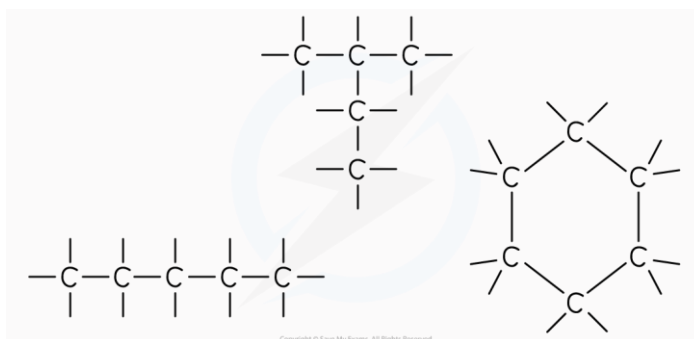


# Homologous Series

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



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

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

Homologous Series of Alkanes Table

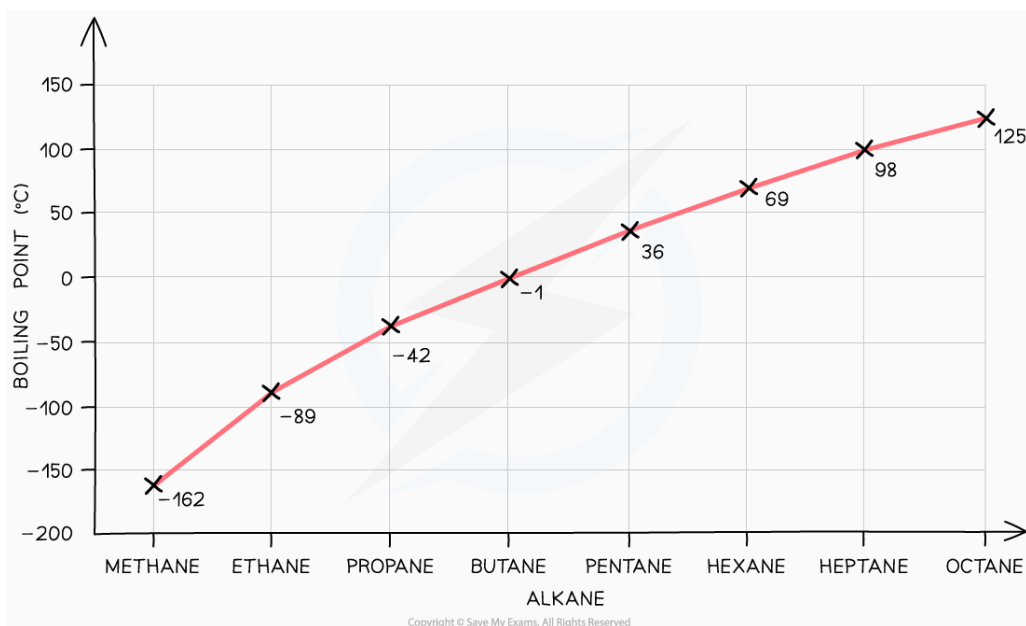
Name of alkane	Number of carbons	Chemical formula	Boiling point in °C	State at room temperature	Melting point in °C
Methane	1	CH <sub>4</sub>	-162	gas	-182
Ethane	2	C <sub>2</sub> H <sub>6</sub>	-89	gas	-183
Propane	3	C <sub>3</sub> H <sub>8</sub>	-42	gas	-188
Butane	4	C <sub>4</sub> H <sub>10</sub>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

- Things we can say about a homologous series:

- each member has the same functional group
- each member has the same general formula
- each member has similar chemical properties
- each member differs by  $\text{-CH}_2\text{-}$
- 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

## Boiling Point Trends

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

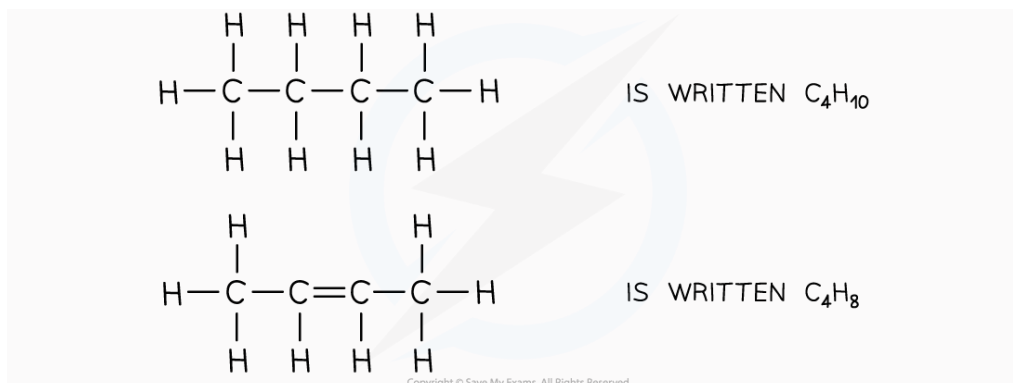


- The broad trend is that boiling point increases with increased molecular size
- Each additional  $\text{-CH}_2\text{-}$  (called the homologous increment) adds 8 more electrons to the molecule
- This increases the strength of the London Dispersion Forces
- Stronger LDF leads to a higher boiling point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

## Representing Formulae

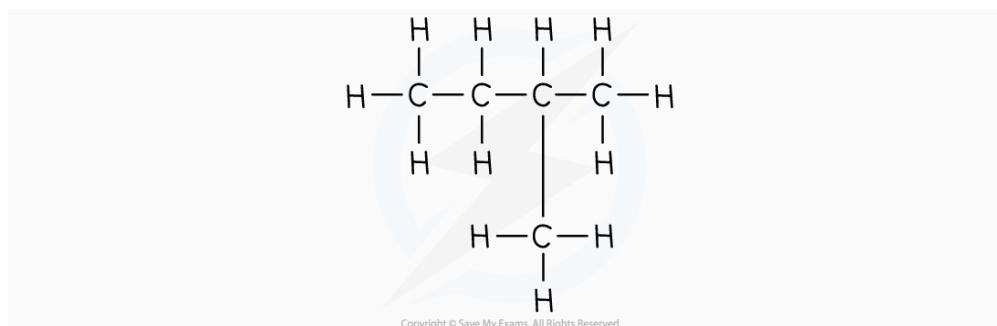
- Organic compounds can be represented in a number of ways:
  - Empirical Formulae
  - Molecular Formulae
  - Structural Formulae
  - Condensed Structural Formulae
- The empirical formula shows the simplest possible ratio of the atoms in a molecule
- For example:

- Hydrogen peroxide is  $\text{H}_2\text{O}_2$  but the empirical formula is  $\text{HO}$
- The molecular formula shows the actual number of atoms in a molecule
- For example:



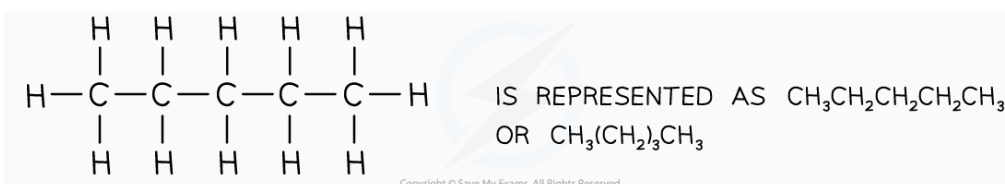
### *The molecular formulae of butane and butene*

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



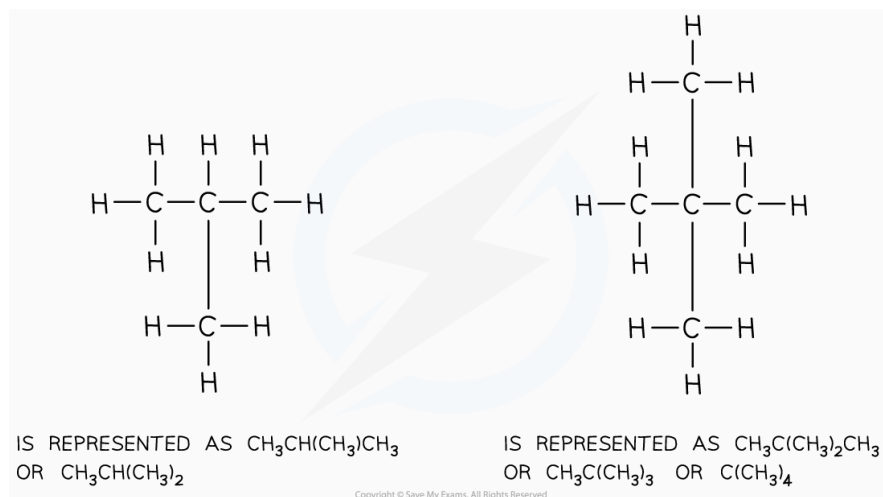
### *The structural formula of 2-methylbutane*

- In a condensed structural formulae enough information is shown to make the structure clear, but most of the actual covalent bonds are omitted
- Only important bonds are always shown, such as double and triple bonds
- Identical groups can be bracketed together
- Side groups are also shown using brackets
- Straight chain alkanes are shown as follows:



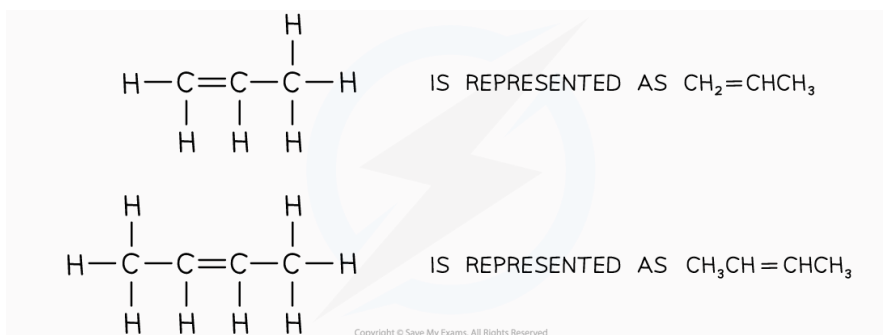
### Representing condensed structural formulae of straight chains

- Branched alkanes are shown as follows:



