & \text{C}-\text{H} \\ & & \\ \text{H} & & \end{array}$	Ethanal
Ketone	-one	$\begin{array}{c} \text{CH}_3 & & \text{O} \\ & & // \\ & & \text{C} \\ & & \backslash \\ & & \text{CH}_3 \end{array}$	Propanone
Carboxylic Acid	-oic acid	$\begin{array}{c} \text{H} & & \text{O} \\ & & // \\ \text{H}-\text{C}- & \text{C}-\text{OH} \\ & & \\ \text{H} & & \end{array}$	Ethanoic acid
Ester	alkyl -oate	$\begin{array}{c} \text{H} & \text{H} & \text{H} & & \text{O} & \text{H} \\ & & & & // & \\ \text{H}-\text{C}- & \text{C}- & \text{C}-\text{O}- & \text{C}- & \text{C}-\text{H} \\ & & & & & \\ \text{H} & \text{H} & \text{H} & & & \text{H} \end{array}$	Propyl Ethanoate
Amine	alkyl -amine	$\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C}- & \text{C}-\text{NH}_2 \\ & \\ \text{H} & \text{H} \end{array}$	Ethylamine
Nitrile	-nitrile	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{C}=\text{N} \\ \\ \text{H} \end{array}$	Ethane nitrile

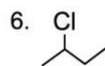
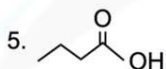
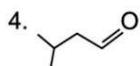
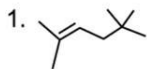
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Worked Example

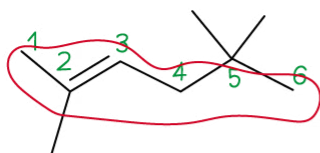
Naming organic molecules

Name the following molecules using correct systematic nomenclature:



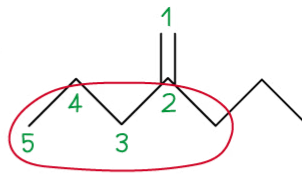
Answer

1.



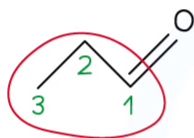
2, 5, 5 - TRIMETHYLHEX-2-ENE

2.



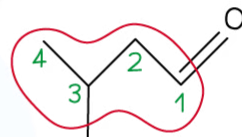
2-PROPYLPENT-1-ENE

3.



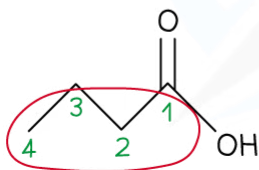
PROPANAL

4.



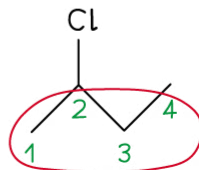
3-METHYLBUTANAL

5.



BUTANOIC ACID

6.



2-CHLOROBUTANE

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3.1.4 Structural Isomerism

YOUR NOTES

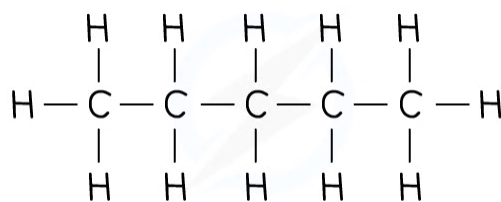


Molecules: Straight, Branched & Cyclic

- Straight, branched and cyclic organic molecules are also called **aliphatic** compounds as long as they do not contain a **benzene ring**

Straight-chain

- **Straight-chain** organic molecules are those in which the carbon atoms are connected to each other in one continuous chain

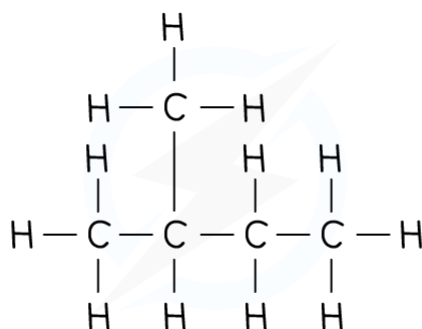


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Pentane is a straight-chain organic molecule as the carbon atoms are connected in one continuous chain

Branched

- **Branched** organic molecules have side groups attached to the main chain of carbon atoms

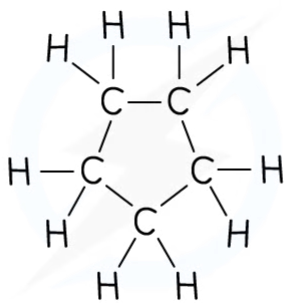


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2-methylbutane is a branched organic molecule as the main chain (consisting of 4 carbon atoms) has a methyl branch

Cyclic

- **Cyclic** organic molecules are those in which the carbon atoms are connected to each other in a ring shape



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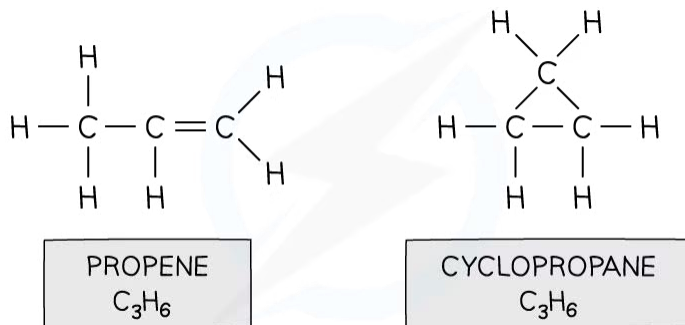
Cyclopentane is a cyclic organic molecule as the carbons are attached to each other in a ring structure

YOUR NOTES



Structural Isomerism

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

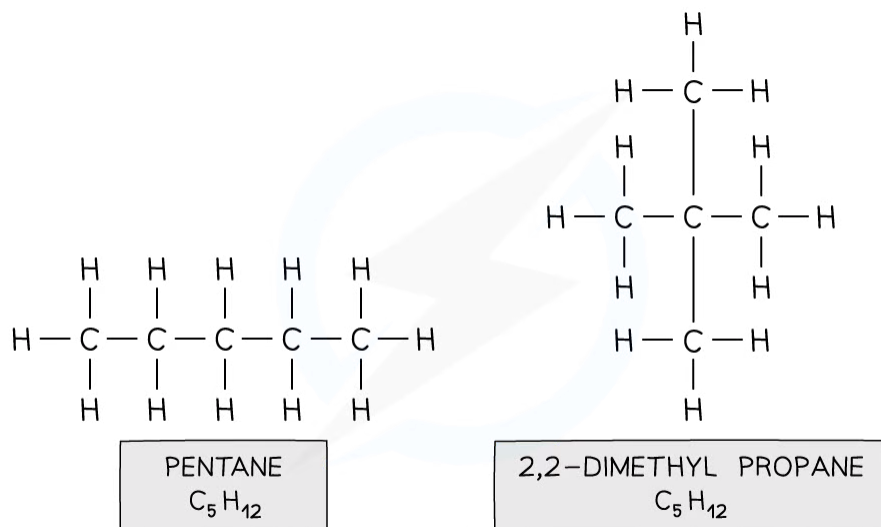


Both propene and cyclopropane are made up of 3 carbon and 6 hydrogen atoms but the structure of the two molecules differs

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

Chain isomerism

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



YOUR NOTES

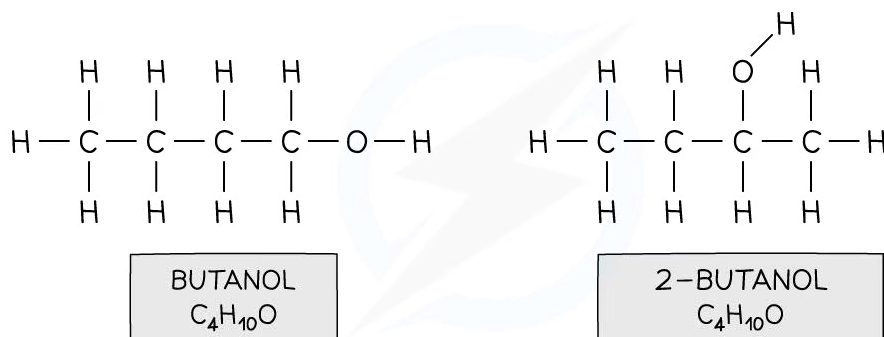




Both compounds are made up of the same atoms, however the longest carbon chain in pentane is 5 and in 2,2-dimethylpropane it is 3 (with two methyl branches)

Positional isomerism

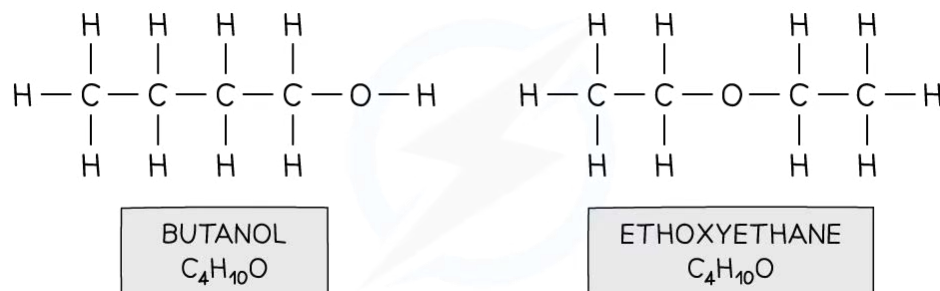
- **Positional isomers** arise from differences in the position of a functional group in each isomer
 - The functional group can be located on different carbons
 - For example, butan-1-ol and butan-2-ol



Both compounds have an alcohol group and are made up of 4 carbons, 10 hydrogens and one oxygen, however in butanol the functional group is located on the first carbon and in 2-butanol 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



Both compounds have the same molecular formula however butanol contains an alcohol functional group and ethoxyethane an ether functional group

Deducing Isomers

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

? Worked Example

Isomers of dibromopropane

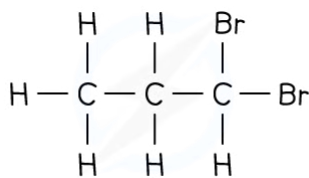
How many isomers are there of dibromopropane, $C_3H_6Br_2$?

YOUR NOTES



Answer

Step 1: Draw the structural formula of the compound



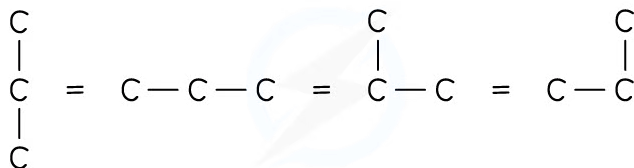
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Step 2: Determine whether it is a stereo or structural isomer

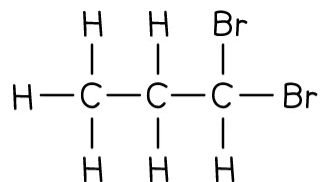
There is no restricted bond rotation around the C-C bond, so it is structural isomerism

Step 3: Determine whether it is a functional group, chain or positional isomerism

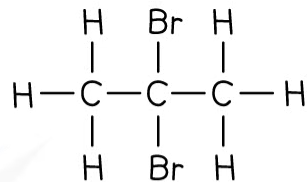
- Functional group? No, as Br is the only functional group possible
- Chain? No, as the longest chain can only be 3
- Positional? Yes, as the two bromine atoms can be bonded to different carbon atoms



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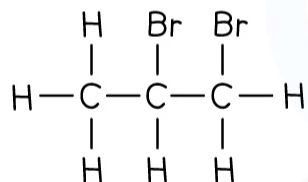


AND

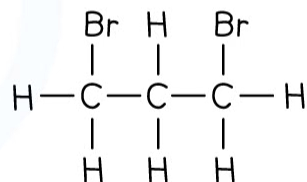


1,1-DIBROMOPROPANE

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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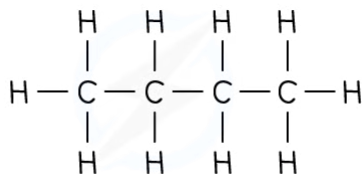
Worked Example

Deducing isomers of C_4H_{10}

How many isomers are there of the compound with molecular formula C_4H_{10} ?

Answer

Step 1: Draw the structural formula of the compound



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Step 2: Determine whether it is a stereo or structural isomer.

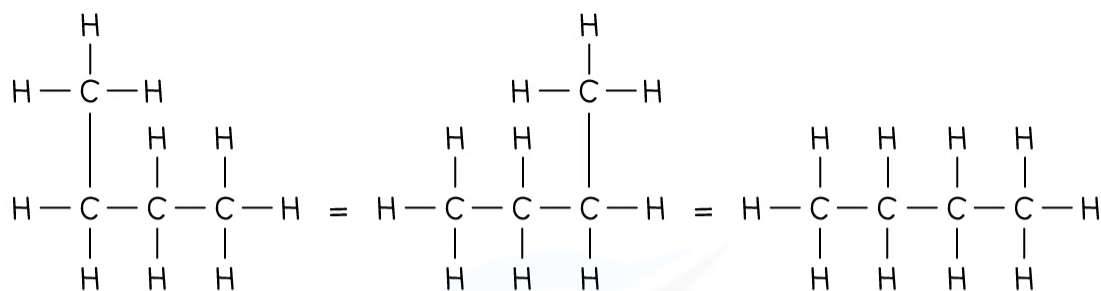
There is no restricted bond rotation around the C-C bond so it is structural isomerism

Step 3: Determine whether it is a functional group, chain or positional isomerism

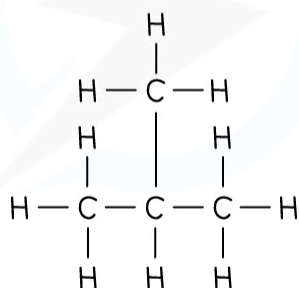
- Functional group? No, as there are no functional groups
- Positional? No, as there are no functional groups which can be positioned on different carbon atoms
- Chain? Yes!

YOUR NOTES





BUTANE



2-METHYLPROPANE

C_4H_{10} THEREFORE HAS 2 STRUCTURAL ISOMERS

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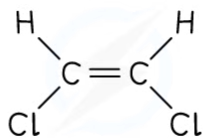
? Worked Example

Deducing isomers of $\text{C}_2\text{H}_2\text{Cl}_2$

How many isomers are there of the compound with molecular formula $\text{C}_2\text{H}_2\text{Cl}_2$?

Answer

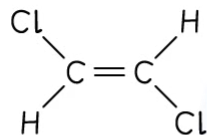
Step 1: Draw the possible structural formula of the compound



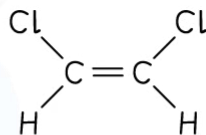
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Step 2: Determine whether it is a stereo or structural isomer

The compound has to be unsaturated for it to have molecular formula $C_2H_2Cl_2$; Due to the double bond there is restricted rotation about the C-C bond; This compound will therefore display geometrical isomerism



AND



TRANS-1,2-DICHLOROETHENE

CIS-1,2-DICHLOROETHENE

$C_2H_2Cl_2$ THEREFORE HAS 2 GEOMETRIC ISOMERS

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YOUR NOTES



3.1.5 Stereoisomerism

YOUR NOTES



Stereoisomerism: Geometrical Isomerism

- **Stereoisomers** are compounds that have the same atoms connected to each other, however the atoms are differently arranged in space
- There are two types of **stereoisomerism**:
 - Geometrical (E/Z) isomerism
 - Optical isomerism (this will be covered in the Second Year of the A Level course)

Geometrical (E/Z) isomerism

- **Geometrical isomerism** is seen in unsaturated (double bond containing) or ring compounds that have the same molecular formula and order of atoms (the atoms are connected similarly to each other) but different shapes
- **E/Z** nomenclature is used to distinguish between the isomers
 - Z isomers have functional groups on the same side of the double bond/carbon ring
 - E isomers have functional groups on opposite sides of the double bond/carbon ring
- You may see this type of isomerism referred to in other sources as cis/trans isomerism
 - This is a special case of E/Z isomerism
 - A "cis" isomer would essentially be the same as a "Z" isomer and a "trans" isomer would also essentially be the same as an "E" isomer

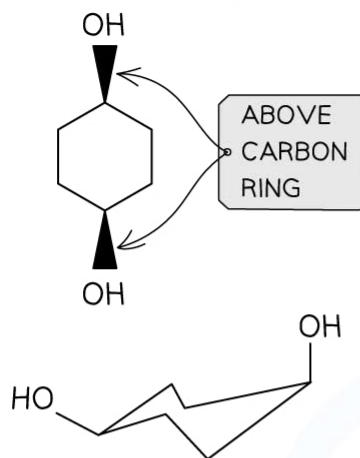


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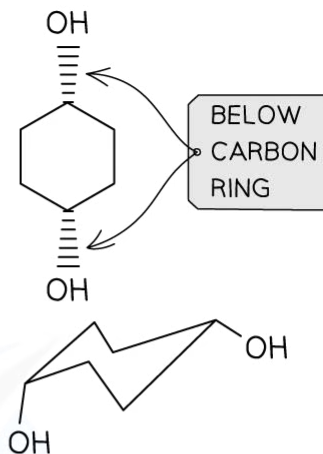
Geometrical isomerism in unsaturated compounds



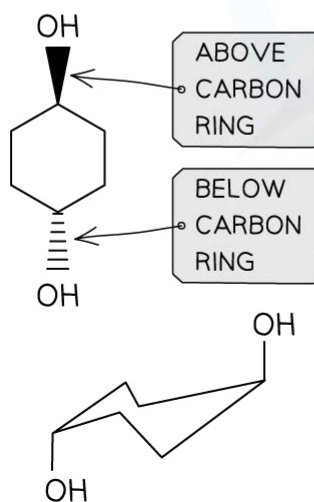
CIS-1, 4-CYCLOHEXADIOL



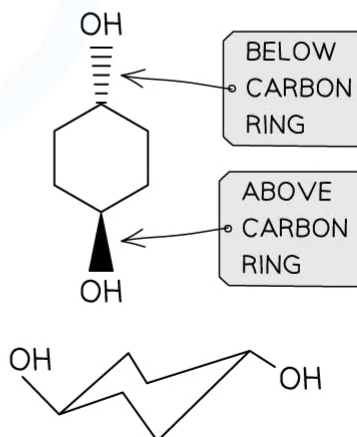
CIS-1, 4-CYCLOHEXADIOL



TRANS-1, 4-CYCLOHEXADIOL



TRANS-1, 4-CYCLOHEXADIOL



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Geometrical isomerism in cyclic compounds

- This causes the compounds to have different **chemical** and **physical** properties
- For example, they may have different reaction rates for the same reaction (chemical property) or different melting/boiling points (physical property)

3.2 Alkanes

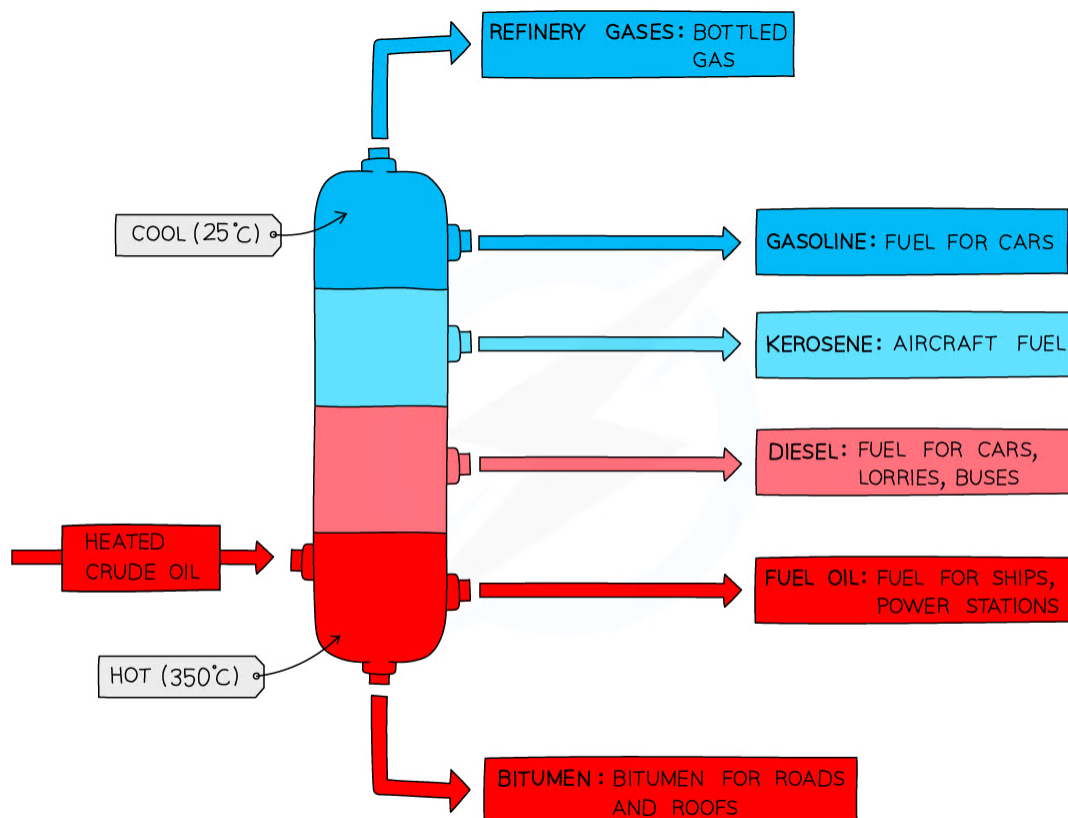
3.2.1 Fractional Distillation of Crude Oil

Fractional Distillation

- Crude oil is currently the world's main source of organic chemicals
- As a mixture, it isn't a very useful substance, but the different hydrocarbons that make up the mixture, called fractions, are useful, with each fraction having different applications
- It is a mixture of mostly alkanes, unbranched and branched chain
 - The mixture is separated into **fractions**, based on boiling points
- Each fraction consists of groups of hydrocarbons of **similar** chain lengths
 - Hydrocarbons of similar chain length have similar boiling points
- The fractions are separated from each other in a process called **fractional distillation**
- The size and length of each hydrocarbon molecule determines in which fraction it will be separated into
- The size of each molecule is directly related to how many carbon and hydrogen atoms the molecule contains
- Most fractions contain mainly **alkanes**, which are compounds of carbon and hydrogen with only **single** bonds between them

YOUR NOTES





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The Process of Fractional Distillation of Crude Oil

- ♦ Fractional distillation is carried out in a **fractionating column** which is very **hot** at the **bottom** and **cool** at the **top**
- ♦ Crude oil enters the fractionating column and is heated so **vapours rise**
- ♦ Vapours of hydrocarbons with very **high** boiling points will immediately condense into liquid at the higher temperatures lower down and are tapped off at the bottom of the column
- ♦ Vapours of hydrocarbons with **low** boiling points will rise up the column and condense at the top to be tapped off
- ♦ The different fractions condense at different heights according to their **boiling points** and are tapped off as liquids
- ♦ The fractions containing **smaller** hydrocarbons are collected at the top of the fractionating column as gases
- ♦ The fractions containing **bigger** hydrocarbons are collected at the lower sections of the fractionating column
- ♦ The crude oil contains small amounts of other compounds
- ♦ Some of these compounds may contain sulfur, and when burned sulfur dioxide can be produced
 - This is one of the causes of acid rain



Exam Tip

Fractional distillation is a physical process and **not** a chemical one, so no covalent bonds are broken. The intermolecular forces between molecules are broken as the crude oil is heated. You do not need to memorise the fractions, you just need to understand the principle of what is happening during the process, and why it is used.

