



OCR A Chemistry A-level

Module 4.1: Basic Concepts and Hydrocarbons Detailed Notes



4.1.1 Basic Concepts of Organic Chemistry

Naming and Representing the Formulae of Organic Compounds

Hydrocarbons

Organic chemistry mainly concerns the properties and reactions of **hydrocarbons**, compounds that contain **only carbon and hydrogen** atoms. Hydrocarbons form series of compounds with similar structures and formulas that can be represented in many different ways.

Nomenclature

Nomenclature is the set of rules that outline how different organic compounds should be **named** and how their **formulas are represented**.

Naming compounds

Compounds are named according to rules laid out by the **International Union of Pure and Applied Chemistry (IUPAC)**. This ensures each compound is universally named the same - which helps to avoid potentially dangerous confusion.

As well as being able to name compounds from their structures, you should be able to **draw** structures from IUPAC names.

Stem

The prefix of the chemical tells you **the length of the longest unbroken chain of carbon atoms** in the compound. The first 10 are given below, using alkanes as an example:

| Number of C atoms | Prefix | Alkane example |
|-------------------|--------|----------------|
| 1 | Meth- | Methane |
| 2 | Eth- | Ethane |
| 3 | Prop- | Propane |
| 4 | But- | Butane |
| 5 | Pent- | Pentane |
| 6 | Hex- | Hexane |
| 7 | Hept- | Heptane |
| 8 | Oct- | Octane |
| 9 | Non- | Nonane |
| 10 | Dec- | Decane |





Functional groups

The **ending (suffix)** of the compound's name tells you the **functional group** present. If there is more than one functional group present, they are added as a **prefix**.

| Functional group | Suffix |
|------------------|-----------|
| Alkane | -ane |
| Alkene | -ene |
| Alcohol | -ol |
| Carboxylic acid | -oic acid |
| Ketone | -one |
| Aldehyde | -al |
| Ester | -ate |
| Amine | -amine |

If a **halogen** is present, it is represented by a **prefix**:

| Functional group | Prefix |
|------------------|---------|
| Fluorine | Fluoro- |
| Chlorine | Chloro- |
| Bromine | Bromo- |
| Iodine | Iodo- |

Side chains

Carbon side chains that are **branched** from the longest carbon chain are represented by a **prefix** at the start of the word. These **alkyl groups** are made using the **stems** given above (meth-, eth-, prop-, etc), and the **suffix -yl**.

General rules

1. **Functional groups** and **side chains** are given, if necessary, with the number corresponding to the carbon they are attached to.
2. **Numbers** are separated by **commas**.
3. Numbers and words are separated by **hyphens**.
4. If **more than one** particular side chain or functional group is present then one of the following prefixes is added: di- (2), tri- (3), tetra- (4), etc.
5. The carbon chain is **numbered in ascending order** from the end of the chain nearest a functional group.
6. If multiple prefixes are present, they are included in **alphabetical** order.

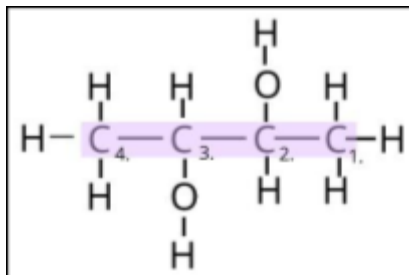




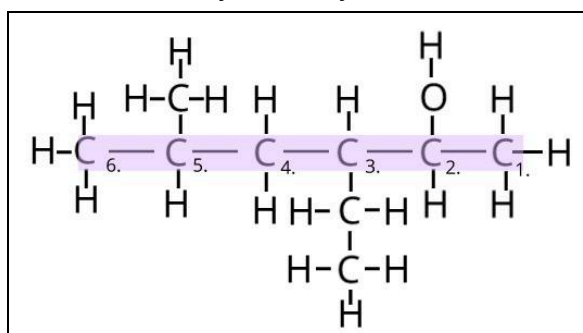
Examples

Example: The displayed structure of butan-2,3-diol.

This compound only has single carbon-carbon bonds, so is an alkane. Its longest chain of carbon atoms is 4, giving the stem butan-, and it has two alcohol functional groups on carbons 2 and 3.

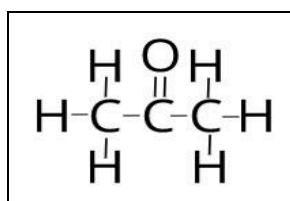


Example: The displayed structure of 3-ethyl,5-methylhexan-2-ol.

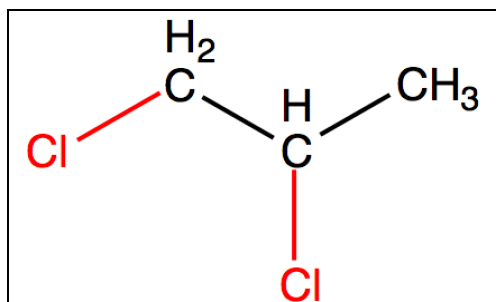


Example: The displayed structure of propanone.

Propan-2-one is also correct, but since the C=O can only be in the 2 position for the compound to be a ketone, the number is not necessary.



Example: The skeletal structure of 1,2-dichloropropane





Formulas

There are many different ways of writing and representing organic compounds:

1. Empirical Formula

- The simplest whole number ratio of atoms of each element in a compound.

2. Molecular Formula

- The true number of atoms of each element in a compound.

3. General Formula

- The simplest algebraic formula of a member of a homologous series. All members of a homologous organic series follow the general formula.

Example: Alkanes have the general formula C_nH_{2n+2} .