### Representing condensed structural formulae of branched alkanes

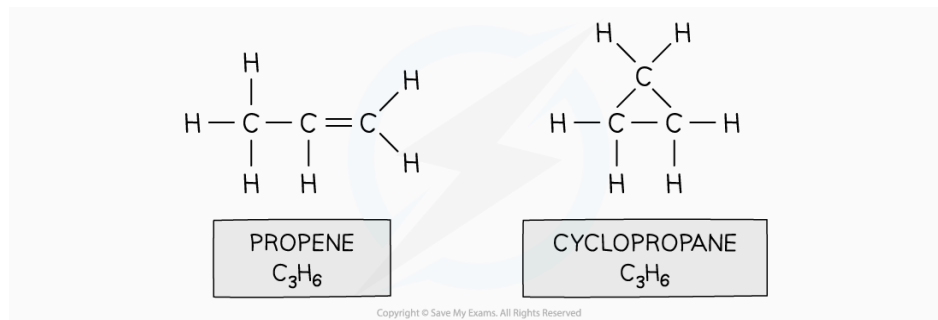
- Alkenes are shown as follows:



### Representing condensed structural formulae of alkenes

## Isomers

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

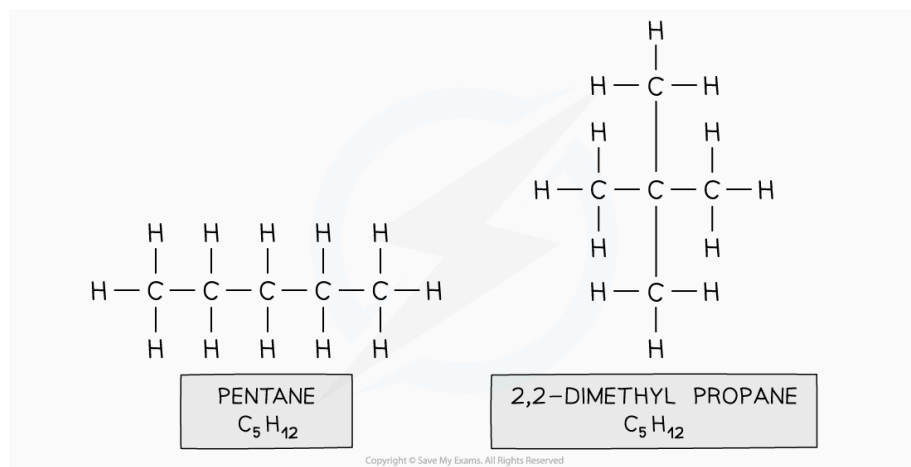


*Both propene and cyclopropane are made up of 3 carbon and 6 hydrogen atoms but the structure of the two molecules differs*

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

### Branch-Chain isomerism

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

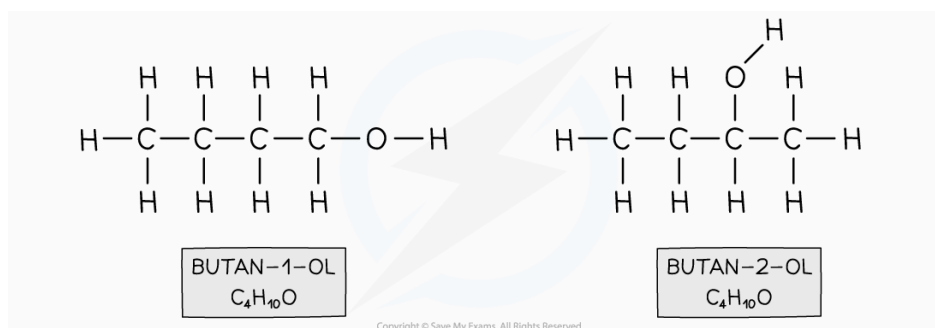


*Both compounds are made up of the same atoms however the longest carbon chain in pentane is 5 and in 2,2-dimethylpropane it is 3 (with two methyl branches)*

### Positional isomerism

- Positional isomers arise from differences in the position of a functional group in each isomer

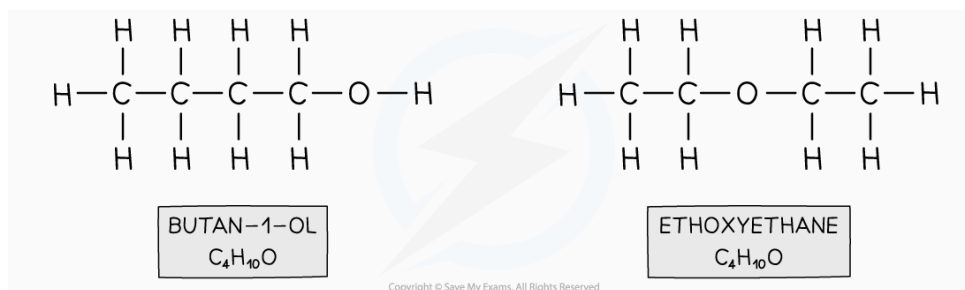
- The functional group can be located on different carbons
- For example, butan-1-ol and butan-2-ol



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

### Functional group isomerism

- When different functional groups result in the same molecular formula, functional group isomers arise
- The isomers have very different chemical properties as they have different functional groups
  - For example, butanol and ethoxyethane



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

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

## Nomenclature

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

## Nomenclature of Organic Compounds Table

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

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**Exam Tip**

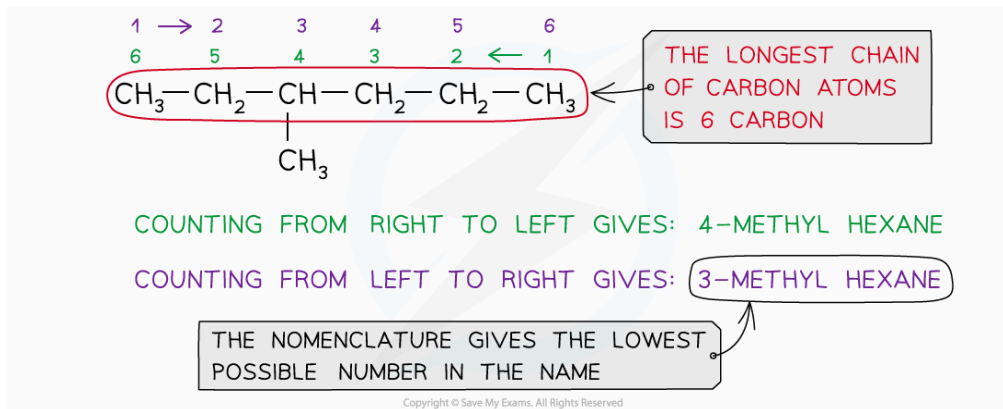
Although the table shows up to 10 carbons for reference, in your IB Chemistry exam you are only required to name molecules with up to 6 carbons

**Chains & Branches**

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

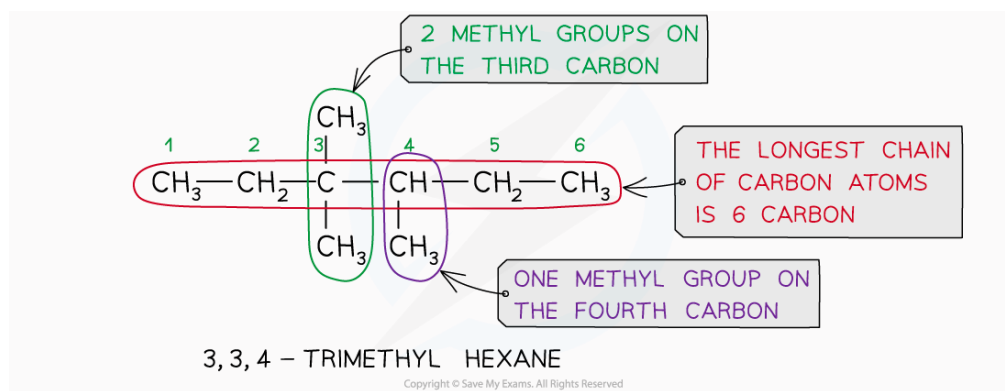


- The side-chain is named by adding '-yl' to the normal alkane stem
- This type of group is called an alkyl group



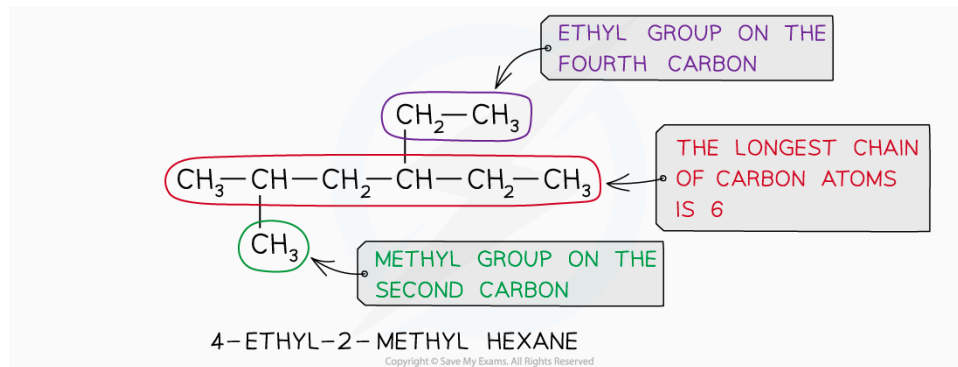
### Naming Side Chains

- 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



### Naming Multiple Side Chains

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



### 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

**Alkanes**

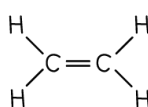
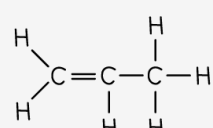
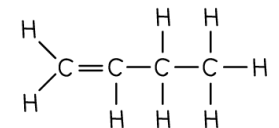
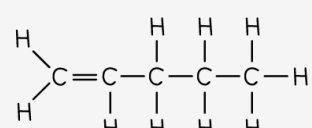
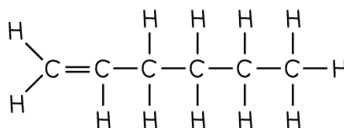
- Hydrocarbons are compounds containing hydrogen and carbon only
- There are four families of hydrocarbons you should know: alkanes, alkenes, alkynes and arenes
- Alkanes have the general molecular formula  $C_nH_{2n+2}$ . They contain only single bonds and are said to be saturated
- Alkanes are named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

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

*The first six members of the alkane family*

## Alkenes

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

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

*The first five members of the alkene family*

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

## Alkynes

- Alkynes have the general molecular formula  $C_nH_{2n-2}$
- The triple bond makes them unsaturated molecules
- Alkynes are named using the nomenclature rule alk + yne

