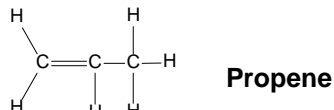
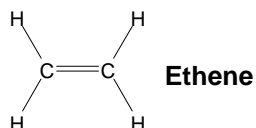


3.4 Alkenes

Alkenes are unsaturated hydrocarbons

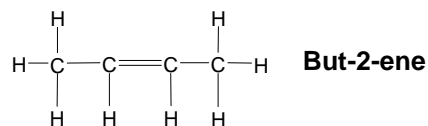
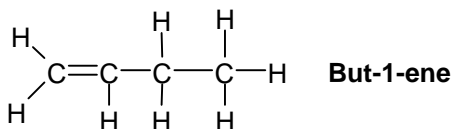
General formula is C_nH_{2n}

Alkenes contain a carbon-carbon double bond somewhere in their structure.

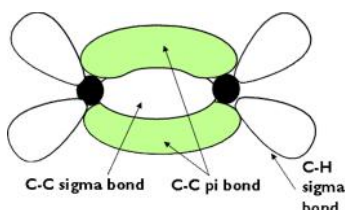


The arrangement of bonds around the $>C=C<$ is planar and has the bond angle 120°

Numbers need to be added to the name when positional isomers can occur.



$C=C$ double covalent bond consists of **one sigma (σ) bond and one pi (π) bond.**



bonds are **exposed** and have **high electron density**.

They are therefore vulnerable to attack by species which 'like' electrons: these species are called **electrophiles**.

Stereoisomerism

Stereoisomers have the same structural formulae but have a different spatial arrangement of atoms.

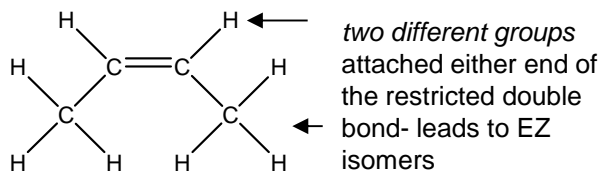
Alkenes can exhibit a type of isomerism called **E-Z stereoisomerism**

E-Z isomers exist due to restricted rotation about the $C=C$ bond

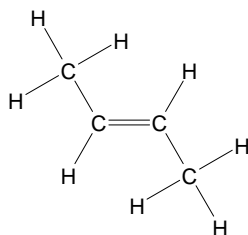
E-Z stereoisomers arise when:

- There is **restricted rotation** around the $C=C$ double bond.
- There are **two different groups/atoms** attached both ends of the double bond.

Single carbon-carbon covalent bonds can easily rotate

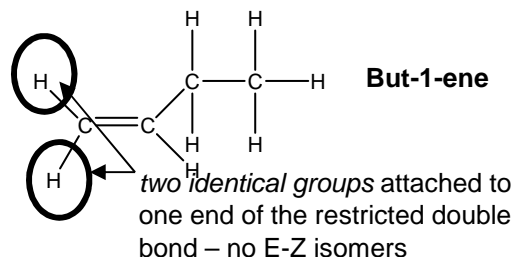


Z-but-2-ene



E-but-2-ene

These are two isomers as the lack of rotation around the double bonds means one cannot be switched to the other.

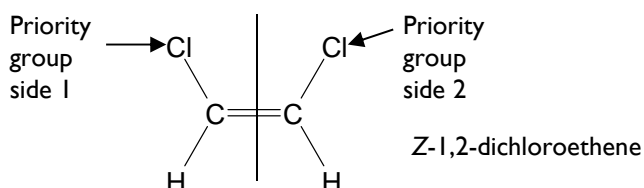


But-1-ene is a structural isomer of But-2-ene but does not show E-Z isomerism.

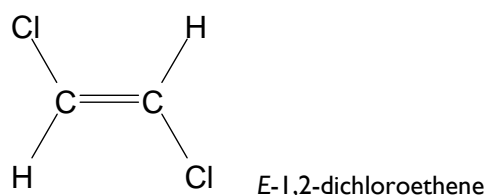
Naming E-Z stereoisomers

First determine the priority groups on both sides of the double bond

Priority Group: The atom with the bigger Atomic number is classed as the priority atom



If the priority atom is on the same side of the double bond it is labelled Z from the german *zusammen* (The Zame Zide!)