4. Structural Formula

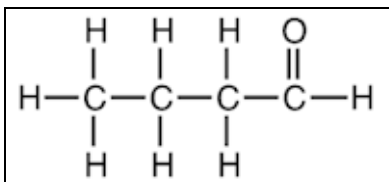
- The minimal detail that shows the arrangement of atoms in a molecule.
- The carboxyl group will be represented as COOH and the ester group as COO.

Example: The structural formula of 2-methylpropanoic acid is $(CH_3)_2CHCOOH$.

5. Displayed Formula

- The relative positioning of atoms and the bonds between them. Shows every atom and every bond in an organic compound.

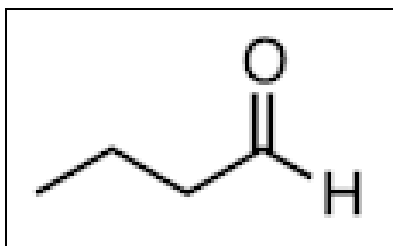
Example:



6. Skeletal Formula

- The simplified organic formula of just a carbon skeleton and functional groups.
- Shows only the bonds in a compound and any non-carbon atoms.
- Vertices are carbon atoms.
- Hydrogen is assumed to be bonded to them unless stated otherwise.

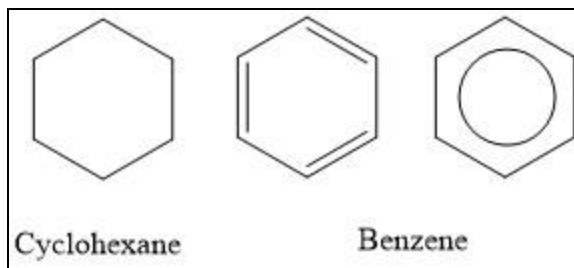
Example:





7. Cyclic Compounds and Benzene

- These compounds are represented by the symbols below.
- Benzene can be represented in two equivalent ways.



Functional Groups

Homologous Series

A **homologous series** is a series of organic compounds with the same functional group but with each successive member **differing by CH_2** . Organic compounds are often part of a homologous series, in which all members follow a **general formula** and react in a very similar way. There is an **increase in boiling points** as the chain length increases.

Example:

| TABLE 25.1 First Several Members of the Straight-Chain Alkane Series | | | |
|--|--|---------|--------------------------------------|
| Molecular Formula | Condensed Structural Formula | Name | Boiling Point ($^{\circ}\text{C}$) |
| CH_4 | CH_4 | Methane | -161 |
| C_2H_6 | CH_3CH_3 | Ethane | -89 |
| C_3H_8 | $\text{CH}_3\text{CH}_2\text{CH}_3$ | Propane | -44 |
| C_4H_{10} | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ | Butane | -0.5 |
| C_5H_{12} | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ | Pentane | 36 |
| C_6H_{14} | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ | Hexane | 68 |
| C_7H_{16} | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ | Heptane | 98 |
| C_8H_{18} | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ | Octane | 125 |
| C_9H_{20} | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ | Nonane | 151 |
| $\text{C}_{10}\text{H}_{22}$ | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ | Decane | 174 |

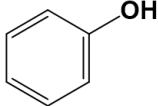




Functional Group

Each homologous series has a **functional group** that allows that molecule to be recognised. A functional group is a group of atoms responsible for the **characteristic reactions** of a compound.

Example: Table of functional groups

| Name | Functional Group | IUPAC Ending |
|------------------|---|--------------|
| Alcohols | $R-OH$ | -ol |
| Phenols |  | phenol |
| Aldehydes | $R-\overset{\overset{O}{\parallel}}{C}-H$ | -al |
| Ketones | $R-\overset{\overset{O}{\parallel}}{C}-R'$ | -one |
| Carboxylic Acids | $R-\overset{\overset{O}{\parallel}}{C}-OH$ | -oic acid |
| Esters | $R-\overset{\overset{O}{\parallel}}{C}-O-R'$ | -ate |

Alkyl Group

An alkyl group is a **hydrocarbon** chain with the general formula C_nH_{2n+1} . Sometimes **R** may be used to represent alkyl groups, as well as other fragments of organic compounds not involved in reactions.

Aliphatic

An aliphatic compound is a compound containing carbon and hydrogen joined together in **straight chains**, **branched chains** or **non-aromatic rings**.

Alicyclic

An alicyclic compound is an **aliphatic** compound arranged in **non-aromatic rings**, with or without side chains.





Aromatic

An aromatic compound is a compound containing a fully **conjugated ring**. Benzene is aromatic.

Saturated

A compound is described as being saturated if it contains **single carbon-carbon bonds** only.

Unsaturated

A compound is described as being unsaturated if it contains multiple carbon-carbon bonds, including $C=C$, $C\equiv C$, and aromatic rings.