YOUR NOTES



3.2.2 Modification of Alkanes by Cracking

YOUR NOTES

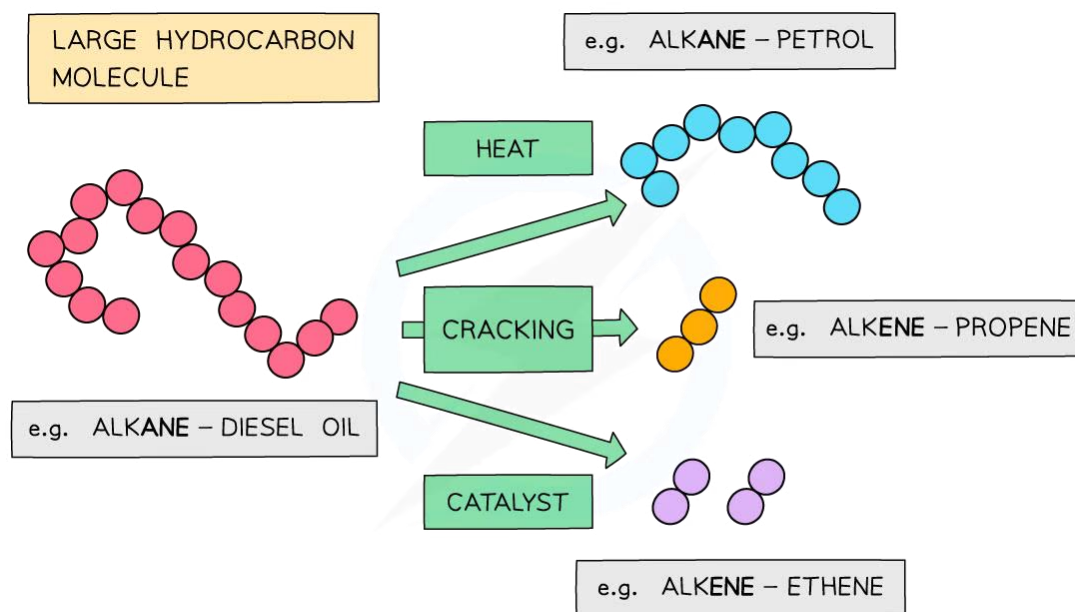


Cracking

- Alkanes are hydrocarbons that can be produced by the **addition reaction** of hydrogen to an alkene or by **cracking** of longer alkane chains

Crude oil

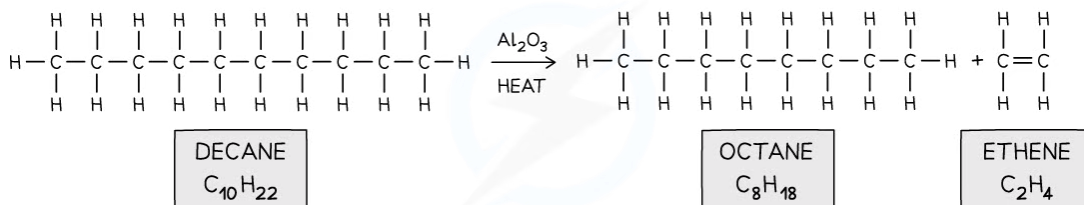
- Crude oil is a **mixture** of hydrocarbons containing **alkanes**, **cycloalkanes** and **arenes** (compounds with a benzene ring)
- The crude oil is **extracted** from the earth in a **drilling process** and transported to an **oil refinery**
- At the oil refinery the crude oil is separated into useful fuels by **fractional distillation**
- This is a separating technique in which the wide range of different hydrocarbons are separated into fractions based on their boiling points
- However, the smaller hydrocarbon fractions (such as gasoline fractions) are in high demand compared to the larger ones
- Therefore, some of the **excess** heavier fractions are broken down into smaller, **more useful compounds**
- These more useful compounds include **alkanes** and **alkenes** of **lower** relative formula mass (M_r)
- This process is called **cracking**



The heavier fractions that are obtained in fractional distillation are further cracked into useful alkane and alkenes with lower M_r values

Production of alkanes from cracking

- ♦ In **cracking** these large, less useful hydrocarbon molecules found in crude oil are broken down into smaller, more useful molecules
- ♦ The large hydrocarbon molecules are fed into a **steel chamber** and **heated** to a high temperature and then passed over an **aluminium oxide** (Al_2O_3) catalyst
 - The chamber does not contain any **oxygen** to prevent **combustion** of the hydrocarbon to water and carbon dioxide
- ♦ When a large hydrocarbon is cracked, a **smaller alkane** and one (or more) **alkene** molecules are formed
 - E.g. octane and ethene from decane



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Long hydrocarbons are cracked by heating them and using aluminium oxide catalyst into a smaller alkane and an alkene



Exam Tip

Remember that cracking is an **endothermic** reaction.

YOUR NOTES





3.2.3 Combustion of Alkanes

Combustion

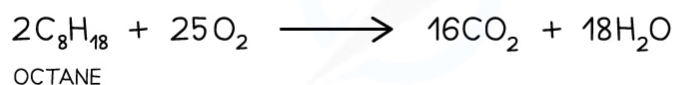
- Alkanes are **combusted** (burnt) on a large scale for their use as fuels

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 -----> CARBON DIOXIDE + WATER



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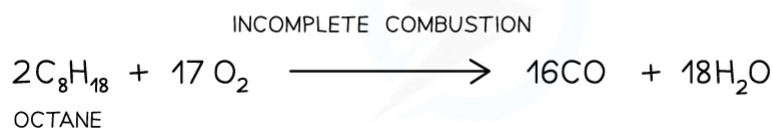
The complete combustion of alkanes

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

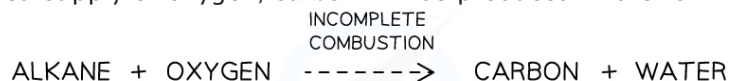
ALKANE + OXYGEN -----> CARBON MONOXIDE + WATER



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The incomplete combustion of alkanes

- 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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Combustion & The Environment

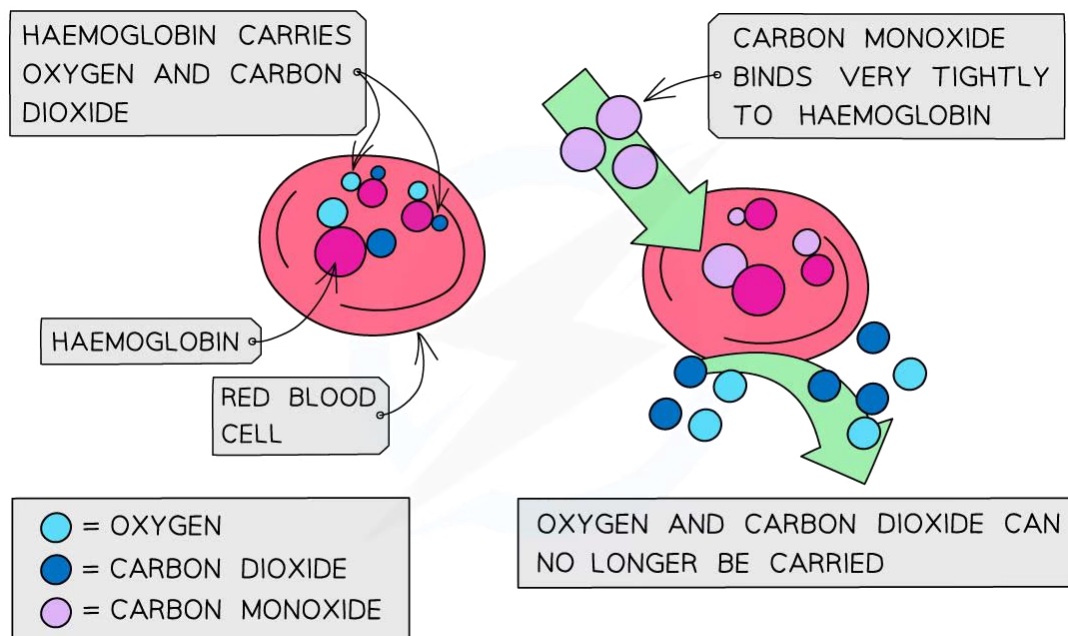
YOUR NOTES



- Car **exhaust fumes** include toxic gases such as **carbon monoxide (CO)**, **oxides of nitrogen (NO/NO₂)** and **volatile organic compounds (VOCs)**
- When released into the atmosphere, these pollutants have serious environmental consequences damaging nature and health

Carbon monoxide

- CO is a toxic and odourless gas which can cause dizziness, loss of consciousness and eventually death
 - The CO binds well to haemoglobin which therefore cannot bind oxygen and carbon dioxide
 - Oxygen is transported to organs
 - Carbon dioxide is removed as waste material from organs



The high affinity of CO to haemoglobin prevents it from binding to O₂ and CO₂

Oxides of nitrogen

- Normally, nitrogen is too unreactive to react with oxygen in air
- However, in a car engine, high temperatures and pressures are reached causing the oxidation of nitrogen to take place:



- The **oxides of nitrogen** are then released in the exhaust fumes into the atmosphere

- Car exhaust fumes also contain **unburnt hydrocarbons** from fuels and their **oxides** (VOCs)
- In air, the nitrogen oxides can react with these VOCs to form **peroxyacetyl nitrate** (PAN) which is the main pollutant found in **photochemical smog**
 - PAN is also harmful to the lungs, eyes and plant-life
- Nitrogen oxides can also dissolve and react in water with oxygen to form nitric acid which is a cause of **acid rain**
- Acid rain can cause corrosion of buildings, endangers plant and aquatic life (as lakes and rivers become too **acidic**) as well as directly damaging human health

Catalytic removal

- To reduce the amount of pollutants released in car exhaust fumes, many cars are now fitted with **catalytic converters**
- Precious metals (such as platinum) are coated on a honeycomb to provide a **large surface area**
- The reactions that take place in the catalytic converter include:
 - Oxidation of CO to CO₂:



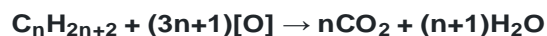
or



- Reduction of NO to N₂:



- Oxidation of unburnt hydrocarbons:



Pollutants, their Effect & Removal Table

YOUR NOTES



YOUR NOTES



	Formation	Environmental Consequence	Catalytic Removal
Carbon Monoxide	Incomplete combustion of alkanes in car engines	Toxic gas	Oxidation to CO ₂ : $2\text{CO} + \text{O}_2 \longrightarrow 2\text{CO}_2$ OR $2\text{CO} + 2\text{NO} \longrightarrow 2\text{CO}_2 + \text{N}_2$
Oxides of Nitrogen	Oxidation of nitrogen in car engines	Dissolve in and react in water with oxygen to form acid rain	Reduction to nitrogen gas: $2\text{CO} + 2\text{NO} \longrightarrow 2\text{CO}_2 + \text{N}_2$
VOCs	Unburnt hydrocarbons from fuels and their oxides formed in car engines	React with oxides of nitrogen in the atmosphere to produce PAN	Oxidise unburnt hydrocarbons to carbon dioxide and water: $\text{C}_n\text{H}_{2n+2} + (3n + 1)[\text{O}] \longrightarrow$ $n\text{CO}_2 + (n + 1)\text{H}_2\text{O}$
PAN	From the photochemical reaction of VOCs and nitrogen oxides in the atmosphere	Photochemical smog	Oxidise unburnt hydrocarbons and reduce nitrogen oxides to prevent formation of PAN in the atmosphere

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Exam Tip

Though CO₂ is not a **toxic** gas, it is still a **pollutant** causing **global warming** and **climate change**.

3.2.4 Chlorination of Alkanes

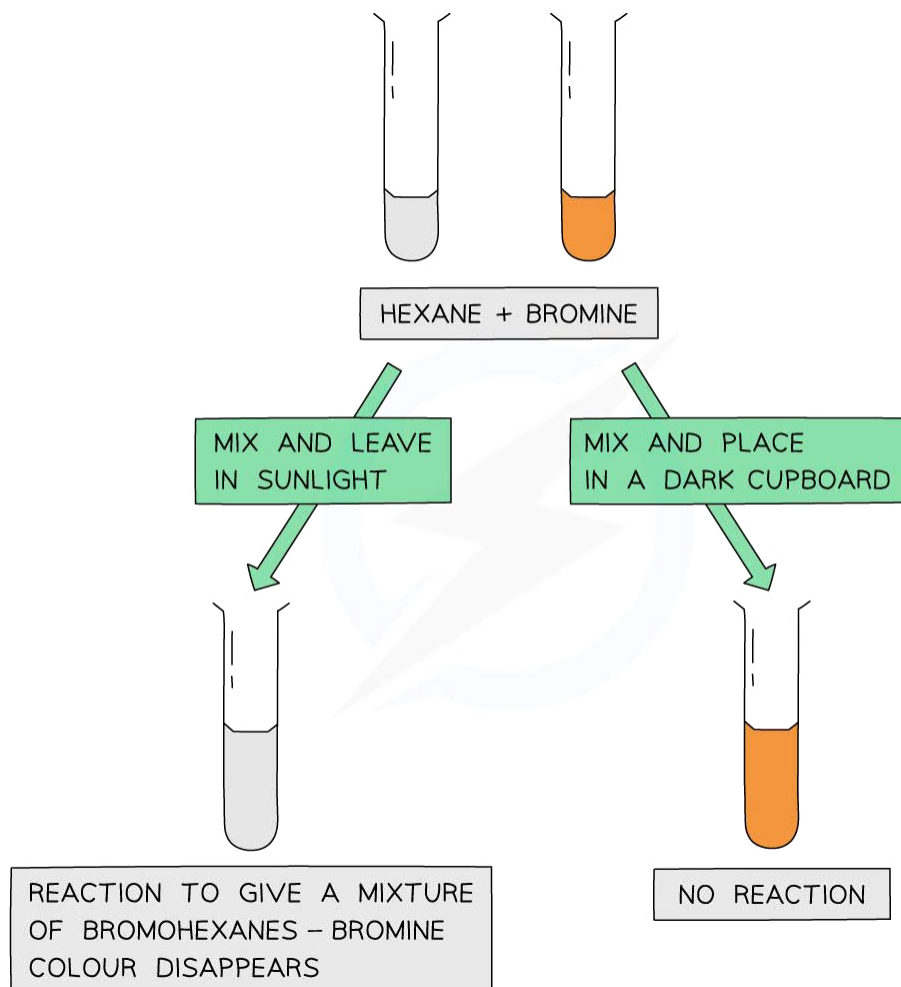
Free Radical Substitution

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 reaction called the **propagation step**
 - The reaction is terminated when two radicals collide with each other in a **termination step**
- Alkanes can undergo **free-radical substitution** in which a hydrogen atom gets **substituted** by a halogen (chlorine/bromine)
 - **Ultraviolet light (sunlight)** is needed for this substitution reaction to occur
- The free-radical substitution reaction consists of three steps

YOUR NOTES



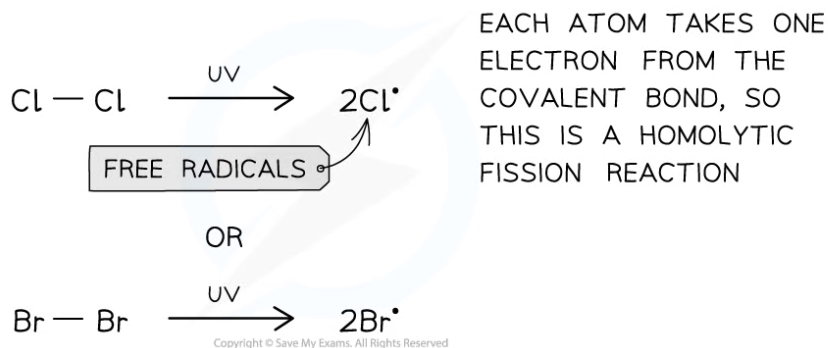


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The fact that the bromine colour has disappeared only when mixed with an alkane and placed in sunlight suggests that the ultraviolet light is essential for the free radical substitution reaction to take place

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



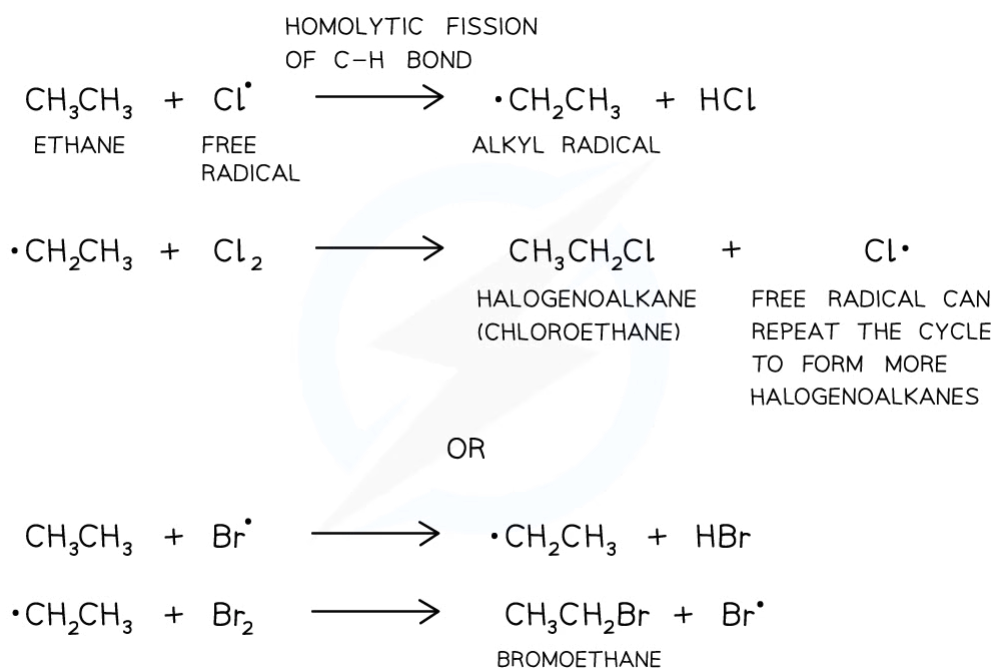
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The first step of the free-radical substitution reaction is the initiation step in which two free radicals are formed by sunlight

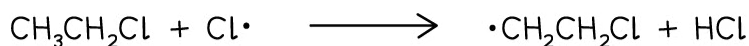
Propagation step

- The **propagation step** refers to the **progression** (growing) of the substitution reaction in a **chain 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

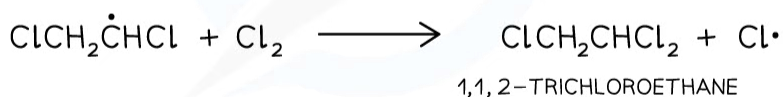
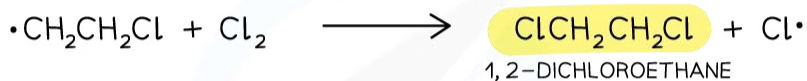


The second step of the free-radical substitution reaction is the propagation step in which the reaction grows in a chain reaction

- 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 C₂Cl₆/C₂Br₆)



THIS CAN BE FOLLOWED BY:



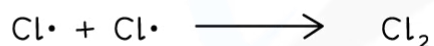
THE SAME PROCESS CAN TAKE PLACE WITH BROMINE INSTEAD OF CHLORINE. THE REACTION WILL CARRY ON TO EVENTUALLY FORM C_2Cl_6

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

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

3.3 Halogenoalkanes

YOUR NOTES



3.3.1 Reactivity of Halogenoalkanes

Reactivity of Halogenoalkanes

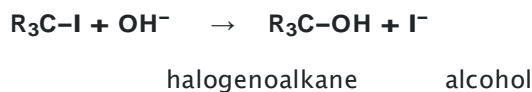
- The halogenoalkanes have different **rates of substitution reactions**
- Since substitution reactions involve **breaking** the **carbon-halogen bond** the **bond energies** can be used to explain their different reactivities

Halogenoalkane Bond Energy Table

Bond	Bond Energy (kJ mol ⁻¹)
C-F	467 (strongest bond)
C-Cl	346
C-Br	290
C-I	228 (weakest bond)

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- The table above shows that the C-I bond requires the least energy to break, and is therefore the **weakest** carbon-halogen bond
- During substitution reactions the C-I bond will therefore **heterolytically** break as follows:



- The C-F bond, on the other hand, requires the most energy to break and is, therefore, the **strongest** carbon-halogen bond
- Fluoroalkanes will therefore be less likely to undergo substitution reactions

Aqueous silver nitrate

- Reacting halogenoalkanes with **aqueous silver nitrate solution** will result in the formation of a **precipitate**
- The **rate of formation** of these precipitates can also be used to determine the reactivity of the halogenoalkanes

Halogenoalkane Precipitates Table

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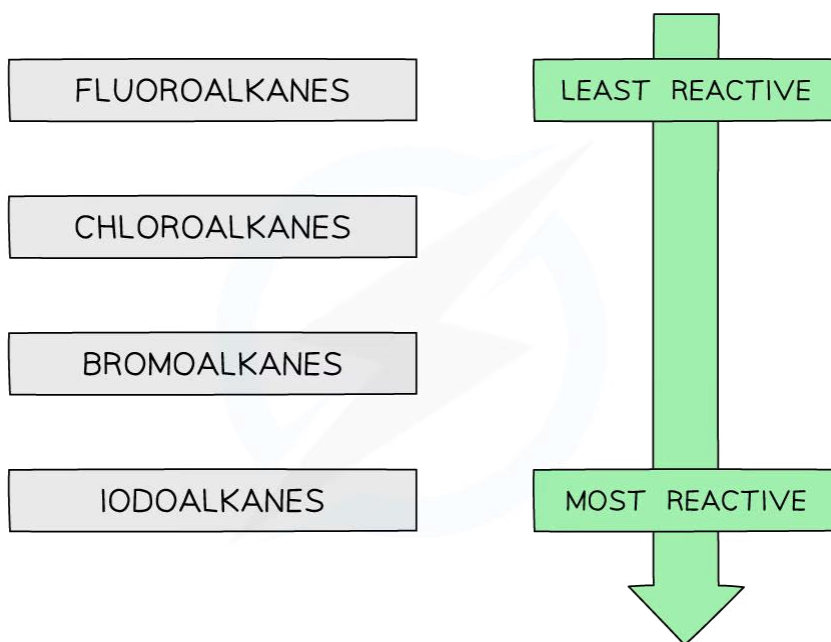
YOUR NOTES



Halogenoalkane	Precipitate
Chlorides	White (silver chloride)
Bromides	Cream (silver bromide)
Iodides	Pale yellow (silver iodide)

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- The formation of the pale yellow silver iodide is the fastest (fastest **nucleophilic substitution** reaction) whereas the formation of the silver fluoride is the slowest (slowest **nucleophilic substitution** reaction)
- This confirms that fluoroalkanes are the least reactive and iodoalkanes are the most reactive halogenoalkanes



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The trend in reactivity of halogenoalkanes

3.3.2 Reactions of Halogenoalkanes

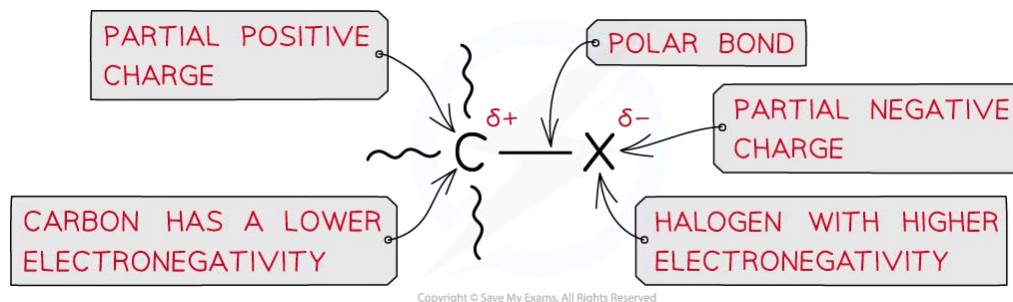
YOUR NOTES



The Key Reactions of the Halogenoalkanes

Types of Reactions that halogenoalkanes undergo:

- ♦ **Halogenoalkanes** are much more reactive than alkanes due to the presence of the **electronegative** halogens
 - The carbon-halogen bond is polar causing the carbon to carry a partial positive and the halogen a partial negative charge

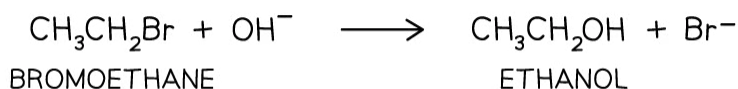


Due to the large difference in electronegativity between the carbon and halogen atom, the C-X bond is polar

- ♦ Because of this, halogenoalkanes will undergo two key types of reaction
- ♦ **Nucleophilic substitution** reactions
 - A halogen is substituted for another atom or group of atoms
 - The products formed when halogenoalkanes undergo this type of reaction are alcohols, amines and nitriles
- ♦ **Elimination** reactions
 - A hydrogen halide is eliminated during the reaction
 - The key product formed from this type of reaction is an alkene

Formation of alcohols

- ♦ The nucleophile in this reaction is the hydroxide, OH⁻ ion
- ♦ An **aqueous** solution of **sodium hydroxide** (NaOH) or **potassium hydroxide** (KOH) with **ethanol** is used
- ♦ This reaction is very slow at room temperature, so the reaction mixture is warmed
- ♦ This is an example of a **hydrolysis reaction** and the product is an alcohol
 - The rate of this reaction depends on the type of halogen in the halogenoalkane
 - The stronger the C-X bond, the slower the rate of the reaction
 - In terms of bond enthalpy, C-F > C-Cl > C-Br > C-I
 - Fluoroalkanes do not react at all, but iodoalkanes have a very fast rate of reaction