- As with alkenes, in molecules with a straight chain of 4 or more carbon atoms, the position of the triple bond must be specified
- The carbon atoms on the straight chain must be numbered, starting with the end closest to the triple bond
- The lowest-numbered carbon atom participating in the triple bond is indicated just before the -yne:

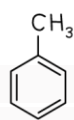
Structural Formula	Name	Molecular Formula
$\text{H}-\text{C}\equiv\text{C}-\text{H}$	ethyne	$\text{C}_2\text{H}_2$
$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}\equiv\text{C}-\text{C}-\text{H} \\   \\ \text{H} \end{array}$	propyne	$\text{C}_3\text{H}_4$
$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}-\text{C}\equiv\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$	but-1-yne	$\text{C}_4\text{H}_6$
$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \\ \text{H}-\text{C}\equiv\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	pent-1-yne	$\text{C}_5\text{H}_8$
$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \\ \text{H}-\text{C}\equiv\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	hex-1-yne	$\text{C}_6\text{H}_{10}$

*The first five members of the alkyne family*

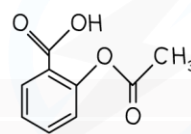
- The name of the functional group is alkynyl

## Arenes

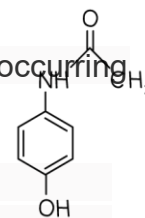
- Arene is the collective name given to compounds with one or more rings with pi electrons that are delocalised throughout the ring(s)
- Compounds with this feature are said to be aromatic
- This doesn't mean they are necessarily smelly, although a lot of naturally occurring arenes do have distinctive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



TOLUENE



ASPIRIN



PARACETAMOL

*Arenes are present in many everyday chemicals and pharmaceuticals*

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

## Halogenoalkanes

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

Haloalkanes Examples Table

Structural Formula	Name	Molecular Formula
$  \begin{array}{c}  \text{H} \quad \text{H} \\    \quad   \\  \text{H}-\text{C}-\text{C}-\text{Cl} \\    \quad   \\  \text{H} \quad \text{H}  \end{array}  $	chloroethane	C <sub>2</sub> H <sub>5</sub> Cl
$  \begin{array}{c}  \text{H} \quad \text{Br} \quad \text{H} \\    \quad   \quad   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\    \quad   \quad   \\  \text{H} \quad \text{H} \quad \text{H}  \end{array}  $	2-bromopropane	C <sub>3</sub> H <sub>7</sub> Br
$  \begin{array}{c}  \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\    \quad   \quad   \quad   \quad   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{I} \\    \quad   \quad   \quad   \quad   \\  \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H}  \end{array}  $	1-iodopentane	C <sub>5</sub> H <sub>11</sub> I
$  \begin{array}{c}  \text{H} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad \text{H} \\    \quad   \quad   \quad   \quad   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\    \quad   \quad   \quad   \quad   \\  \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H}  \end{array}  $	3-chloropentane	C <sub>5</sub> H <sub>11</sub> Cl

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

## Dihaloalkanes Examples Table

Structural Formula	Name	Molecular Formula
$  \begin{array}{c}  \text{H} \quad \text{H} \\    \quad   \\  \text{H}-\text{C}-\text{C}-\text{Cl} \\    \quad   \\  \text{H} \quad \text{Cl}  \end{array}  $	1,1-dichloroethane	$\text{C}_2\text{H}_4\text{Cl}_2$
$  \begin{array}{c}  \text{H} \quad \text{H} \\    \quad   \\  \text{H}-\text{C}-\text{C}-\text{Cl} \\    \quad   \\  \text{Cl} \quad \text{H}  \end{array}  $	1,2-dichloroethane	$\text{C}_2\text{H}_4\text{Cl}_2$
$  \begin{array}{c}  \text{H} \quad \text{H} \quad \text{H} \\    \quad   \quad   \\  \text{Br}-\text{C}-\text{C}-\text{C}-\text{H} \\    \quad   \quad   \\  \text{H} \quad \text{Cl} \quad \text{H}  \end{array}  $	1-bromo-2-chloropropane	$\text{C}_3\text{H}_7\text{BrCl}$

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## Alcohols &amp; Ethers

## Alcohols

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

## The first four Alcohols and their Structures Table

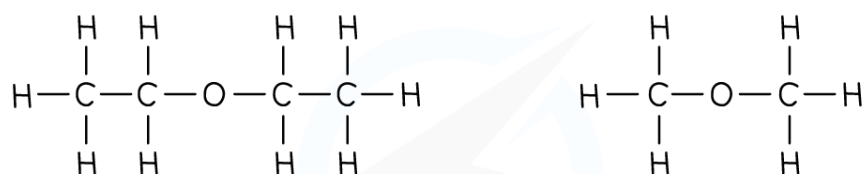
ALCOHOL	STRUCTURAL FORMULA	DISPLAYED FORMULA
METHANOL	$\text{CH}_3\text{OH}$	$  \begin{array}{c}  \text{H} \\    \\  \text{H}-\text{C}-\text{O}-\text{H} \\    \\  \text{H}  \end{array}  $
ETHANOL	$\text{CH}_3\text{CH}_2\text{OH}$	$  \begin{array}{c}  \text{H} \quad \text{H} \\    \quad   \\  \text{H}-\text{C}-\text{C}-\text{O}-\text{H} \\    \quad   \\  \text{H} \quad \text{H}  \end{array}  $
PROPANOL	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	$  \begin{array}{c}  \text{H} \quad \text{H} \quad \text{H} \\    \quad   \quad   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{O}-\text{H} \\    \quad   \quad   \\  \text{H} \quad \text{H} \quad \text{H}  \end{array}  $
BUTANOL	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	$  \begin{array}{c}  \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\    \quad   \quad   \quad   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{O}-\text{H} \\    \quad   \quad   \quad   \\  \text{H} \quad \text{H} \quad \text{H} \quad \text{H}  \end{array}  $

## Classification of alcohols

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

### Ethers

- Ethers are a family of molecules that contain the ether functional group, R-O-R, where R is an alkyl group
- Their general formula is  $C_nH_{2n+2}O$
- The nomenclature of ether follows the pattern alkoxy + alkane
- Sometimes you will see an older nomenclature for ethers where each R group is given an alkyl name
  - For Example:  $CH_3OCH_3$  is dimethyl ether and  $C_2H_5OCH_3$  is ethyl methyl ether
- Ethers are functional group isomers of alcohols



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

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

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*Ethers are useful substances*

## Carbonyls

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

### Aldehydes

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

### Ketones

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

Aldehyde and Ketone Examples Table

Structural Formula	Name	Molecular Formula
$\begin{array}{c} \text{O} \\    \\ \text{H}-\text{C}-\text{H} \end{array}$	methanal (also known as formaldehyde)	CH <sub>2</sub> O
$\begin{array}{c} \text{H} \quad \text{O} \\   \quad    \\ \text{H}-\text{C}-\text{C}-\text{H} \\   \\ \text{H} \end{array}$	ethanal	C <sub>2</sub> H <sub>4</sub> O
$\begin{array}{c} \text{H} \quad \text{H} \quad \text{O} \\   \quad   \quad    \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$	propanal	C <sub>3</sub> H <sub>6</sub> O
$\begin{array}{c} \text{H} \quad \text{O} \quad \text{H} \\   \quad    \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$	propanone (also known as acetone)	C <sub>3</sub> H <sub>6</sub> O
$\begin{array}{c} \text{H} \quad \text{O} \quad \text{H} \quad \text{H} \quad \text{H} \\   \quad    \quad   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	pentan-2-one	C <sub>5</sub> H <sub>10</sub> O

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

- Aldehydes and ketones with the same number of carbons are functional group isomers

## Carboxylic Acids & Esters

### Carboxylic acids

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

Carboxylic Acids Examples Table

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

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### Esters

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

Esters Examples Table

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

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

### Exam Tip

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

## Organic Nitrogen Compounds

### Amines

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

## Amides

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

## Nitriles

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

### Organic Nitrogen Compounds Examples

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

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## Exam Tip

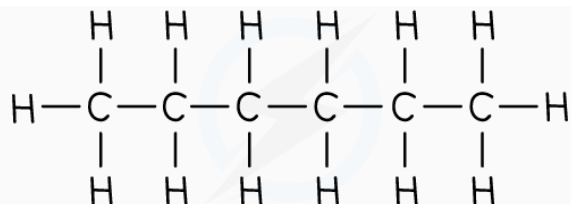
Be careful about counting all the carbons when naming a nitrile. For example  $\text{C}_3\text{H}_7\text{CN}$  is butanenitrile not propanenitrile as the longest chain is 4 carbons.

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

## 3-D Modelling

- Representing 3-D molecules on a 2D surface is not easy and the best way to understand 3-D structures is to use modelling kits or 3-D modelling software, such as ACD Labs ChemSketch

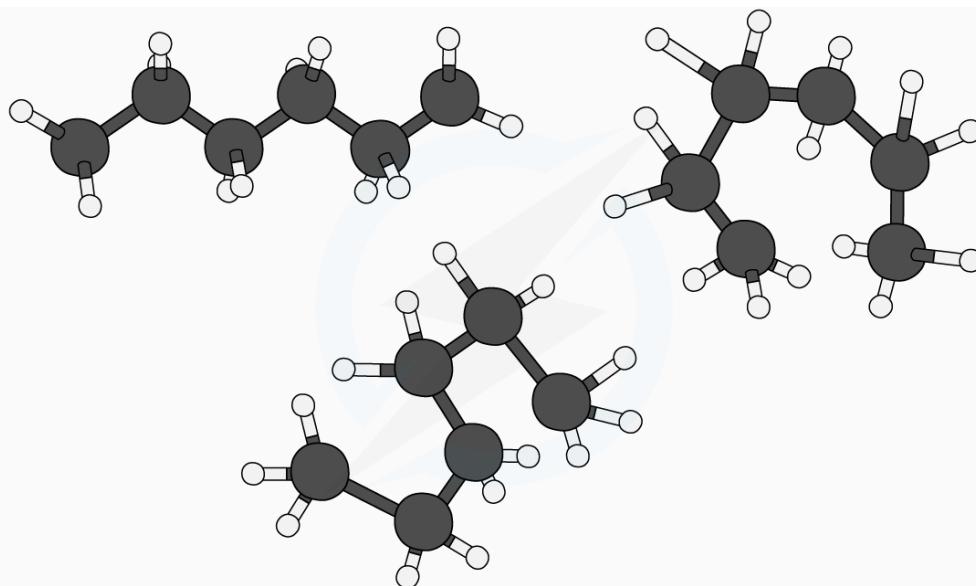
- For simplification, complex organic molecules are shown with 90° bond angles that give the minimum information of which atoms are connected together as in this representation of hexane, C<sub>6</sub>H<sub>14</sub>