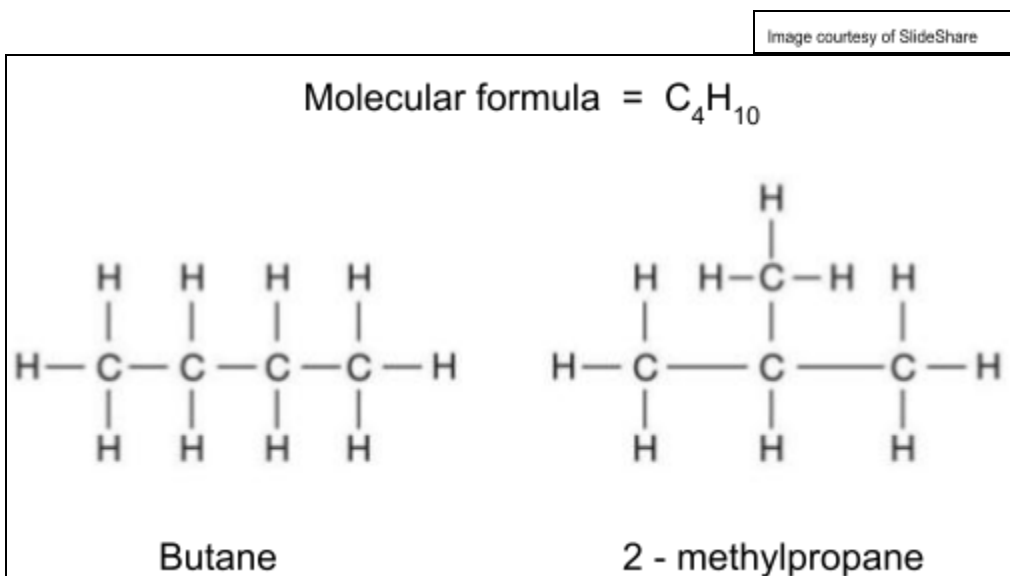
Isomerism

Isomers are molecules with the **same molecular formula** but a **different arrangement** of atoms within the molecule. This gives the isomers a different structural formula.

Chain Isomers

Chain isomers have the same molecular formula but a **different arrangement of the carbon skeleton**. The isomers's carbon chain will differ - they can be **straight** chains or **branched** chains, however they will always have the same molecular formula.

Example: Chain isomers with the molecular formula C_4H_{10} .



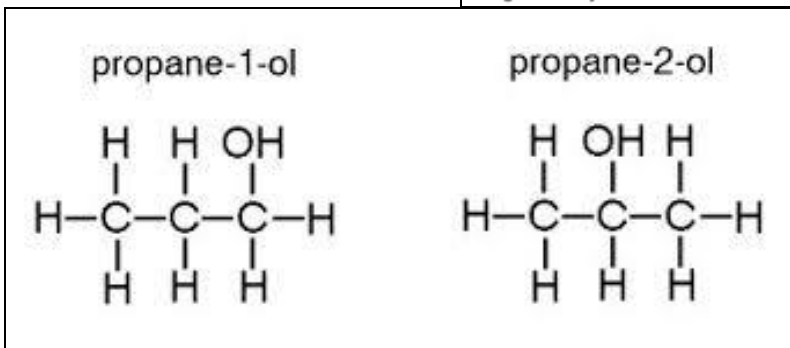


Position Isomers

Position isomers have the **functional group** of the molecule in a **different position** on the carbon chain.

Example: Position isomers with the molecular formula C_3H_8O

Images courtesy of Astan Publications

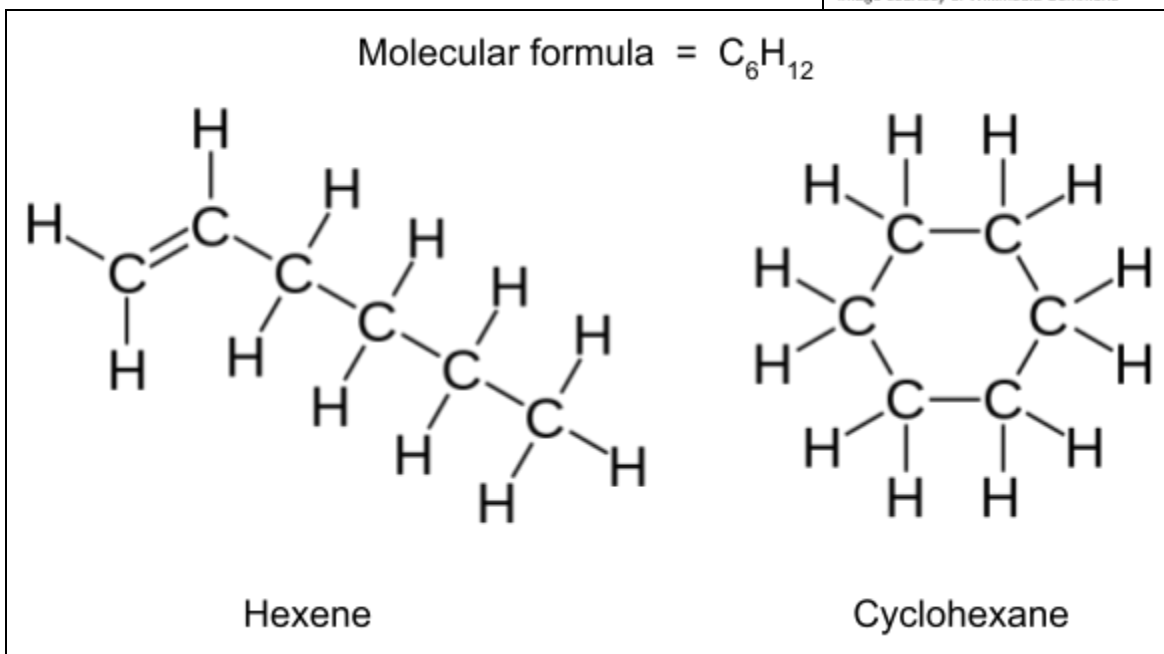


Functional Group Isomers

Functional group isomers have the same molecular formula, but the molecules have a **different functional group**.

Example: Functional group isomers with the molecular formula C_6H_{12}

Image courtesy of Wikimedia Commons





Reaction Mechanisms

Mechanisms

A '**curly arrow**' is used to describe the movement of an electron pair during a reaction. It can show either heterolytic fission or the formation of a covalent bond.