The halogen is replaced by the nucleophile, OH⁻

- This reaction could also be done with water as the nucleophile, but it is very slow
 - The hydroxide ion is a better nucleophile than water as it carries a full negative charge
 - In water, the oxygen atom only carries a partial charge



A hydroxide ion is a better nucleophile as it has a full formal negative charge whereas the oxygen atom in water only carries a partial negative charge; this causes the nucleophilic substitution reaction with water to be much slower than the aqueous alkali

Measuring the rate of hydrolysis

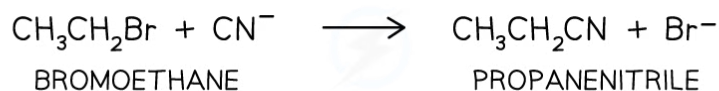
- Acidified silver nitrate can be used to measure the rate of hydrolysis of halogenoalkanes
- Set up three test tubes in a 50 °C water bath, with a mixture of ethanol and acidified silver nitrate
- Add a few drops of a chloroalkane, bromoalkane and an iodoalkane to each test tube and start a stop watch
- Time how long it takes for the precipitates to form
- The precipitate will form as the reaction progresses and the halide ions are formed
- A white precipitate will form from the chloroalkane, a cream precipitate will form from the bromoalkane and a yellow precipitate will form from the iodoalkane
 - The yellow precipitate will form the fastest
 - This is because the C-I bond has the lowest bond enthalpy, so it is the easiest to break and will cause the I⁻ ions to form the fastest
 - The white precipitate will form the slowest
 - This is because the C-Cl bond has the highest bond enthalpy, so it is the hardest to break and will cause the Cl⁻ ions to form the slowest

Formation of nitriles

- The **nucleophile** in this reaction is the **cyanide**, CN⁻ ion
- **Ethanol solution of potassium cyanide** (KCN in ethanol) is **heated under reflux** with the halogenoalkane
- The product is a **nitrile**
 - Eg. bromoethane reacts with ethanolic potassium cyanide when heated under reflux to form propanenitrile

YOUR NOTES





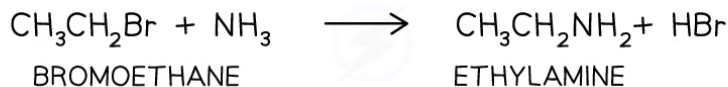
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The halogen is replaced by a cyanide group, CN⁻

- The nucleophilic substitution of halogenoalkanes with KCN adds an **extra** carbon atom to the carbon chain
- This reaction can therefore be used by chemists to make a compound with one more carbon atom than the best available organic starting material

Formation of primary amines by reaction with ammonia

- The **nucleophile** in this reaction is the **ammonia**, NH₃ molecule
- An **ethanolic solution** of **excess ammonia** (NH₃ in ethanol) is **heated under pressure** with the halogenoalkane
- The product is a **primary amine**
 - Eg. bromoethane reacts with excess ethanolic ammonia when heated under pressure to form ethylamine



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The halogen is replaced by an amine group, NH₂

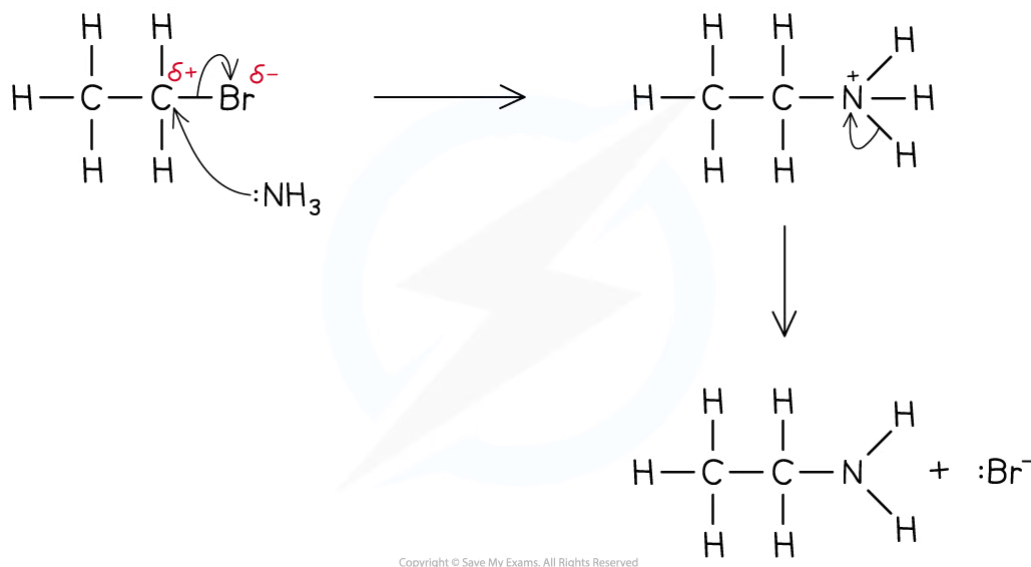
Nucleophilic Substitution

- The nucleophilic substitution mechanisms for the above reactions are as follows:

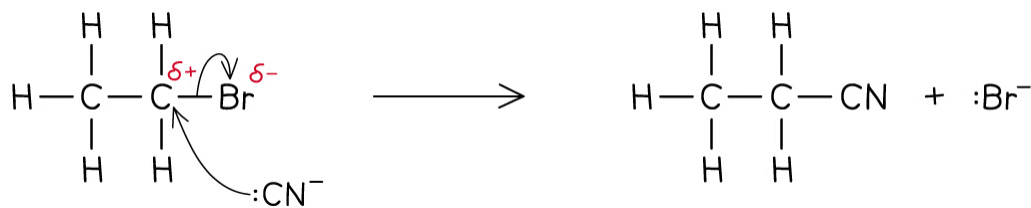
Nucleophilic Substitution with OH⁻



Nucleophilic Substitution with NH₃



Nucleophilic Substitution with CN⁻



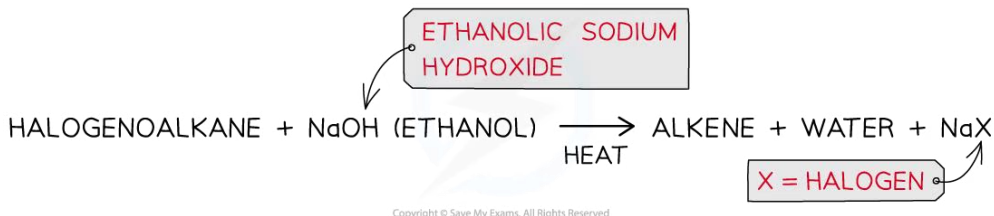
YOUR NOTES



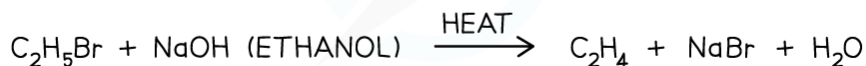
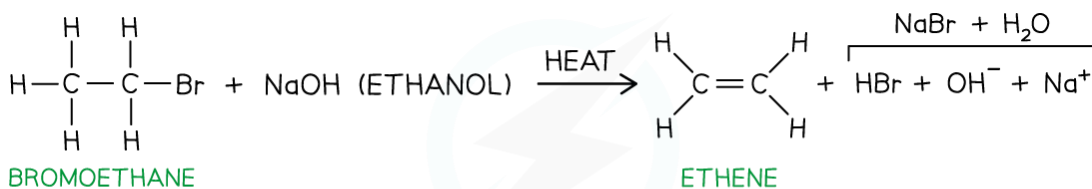


Elimination

- In an **elimination** reaction, an organic molecule loses a small molecule
 - In the case of halogenoalkanes this small molecule is a hydrogen halide (eg. HCl)
- The halogenoalkanes are **heated** with **ethanolic sodium hydroxide** causing the C-X bond to break **heterolytically**, forming an X⁻ ion and leaving an alkene as an organic product
 - For example, bromoethane reacts with **ethanolic sodium hydroxide** when heated to form ethene



Production of an alkene from a halogenoalkane by reacting it with ethanolic sodium hydroxide and heating it

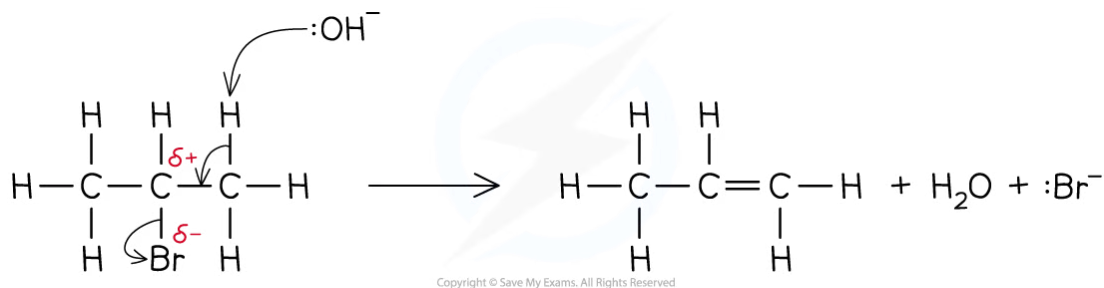


Hydrogen bromide is eliminated to form ethene

Elimination Reactions

- The elimination mechanism for the above reaction is as follows:

Elimination with OH^-



Which product will form?

- Note that the reaction conditions should be stated correctly as different reaction conditions will result in different types of organic reactions
 - NaOH (hot, in ethanol): an **elimination** reaction occurs to form an **alkene**
 - NaOH (warm, aqueous): a **nucleophilic substitution** reaction occurs, and an **alcohol** is formed

YOUR NOTES



3.3.3 Ozone Depletion

YOUR NOTES



Uses

Fluorohalogenoalkanes

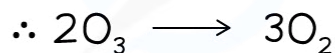
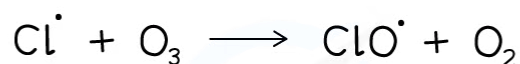
- The most common **halogenoalkanes** are **chlorofluorocarbons** (CFCs)
- These compounds contain carbon atoms with chlorine and fluorine atoms attached to them
 - E.g. CCl_3F and CCl_2F_2
- CFCs have many uses due to their **chemical inertness** as they are **non-flammable** and **non-toxic**
 - They are used as refrigerators
 - Propellants for aerosols
 - As solvents for dry cleaning

Hydrofluorocarbons

- **Hydrofluorocarbons** (HFCs) are compounds that contain a carbon attached to hydrogen and fluorine atoms only
 - E.g. $\text{CH}_2\text{F}-\text{CF}_3$
- As with CFCs, HFCs are chemically inert and are therefore used for a wide range of purposes

Halogenoalkanes & The Ozone Layer

- Though **chlorofluorocarbons** (CFCs) have many beneficial uses, they also have devastating effects on the ozone layer:
 - CFCs absorb a lot of UV radiation in the upper atmosphere
 - The CFCs are then broken down by the UV light causing the formation of chlorine radicals
 - These radicals react with ozone and break down the ozone layer
- This is why **hydrofluorocarbons** (HFCs) are often used as an alternative to CFCs
- As these compounds don't contain any chlorine atoms, they will not have adverse effects on the **ozone layer**



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Chlorine radicals and the ozone layer

3.4 Alkenes

3.4.1 Structure, Bonding & Reactivity

Shapes & Bond Angles in Organic Molecules

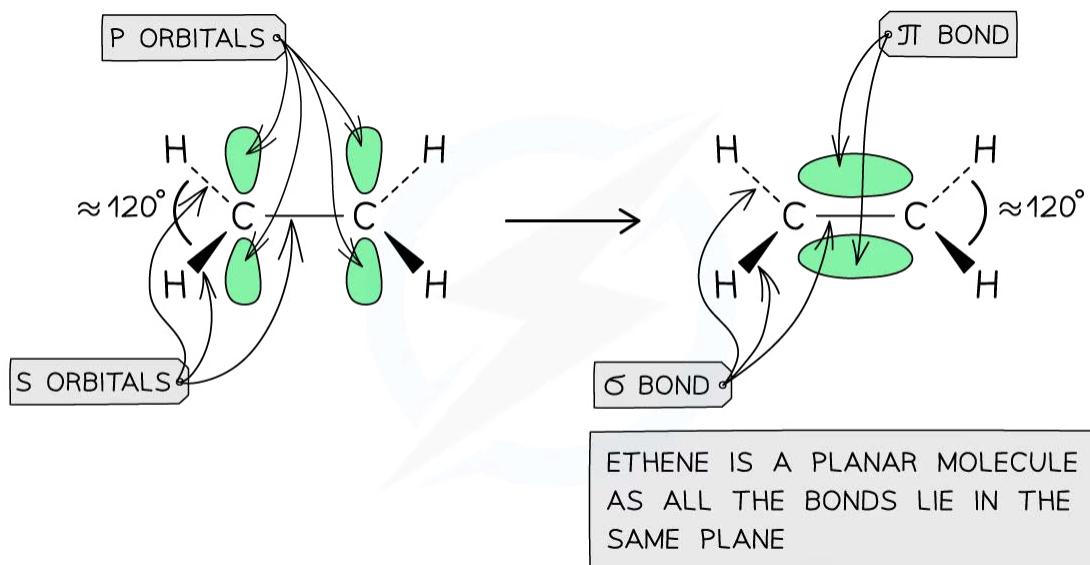
- Each carbon atom has four electrons in its outer shell (**electronic configuration:** $1s^2 2s^2 2p^2$)
- Carbon atoms share these four electrons in four covalent bonds with other atoms to achieve a **full outer shell configuration**
- These electrons are found in orbitals within the respective atoms
- When forming a covalent bond, the orbitals overlap in such a way to form two types of bonds
 - Sigma bonds (σ)
 - Pi bonds (π)
- When carbon atoms use only three of their electron pairs to form a σ bond, each carbon atom will have a p orbital which contains **one** spare electron
- When the p orbitals of two carbon atoms overlap with each other, a π bond is formed (the π bond contains two electrons)
- The two orbitals that form the π bond lie above and below the plane of the two carbon atoms to maximise bond overlap
- The three bonding pair of electrons are in the plane of the molecule and repel each other
- The molecule adopts a **planar** arrangement with bond angles of **120°**

Ethene

- Each carbon atom uses **three** of its **four** electrons to form σ bonds
- Two σ bonds are formed with the hydrogen atoms
- One σ bond is formed with the other carbon atom
- The fourth electron from each carbon atom occupies a p orbital which overlaps **sideways** with another p orbital on the other carbon atom to form a π bond
- This means that the C-C is a **double bond**: one σ and one π bond

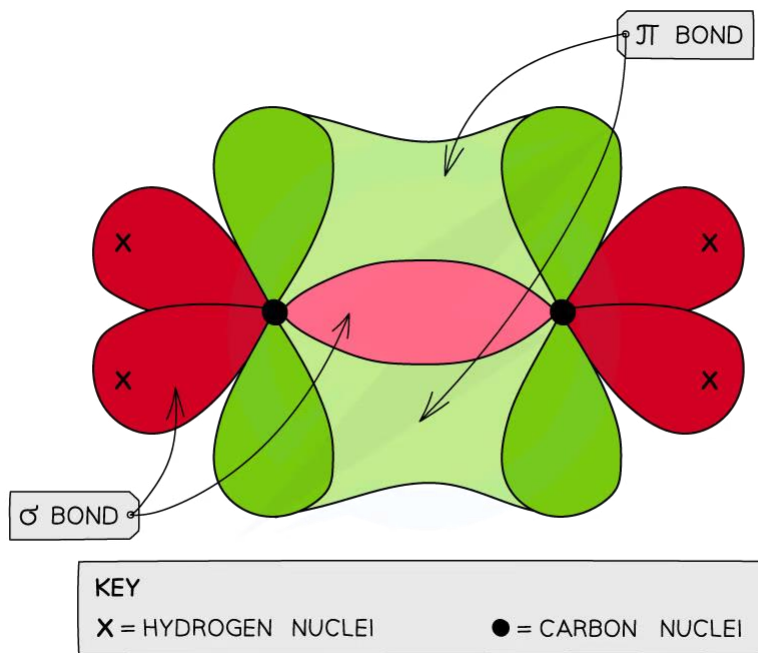
YOUR NOTES





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The overlap of the two p orbitals results in the formation of a π bond in ethene in which the bonding pair of electrons repel each other to force the molecule into a planar configuration with bond angles of 120°



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Each carbon atom in ethene forms two sigma bonds with hydrogen atoms and one σ bond with another carbon atom. The fourth electron is used to form a π bond between the two carbon atoms

YOUR NOTES
↓



Exam Tip

A **double bond** is a combination of a σ and π bond and a **triple bond** is a combination of one σ and two π bonds. The strength of the bonds increases as follows: **single < double < triple bond**. This is due to the increased electron density around the carbon-carbon bond, making the bond stronger and more difficult to break. You must be able to draw and explain these diagrams for the exam.

YOUR NOTES





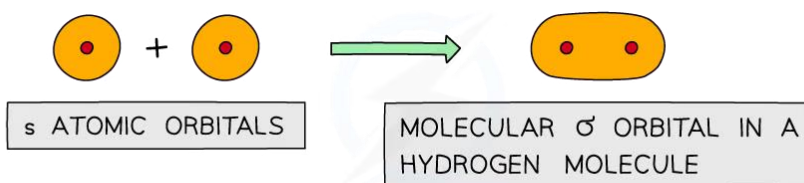
Molecular Orbitals

Bond overlap in covalent bonds

- A single **covalent bond** is formed when two nonmetals combine
- Each atom that combines has an **atomic orbital** containing a single unpaired electron
- When a covalent bond is formed, the **atomic orbitals** overlap to form a **combined orbital** containing two electrons
 - This new orbital is called the **molecular orbital**
- The **greater** the atomic orbital overlap, the **stronger** the bond
- **Sigma (σ)** bonds are formed by **end-to-end overlap** of orbitals between the bonding atoms
- **Pi (π)** bonds are formed by the **sideways overlap** of **adjacent above and below** the σ bond

σ bonds

- **Sigma (σ)** bonds are formed from the **end to end overlap** of atomic orbitals
- s orbitals overlap this way as well as p orbitals



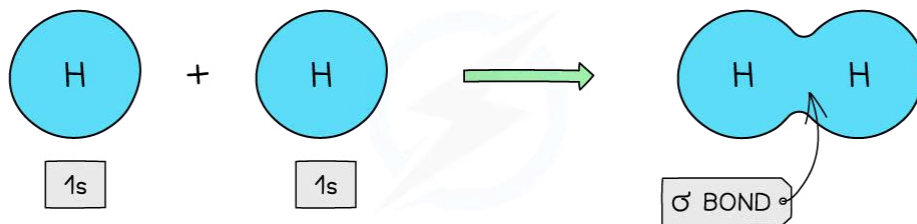
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Sigma orbitals can be formed from the end to end overlap of s orbitals

- The electron density in a σ bond is symmetrical about a line joining the nuclei of the atoms forming the bond
- The pair of electrons is found between the nuclei of the two atoms
- The electrostatic attraction between the electrons and nuclei bonds the atoms to each other

Hydrogen

- The hydrogen atom has only one s orbital
- The s orbitals of the two hydrogen atoms will overlap to form a σ bond

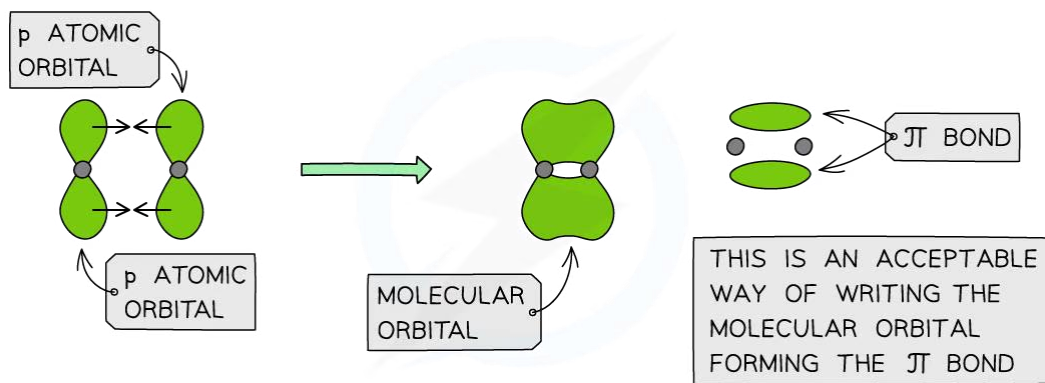


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π bonds

- Pi (π) bonds are formed from the **sideways overlap** of **adjacent p orbitals**
- The two lobes that make up the π bond lie **above and below the plane** of the σ bond
- This maximises overlap of the p orbitals
- A single π bond is drawn as **two electron clouds**, one arising from each lobe of the p orbitals
- The two clouds of electrons in a π bond represent **one bond** containing **two electrons**

YOUR NOTES



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π orbitals can be formed from the sideways overlap of p orbitals

3.4.2 Isomerism in Alkenes

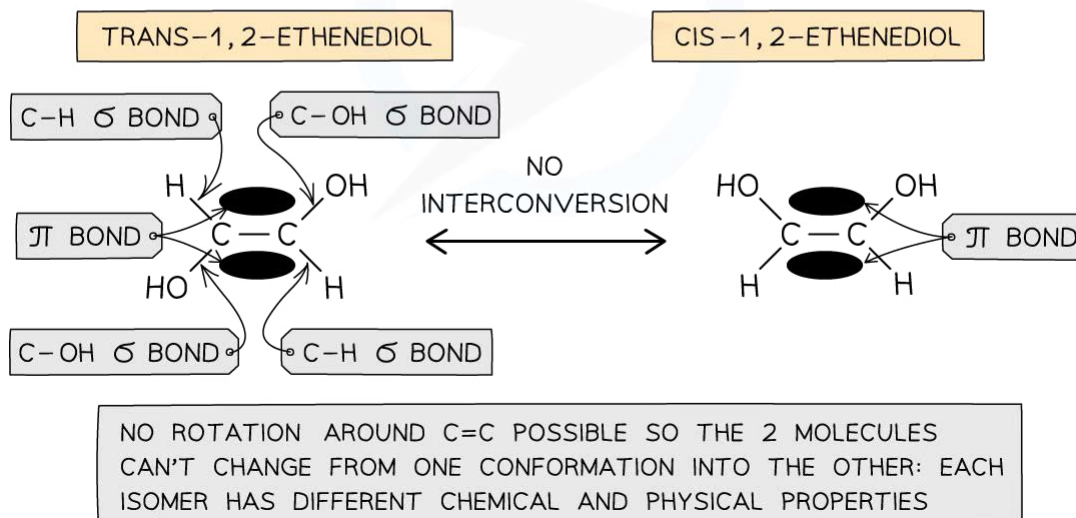
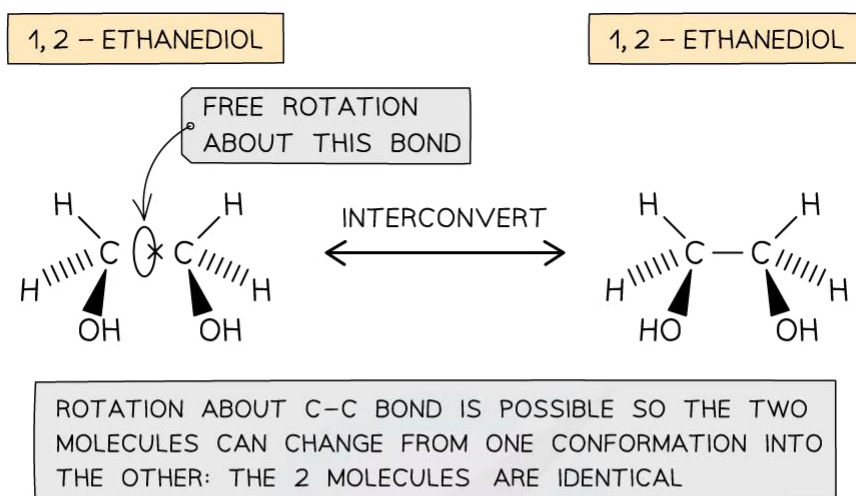
YOUR NOTES



Isomerism in Alkenes

Unsaturated compounds

- In unsaturated compounds, the groups attached to the C=C carbons remain fixed in their position
- This is because free rotation of the bonds about the C=C bond is not possible due to the presence of a π bond



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The presence of a π bond in unsaturated compounds restricts rotation about the C=C bond forcing the groups to remain fixed in their position and giving rise to the formation of geometrical isomers



Exam Tip

Geometrical isomerism is also possible in **cyclic compounds** because there is limited rotation about C–C single bonds that make up the rings.

Therefore, the substitutions in cyclic compounds are fixed in their position (to stay either above or below the ring of carbon atoms).