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*A simplified displayed structure for hexane*

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



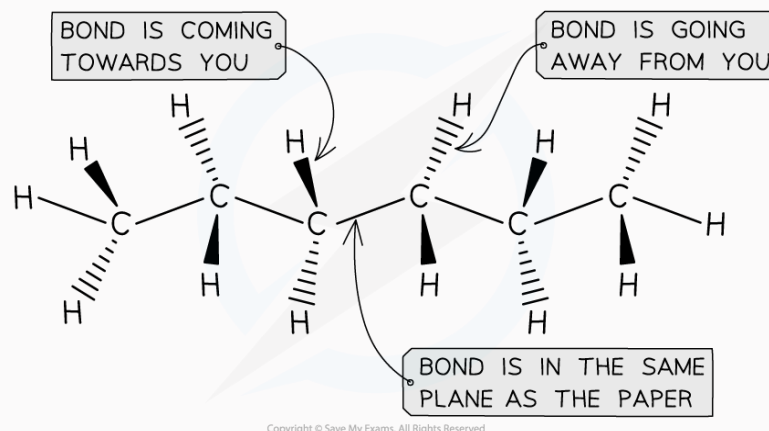
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*Different 3-D structures for hexane*

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

## Stereochemical drawings

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



*A stereochemical drawing for hexane*

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

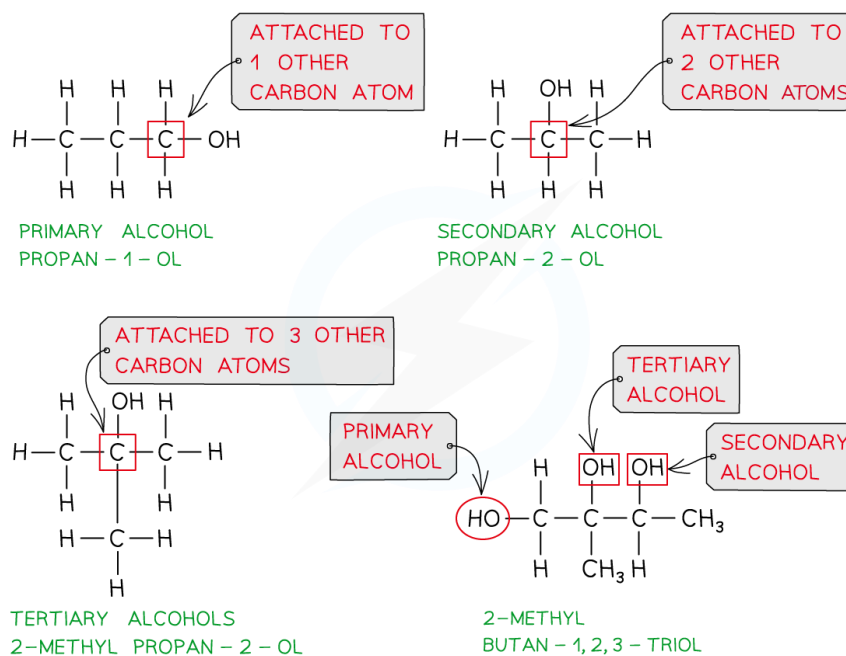
### Exam Tip

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

## Primary, Secondary & Tertiary Atoms

### Alcohols and halogenoalkanes

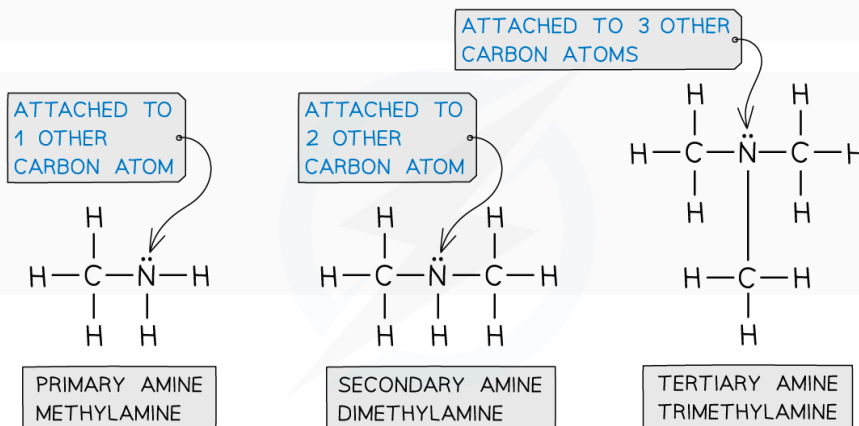
- Primary alcohols and halogenoalkanes are those in which the carbon atom bonded to the functional group is attached to one other carbon atom (or alkyl group)
- In secondary alcohols and halogenoalkanes the functional group carbon atom is attached to two other carbon atoms (or alkyl groups)
- In tertiary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



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

## Amines

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



*Primary, secondary and tertiary Amines*

# Benzene

## Kekulé structure for benzene

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

## Problems with Kekulé's structure for benzene

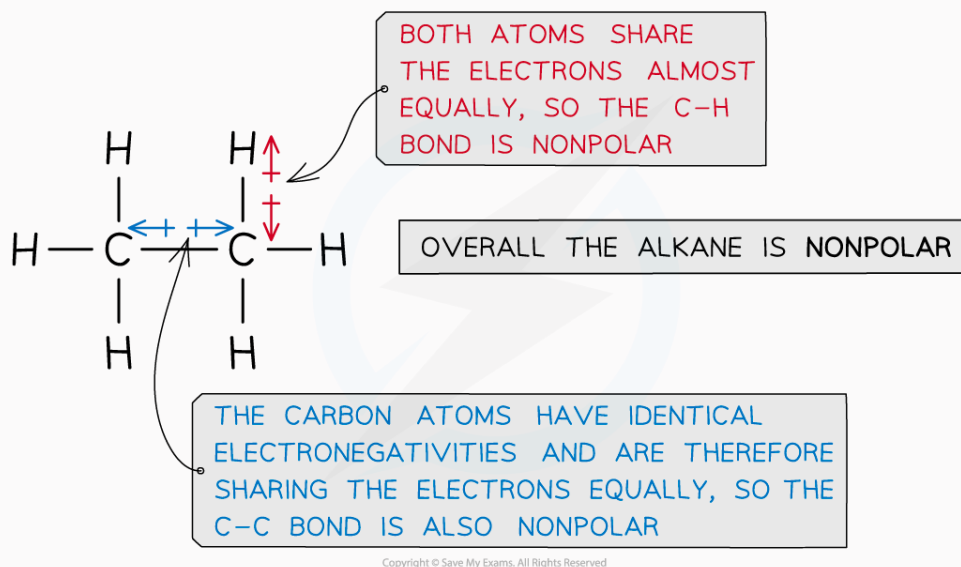
- Since benzene has three double bonds, it should have similar reactivity to ethene
- However, this turned out not to be the case
  - Ethene undergoes addition reactions whereas benzene rarely does (only under very harsh conditions) and instead undergoes substitution reactions
- The presence of three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

## Shape of benzene

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



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



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

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

### Exam Tip

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

## Combustion of Alkanes

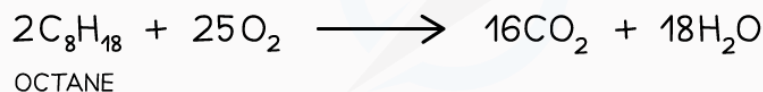
- Alkanes are combusted (burnt) on a large scale for their use as fuels
- They also react in free-radical substitution reactions to form more reactive halogenoalkanes

### Complete combustion

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

## COMPLETE COMBUSTION

ALKANE + OXYGEN  $\dashrightarrow$  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  $\dashrightarrow$  CARBON MONOXIDE + WATER



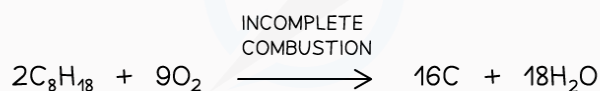
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*The incomplete combustion of alkanes*

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

## INCOMPLETE COMBUSTION

ALKANE + OXYGEN  $\dashrightarrow$  CARBON + WATER



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*The incomplete combustion of alkanes (2)*

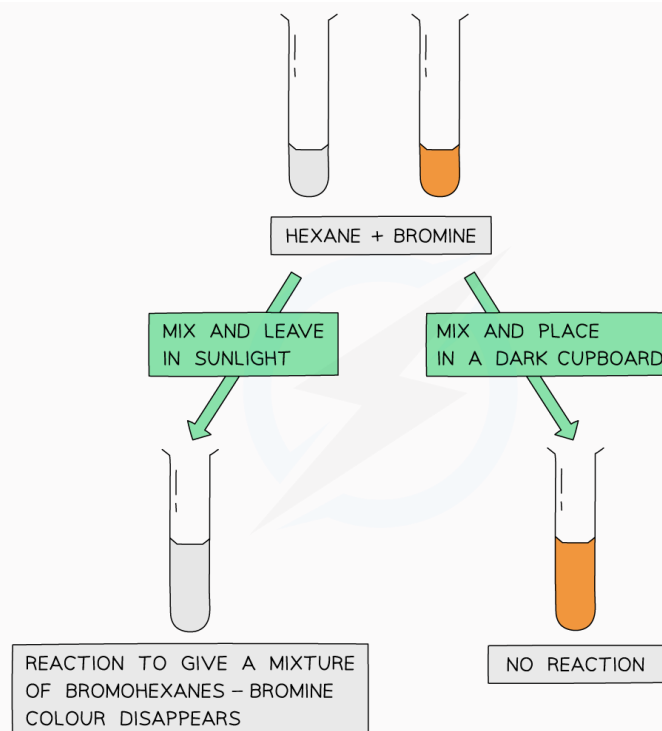
**Exam Tip**

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

## Halogenation of Alkanes

### Free-radical substitution of alkanes

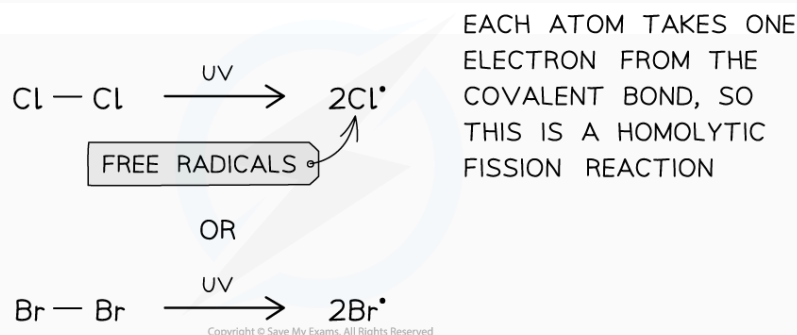
- Alkanes can undergo free-radical substitution in which a hydrogen atom gets substituted by a halogen (chlorine/bromine)
- Since alkanes are very unreactive, ultraviolet light (sunlight) is needed for this substitution reaction to occur
- The free-radical substitution reaction consists of three steps: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