Example:



Breaking a covalent bond is called **fission**.

In **homolytic fission**, each bonding atom receives one electron from the bonded pair, forming two **radicals**. Movement of one electron is shown by a single-headed curly arrow.



In **heterolytic fission**, one bonding atom receives both electrons from the bonded pair. This leads to the formation of a **positive and negative ion**. Movement of two electrons is shown by a double-headed curly arrow. Most mechanisms involve heterolytic fission.



A **radical** is a species with an unpaired electron. Radicals are represented by a dot, as shown above in the homolytic fission of Cl_2 .

Types of reactions

Reactions can be classified according to what happens to the reactants during the reaction and what the end products are. The main types of reaction are:

- **Addition** - the reactants combine to form a **single product**.
- **Substitution** - one functional group is **replaced** by a **different functional group**.
- **Oxidation** - a species **loses** at least one electron, and is oxidised.



- **Reduction** - a species **gains** at least one electron, and is reduced.
- **Polymerisation** - a reaction in which many small molecules, known as **monomers**, join together to form a long, repeating molecule called a **polymer**.
- **Elimination** - a small molecule is **removed** from a larger molecule.

4.1.2 Alkanes

Properties of Alkanes

Alkanes are **saturated hydrocarbons** containing single C-C and C-H bonds. These single bonds are called **σ bonds**. The overlap of orbitals is directly between the two atoms and there is **free rotation** around the σ bond.

Alkanes are part of a **homologous series** with the general formula **C_nH_{2n+2}** . Cycloalkanes are an exception to this general formula but are still saturated hydrocarbons.

Each carbon atom in an alkane forms four σ bonds. They have **tetrahedral** geometry and a bond angle of **109.5°** . This shape minimises electron-electron repulsion between bonding pairs.

Variations in Boiling Points

Induced dipole-dipole interactions act between organic **alkane chains** and are affected by the **chain length** and any **branching**. As the chain length of the alkane increases, so does the **Mr** of the molecule. This results in **stronger** intermolecular forces between the chains and the compound has a **higher boiling point** as a result.

Branching of alkane chains weakens van der Waals forces between the chains as they are less able to **pack tightly** together. Therefore, the distance over which the intermolecular forces act is increased and the **attractive forces weakened**. This means branched chain alkanes have **lower boiling points** than straight chain alkanes.

Fractional distillation makes use of this variation in boiling points. The mixture of hydrocarbons is **vaporised** and fed into the fractionating column. Vapours **rise, cool** and **condense** at their different boiling points. The column is hotter at the bottom and cooler at the top. Products with **short** carbon chains have **lower** boiling points, meaning they **rise higher** up the column before reaching their boiling point. Therefore, they are **collected at the top** of the column. Products with **long** carbon chains have **higher** boiling points, meaning they don't rise very far up the column before reaching their boiling point. They condense and are **collected at the bottom** of the fractionating column.





Reactions of Alkanes

Alkanes have a **low reactivity** with many reagents due to the high bond enthalpy of the C-C bonds and very low polarity of the σ -bonds present.

Combustion of Alkanes

Alkanes make good fuels as they **release a lot of energy** when burned. With **sufficient oxygen** present, they undergo **complete combustion** to produce carbon dioxide and water.

Example:



If the oxygen present is **insufficient**, combustion is **incomplete** and **carbon monoxide or carbon particulates** are produced alongside water.

Example:



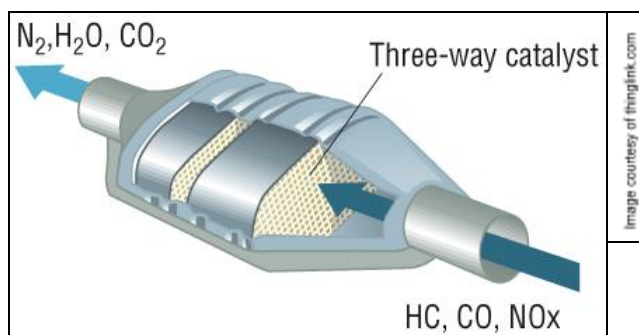
Carbon monoxide is a **toxic**, gaseous product that is especially dangerous to humans as it is odourless and colourless. Carbon monoxide is dangerous because it **replaces oxygen** in the blood, starving the brain and other organs of oxygen and causing people to **suffocate**.

Oxides of **nitrogen** and **sulfur** are also produced as a byproduct of alkane combustion along with **carbon particulates** from unburnt fuel. In clouds, these oxides can react with water and form dilute acids, which result in **acid rain**.

Catalytic Converters

Oxides of nitrogen and carbon monoxide can be removed from systems using a **catalytic converter**. This uses a **rhodium catalyst** to convert harmful products into more stable products such as CO_2 , N_2 or H_2O .

Example:





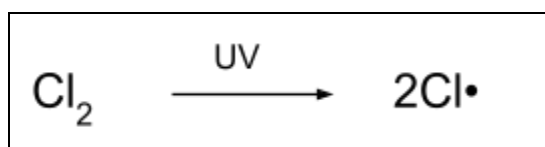
Chlorination of Alkanes

Alkanes react with halogens in the presence of **UV light** to produce **haloalkanes**. The UV light breaks down the halogen bonds (homolytic fission), producing reactive intermediates called **free radicals**.

Free radicals are species containing an **unpaired electron** which is shown using a single dot. These attack the alkanes, resulting in a series of reactions; **initiation, propagation and termination**.