YOUR NOTES



Stability of Cations & Markovnikov's Rule

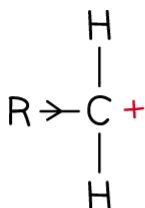
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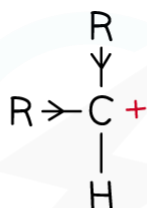
- **Carbocations** are positively charged carbon atoms with only three covalent bonds instead of four
- There are three types of carbocations: primary, secondary and tertiary

Inductive effect

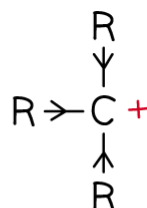
- The alkyl groups attached to the positively charged carbon atoms are '**electron donating groups**'
- This is also known as the **inductive effect** of alkyl **groups**
- The inductive effect is illustrated by the use of arrowheads on the bonds
- The alkyl groups **push** electrons away from themselves towards the positively charged carbon
- This causes the carbocation to become **less positively charged**
- As a result of this, the **charge is spread around** the carbocation which makes it **energetically more stable**
- This means that tertiary carbocations are the most stable as they have **three** electron-donating alkyl groups which energetically stabilise the carbocation
- Due to the positive charge on the carbon atom, carbocations are electron-loving species (**electrophiles**)



PRIMARY CARBOCATION
 (LEAST STABLE)



SECONDARY
 CARBOCATION



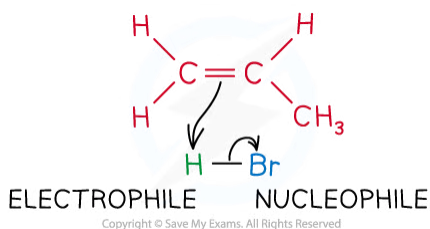
TERTIARY CARBOCATION
 (MOST STABLE)

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Alkyl groups push electron density towards the carbocation making it energetically more stable; the more alkyl groups the carbocation is bonded to, the more stabilised it is

Markovnikov's rule

- In addition reactions, an electrophile reacts with the double bond of alkenes

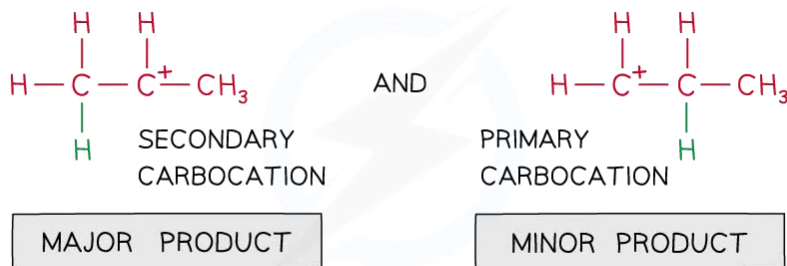


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The electrophile reacts with the electron-rich C-C double bond

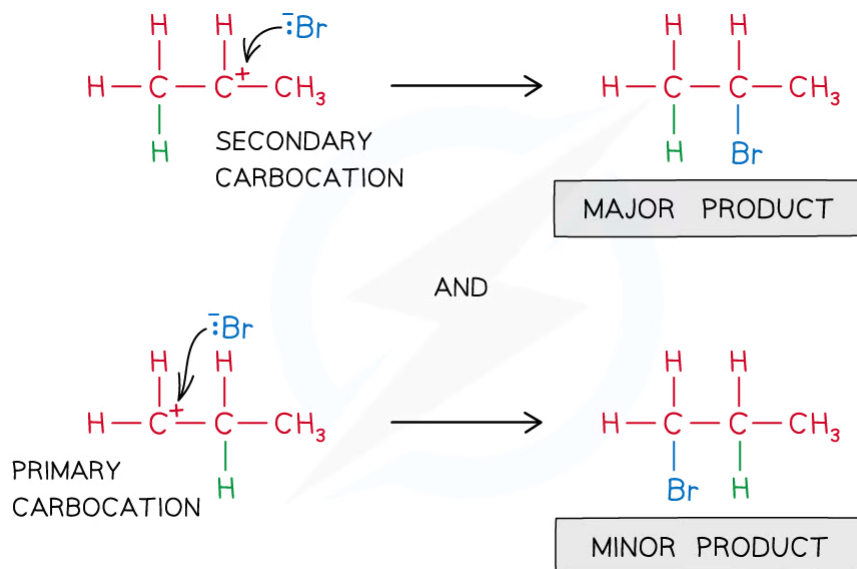
- The **electrophile** will add to the carbon to give the most **stable carbocation**



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The most stable carbocation is the major product of the nucleophilic attack on the C-C double bond

- Therefore, the nucleophile will bond to the C-C carbon atom with the highest number of alkyl groups bonded to it



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The nucleophile ends up to the most substituted C-C carbon atom

- This is also known as the **Markovnikov's rule** which predicts the outcome of **addition reactions** and states that:
 - In an **addition reaction** of a hydrogen halide (HX) to an alkene, the halogen ends up bonded to the most substituted carbon atom.

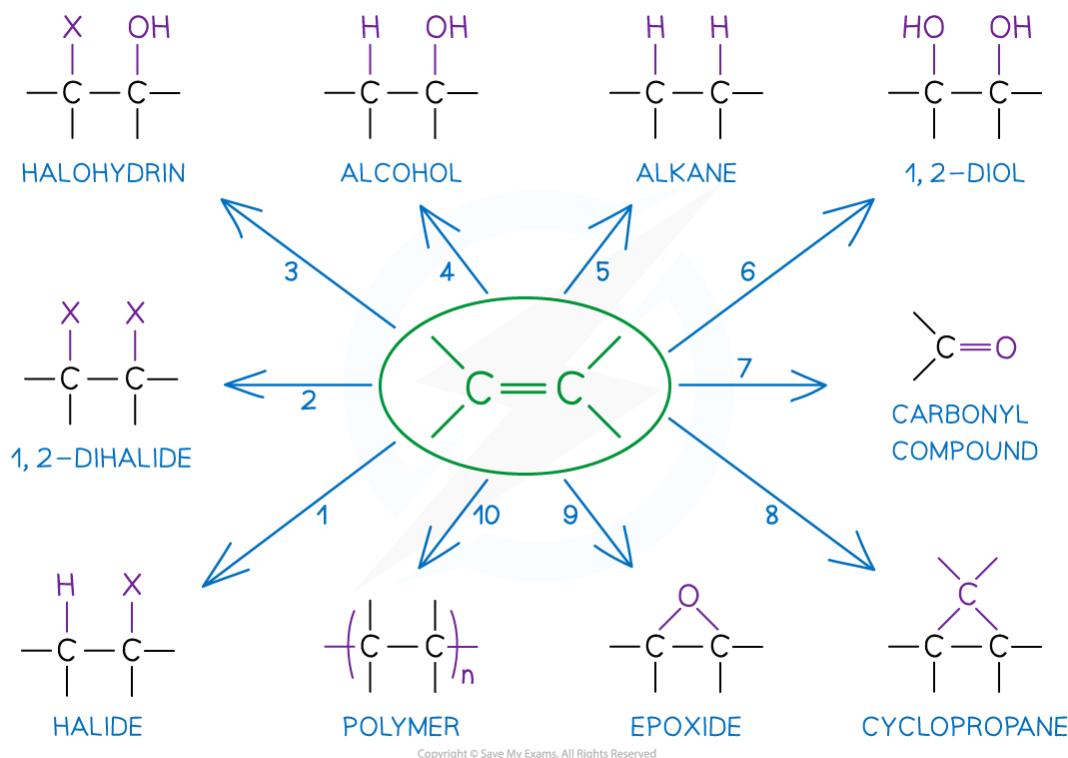
3.4.3 Reactions of Alkenes

YOUR NOTES



Alkenes: Reactions

- 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



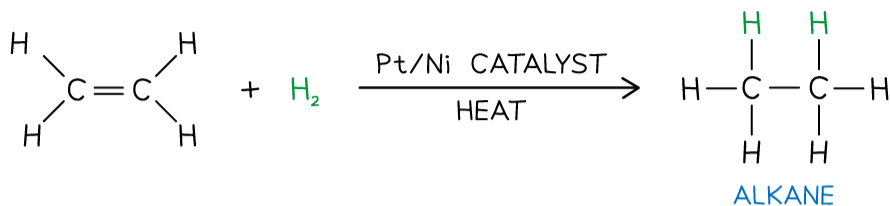
Electrophilic addition

- Electrophilic addition** is the addition of an electrophile 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
- Electrophilic addition reactions include the addition of:
 - Steam (H₂O (g))
 - Hydrogen halide (HX)
 - Halogen

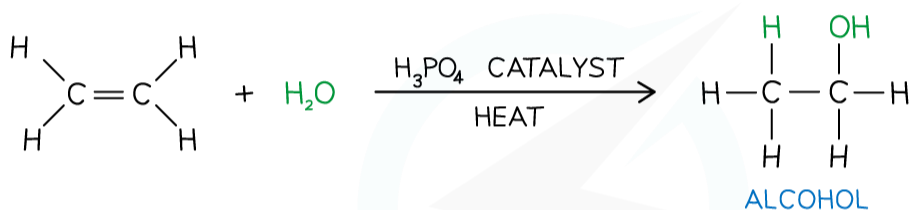


ELECTROPHILIC ADDITION

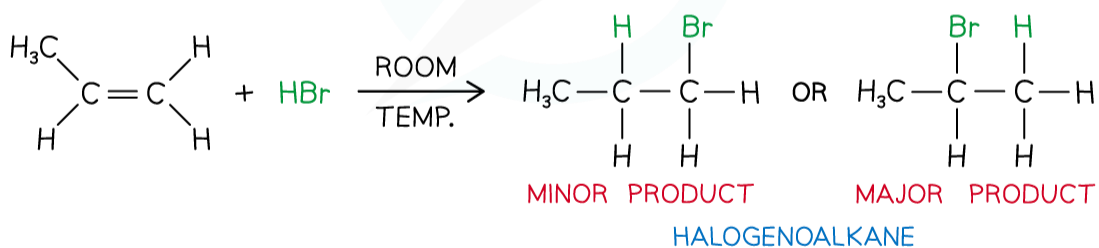
HYDROGENATION



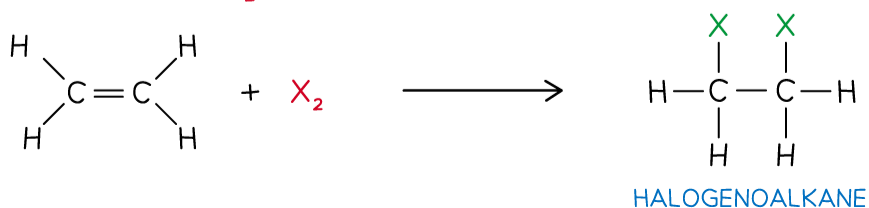
STEAM



HYDROGEN HALIDES (HX)



HALOGENS (X₂)



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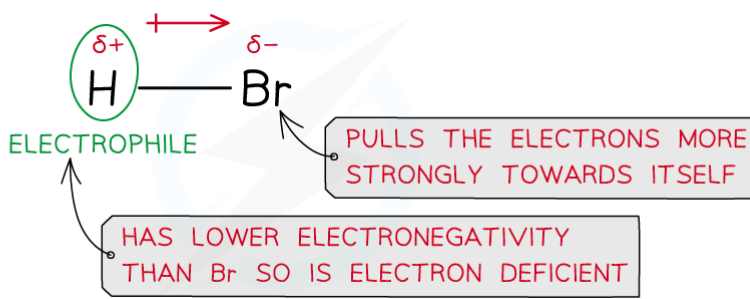
The diagram shows an overview of the different electrophilic addition reactions alkenes can undergo

Electrophilic Addition

- The double bond in alkenes is an area of high electron density (there are four electrons found in this double bond)
- This makes the double bond susceptible to attack by electrophiles (electron-loving species)
- An **electrophilic addition** is the addition of an **electrophile** to a double bond

Electrophilic addition of hydrogen bromide

- A molecule of hydrogen bromide (HBr) is polar as the hydrogen and bromine atoms have different electronegativities
- The bromine atom has a stronger pull on the electrons in the H-Br bond
- As a result of this, the Br atom has a partial negative and the H atom a partial positive charge

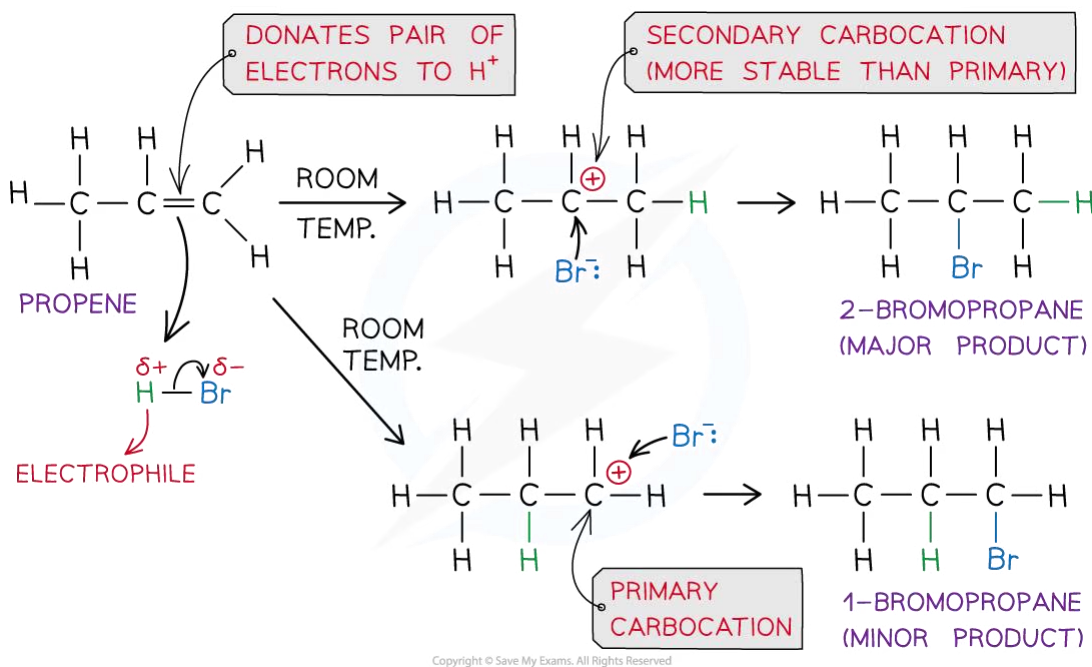


Due to differences in electronegativities of the hydrogen and bromine atom, HBr is a polar molecule

- In an addition reaction, the H atom acts as an electrophile and accepts a pair of electrons from the C=C bond in the alkene
 - The H-Br bond breaks heterolytically, forming a Br⁻ ion
- This results in the formation of a highly reactive carbocation intermediate which reacts with the Br⁻ (nucleophile)

YOUR NOTES

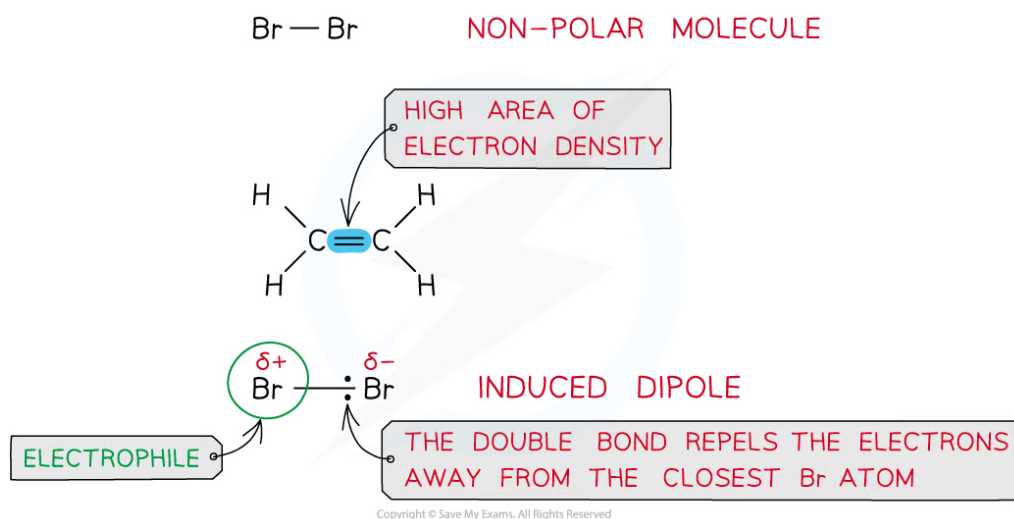




Example of an electrophilic addition reaction of HBr and propene to form 1-bromopropane and 2-bromopropane

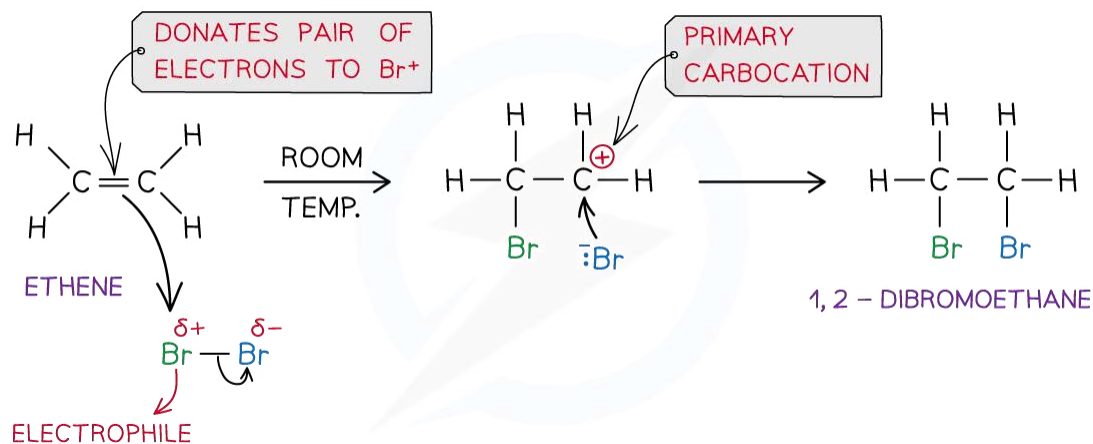
Electrophilic addition of bromine

- Bromine (Br_2) is a non-polar molecule as both atoms have similar electronegativities and therefore share equally the electrons in the covalent bond
- However, when a bromine molecule gets closer to the double bond of an alkene, the high electron density in the double bond repels the electron pair in $\text{Br}-\text{Br}$ away from the closest Br atom
- As a result of this, the closest Br atom to the double bond is slightly positive and the further Br atom is slightly negatively charged



Br₂ is a non-polar molecule however when placed close to an area of high electron density it can get polarised

- In an addition reaction, the closest Br atom acts as an electrophile and accepts a pair of electrons from the C=C bond in the alkene
 - The Br-Br bond breaks heterolytically, forming a Br⁻ ion
- This results in the formation of a highly reactive carbocation intermediate which reacts with the Br⁻ (nucleophile)



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Example of an electrophilic addition reaction of Br₂ and ethene to form dibromoethane



Exam Tip

The stability of the carbocation intermediate is as follows: **tertiary > secondary > primary**. When more than one carbocations can be formed, the major product of the reaction will be the one that results from the nucleophilic attack of the most stable carbocation.

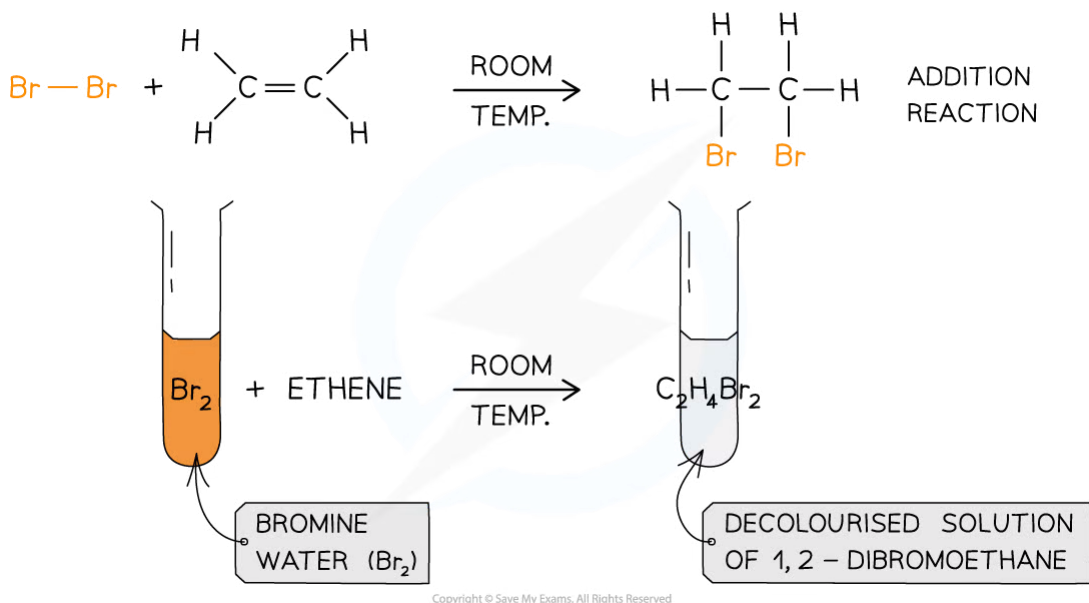
YOUR NOTES



3.4.4 Test for Unsaturation

Test for Unsaturation

- Halogens can be used to test if a molecule is **unsaturated** (i.e. contains a double bond)
- Br₂(aq) is an orange or yellow solution, called **bromine water** and this is the halogen most commonly used
- 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 decolourisation of bromine water by an unsaturated compound as a result of an addition reaction

YOUR NOTES



3.4.5 Addition Polymers

YOUR NOTES

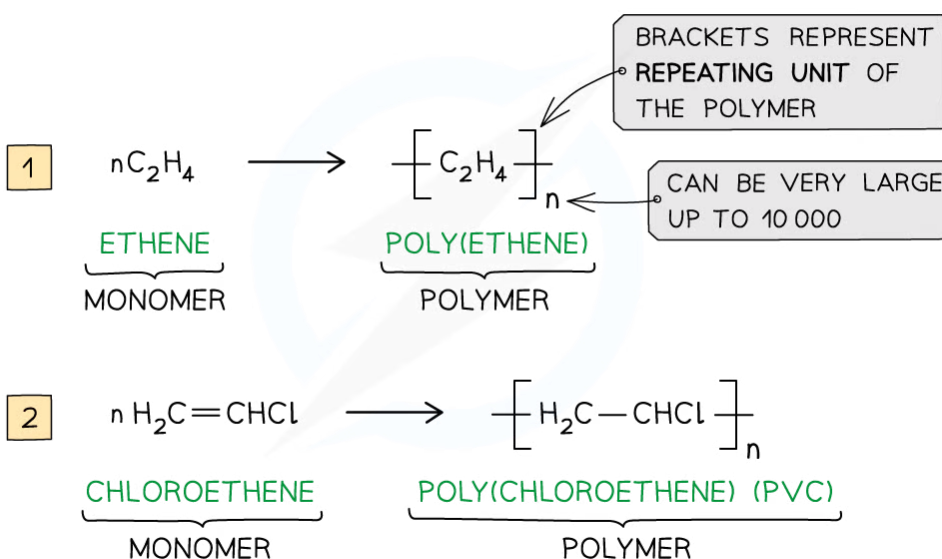


Addition Polymers

Addition polymerisation

- **Addition polymerisation** is one of the most important addition reactions of alkenes which form the basis of the plastics 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 join together to form the polymer are called **monomers**
- A polymerisation reaction can be represented by a **general formula** or by using **displayed formulae**
 - Eg. 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

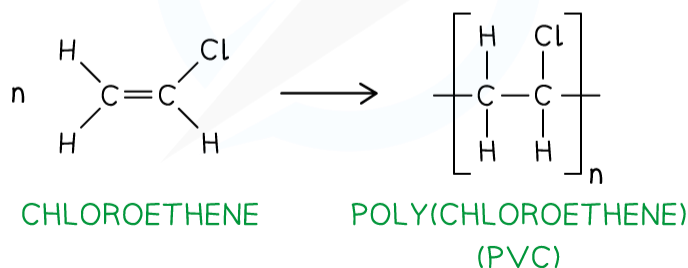
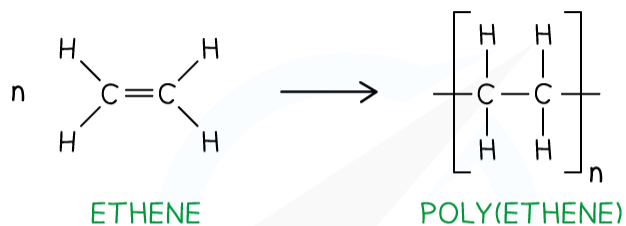
GENERAL FORMULA ADDITION POLYMERISATION