If the priority atom is on the opposite side of the double bond it is labelled E from the german *entgegen* (The Epposite side!)

Electrophilic Addition Reactions of Alkenes

The double bonds in alkenes are areas with high electron density. This attracts electrophiles and the alkenes undergo addition reactions.

Definition Electrophile: an **electron pair acceptor**

Addition reaction: a reaction where two molecules react together to produce one

1. Reaction of Bromine with Alkenes

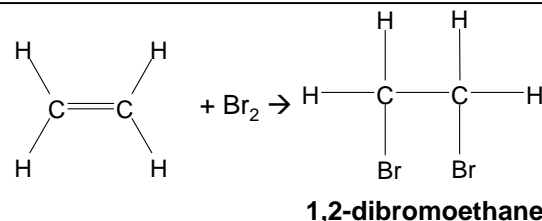
Change in functional group: alkene \rightarrow dihalogenoalkane

Reagent: Bromine

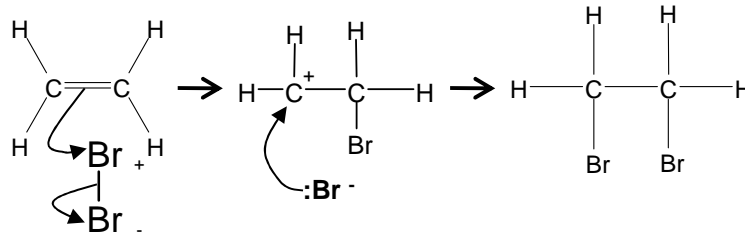
Conditions: Room temperature (not in UV light)

Mechanism: Electrophilic Addition

Type of reagent: Electrophile, $\text{Br}^{\delta+}$



As the Br_2 molecule approaches the alkene, the pi bond electrons repel the electron pair in the Br-Br bond. This **INDUCES** a **DIPOLE**. Br_2 becomes **polar** and **ELECTROPHILIC** (Br^+).



The **INTERMEDIATE** formed, which has a positive charge on a carbon atom is called a **CARBICATION**

2. Reaction of Hydrogen Bromide with Alkenes

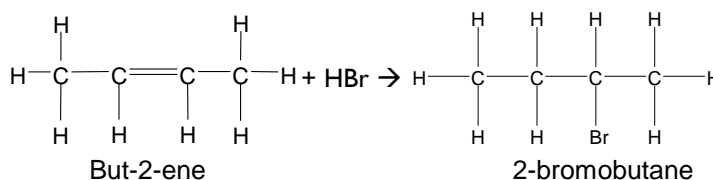
Change in functional group: alkene \rightarrow halogenoalkane

Reagent: HCl or HBr

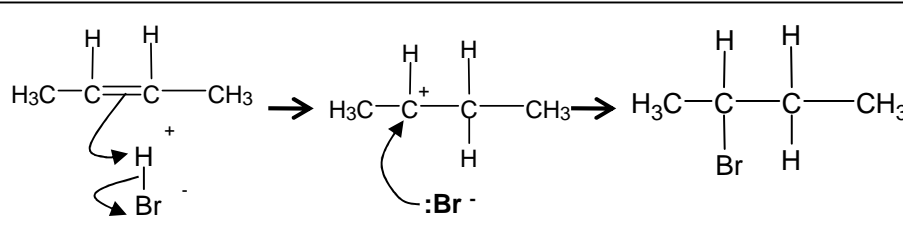
Conditions: Room temperature

Mechanism: Electrophilic Addition

Type of reagent: Electrophile, $\text{H}^{\delta+}$



HBr is a polar molecule because Br is more electronegative than H. The H^+ is attracted to the electron-rich pi bond.