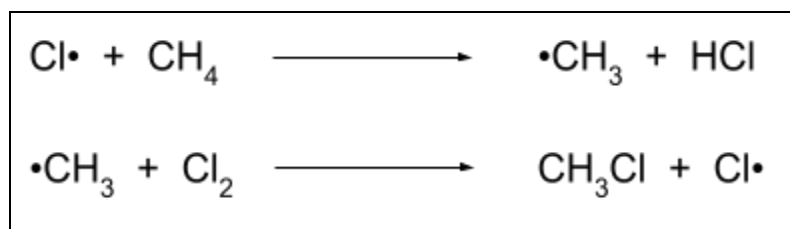
Example:

1. **Initiation** - The halogen-halogen bond is broken to form two free radicals.

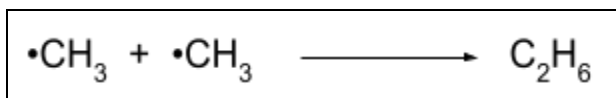


Free radicals are shown using a dot

2. **Propagation** - In each propagation step, the molecule containing the radical changes through single electron transfer. Overall, a hydrogen is replaced and the $\text{Cl}\cdot$ radical is reformed as a catalyst.



3. **Termination** - Two radicals join to end the chain reaction and form a stable product.



The propagation step can continue many times to result in **multiple substitutions** - this is a **chain reaction**. The **conditions** of the reaction can be altered to favour the termination step and limit the number of substitutions, however, termination could also occur at different positions in the carbon chain. The nature of this reaction to produce **multiple products** limits its use in organic synthesis.





4.1.3 Alkenes

Properties of Alkenes

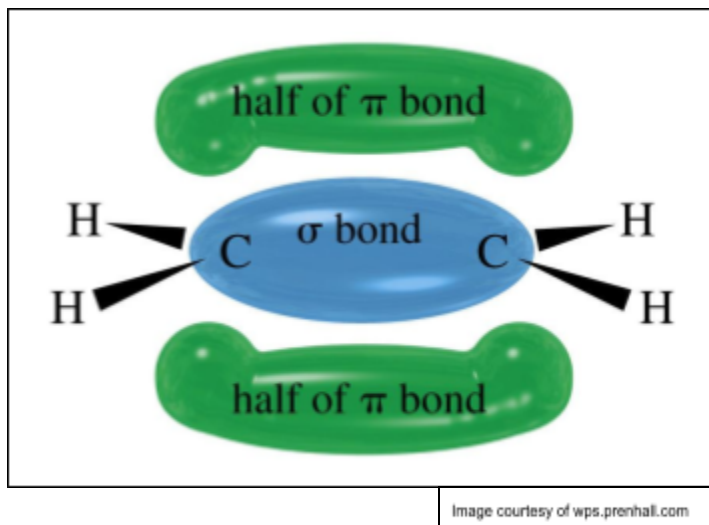
Introduction to Alkenes

Alkenes and cycloalkenes are **unsaturated hydrocarbons** with at least one carbon-carbon **double bond**. They are part of a homologous series with the general formula C_nH_{2n} .

The carbon-carbon double bond is an area of **high electron density**, making it susceptible to attack from electrophiles (species that are attracted to electron dense areas). It consists of a normal covalent **σ bond** and a **π bond**.

The **π -bond** is formed by **sideways overlap** of adjacent p-orbitals above and below the bonding C atoms. The **σ -bond** is formed by overlap of orbitals directly between the bonding atoms.

Example:



The C-H bonds are in the same **plane** as the C-C σ bond. There is **trigonal planar geometry** around the carbon atom and a bond angle of **120°** . This angle minimises electron-electron **repulsion** between bonding pairs. The π bond has electron density above and below the plane of the σ bonds. There is **restricted rotation** in alkenes due to this π bond.

Bromine water is used to identify an alkene double bond and other unsaturated compounds. Alkenes cause bromine water to change colour from **orange-brown to colourless**. This is because bromine forms bonds to the carbon atoms, removing the C=C bond, causing the compound to become **saturated**.





Stereoisomerism in Alkenes

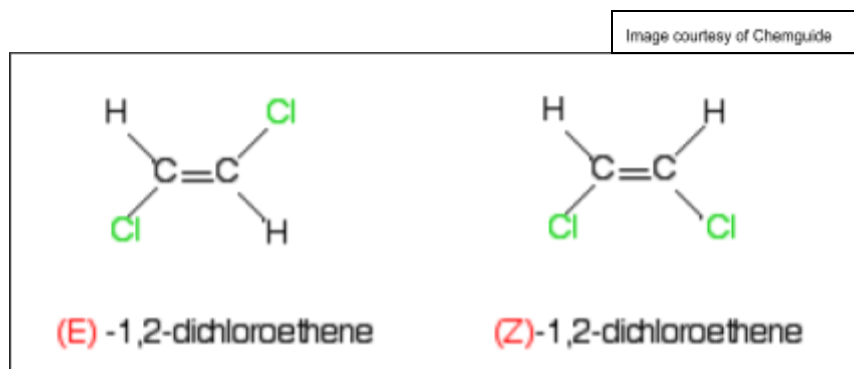
Stereoisomers

Stereoisomers are compounds with the **same structural formula** but with a **different arrangement of atoms in space**.