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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 displayed formulae of 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

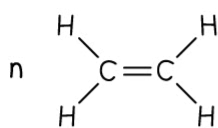
- ♦ A **repeat unit** is the smallest group of atoms that when connected one after the other make up the polymer chain
 - It is represented by **square brackets** in the displayed and general formula
- ♦ In **poly(alkenes)** (such as poly(ethene)) and **substituted poly(alkenes)** (such as PVC) made 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

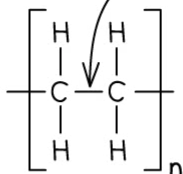


YOUR NOTES
↓

1



ETHENE
MONOMER

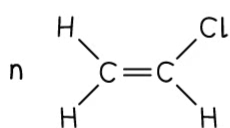


POLY(ETHENE)
REPEATING UNIT
OF POLYMER

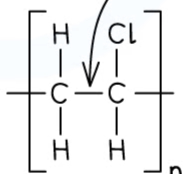
DOUBLE BOND HAS
CHANGED INTO A
SINGLE BOND

MONOMER AND REPEATING
UNIT ARE THE SAME

2



CHLOROETHENE
MONOMER



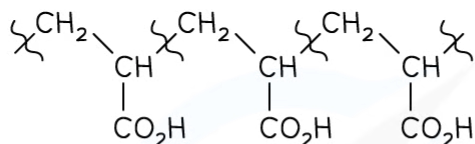
POLY(CHLOROETHENE)
REPEATING UNIT
OF POLYMER

DOUBLE BOND HAS
CHANGED INTO A
SINGLE BOND

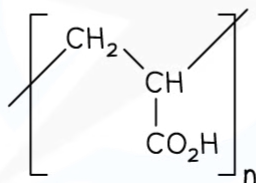
MONOMER AND REPEATING
UNIT ARE THE SAME

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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



ONE REPEATING UNIT

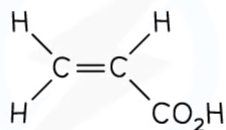


POLY(PROP-2-ENOIC ACID)

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

MONOMER

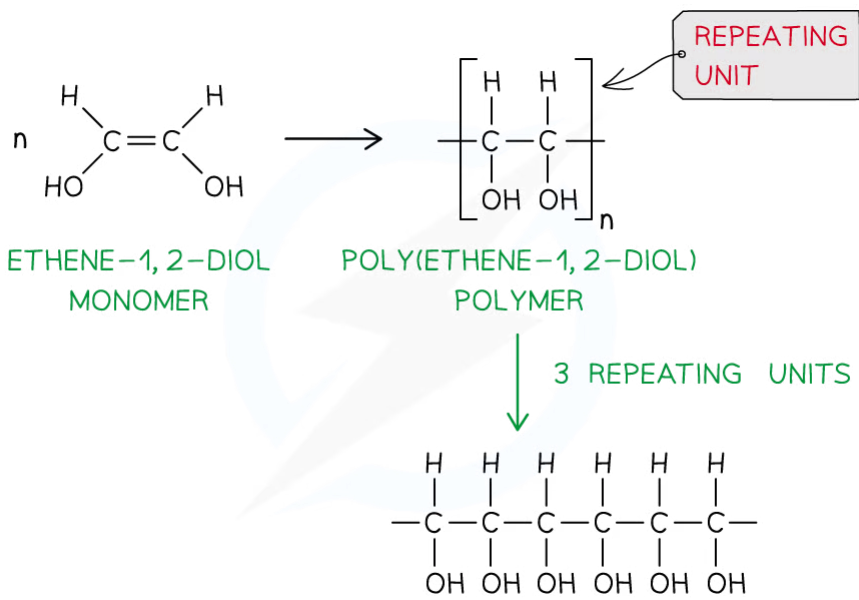


PROP-2-ENOIC ACID

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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, CH(OH)=CH(OH) , is polymerised, the C=C double bond opens to produce a repeating unit of -CH(OH)-CH(OH)- which gives the polymer poly(ethene-1,2-diol)



YOUR NOTES
↓



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.

3.4.6 Solution to Plastic Pollution

Disposing of Polymers

- ♦ Though poly(alkenes)s are extremely important in everyday such as their use as **plastics**, the disposal of these polymers is problematic
- ♦ Poly(alkenes) are very large alkane molecules which are **unreactive** and therefore do not undergo any chemical reactions; they are **resistant to chemical attack**
- ♦ Due to their unreactivity, polymers are **non-biodegradable** and take up to hundreds of years to decompose when dumped in landfill sites
 - Throwing away poly(alkenes) therefore cause the long-term pollution of the environment
- ♦ Burning the polymers results in **harmful combustion products** which again cause the pollution of the environment



Exam Tip

The disposal of polymers is a challenge due to their unreactivity, their non-biodegradability, and the formation of harmful combustion products when burnt.

Solutions to Plastic Pollution

- ♦ Possibly the easiest method to reduce the amount of plastic, is to reuse it rather than throwing it away
- ♦ Since polymers have a long chain full of saturated, non polar C-C bonds
- ♦ This makes them very unreactive molecules, which is why they are said to be non-biodegradable
 - They cannot be attacked and broken down by biological agents, such as enzymes
- ♦ This is what makes throwing plastic away to end up on a landfill such a problem
- ♦ Instead of throwing it away or reusing the plastic, you could recycle it

Feedstock Recycling

- ♦ This is one possible solution to deal with the excess pollution that is caused by plastic
- ♦ This process involves
 - Heating the plastic to a high enough temperature that the polymer bonds break, and monomers are formed
 - The monomers formed are then used to produce new plastics

Mechanical Recycling

- ♦ This is a more straight forward type of recycling
- ♦ The different types of plastic are separated and washed thoroughly
- ♦ Then, they are ground up into small pellets
- ♦ The pellets are heated up until they melt, and then remoulded so that they can be used again

YOUR NOTES



Some Issues

- These types of recycling are not perfect solutions
- Some plastics, like poly(propene), can only be heated and reused a number of times
- Each time the plastic is heated, some of the key chains break
- This means that over time, the properties of the plastic are degraded

YOUR NOTES



3.5 Alcohols

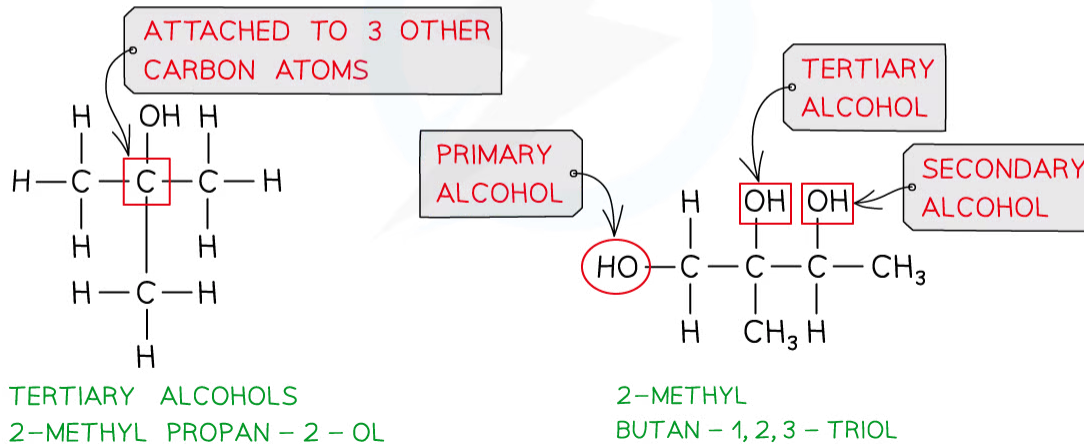
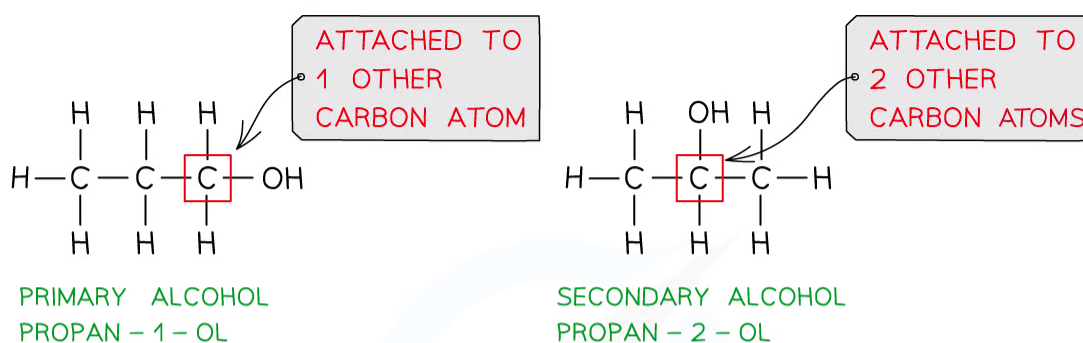
YOUR NOTES



3.5.1 Classifying Alcohols

Classification of Alcohols

- **Primary alcohols** are alcohols in which the carbon atom bonded to the -OH group is attached to **one** other carbon atom (or alkyl group)
- **Secondary alcohols** are alcohols in which the carbon atom bonded to the -OH group is attached to **two** other carbon atoms (or alkyl groups)
- **Tertiary alcohols** are alcohols in which the carbon atom bonded to the -OH group is attached to **three** other carbon atoms (or alkyl groups)

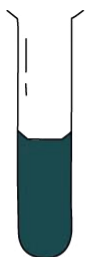


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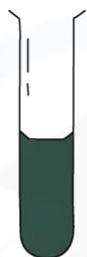
Classifying primary, secondary and tertiary alcohols and alcohols with more than one alcohol group

- Only **primary** and **secondary alcohols** can get oxidised when **mildly oxidised** with acidified $K_2Cr_2O_7$
 - Primary alcohols get mildly oxidised to aldehydes
 - Secondary alcohols get mildly oxidised to ketones
- **Tertiary alcohols** do **not** undergo oxidation with acidified $K_2Cr_2O_7$

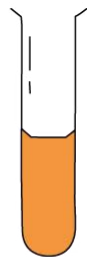
- Therefore, only the oxidation of primary and secondary alcohols will change the colour of $\text{K}_2\text{Cr}_2\text{O}_7$ solution as the **orange** $\text{Cr}_2\text{O}_7^{2-}$ ions are reduced to **green** Cr^{3+} ions



PROPAN-1-OL
(PRIMARY ALCOHOL)



PROPAN-2-OL
(SECONDARY ALCOHOL)



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

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Only primary and secondary alcohols can be oxidised, turning the orange solution green

No colour change is observed with a tertiary alcohol

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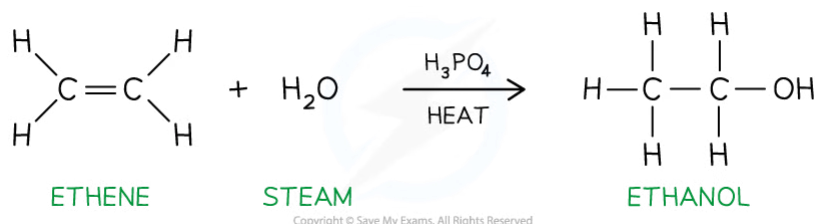
3.5.2 Alcohol Production

Alcohol Production

- Alcohols are compounds that contain at least one hydroxy (-OH) group
- The general formula of alcohols is $C_nH_{2n+1}OH$
- Alcohols can be prepared by a wide range of chemical reactions

Electrophilic addition to alkenes

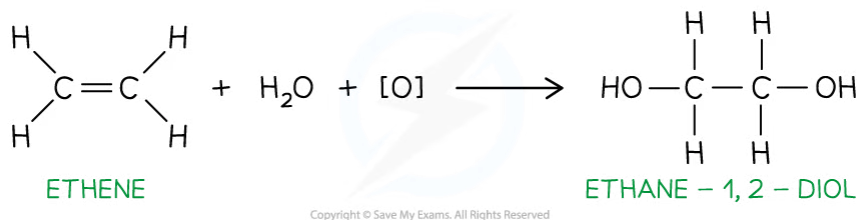
- When hot steam is reacted with an alkene, using concentrated phosphoric(VI) acid (H_3PO_4) or sulfuric acid as a catalyst, **electrophilic addition** takes place to form an alcohol



Electrophilic addition of steam to alkenes to form an alcohol

Oxidation of alkenes

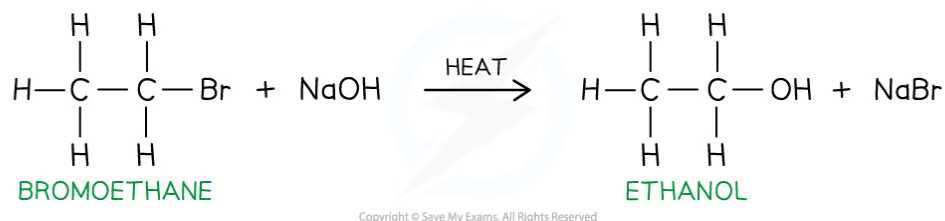
- Cold, dilute $KMnO_4$ is a **mild oxidising agent** and oxidises alkenes
- The $C=C$ double bond is broken open and a diol is formed
 - A diol is a compound with two hydroxy, -OH, groups



Oxidation of alkenes using cold, dilute $KMnO_4$ to form a diol

Nucleophilic substitution of halogenoalkanes

- The halide atom in halogenoalkanes can be substituted when heated with aqueous NaOH in a **nucleophilic substitution** reaction



Nucleophilic substitution of halogenoalkanes using NaOH to form an alcohol

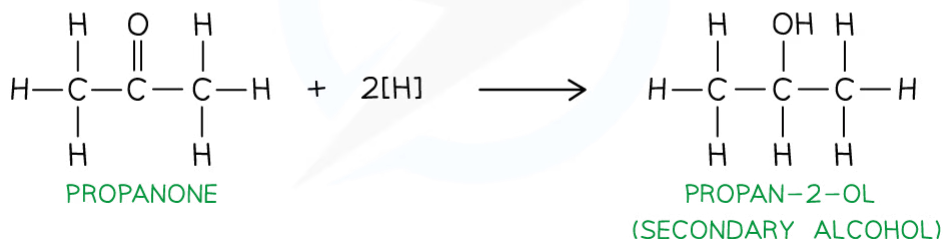
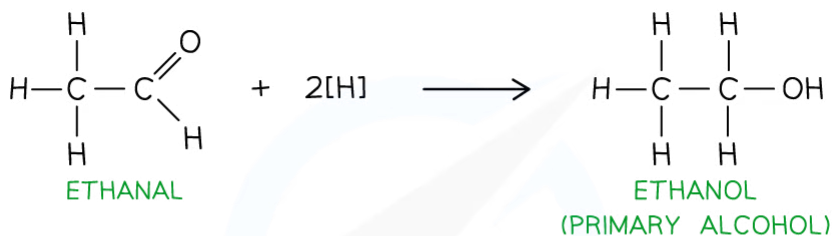
YOUR NOTES





Reduction of aldehyde & ketones

- **Aldehydes** and **ketones** can be reduced by reducing agents such as NaBH_4 or LiAlH_4
- Aldehydes are reduced to **primary alcohols**
 - The carbon attached to the hydroxy group is bonded to one other alkyl group
- Ketones are reduced to **secondary alcohols**
 - The carbon attached to the hydroxy group is bonded to two other alkyl groups



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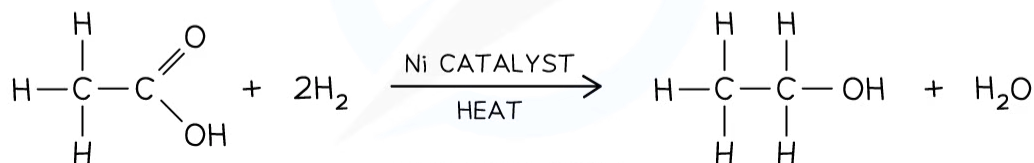
Reduction of aldehydes and ketones to form primary and secondary alcohols

Reduction of carboxylic acids

- Similarly, carboxylic acids are reduced by NaBH_4 or LiAlH_4 to primary alcohols
- Carboxylic acids can also be reduced by H_2 using a nickel catalyst and heat



OR



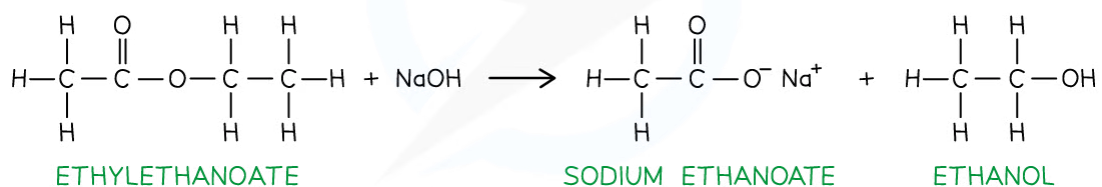
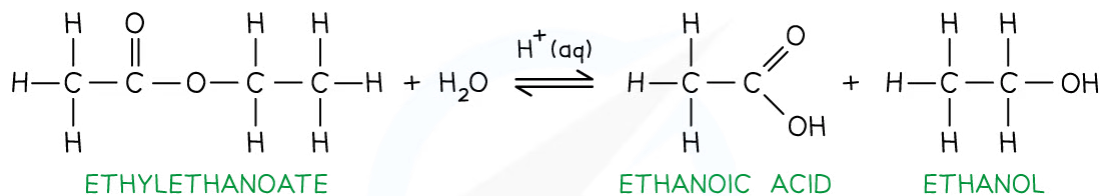
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Reduction of carboxylic acids to primary alcohols

Hydrolysis of ester

- Esters are made by a **condensation reaction** between an alcohol and a carboxylic acid
- When an ester is heated with dilute acid or alkali, **hydrolysis** will take place and the carboxylic acid and alcohol will be reformed

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Hydrolysis of esters to form alcohols

Alcohol Production Reactions Table

Reaction Type	Reagents	Conditions	Product
Electrophilic addition	Alkene Steam	Heat H ₃ PO ₄ Catalyst	Alcohol
Oxidation	Alkenes Cold, dilute KMnO ₄	Shaking of reagents	Diol
Nucleophilic Substitution	Halogenoalkanes Aqueous NaOH	Heat	Alcohol
Reduction	Aldehydes/ ketones	NaBH ₄ or LiAlH ₄	Primary/ secondary alcohol
Reduction	Carboxylic acid	NaBH ₄ or LiAlH ₄ Or H ₂ , Ni catalyst and heat	Primary alcohol
Hydrolysis	Esters	Dilute acid or alkali heat	Alcohol

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Exam Tip

The symbol [O] is used to represent oxygen provided by an oxidising agent.

3.5.3 Oxidation of Alcohols

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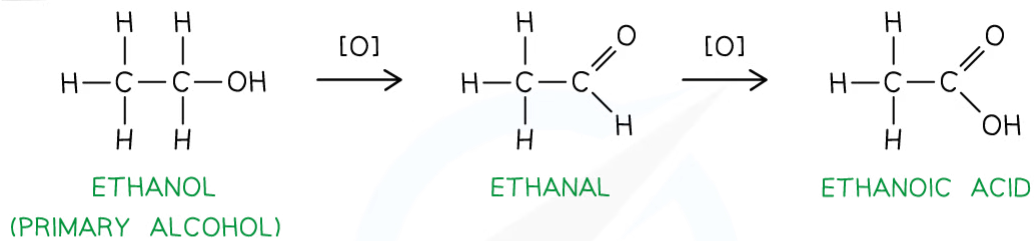


Oxidation of Alcohols

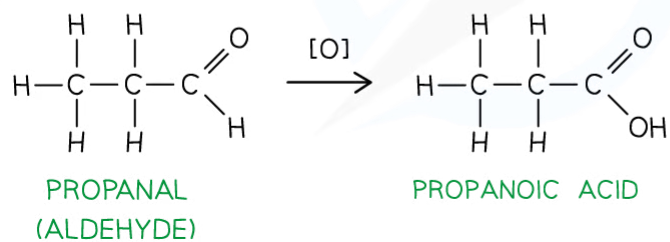
Oxidation of alcohols

- ♦ Primary alcohols can be oxidised to form **aldehydes** which can undergo further oxidation to form **carboxylic acids**
- ♦ Secondary alcohols can be oxidised to form **ketones** only
- ♦ Tertiary alcohols do not undergo oxidation
- ♦ 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 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
 - This reduction requires hydrogen (H^+) ions which are provided by the acidic medium
 - 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 $K_2Cr_2O_7$ 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 (MnO_4^-) are reduced to colourless Mn^{2+} ions
- ♦ The primary alcohol is added to the oxidising agent and warmed
- ♦ The aldehyde product has a lower boiling point than the alcohol reactant so it can be **distilled off** as soon as it forms
- ♦ If the aldehyde is not distilled off, further **refluxing** with excess oxidising agent will oxidise it to a carboxylic acid
- ♦ Since ketones cannot be further oxidised, the ketone product does not need to be **distilled off** straight away after it has been formed

1



2



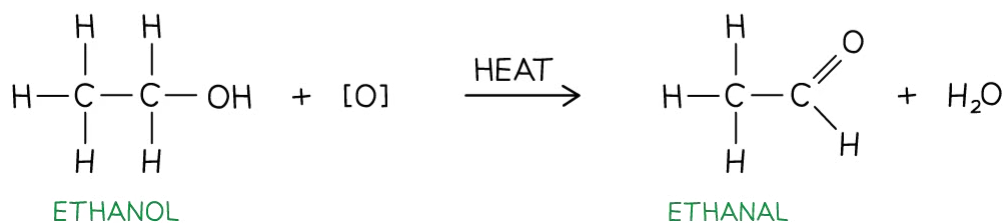
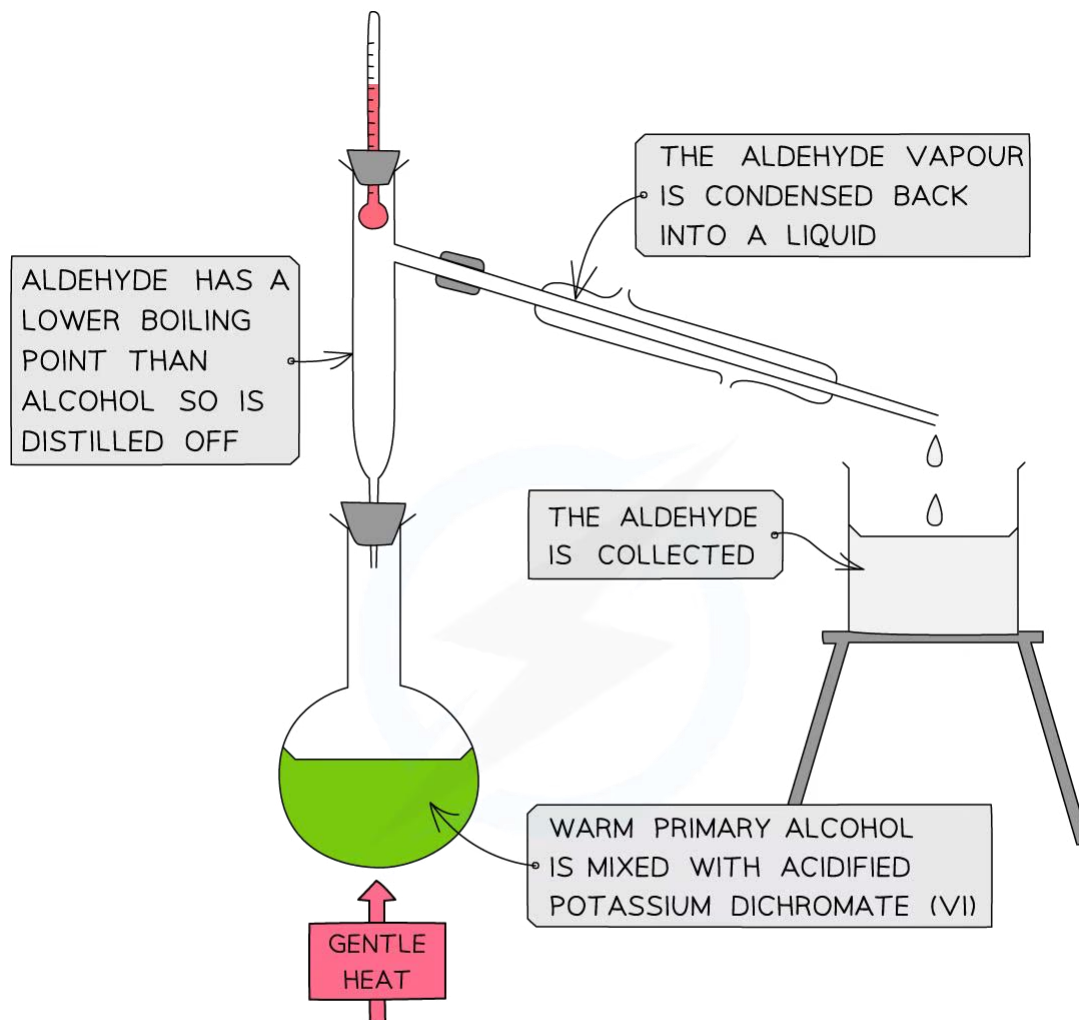
[O] = ACIDIFIED $\text{K}_2\text{Cr}_2\text{O}_7$
OR
ACIDIFIED KMnO_4