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

## Initiation step

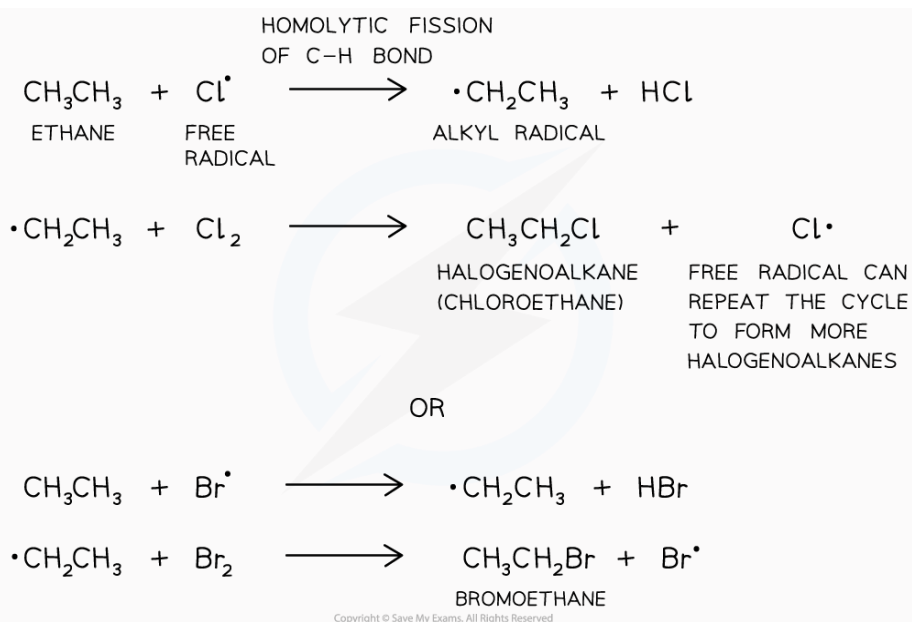
- In the initiation step the Cl-Cl or Br-Br is broken by energy from the UV light
- This produces two radicals in a homolytic fission reaction



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

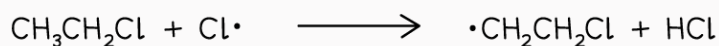
## Propagation step

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

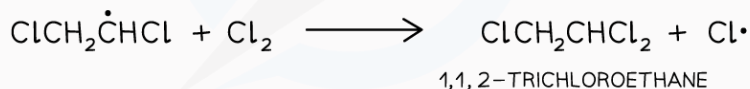


*The second step of the free-radical substitution reaction is the propagation step in which the reaction grows in a chain type reaction*

- This reaction is not very suitable for preparing specific halogenoalkanes as a mixture of substitution products are formed
- If there is enough chlorine/bromine present, all the hydrogens in the alkane will eventually get substituted (eg. ethane will become  $C_2Cl_6/C_2Br_6$ )



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*

**Exam Tip**

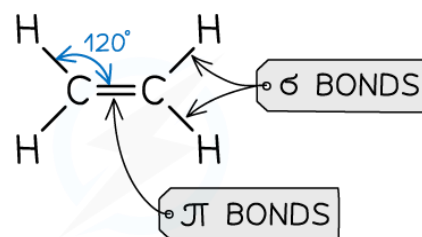
Make sure you practice and are able to write out these equations, especially the propagation steps which students frequently get wrong. It is quite common for students to incorrectly show a hydrogen radical produced in propagation, which does not happen:



Do not fall into this trap!

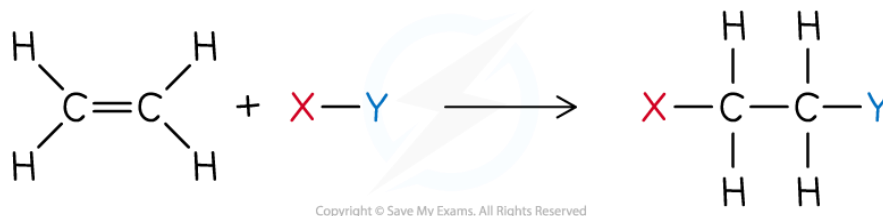
## Reactivity of Alkenes

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



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

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



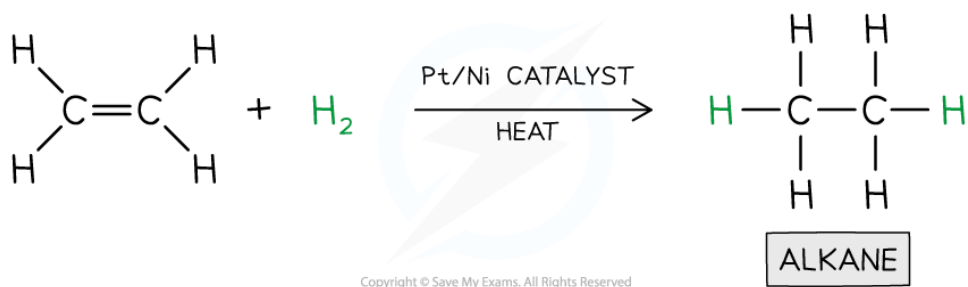
### *Addition reactions in alkenes*

- Molecules which contain  $\pi$ -bonds and which can hence undergo addition are said to be unsaturated
- Molecules which do not contain  $\pi$ -bonds and which hence cannot undergo addition are said to be saturated.

- Alkenes are unsaturated and can hence undergo addition
- Addition is the combination of two or more molecules to form a single molecule
- Addition reactions are generally faster than substitution reactions since only weak  $\pi$ -bonds are broken, rather than stronger  $\sigma$ -bonds
- The ability of alkenes to undergo addition means that they are much more reactive than alkanes

## Hydrogenation of Alkenes

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

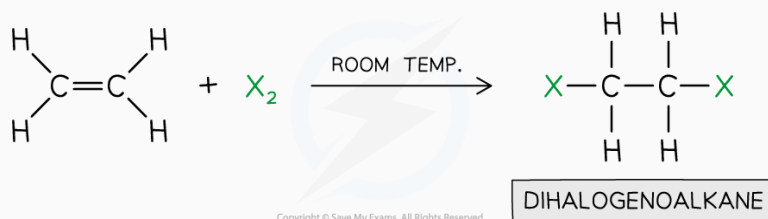


*Catalytic hydrogenation converts alkenes into useful alkanes*

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

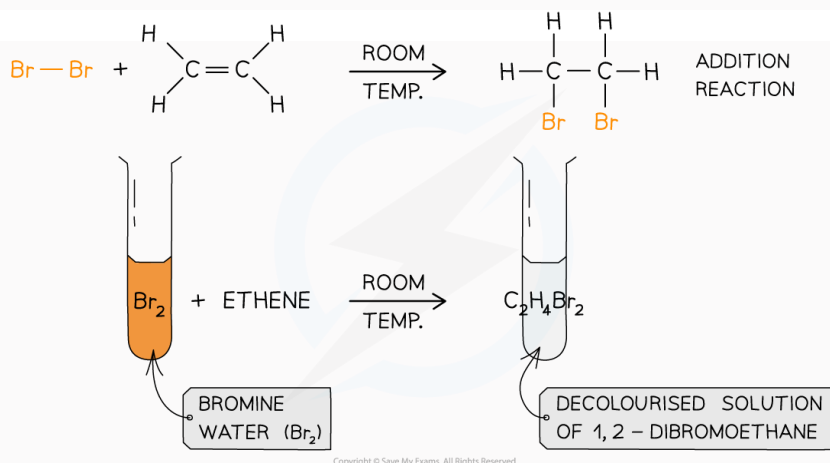
## Halogenation of Alkenes

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



### Halogenation in alkenes

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



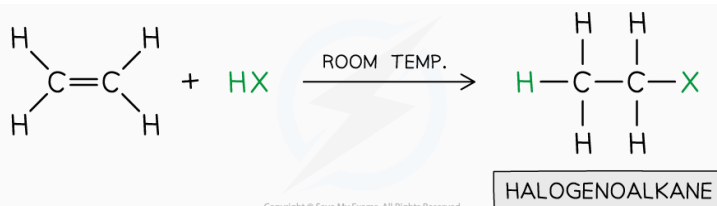
*The bromine water test is the standard test for unsaturation in alkenes*

### Exam Tip

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

## Hydrohalogenation of Alkenes

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

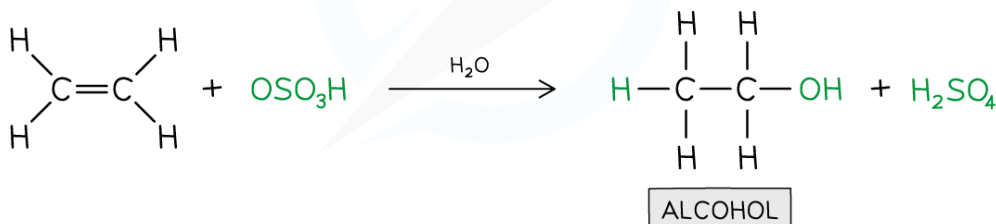
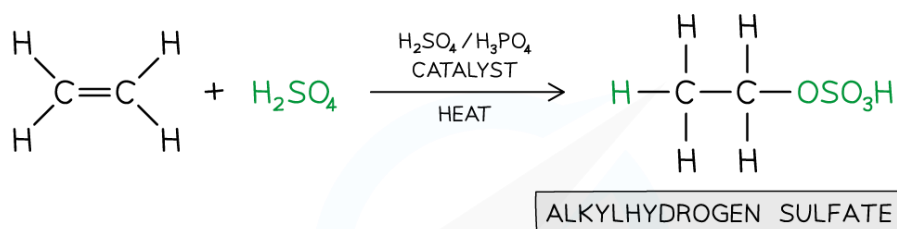