E-Z Isomerism

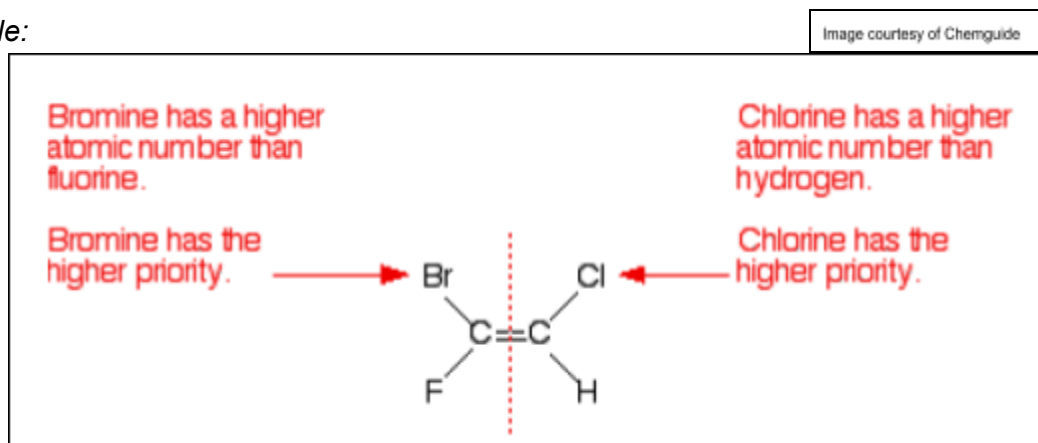
E-Z isomerism is a type of **stereoisomerism**, which occurs due to the **limited rotation** around a double carbon bond. The limited rotation means that 'high priority' groups attached to the C=C can either be 'together' or 'opposite'. The **E** isomer has these groups **apart** on opposite sides (one above, one below). The **Z** isomer has these groups **together** on the same side (both above or both below).

Example:



There is a **priority of different groups** in molecules that can display E-Z isomerism. The first atom which is directly bonded to the carbon with the double bond with the **higher atomic number** is given the **higher priority**. These groups are used to determine if it is the E or Z isomer.

Example:

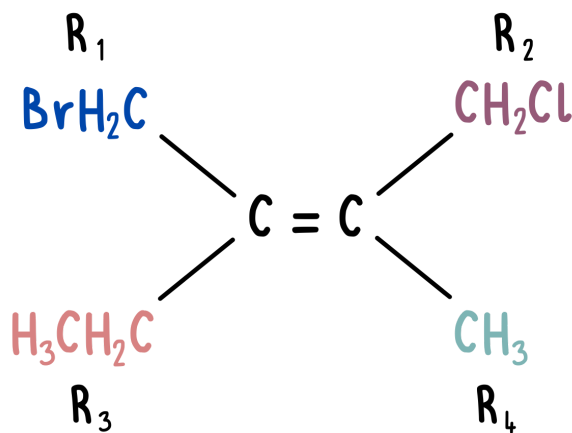


Therefore this molecule is the Z isomer as the highest priority atoms are on the same side.





How to determine a more complicated E/Z isomers



Compound A

- **Step 1: Apply the CIP priority rules**

- Look at R1 and R3:
 - Carbon is the **first atom** attached to the C=C bond, on the left hand side
- Look at R2 and R4:
 - Carbon is the first atom attached to the C=C bond, on the right hand side
- This means that we cannot deduce if compound A is an *E* or *Z* isomer by applying the CIP priority rules to the first atom attached to the C=C bond
 - Therefore, we now have to look at the **second atoms** attached

- **Step 2: Apply the CIP priority rules (using the second atoms)**

- Look again at R1 and R3:
 - The second atoms attached to R1 are **hydrogens** and **bromine**
 - The second atoms attached to R3 are **hydrogens** and another **carbon**
 - We can ignore the hydrogens as both R groups have hydrogens
 - Bromine has a **higher atomic number** than carbon, so bromine is the **higher priority**
 - Therefore, the CH₂Br group has priority over the CH₃CH₂ group
- Look again at R2 and R4:
 - The second atoms attached to R2 are **hydrogens** and **chlorine**
 - The second atoms attached to R4 are **hydrogens**
 - Chlorine has a **higher atomic number** than hydrogen, so chlorine is the **higher priority**
 - Therefore, the CH₂Cl group has priority over the CH₃ group





- **Step 3: Deduce E or Z**

- In compound A, the two highest priority groups are on the **same side** (both above) the C=C bond
 - Therefore, compound A is the **Z isomer**

Cis-Trans Isomerism

Cis-trans isomerism is a special case of E/Z isomerism in which two of the substituent groups attached to each carbon atom of the C=C group are the same. These stereoisomers can be named in the same process as above, but instead using **Cis-** for when the groups are on the **same side** and **trans-** for when they are **different sides**. It is important to remember that use of E as equivalent to trans and Z as equivalent to cis is only consistently correct when there is an H on each carbon atom of the C=C bond.

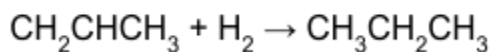
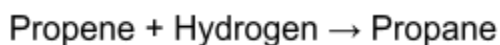
Addition Reactions of Alkenes

The **carbon-carbon double bond** in alkenes has a relatively low bond enthalpy. This makes them relatively reactive. During their reactions, the double bond opens up to form single bonds to other atoms. These are called **addition** reactions. The **pi bond** is an area of high electron density. This attracts electrophiles.

Producing Alkanes

Alkenes can undergo **electrophilic addition** with **hydrogen** to produce **alkanes**. The C=C bond opens up and forms single bonds to each of the hydrogen atoms. This reaction requires a **nickel catalyst**.

Example:



This reaction is also known as a **hydrogenation** reaction. **Catalytic hydrogenation** is used in the manufacture of **margarine** from **unsaturated vegetable oils**.