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Oxidation Stages of Primary Alcohols

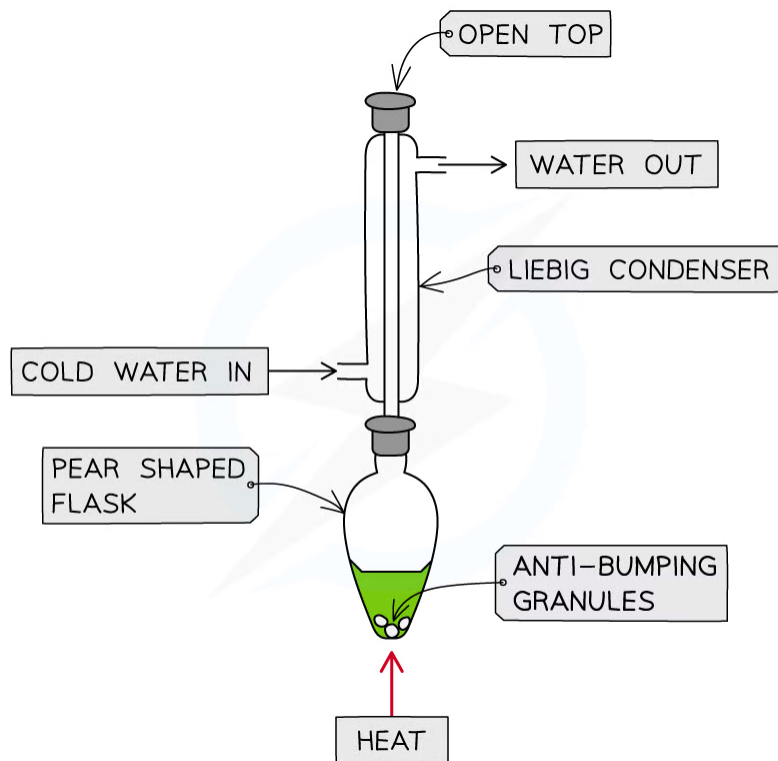
YOUR NOTES





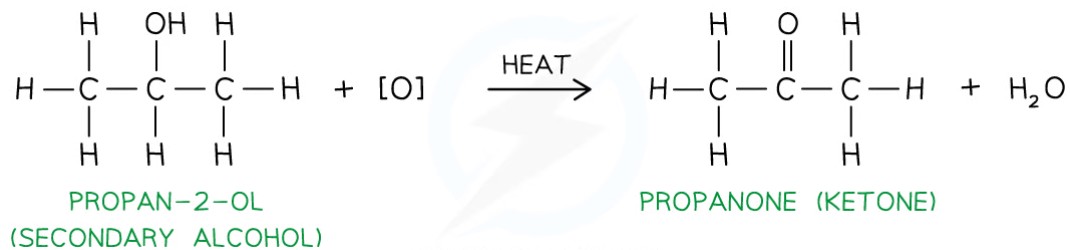
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Oxidation of ethanol by acidified $\text{K}_2\text{Cr}_2\text{O}_7$ to form an aldehyde by distillation



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Further oxidation of the aldehyde via reflux can be done to produce a carboxylic acid



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Oxidation of propan-2-ol by acidified $\text{K}_2\text{Cr}_2\text{O}_7$ to form a ketone

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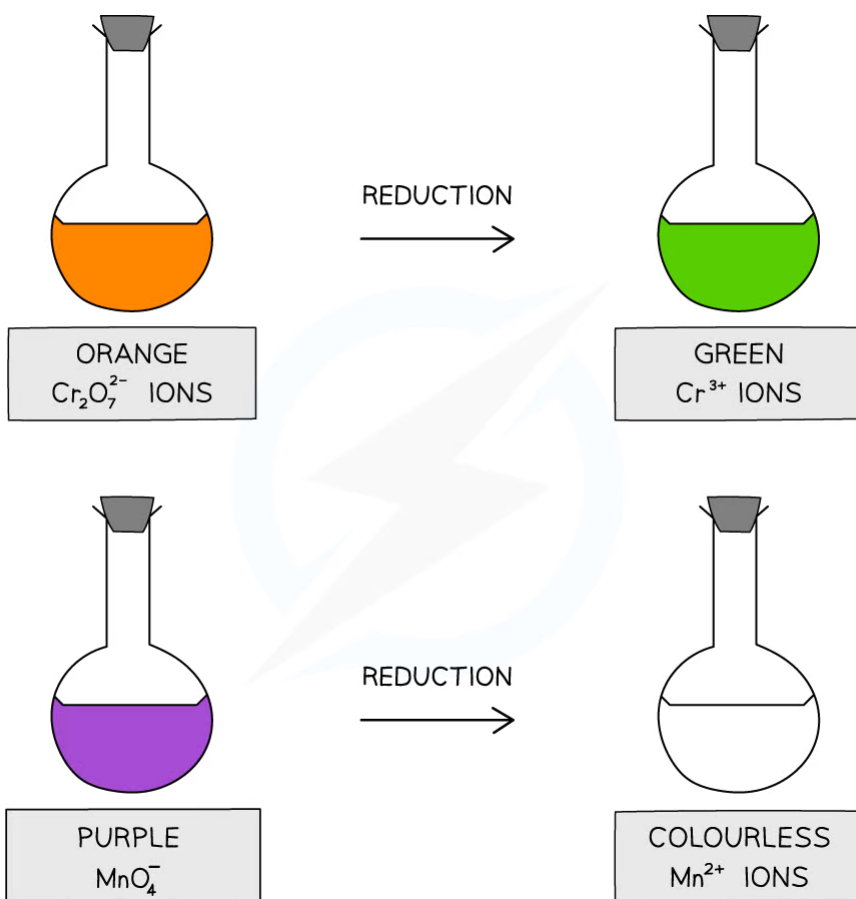


Oxidation Products

- **Aldehydes** and **ketones** are carbonyl compounds containing a C=O group
- They can be prepared from the oxidation of **primary** and **secondary alcohols** respectively

Oxidising agents

- The oxidising agents used to prepare aldehydes and ketones from alcohols include **acidified potassium dichromate** ($K_2Cr_2O_7$) and **acidified potassium manganate** ($KMnO_4$)
- The acidified **potassium dichromate(VI)**, $K_2Cr_2O_7$, is an orange oxidising agent
 - When the alcohols are **oxidised** the orange dichromate ions ($Cr_2O_7^{2-}$) are reduced to green Cr^{3+} ions
- The acidified **potassium manganate(VII)**, $KMnO_4$ is a purple oxidising agent
 - When the alcohols are **oxidised** the purple manganate ions (MnO_4^-) are reduced to colourless Mn^{2+} ions



The oxidising agents change colour when they oxidise an alcohol and get reduced themselves

YOUR NOTES



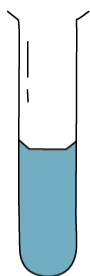


Testing for Oxidation Products

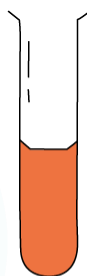
- The presence of an aldehyde group ($-CHO$) in an **unknown compound** can be determined by the **oxidising agents** Fehling's and Tollens' reagents

Fehling's solution

- Fehling's solution** is an alkaline solution containing copper(II) ions which act as the oxidising agent
- When **warmed** with an aldehyde, the aldehyde is oxidised to a carboxylic acid and the Cu^{2+} ions are reduced to Cu^+ ions
 - In the alkaline conditions, the carboxylic acid formed will be neutralised to a carboxylate ion (the $-COOH$ will lose a proton to become $-COO^-$)
 - The carboxylate ion ($-COO^-$) will form a salt with a positively charged metal ion such as sodium ($-COO^-Na^+$)
- The **clear blue** colour of the solution turns **opaque** red due to the formation of a **copper(I) oxide precipitate**
- Ketones** cannot be oxidised and therefore give a **negative test** when warmed with Fehling's solution



CLEAR BLUE FEHLING'S SOLUTION WITH Cu^{2+} IONS



OPAQUE RED PRECIPITATE OF Cu_2O AS:
 - Cu^{2+} IS REDUCED TO Cu^+
 - ALDEHYDE IS OXIDISED TO CARBOXYLIC ACID

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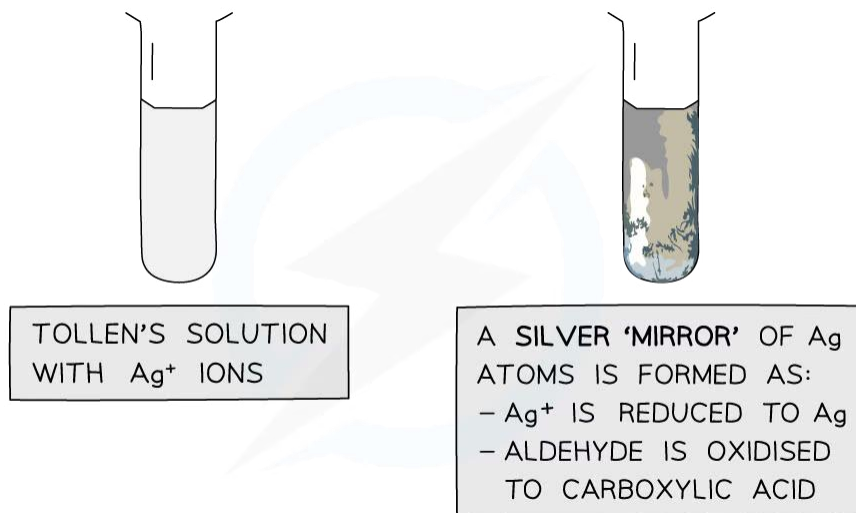
The copper(II) ions in Fehling's solution are oxidising agents, oxidising the aldehyde to a carboxylic acid and getting reduced themselves to copper(I) ions in the Cu_2O precipitate

Tollens' reagent

- Tollens' reagent** is an aqueous alkaline solution of silver nitrate in excess ammonia solution
 - Tollen's reagent is also called **ammoniacal silver nitrate solution**
- When **warmed** with an aldehyde, the aldehyde is oxidised to a carboxylic acid and the Ag^+ ions are reduced to Ag atoms
 - In the alkaline conditions, the carboxylic acid will become a carboxylate ion and form a salt
- The Ag atoms form a silver 'mirror' on the inside of the tube

- **Ketones** cannot be oxidised and therefore give a **negative test** when warmed with Tollens' reagent

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The Ag^+ ions in Tollens' reagent are ~~oxidising agents~~, oxidising the aldehyde to a carboxylic acid and getting reduced themselves to silver atoms

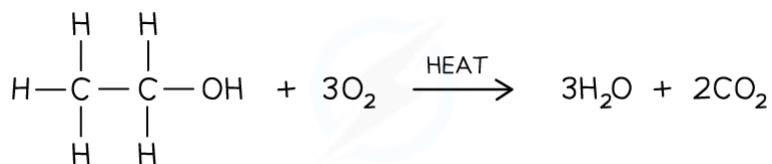
3.5.4 Combustion of Alcohols

Combustion of Alcohols

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.

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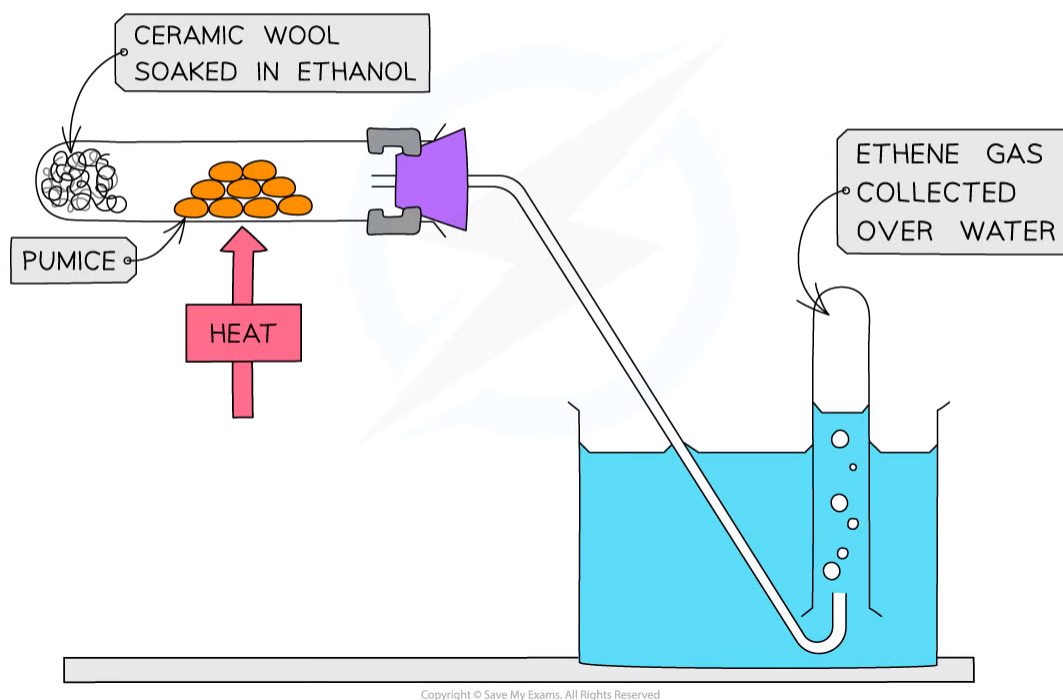
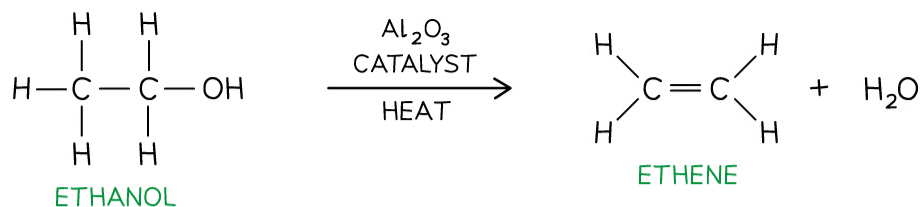


3.5.5 Elimination Reactions of Alcohols

Elimination Reactions

Elimination Reaction of Alcohols

- Alcohols can also undergo **dehydration** to form alkenes
 - This is an example of an elimination reaction
 - Elimination reactions involve a small molecule leaving the parent molecule as a byproduct
 - In this case, the small molecule is a water molecule
 - The water molecule is formed from the -OH group and a hydrogen atom from the adjacent carbon atom
- Alcohol vapour is passed over a **hot catalyst** of aluminium oxide (Al_2O_3) powder or pieces of porous pot
 - Excess hot, concentrated sulfuric acid or phosphoric acid is used as a catalyst



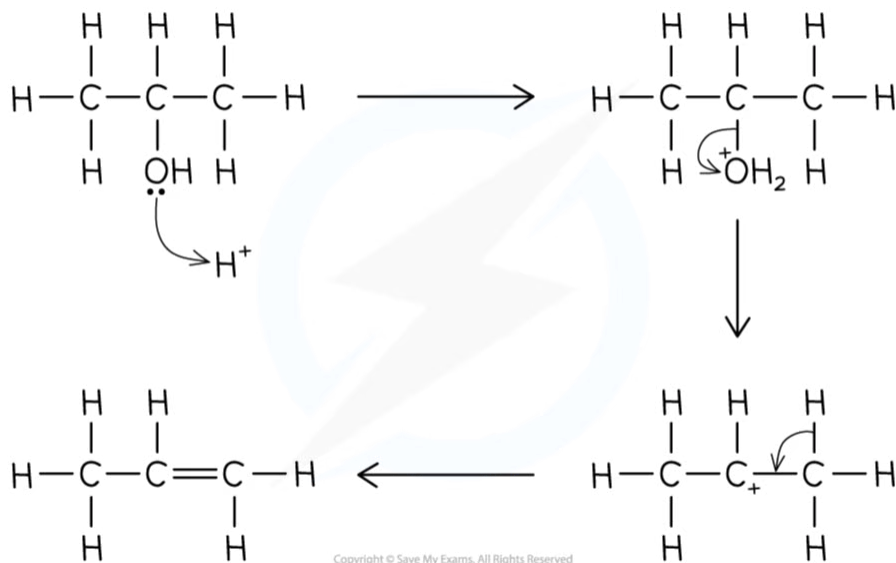
Dehydration of ethanol using aluminium oxide as a catalyst forms ethene gas, which can be collected over water

- The reaction and mechanism for the dehydration of propan-1-ol is shown below

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Dehydration of propan-1-ol mechanism

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3.6 Organic Analysis

3.6.1 Identification of Functional Groups by Test-Tube Reactions

Test-Tube Reactions

- Often, chemists will need to identify the functional groups present in an organic compound
- Some simple questions which can be considered are:
 - Is the compound acidic?
 - If so, it could be a carboxylic acid
 - What state is the compound in?
 - If solid, it could suggest long C-C chains or strong intermolecular forces
 - If liquid, it could suggest medium C-C chain length, or something polar
 - If gas, it will likely have very short C-C chain length and is unlikely to be polar
 - Is it soluble in water?
 - If so, then it suggests that the compound has polar groups and if not, then it suggests that it does not have polar groups present
- Following this, simple chemical tests can also be done, to determine the functional groups which are present
- These are known as test-tube reactions, and are simple but highly effective tests

Simple Test Tube Reactions

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Functional Group	Test	Result
Alkene C=C	Shake with bromine water	Orange turns to colourless
Halogenoalkane R-X	Add aqueous sodium hydroxide and warm gently Acidify with nitric acid (HNO ₃) Add silver nitrate (AgNO ₃)	Coloured precipitate of AgX forms AgCl = white AgBr = cream AgI = yellow
Alcohol R-OH	Add acidified potassium dichromate solution (K ₂ Cr ₂ O ₇)	Orange turns to green with primary and secondary alcohols No colour change (no reaction) with tertiary alcohols
Aldehydes R-CHO	Warm with Tollen's reagent OR Warm with Fehling's solution	Silver mirror forms OR Blue solution turns to a red precipitate
Carboxylic Acids R-COOH	Add sodium hydrogen carbonate (NaHCO ₃)	CO ₂ gas formed

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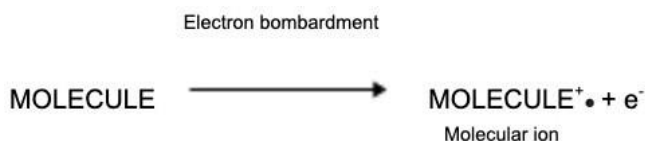
3.6.2 Mass spectrometry

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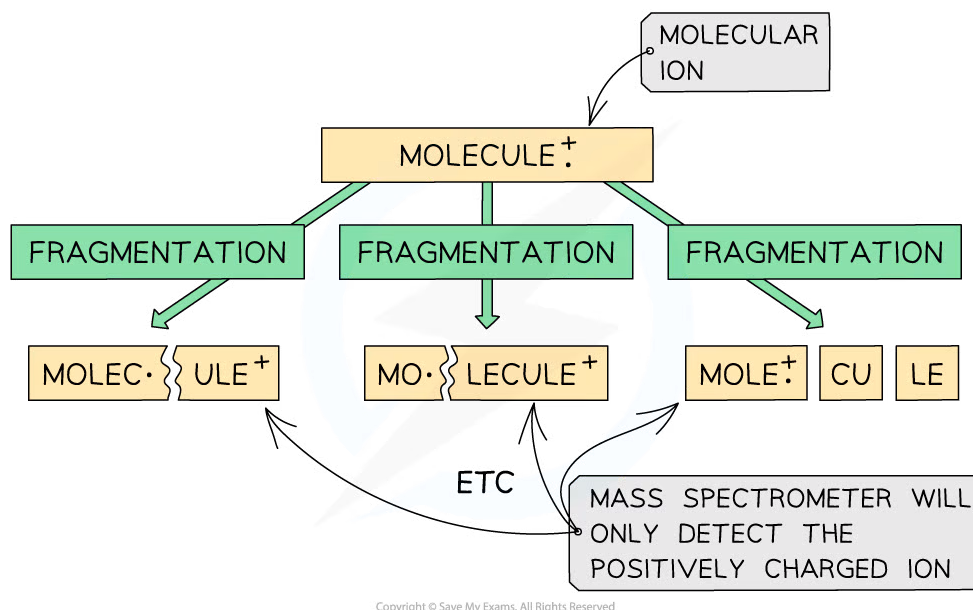


Interpreting a Mass Spectrum

- **Mass spectroscopy** is an analytical technique used to identify unknown compounds
- The molecules in the small sample are **bombarded** with high energy electrons which can cause the molecule to lose an electron
- This results in the formation of a positively charged **molecular ion** with one unpaired electron
 - One of the electrons in the pair has been **removed** by the beam of electrons



- The molecular ion can further **fragment** to form new ions, molecules, and radicals



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Fragmentation of a molecule in mass spectroscopy

- These **fragmented** ions are **accelerated** by an electric field
- Based on their mass (**m**) to charge (**z**) ratio, the ion fragments are then separated by deflecting them into the **detector**
 - Most ions will only gain a charge of 1+ and therefore a ion with mass 12 and charge 1+ will have an m/z value of 12
 - It is, however, possible for a greater charge to occur. For example, an ion with mass 16 and charge 2+ will have a m/z value of 8

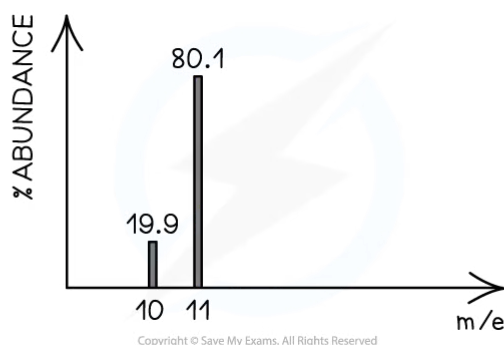
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- The smaller and more positively charged fragment ions will be **detected** first as they will get **deflected** the most and are more attracted to the **negative pole** of the magnet
- Each fragment corresponds to a specific **peak** with a particular m/z value in the mass spectrum
- The **base peak** is the peak corresponding to the most **abundant** ion
- The m/z is sometimes referred to as the m/e ratio and it is almost always 1:1

Isotopes

- Isotopes are different atoms of the **same element** that contain the same number of **protons** and **electrons** but a different number of **neutrons**.
 - These are atoms of the same **elements** but with different mass number
 - For example, Cl-35 and Cl-37 are isotopes as they are both atoms of the same element (chlorine, Cl) but have a different mass number (35 and 37 respectively)
- Mass spectroscopy can be used to find the **relative abundance** of the isotopes experimentally
- The **relative abundance** of an isotope is the proportion of one particular isotope in a mixture of isotopes found in nature
 - For example, the relative abundance of Cl-35 and Cl-37 is 75% and 25% respectively
 - This means that in nature, 75% of the chlorine atoms is the Cl-35 isotope and 25% is the Cl-37 isotope
- The **heights** of the peaks in mass spectroscopy show the proportion of each isotope present



The peak heights show the relative abundance of the boron isotopes: boron-10 has a relative abundance of 19.9% and boron-11 has a relative abundance of 80.1%



Worked Example

Calculating m/z ratio

In a sample of iron, the ions $^{54}\text{Fe}^{2+}$ and $^{56}\text{Fe}^{3+}$ are detected. Calculate their m/z ratio and determine which ion is detected more inside the spectrometer.

Answer

$$m/e (^{54}\text{Fe}^{2+}) = \frac{54}{2}$$

$$= 27$$

$$m/e (^{56}\text{Fe}^{3+}) = \frac{56}{3}$$

$$= 18.7$$

$$= 19$$

- $^{56}\text{Fe}^{3+}$ has a smaller m/z ratio and will therefore be deflected more.
- It also has the largest positive charge and will be more attracted to the negative pole of the magnet within the mass spectrometer.