### Hydrohalogenation reactions in alkenes

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

## Hydration of Alkenes

- When alkenes are treated with steam at 300 °C, a pressure of 60 atmospheres and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) or phosphoric acid ( $\text{H}_3\text{PO}_4$ ) catalyst, the water is added across the double bond in a reaction known as hydration
- An alkene is converted into an alcohol
- The reaction processes via an intermediate in which  $\text{H}^+$  and  $\text{HSO}_4^-$  ions are added across the double bond
- The intermediate is quickly hydrolysed by water, reforming the sulfuric acid



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### Hydration in Alkenes

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

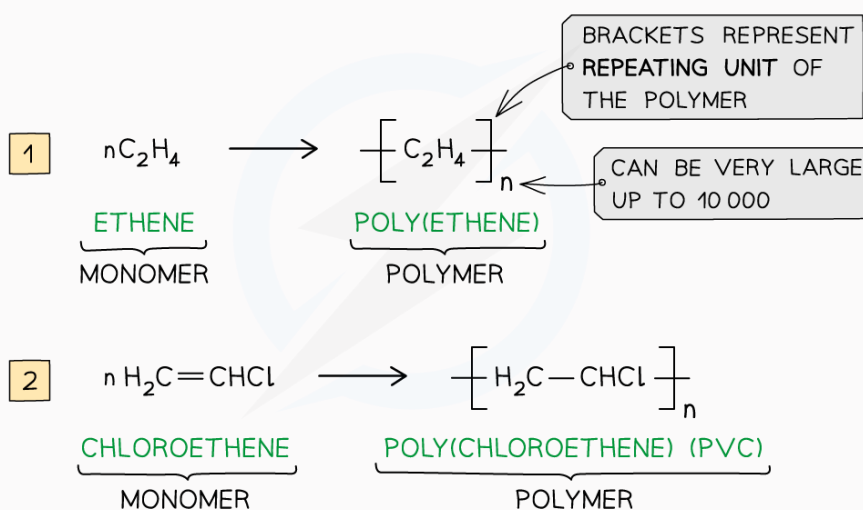
## Polymers

### Addition polymerisation

- Addition polymerisation is one of the most important addition reactions of alkenes which form the basis of the plastic industry
- Addition polymerisation is the reaction in which many monomers containing at least one  $\text{C}=\text{C}$  double bond form long chains of polymers as the only product

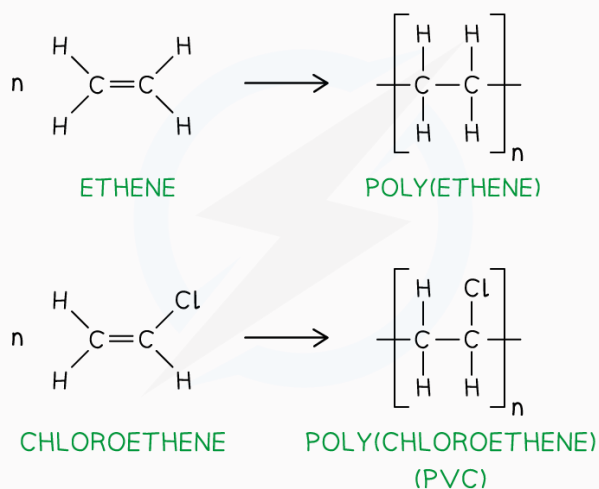
- Just like in other addition reactions of alkenes, the  $\pi$ -bond in each C=C bond breaks and then the monomers link together to form new C-C single bonds
- A polymer is a long-chain molecule that is made up of many repeating units
- The small, reactive molecules that react together to form the polymer are called monomers
- A polymerisation reaction can be represented by a general formula or by using displayed formulae
  - E.g. poly(ethene) and poly(chloroethene) (also known as PVC) are polymers made up of the ethene and chloroethene monomers respectively and are commonly used in making plastics

### GENERAL FORMULA ADDITION POLYMERISATION



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

### DISPLAYED FORMULAE ADDITION POLYMERISATION

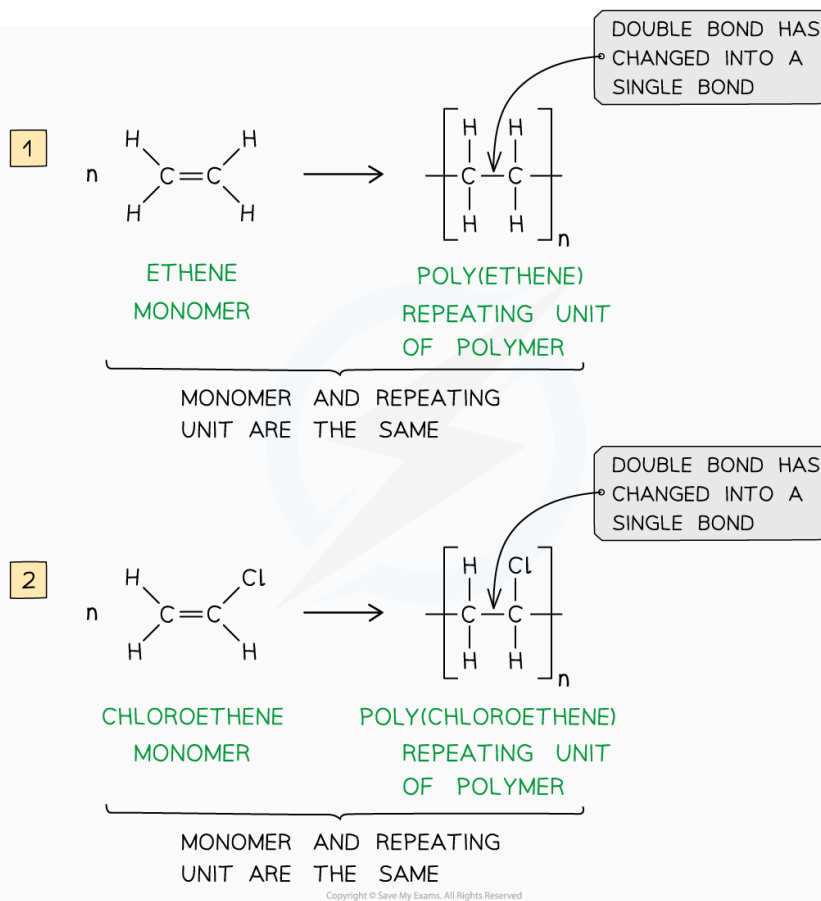


The addition polymerisation of ethene (1) and chloroethene (2)

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

### Deducing repeat units

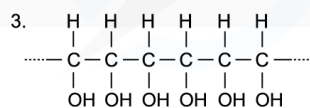
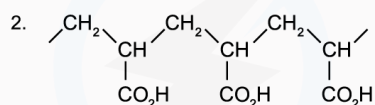
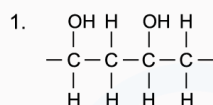
- A repeat unit is the smallest group of atoms that when connected one after the other make up the polymer chain
  - It is represented by square brackets in the displayed and general formula
- In poly(alkenes) (such as poly(ethene)) and substituted poly(alkenes) (such as PVC) made of one type of monomer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



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

### Worked example

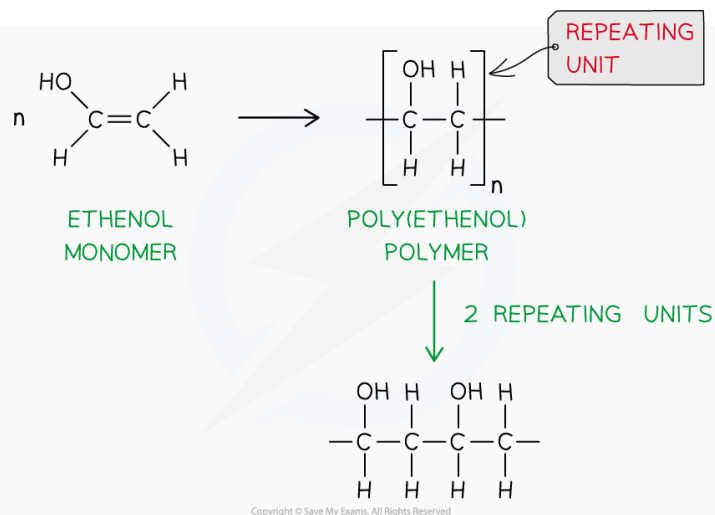
Identify the monomers present in the given sections of addition polymer molecules:



Answers:

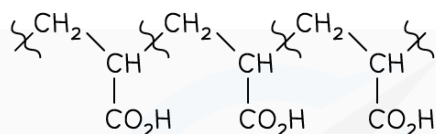
Answer 1:

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

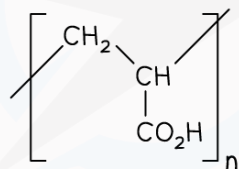


Answer 2:

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



ONE REPEATING UNIT

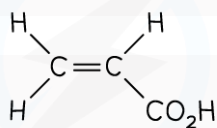


POLY(PROP-2-ENOIC ACID)

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

MONOMER

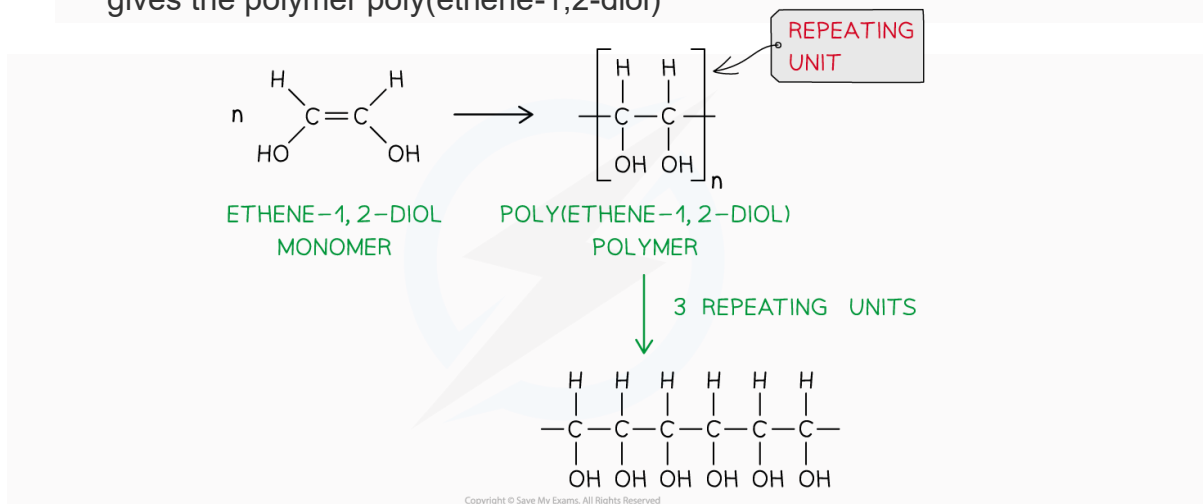


PROP-2-ENOIC ACID

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Answer 3:

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



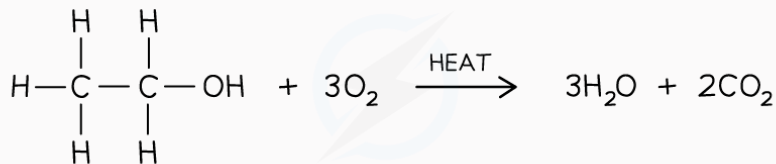
### Exam Tip

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  $\text{C}=\text{C}$  bonds instead of  $\text{C}-\text{C}$  bonds.