Producing Haloalkanes

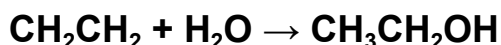
Haloalkanes are organic compounds with single carbon bonds only and halogen functional groups. Alkenes undergo **addition** reactions with **halogens** to form **di-substituted haloalkanes**, and with **hydrogen halides** to form **mono-substituted haloalkanes**. The electrophilic addition mechanism for this reaction is given on the following page of these notes.

Br₂ is present in bromine water in the **test for unsaturation**. This is an electrophilic addition reaction, forming a **dihaloalkane**.

Producing Alcohols

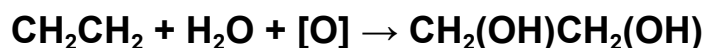
Alcohols are organic compounds with a **hydroxyl** functional group, -OH. Alkenes undergo **addition** reactions with **steam** to form alcohols. This reaction requires an **acid catalyst**, such as phosphoric acid.

Example:



Diols, alcohols with two hydroxyl functional groups, can also be formed from alkenes through an **oxidation** reaction. The double bond is oxidised by **acidified potassium manganate(VII) (KMnO₄)**. The manganate ions must be cold, dilute and acidified.

Example:





Electrophilic Addition

Electrophiles

Electrophiles are **electron pair acceptors** and are attracted to areas of **high electron density**. Some of the most common electrophile sources are:

- HBr
- Br₂
- H₂SO₄

Electrophilic Addition

Electrophilic addition is the reaction mechanism that shows how electrophiles attack the double bond in alkenes. When the double bond is broken, a **carbocation intermediate** forms. This is a carbon atom with only **three bonds**, so it has a **positive** charge.

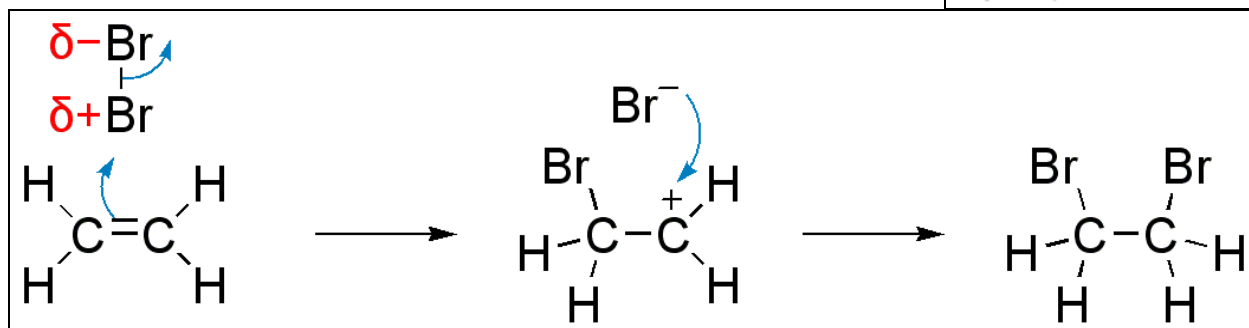
Carbocations can have **varying stability**, with tertiary being the most stable and primary the least. The **more stable** the carbocation, the **more likely** it is to form. Therefore, in an addition reaction of a hydrogen halide, multiple products can form but the **major product** will always be the one that is formed via the **most stable carbocation** possible.

Mechanisms

Mechanism: alkene + halogen → dihaloalkane

Example: Electrophilic addition of bromine to ethene

Image courtesy of Wikimedia Commons



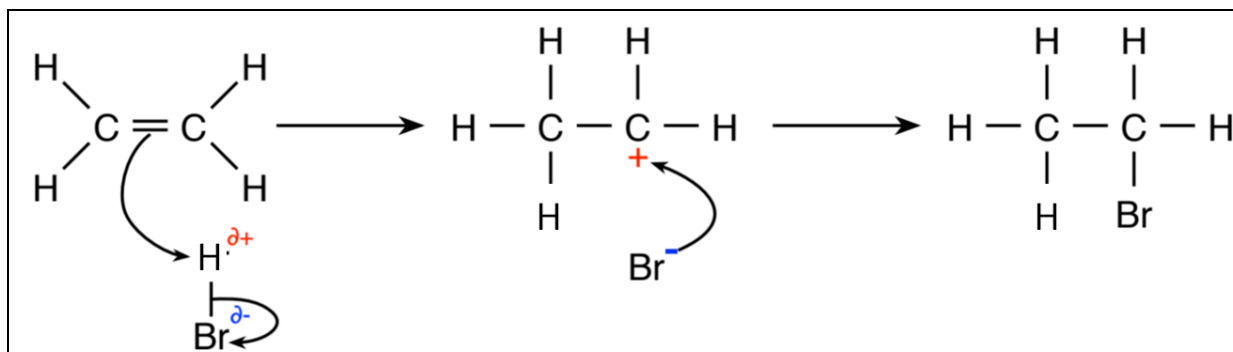
The electron-rich π bond causes the bromine molecule to gain a temporary dipole. This allows electrons to be transferred.





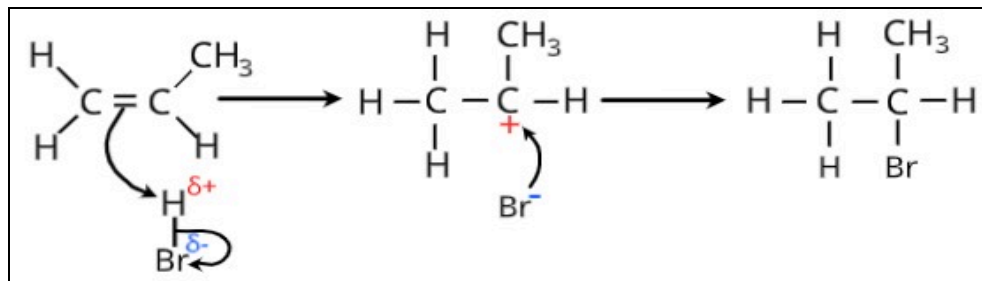
Mechanism: alkene + hydrogen halide → haloalkane

Example: Electrophilic addition of hydrogen bromide to ethene



There is a permanent dipole in HBr due to the electronegativity difference between hydrogen and bromine.