Exam Tip

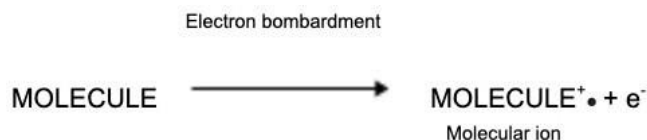
A small m/z value corresponds to fragments that are either **small** or have a **high positive charge** or a combination of **both**.

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Deducing Molecular Formula

- Each **peak** in the mass spectrum corresponds to a certain **fragment** with a particular **m/z** value
- The peak with the highest **m/z** value is the molecular ion (**M^+**) peak which gives information about the **molecular mass** of the compound
- The molecular ion is the entire molecule that has lost one electron when bombarded with a beam of electrons



- The **[M+1]** peak is a smaller peak which is due to the natural abundance of the isotope carbon-13
- The amount of naturally occurring C-13 is a little over 1%, so the [M+1] peak is very small
- The height of the [M+1] peak for a particular ion depends on how many carbon atoms are present in that molecule; the more carbon atoms, the larger the [M+1] peak is
 - For example, the height of the [M+1] peak for an hexane (containing six carbon atoms) ion will be greater than the height of the [M+1] peak of an ethane (containing two carbon atoms) ion

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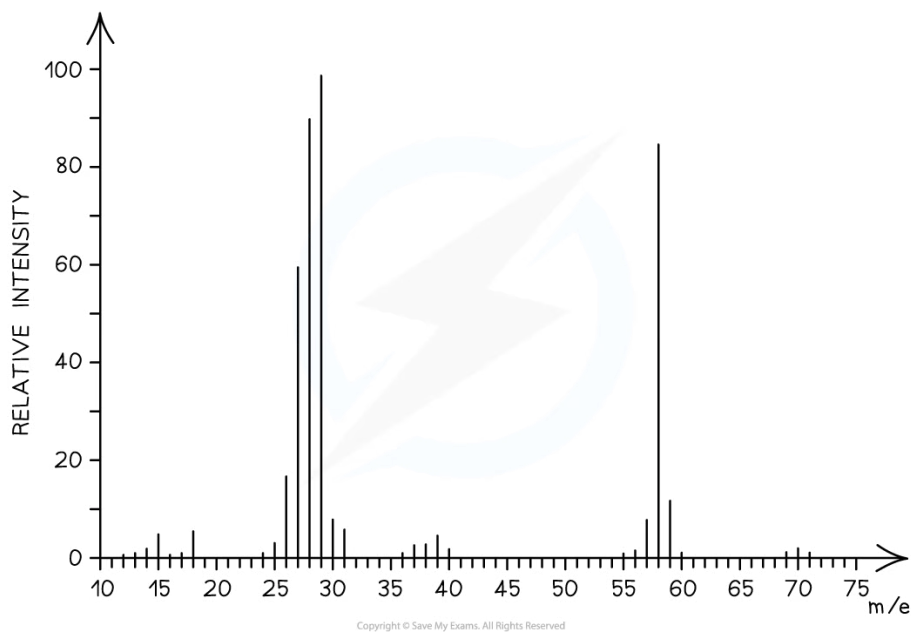




Worked Example

Analysing mass spectra

Determine whether the following mass spectrum corresponds to but-1-ene or pent-1-ene:



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Answer

- The mass spectrum corresponds to pent-1-ene as the molecular ion peak is at $m/z = 70$
 - The small peak at $m/z = 71$ is a C-13 peak, which does not count as the molecular ion peak
- But-1-ene arises from the $C_4H_8^+$ ion which has a molecular mass of 56
- Pent-1-ene arises from the $C_5H_{10}^+$ ion which has a molecular mass of 70

Fragmentation

- The molecular ion peak can be used to identify the **molecular mass** of a compound
- However, different compounds may have the same molecular mass
- To further determine the structure of the unknown compound, **fragmentation** is used
- Fragments may appear due to the formation of **characteristic fragments** or the **loss of small molecules**
 - For example, a peak at 29 is due to the characteristic fragment C_2H_5^+
 - Loss of small molecules give rise to peaks at 18 (H_2O), 28 (CO), and 44 (CO_2)

Alkanes

- Simple alkanes are fragmented in mass spectroscopy by breaking the C-C bonds
- ***m/e*** values of some of the common alkane fragments are given in the table below

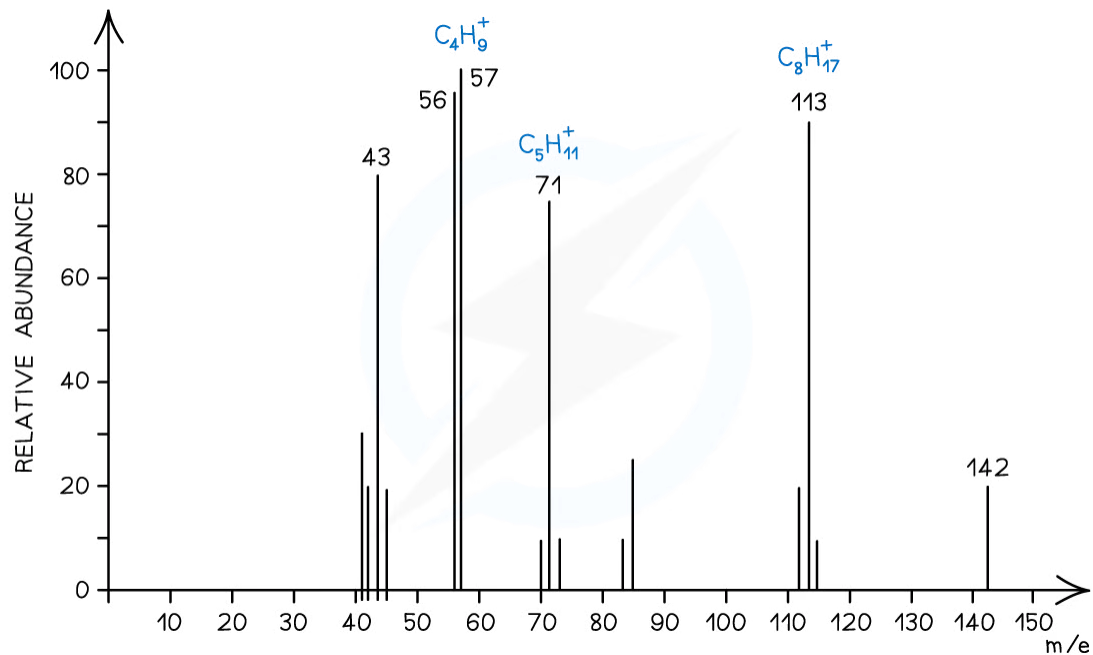
***m/e* Values of Fragments Table**

Fragment	<i>m/e</i>
CH_3^+	15
C_2H_5^+	29
C_3H_7^+	43
C_4H_9^+	57
$\text{C}_5\text{H}_{11}^+$	71
$\text{C}_6\text{H}_{13}^+$	85

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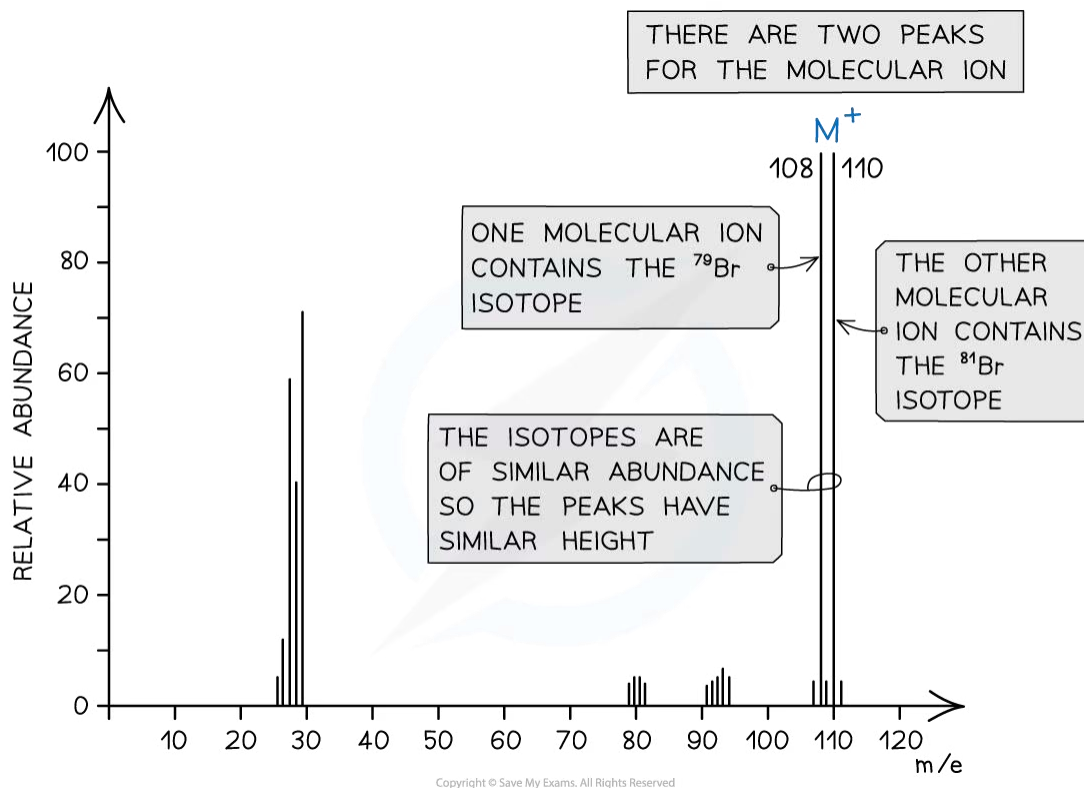
Mass spectrum showing the fragmentation of $C_{10}H_{22}$

Halogenoalkanes

- Halogenoalkanes often have multiple peaks around the molecular ion peak
- This is caused by the fact that there are different isotopes of the halogens

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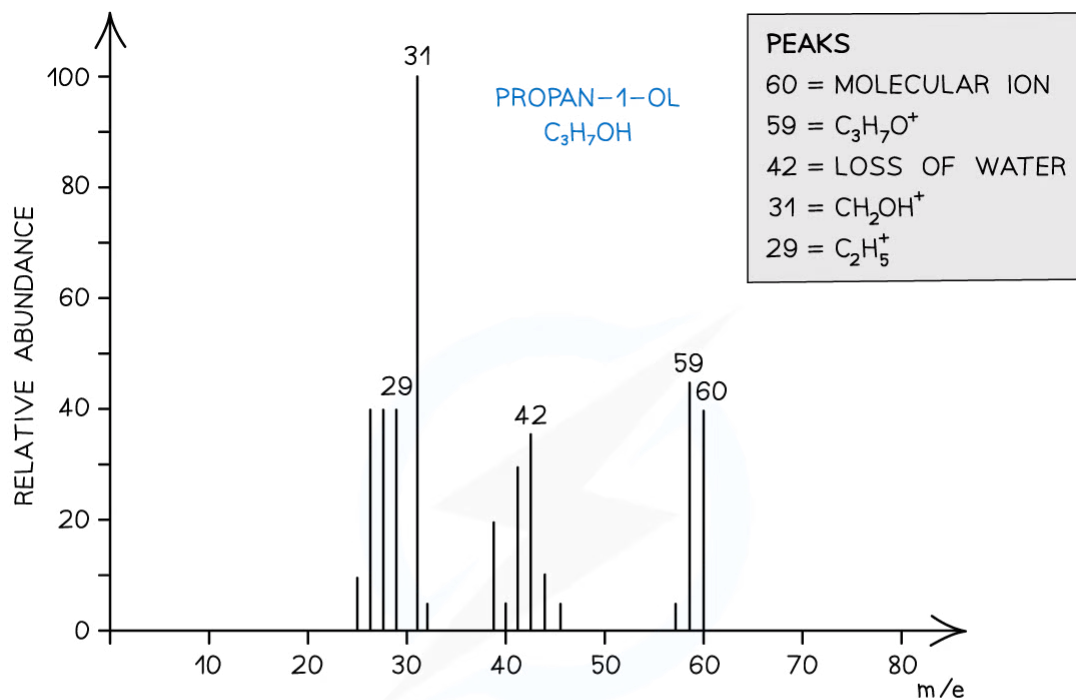
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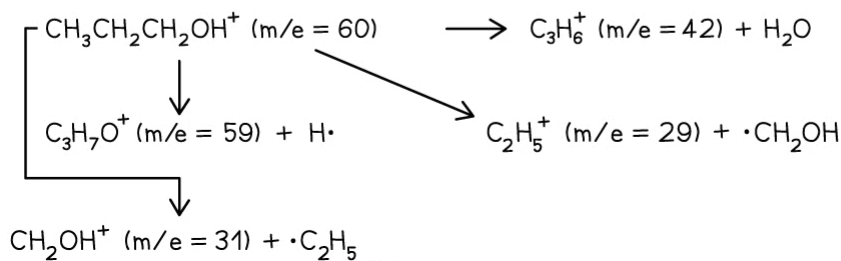
Mass spectrum showing different isotopes of bromine in the molecular ion

Alcohols

- Alcohols often tend to lose a **water molecule** giving rise to a peak at **18 below the molecular ion**
- Another common peak is found at m/e value 31 which corresponds to the CH_2OH^+ fragment
- For example, the mass spectrum of propan-1-ol shows that the compound has fragmented in four different ways:
 - Loss of H^\cdot to form a $\text{C}_3\text{H}_7\text{O}^+$ fragment with $m/e = 59$
 - Loss of a water molecule to form a C_3H_6^+ fragment with $m/e = 42$
 - Loss of a $\cdot\text{C}_2\text{H}_5$ to form a CH_2OH^+ fragment with $m/e = 31$
 - And the loss of $\cdot\text{CH}_2\text{OH}$ to form a C_2H_5^+ fragment with $m/e = 29$



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Mass spectrum showing the fragmentation patterns in propan-1-ol (alcohol)



Worked Example

Ion fragmentation

Which of the following statements about the mass spectrum of CH_3Br is correct?

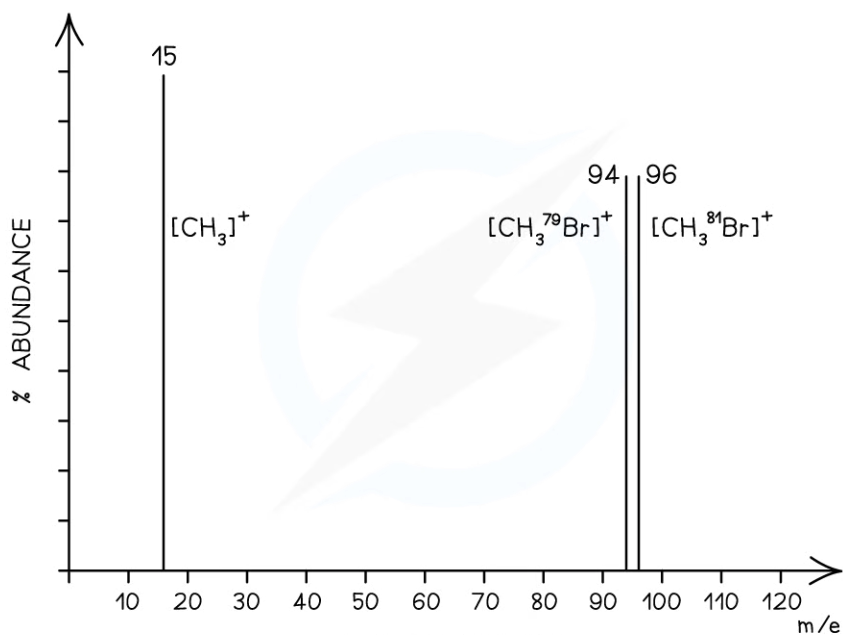
- A. There is one peak for the molecular ion with an m/e value of 44
- B. There is one peak for the molecular ion with an m/e value of 95
- C. The last two peaks have abundances in the ratio 3:1 and occur at m/e values of 94 and 96
- D. The last two peaks are of equal size and occur at m/e values of 94 and 96

Answer



The correct answer is option **D**

- Bromomethane (CH_3Br) can produce 3 peaks
 - $\text{CH}_3^{81}\text{Br} - [\text{CH}_3^{81}\text{Br}]^+ + e^-$ at m/e 96
 - $\text{CH}_3^{79}\text{Br} - [\text{CH}_3^{79}\text{Br}]^+ + e^-$ at m/e 94
 - $\text{CH}_3\text{Br} - [\text{CH}_3]^+ + \cdot\text{Br}$ at m/e 15
- The last two peaks (which correspond to the molecular ion peak) therefore are equal in size and occur at m/e values of 94 and 96



Worked Example

Alcohol fragmentation

Which alcohol is not likely to have a fragment ion at m/e at 43 in its mass spectrum?

- A. $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$
- B. $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_3$
- C. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
- D. $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$

Answer

The correct answer is option **D**

- Because a line at $m/e = 43$ corresponds to an ion with a mass of 43 for example:
 - $[\text{CH}_3\text{CH}_2\text{CH}_2]^+$

- $[(\text{CH}_3)_2\text{CH}]^+$
- 2-butanol is not likely to have a fragment at $m/e = 43$ as it does not have either of these fragments in its structure.

YOUR NOTES



3.6.3 Infrared Spectroscopy

YOUR NOTES



Interpreting an IR Spectrum

- **Infrared (IR) spectroscopy** is a technique used to identify compounds based on changes in **vibrations** of atoms when they **absorb** IR of certain **frequencies**
- A **spectrophotometer** irradiates the sample with electromagnetic waves in the infrared region and then detects the **intensity** of the wavelength of IR radiation which goes through the sample
- All organic molecules absorb IR radiation and depending on which energies of radiation are absorbed, bonds between atoms will vibrate by **stretching, bending** and **twisting**
- The molecules will only vibrate at a specific frequency
- The **resonance frequency** is the specific frequency at which the molecules will vibrate to stimulate larger vibrations
- Depending on the rest of the molecule, each vibration will absorb specific wavelengths of IR radiation which are also shown as the **reciprocal** of the wavelength
 - This unit is called the **wavenumber** (cm^{-1})
- Particular absorbance have characteristic **widths** (broad or sharp) and **intensities** (strong or weak)
 - For example, hydrogen bonds cause the O-H bonds in alcohols and carboxylic acids to be **broad** whereas the C-O bond in carbonyl (C=O) groups have a strong, sharp absorbance peak
- The energies absorbed by different functional groups are given as a range and an unknown compound can be identified by comparing its IR spectrum to the IR spectrum of a known compound

Absorption Range of Bonds Table

Bond	Functional groups containing the bond	Characteristic infrared absorption range (in wavenumbers) (cm^{-1})
C-O	Hydroxy, ester	1040-1300
C=C	Aromatic compound, alkene	1500-1680
C=O	Amide carbonyl, carboxyl ester	1640-1690 1670-1740 1710-1750
C≡N	Nitrile	2200-2250
C-H	Alkane	2850-2950
N-H	Amine, amide	3300-3500
O-H	Carboxyl, hydroxyl	2500-3000 3200-3600

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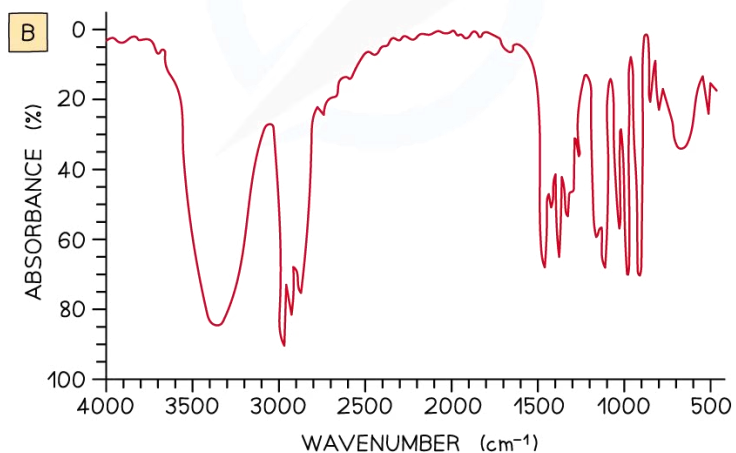
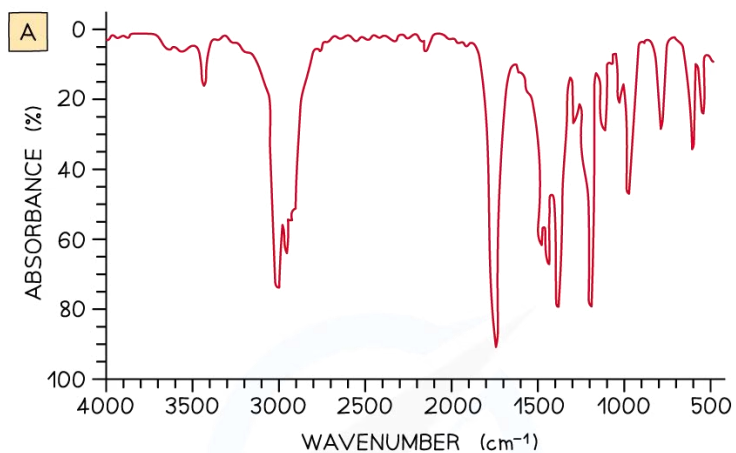
- Due to some absorption bands overlapping each other, other analytical techniques such as mass spectroscopy should be used alongside IR spectroscopy to identify an unknown compound



? Worked Example

Analysing IR Spectra

Look at the two infrared spectra below and determine which one corresponds to propanone and which one to propan-2-ol



Answer

- IR spectrum **A** is **propanone** and spectrum **B** is **propan-2-ol**.
- In IR spectrum **A** the presence of a strong, sharp absorption around 1710 cm^{-1} corresponds to the characteristic $\text{C}=\text{O}$, carbonyl, group in a ketone.
- In spectrum **B** the presence of a strong, broad absorption around $3200\text{--}3500\text{ cm}^{-1}$ suggests that there is an alcohol group present, which corresponds to the -OH group in propan-2-ol.