## Combustion of Alcohols

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

Alcohol + oxygen  $\rightarrow$  carbon dioxide + water



*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

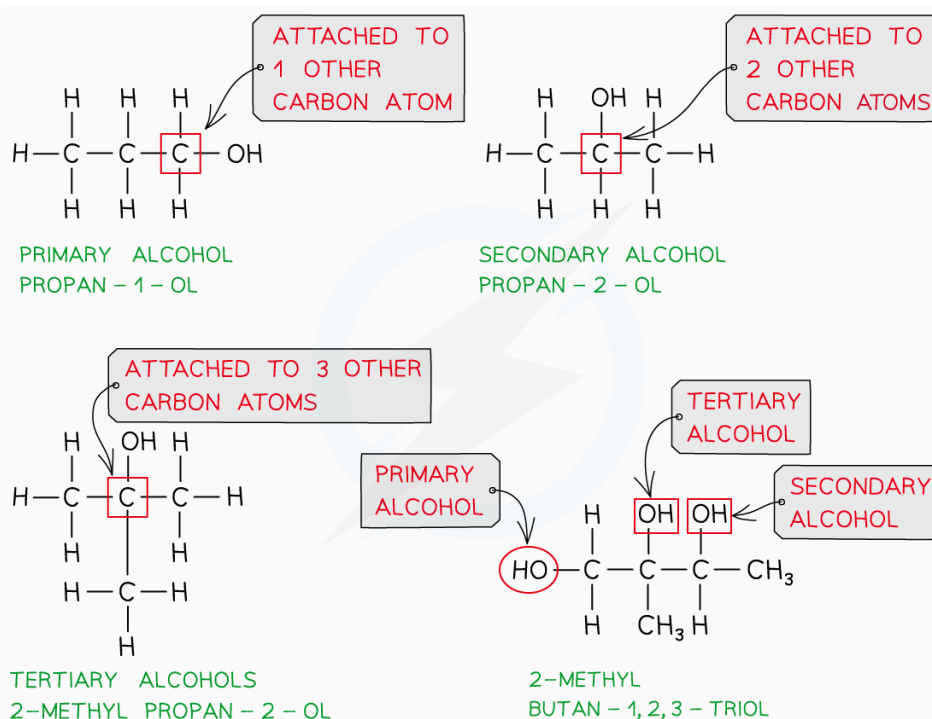
- Blending ethanol with gasoline or diesel increases the energy density and makes it safer in case of fires as it is easier to see the flames compared to pure ethanol burning
- However, there are socio-economic concerns about using large quantities of farm land to produce crops for fermentation, which 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

## Oxidation of Primary Alcohols

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



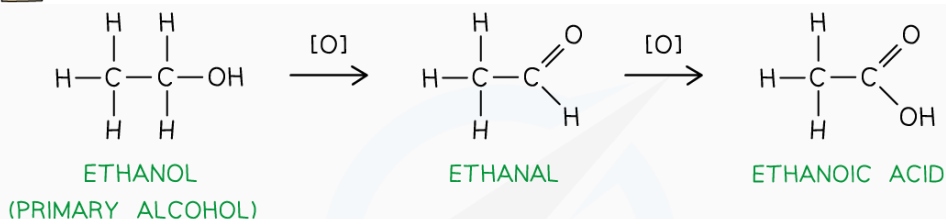
*The three classes of alcohols*

### Primary alcohols

- Primary alcohols can be oxidised to form aldehydes which can undergo further oxidation to form carboxylic acids
- The oxidising agents of alcohols include acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  or acidified  $\text{KMnO}_4$
- Acidified potassium dichromate(VI),  $\text{K}_2\text{Cr}_2\text{O}_7$ , 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

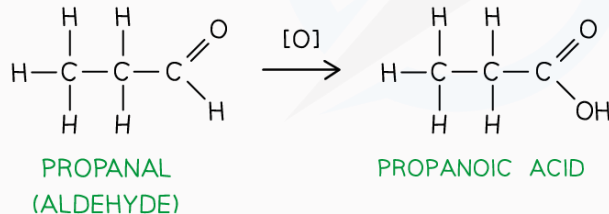
- When alcohols are oxidised the orange dichromate ions ( $\text{Cr}_2\text{O}_7^{2-}$ ) are reduced to green  $\text{Cr}^{3+}$  ions
- Acidified potassium manganate(VII),  $\text{KMnO}_4$ , is a purple oxidising agent
  - As with acidified  $\text{KMnO}_4$  the potassium manganate(VII) is in an acidic medium to allow reduction of potassium manganate(VII) to take place
    - When alcohols are oxidised, the purple manganate ions ( $\text{MnO}_4^-$ ) are reduced to colourless  $\text{Mn}^{2+}$  ions

1



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

2



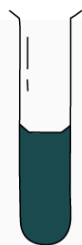
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### Further Oxidation

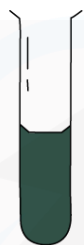
- If the aldehyde is not distilled off, further oxidation with excess oxidising agent will oxidise it to a carboxylic acid
- The reaction takes some time to complete and requires sustained heating

### Test for alcohols

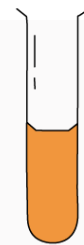
- The oxidation using acidified dichromate provides the basis for the test for alcohols as the reaction gives a strong colour change from orange to green
- Unfortunately, it does not work for tertiary alcohols, which cannot be oxidised



PROPAN-1-OL  
(PRIMARY ALCOHOL)



PROPAN-2-OL  
(SECONDARY ALCOHOL)



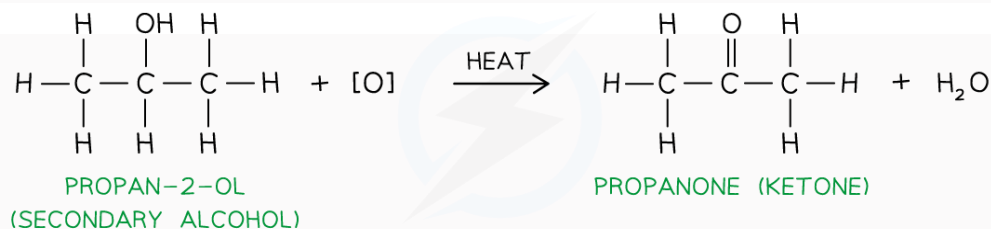
2-METHYL-PROPAN-2-OL  
(TERTIARY ALCOHOL)

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*The test for primary and secondary alcohols*

## Oxidation of Secondary Alcohols

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



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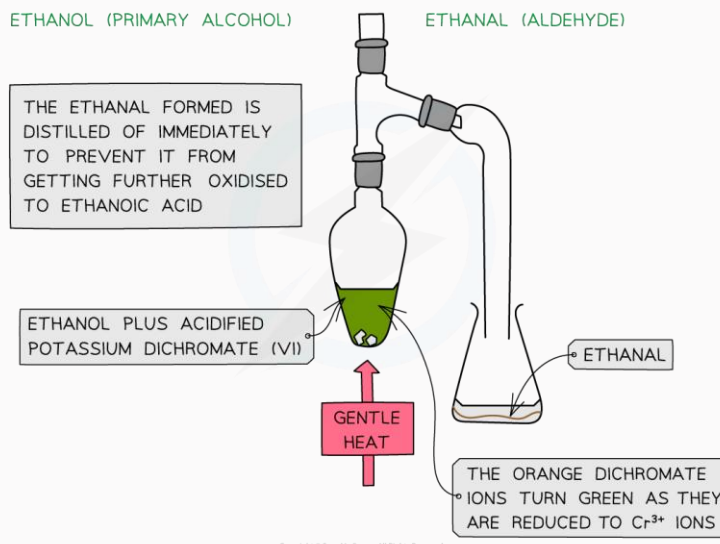
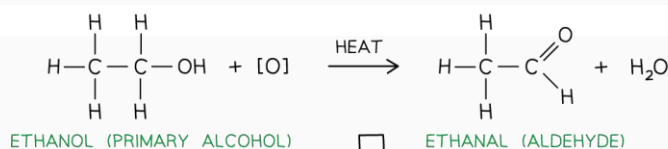
### Oxidation of Secondary Alcohols

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

## Distillation & Reflux

The difference between using distillation and heating under reflux

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

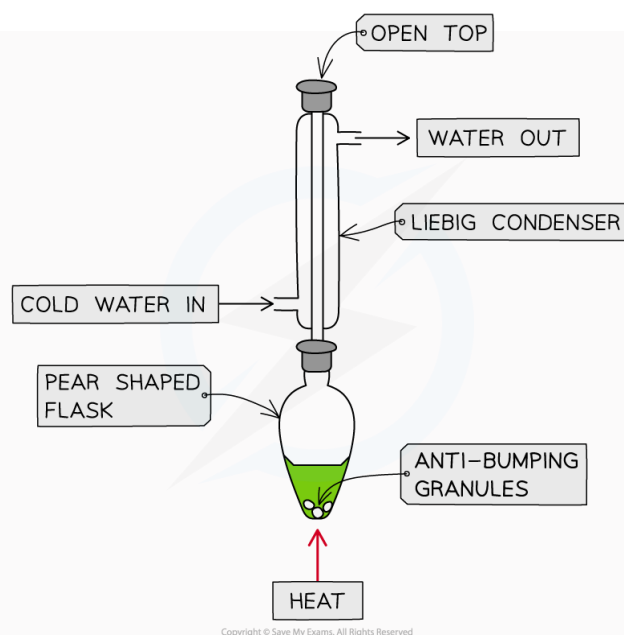


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### Oxidation of ethanol by acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> to form an aldehyde by distillation