Example: Electrophilic addition of hydrogen bromide to propene



Hydrogen bromide is **polar** due to the difference in the electronegativities of hydrogen and bromine. The **electron pair** in the double bond transfers electrons to form a covalent σ bond to **H**. This produces a positively charged **carbocation intermediate** on the other carbon, which attracts the negatively charged bromide ion formed by cleavage of the H-Br bond in the first step.

The hydrogen joins to the carbon atom which is bonded to the most hydrogen atoms. The bromide ion bonds to the carbon atom which is joined to the most carbon atoms. This is due to the tendency for the reaction to proceed via the **most stable carbocation intermediate**. Hence, **2-bromopropane** forms more often than 1-bromopropane in the mechanism of propene with hydrogen bromide. This makes 2-bromopropane the **major product**.



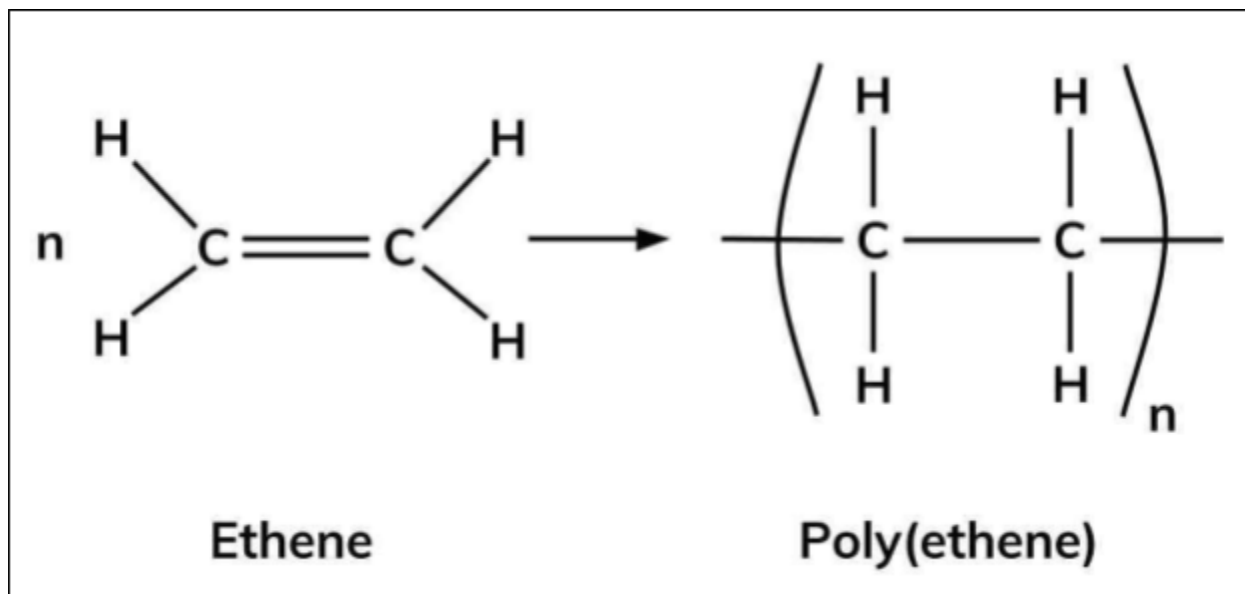


Polymers from Alkenes

Addition Polymers

Addition polymers are produced from **alkenes** which are short chain **monomers** which join together to form **long chain** polymers. The double bond of the alkene is broken to form a **repeating unit** - the repetition of which would form the complete polymer chain.

Example: Addition polymerisation of ethene to form poly(ethene)



The repeating unit must always be shown with **extended bonds through the brackets**, showing that it bonds to other units on both sides.

Waste Polymers and Alternatives

The **energy** and **resources** used to make polymers are large. Polymers are made from alkenes which are obtained from **crude oil**, a **non-renewable** resource. The extraction and cracking of crude oil are both high energy processes and additional energy is then needed to convert these alkenes into polymers.





Uses of Polymers

Polymers are **unreactive** hydrocarbon chains with **multiple strong, non-polar covalent bonds**. This makes them useful for manufacturing many everyday plastic products such as **poly(ethene) shopping bags**.

However, the unreactive nature of the bonds in addition polymers means they are **not biodegradable** and cannot be broken down by species in nature.

Benefits of using cheap oil-derived plastics are counteracted by problems for the environment if these go to **landfill**. It is important to dispose of plastics effectively to improve the use of resources and reduce the negative impact on the environment.

Disposal of Polymers

Addition polymers are **non-biodegradable** which means disposal of them can be difficult. Waste polymers can be processed in different ways. Some can be **recycled**, some are used as organic **feedstock** for production of plastics and other organic chemicals, and some are **combusted** to produce energy for other industrial processes.

Combustion can release **toxic gases** which must be removed to reduce the impact on the environment. During disposal by combustion of chlorine-containing haloalkanes, HCl may be released. This is toxic and needs to be removed.

As well as this, scientists are developing **biodegradable polymers** and **photodegradable polymers** to overcome these waste issues. This helps to reduce dependency on finite resources and alleviates problems from disposal of persistent plastic waste.