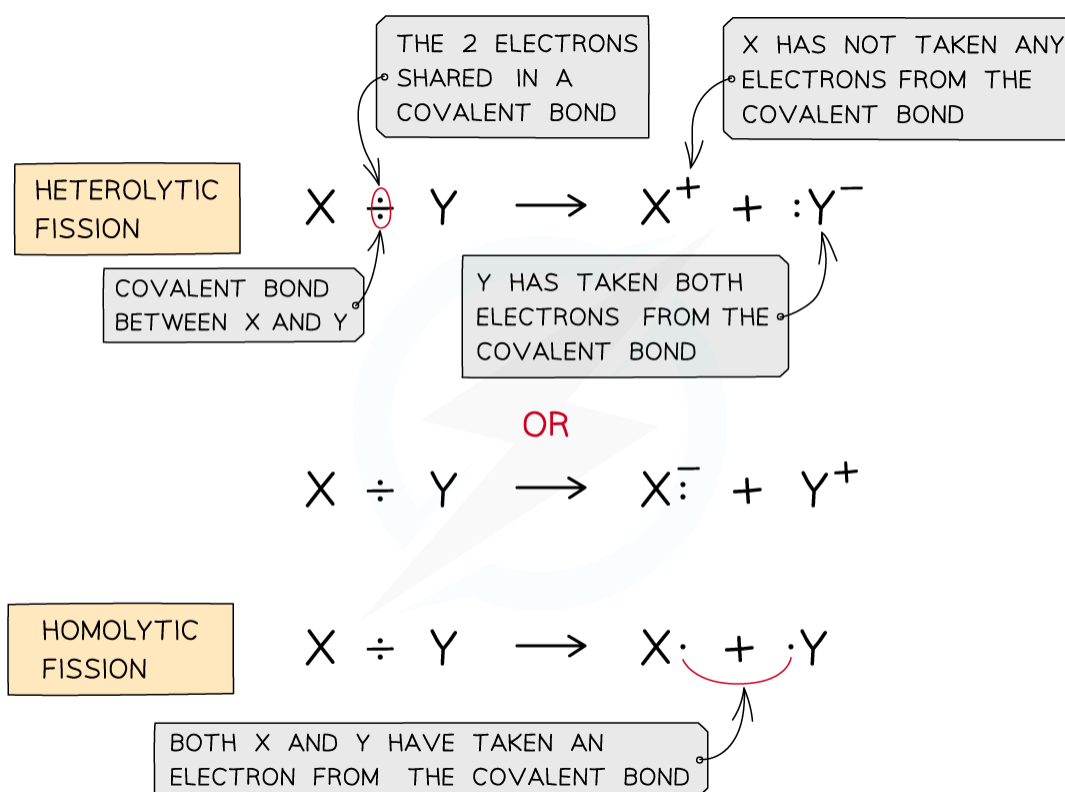
3.7 Organic Mechanisms

3.7.1 Fundamentals of Reaction Mechanisms

Reaction Mechanisms: Terminology

Homolytic & Heterolytic fission

- **Homolytic fission** is breaking a covalent bond in such a way that each atom takes an electron from the bond to form two radicals
- **Heterolytic fission** is breaking a covalent bond in such a way that the more electronegative atom takes both the electrons from the bond to form a negative ion and leaving behind a positive ion



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The diagram shows heterolytic fission in which the most electronegative atom takes both electrons in the covalent bond and homolytic fission in which each atom takes one electron from the covalent bond

Nucleophiles & electrophiles

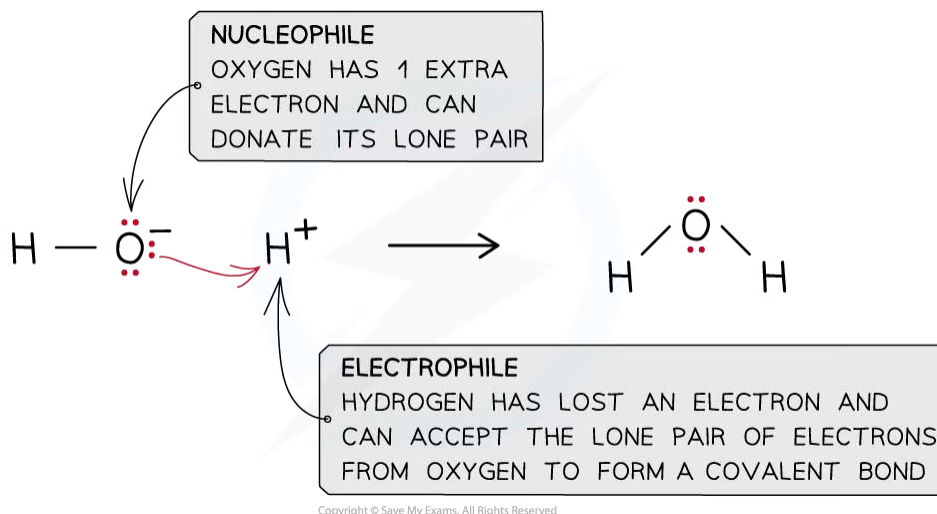
- A **nucleophile** is an electron-rich species that can **donate** a pair of electrons
 - 'Nucleophile' means 'nucleus/positive charge loving' as nucleophiles are attracted to positively charged species
 - **Nucleophilic** refers to reactions that involve a nucleophile
- An **electrophile** is an electron-deficient species that can **accept** a pair of electrons

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YOUR NOTES



- 'Electrophile' means 'electron/negative charge loving' as electrophiles are attracted to negatively charged species
- **Electrophilic** refers to reactions that involve an electrophile



A nucleophile 'loves' a positive charge and an electrophile 'loves' a negative charge

Types of reactions

- An **addition** reaction is an organic reaction in which two (or more) molecules combine to give a **single product** with no other products
- A **substitution** reaction is a reaction that involves **replacing** an atom or group of atoms by another
- An **elimination** reaction is a reaction in which a small molecule (such as H₂O or HCl) is **removed** from an organic molecule
- A **hydrolysis** reaction is a reaction in which a compound is **broken down** by **water** (it can also refer to the breakdown of a substance by dilute acids or alkali)
- A **condensation** reaction is a reaction in which two organic molecules join together and in the process **eliminate** small molecules (such as H₂O or HCl)

Oxidation & reduction

- An **oxidation** reaction is a reaction in which oxygen is added, electrons are removed or the oxidation number of a substance is increased
 - In organic chemistry it often refers to the addition of oxygen or removal of hydrogen atoms to a substance
 - In equations for organic redox reactions, the symbol [O] can be used to represent one atom of oxygen from an oxidising agent
- A **reduction** reaction is a reaction in which oxygen is removed, electrons are added or the oxidation number of a substance is decreased
 - In organic chemistry it often refers to the removal of oxygen or addition of hydrogen atoms to a substance
 - In equations for organic redox reactions, the symbol [H] can be used to represent one atom of hydrogen from a reducing agent

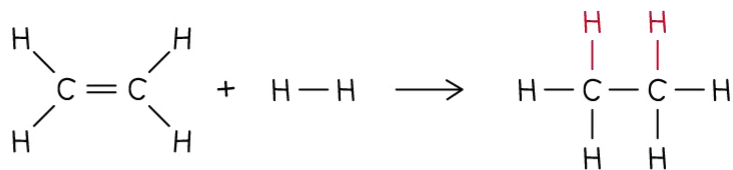
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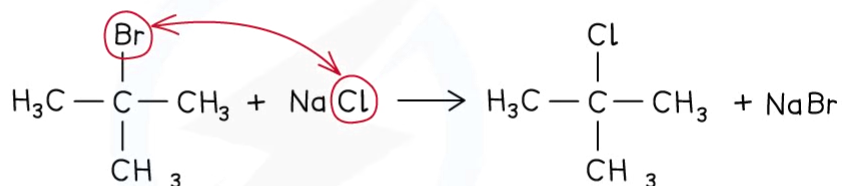


ADDITION
REACTION



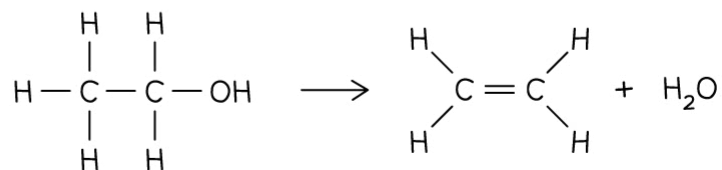
ADDITION OF H₂ TO THE DOUBLE BOND IN
ETHENE TO GIVE A SINGLE PRODUCT ETHANE

SUBSTITUTION
REACTION



CHLORINE HAS REPLACED BROMINE

ELIMINATION
REACTION



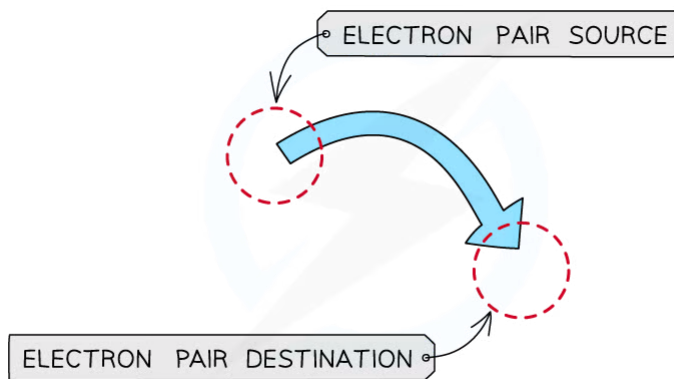
H₂O (SMALL MOLECULE) HAS BEEN REMOVED

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Different types of reactions in organic chemistry

Fundamentals of Mechanisms

- In organic reaction mechanisms, **curly arrows** represent the movement of **electron pairs**
- The arrow begins at a bond or a lone pair of electrons and points to the species that accepts the lone pair of electrons



Curly arrows show electron pairs moving from the source (e.g. a nucleophile) to its destination (e.g. an electrophile)



Exam Tip

You should always include dipoles in your mechanisms, as sometimes they are necessary to gain the mark!

YOUR NOTES

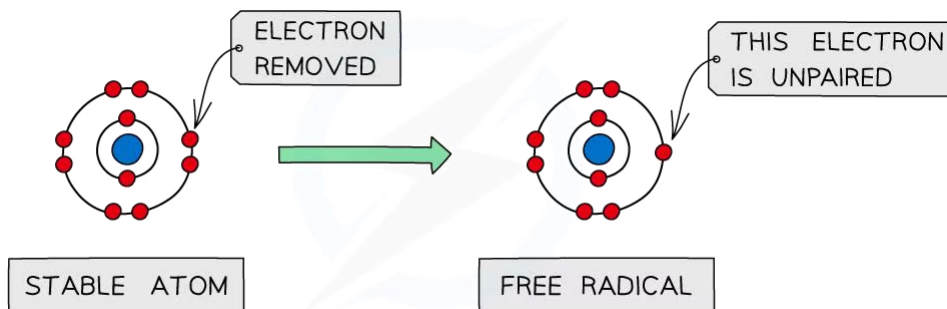


3.7.2 Chlorination of Alkanes

Mechanism: Free Radical Substitution

Chain reactions

- A **free radical** is a species with one (or more than one) unpaired electrons



The diagram shows a free radical which has one unpaired electron

- A **free radical reaction** is a reaction involving free radicals and is a three-step reaction:
 - **Initiation** is the first step and involves breaking a covalent bond using energy from ultraviolet (UV) light from the sun to form two free radicals
 - The **propagation** step is the second step in which the free radical can attack reactant molecules to form even more radicals
 - These in turn can again attack other molecules to form more free radicals and so on
 - In the **termination** step, two free radicals react together to form a product molecule

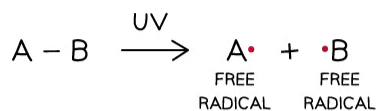
YOUR NOTES





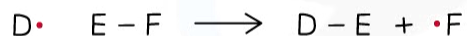
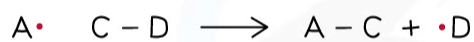
INITIATION

GENERATING THE FREE RADICALS



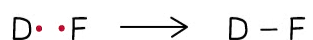
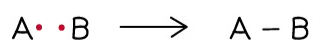
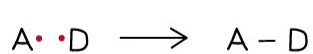
PROPAGATION

GENERATING MORE FREE RADICALS USING THE FREE RADICALS FORMED IN PROPAGATION



TERMINATION

FORMATION OF A PRODUCT/STABLE MOLECULE CAUSED BY COLLISION OF TWO RADICALS

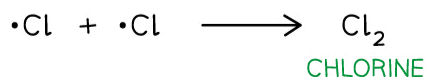
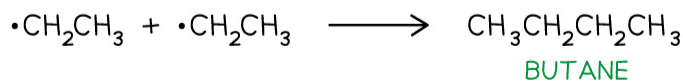
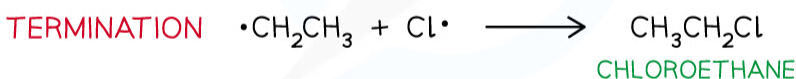
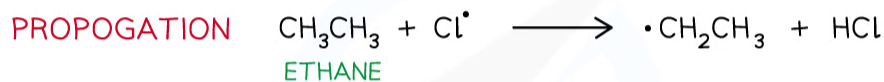
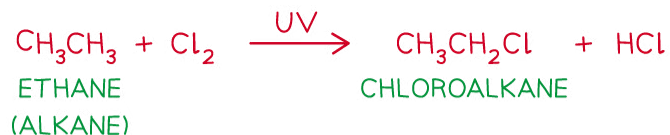


THESE ARE ALL DIFFERENT
COMBINATIONS OF RADICALS
COLLIDING WITH EACH OTHER

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The diagram shows the different stages of a general radical chain reaction

- In an exam, the type of reaction will be a specific alkane and halogen
- For example, ethane and chlorine



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The Free Radical Substitution Reaction of Ethane and Chlorine



Exam Tip

Remember: **Initiation** = a molecule forming two radicals
Propagation = always two steps, a molecule and a radical reacting to form a different molecule and radical
Termination = two radicals reacting to form a molecule
 Read the question carefully – sometimes they specify which termination step you should include.

YOUR NOTES



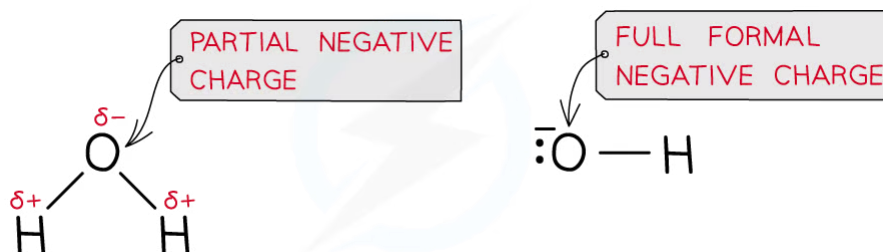
3.7.3 Nucleophilic Substitution

YOUR NOTES



Mechanism: Nucleophilic Substitution

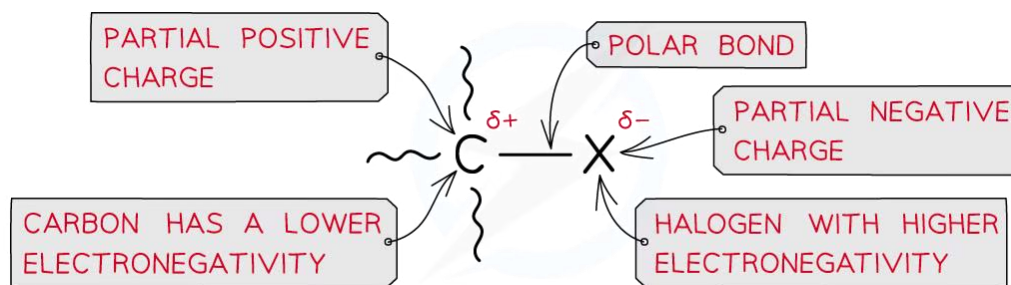
- A **nucleophile** is an electron-rich species that can **donate** a pair of electrons
 - 'Nucleophile' means 'nucleus/positive charge loving' as nucleophiles are attracted to positively charged species
 - **Nucleophilic** refers to reactions that involve a nucleophile
- There are various different species which can behave as nucleophiles, and some make better nucleophiles than others



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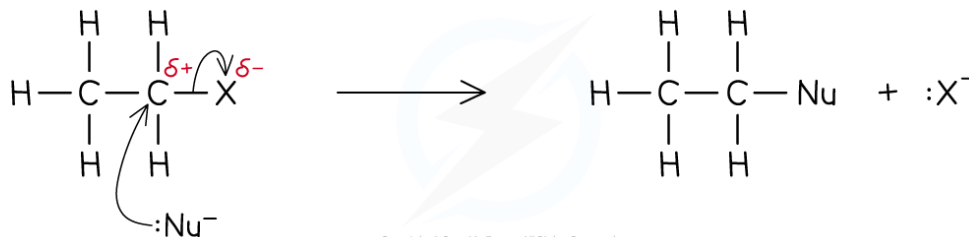
A hydroxide ion is a better nucleophile as it has a full formal negative charge whereas the oxygen atom in water only carries a partial negative charge

- 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
- Halogenoalkanes will undergo nucleophilic substitution reactions due to the polar C-X bond (where X is a halogen)



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

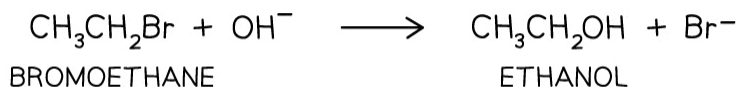


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General Mechanism for Nucleophilic Substitution

- For example, in the following reaction a halogenoalkane reacts with aqueous alkali to form an alcohol



The halogen is replaced by a nucleophile, OH⁻

- The mechanism for the reaction is as follows



Nucleophilic substitution reaction of bromoethane and aqueous alkali (e.g. NaOH)



Exam Tip

Make sure your arrows are clearly **curly** – if they are not curly enough then you will not be awarded the mark. Your first arrow must start at the lone pair of the nucleophile and go clearly to the delta positive carbon atom. Your second arrow must start touching the C-X bond and move clearly to the delta negative X atom. Make sure you show the products formed, including the :X⁻ atom which has been substituted.

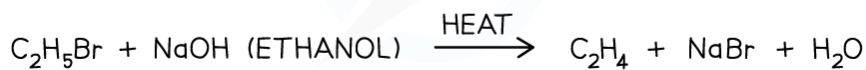
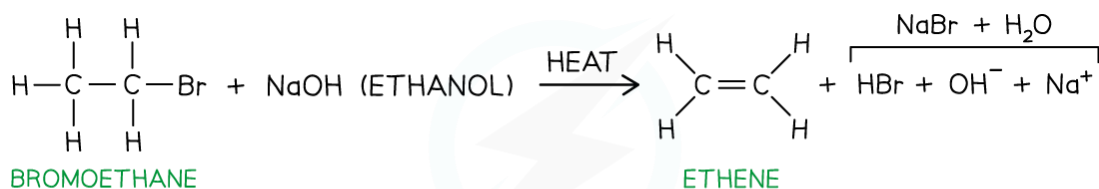
YOUR NOTES



3.7.4 Elimination

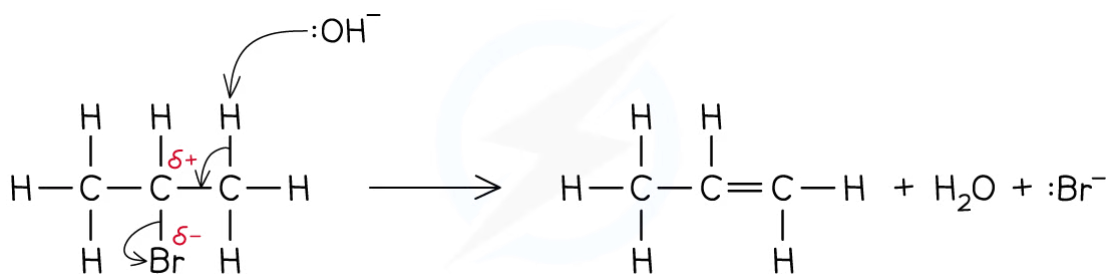
Mechanism: Elimination

- In an elimination reaction, a small molecule is removed leaving behind an alkene
- This is another reaction of halogenoalkanes
- The halogenoalkanes are **heated** with **ethanolic sodium hydroxide** causing the C-X bond to break **heterolytically**, forming a X^- ion and leaving an alkene as organic product
 - E.g. bromoethane reacts with **ethanolic sodium hydroxide** when heated to form ethene



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Hydrogen bromide is eliminated to form ethene



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Elimination Mechanism of 2-bromopropane with hydroxide ions

YOUR NOTES

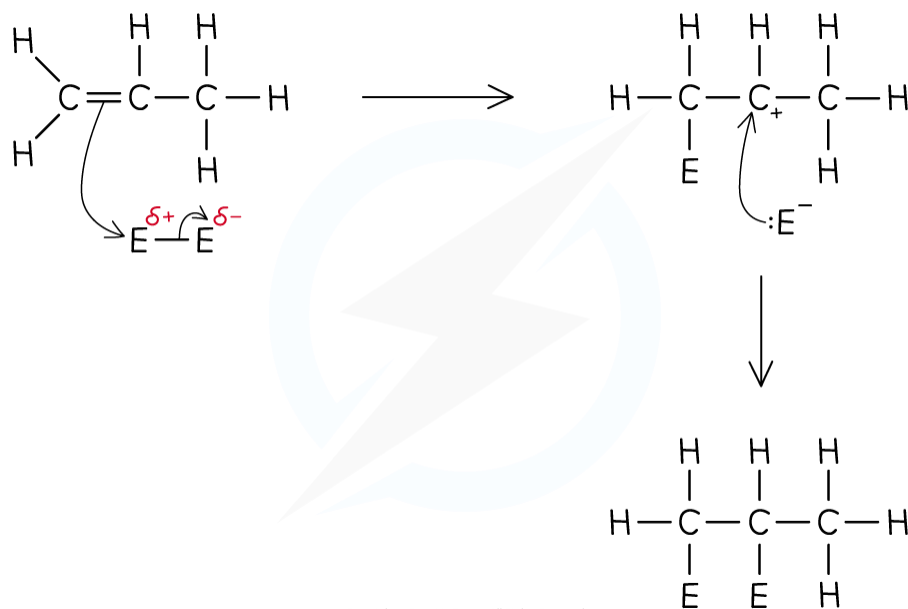


3.7.5 Electrophilic Addition

Mechanism: Electrophilic Addition

Electrophilic addition

- Alkenes undergo electrophilic addition reactions
- In an electrophilic addition reaction, two reactants form only one product
 - So, electrophilic addition reactions will have a 100% atom economy
- It is the double bond in an alkene which makes them so reactive
- The C=C double bond is an electron-rich area of the molecule which is readily attacked by positively charged electrophiles
- Alkenes will undergo electrophilic addition reactions with hydrogen halides, halogens and concentrated sulfuric acid with steam



General mechanism for Electrophilic Addition

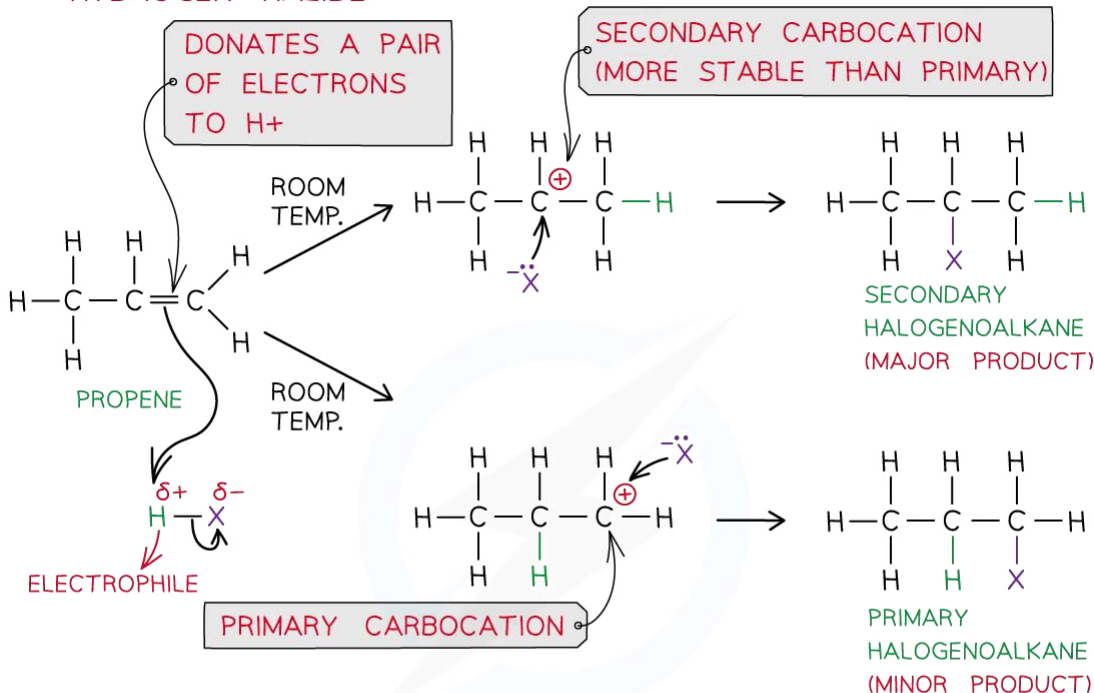
YOUR NOTES



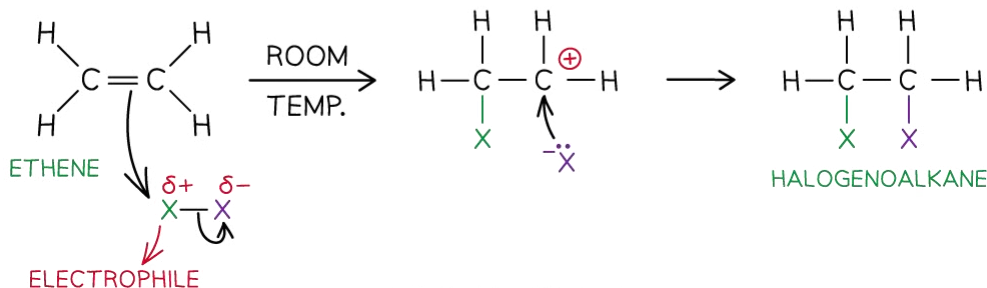


ELECTROPHILIC ADDITION TO ALKENES

• HYDROGEN HALIDE



• HALOGEN



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Electrophilic addition of hydrogen halides or halogens at room temperatures to alkenes results in the formation of halogenoalkanes

- When the reaction takes place with an asymmetrical alkene, then you need to determine which product will form
- This depends on the stability of the carbocation formed as the intermediate
- The stability of carbon carbocations is as follows:
 - Tertiary > secondary > primary
- The major product formed will be from the intermediate with the more stable carbocation, but some of the product from the less stable carbocation intermediate will also form
- In the mechanism above, the secondary halogenoalkane is the major product, because a secondary carbocation is more stable than a primary carbocation