### Heating under reflux

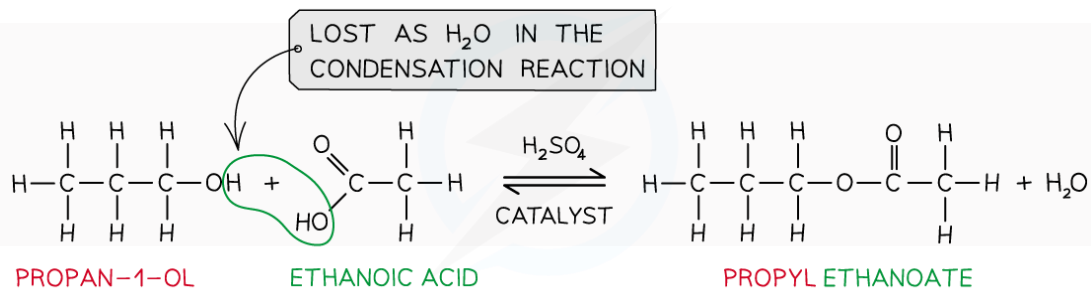
- For reactions that require sustained heating the apparatus has to be modified
- To prevent loss of volatile reactants the apparatus includes a condenser in the vertical position which returns components back into the reaction flask
- This is known as heating under reflux (reflux means re-boiling)



*Heating under Reflux Apparatus*

## Esterification

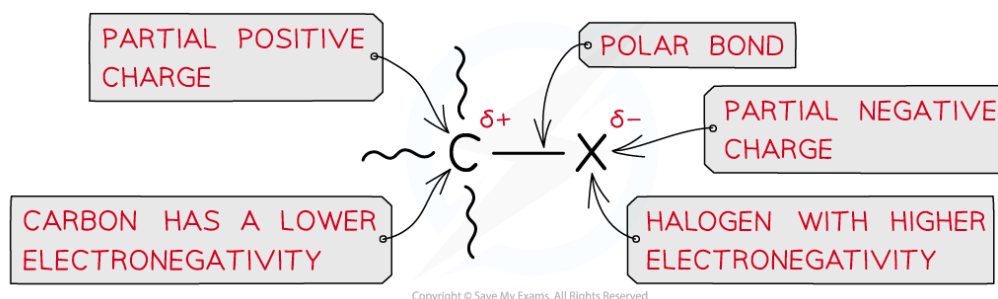
- Esters are compounds with an  $-\text{COOR}$  functional group and are characterised by their sweet and fruity smells
- They are prepared from the condensation reaction between a carboxylic acid and alcohol with concentrated  $\text{H}_2\text{SO}_4$  as catalyst
  - This is also called esterification
- The first part of the ester's name comes from the alcohol and the second part of the name comes from the carboxylic acid
  - E.g. Propanol and ethanoic acid will give the ester propyl ethanoate



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

## Reactions of Halogenoalkanes

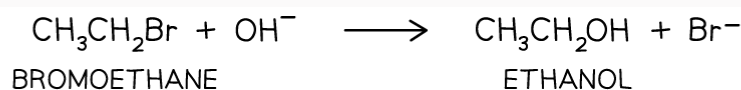
- Halogenoalkanes are much more reactive than alkanes due to the presence of the electronegative halogens
  - The halogen-carbon bond is polar causing the carbon to carry a partial positive and the halogen a partial negative charge
- A nucleophilic substitution reaction is one in which a nucleophile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



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

### Reaction with NaOH

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



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

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

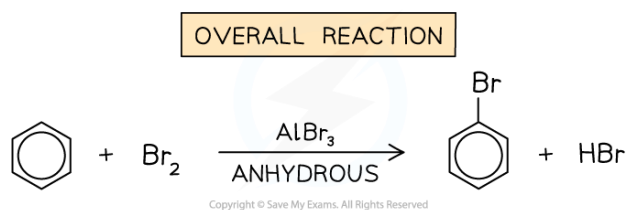
## Reactions of Benzene

- Arenes are very stable compounds due to the delocalisation of  $\pi$  electrons in the ring

- This is because the electron density is spread out over the molecule instead of being confined to a small area
- During chemical reactions such as substitution reactions, this delocalised ring is maintained
- Addition reactions however, disrupt the aromatic stabilisation so they are not favoured

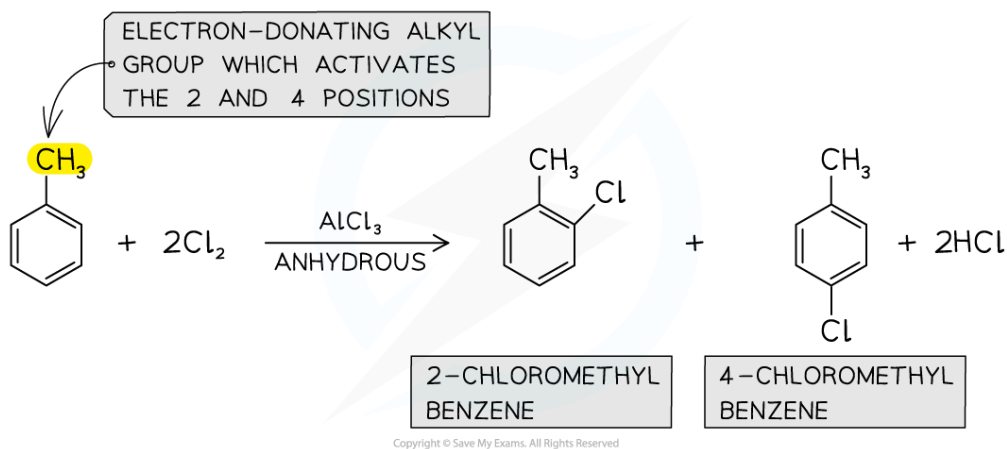
## Substitution

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



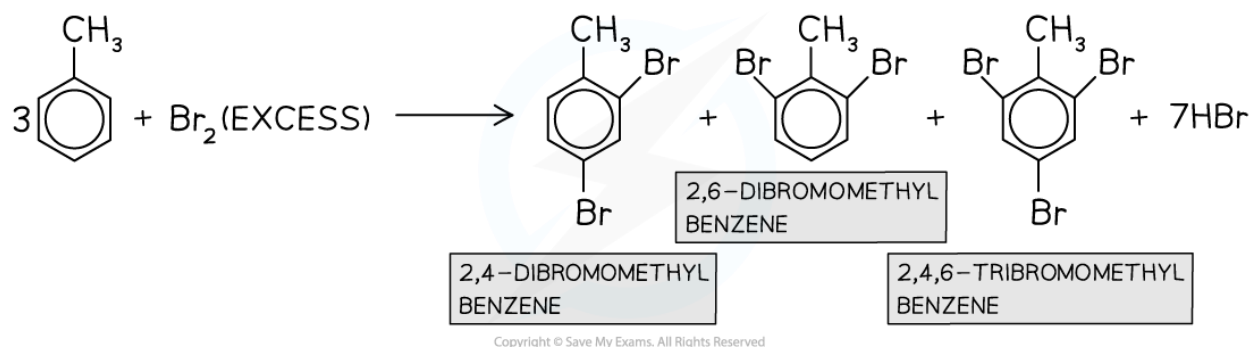
*Arenes undergo substitution reactions with halogens to form aryl halides*

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



*Alkylarenes are substituted on the 2 or 4 position*

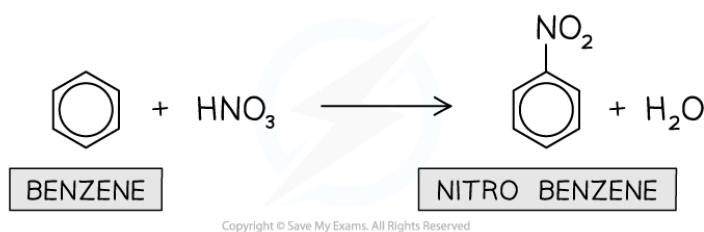
- Multiple substitutions occur when excess halogen is used



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

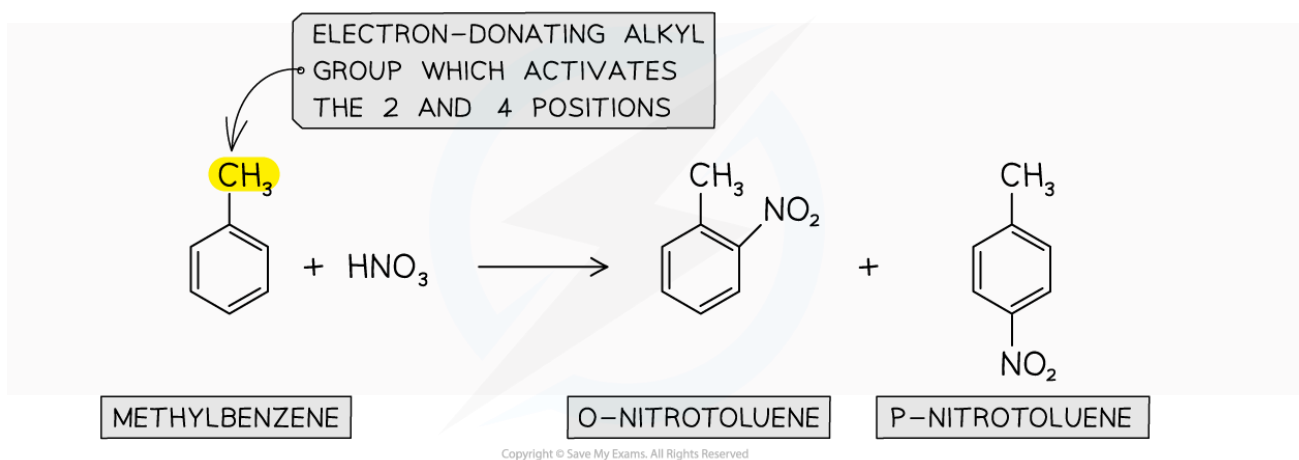
## Nitration

- Another example of a substitution reaction is the nitration of arenes
- In these reactions, a nitro (-NO<sub>2</sub>) group replaces a hydrogen atom on the arene
- The benzene is reacted with a mixture of concentrated nitric acid (HNO<sub>3</sub>) and concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) at a temperature between 25 and 60 °C



### Nitration of benzene

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



### Nitration of alkylarenes