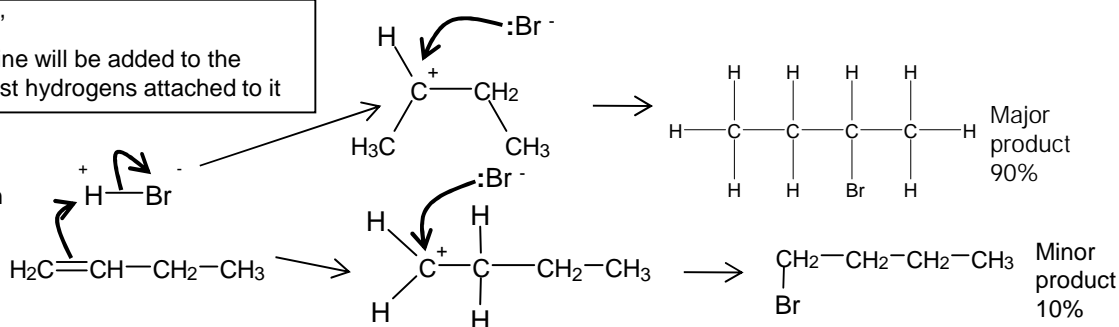


This reaction can lead to two products when the alkene is **unsymmetrical**

'Markownikoff's Rule'

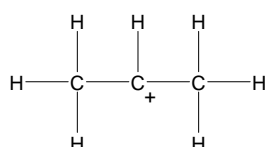
In most cases, bromine will be added to the carbon with the fewest hydrogens attached to it

If the alkene is unsymmetrical, addition of hydrogen bromide can lead to two isomeric products.



Why?

This carbocation intermediate is more stable because the methyl groups on either side of the positive carbon are electron releasing and reduce the charge on the ion which stabilises it.



In **electrophilic addition** to alkenes, the **major product** is formed **via the more stable carbocation** intermediate.

In exam answers

- Draw out both carbocations and identify as primary, secondary and tertiary
- State which is the more stable carbocation e.g. secondary more stable than primary
- State that the more stable carbocation is stabilised because the methyl groups on either (or one) side of the positive carbon are electron releasing and reduce the charge on the ion.
- (If both carbocations are secondary then both will be equally stable and a 50/50 split will be achieved)

The order of stability for carbocations is
tertiary > secondary > primary

3. Reaction of Sulfuric acid with Alkenes

Stage 1

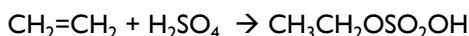
Change in functional group
alkene → alkyl hydrogensulfate

Reagents: concentrated H₂SO₄

Conditions: room temperature

Mechanism: Electrophilic Addition

Type of reagent: Electrophile, H₂SO₄



Stage 2

Change in functional group
alkyl hydrogensulfate → alcohol

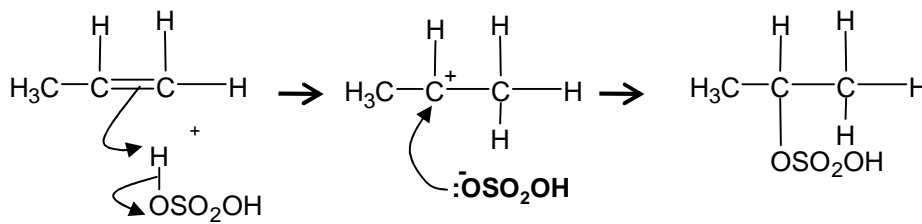
Reagents: water

Conditions: warm mixture

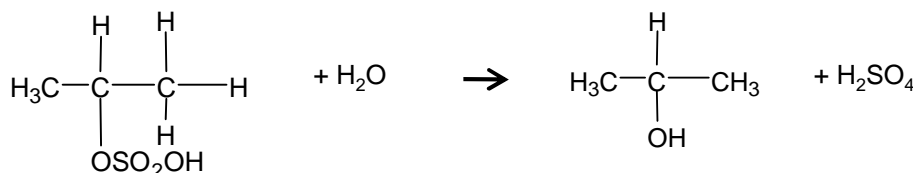
Type of reaction: hydrolysis



Stage 1: electrophilic addition



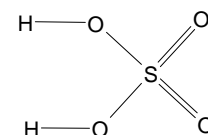
Stage 2: hydrolysis



H₂SO₄ is best drawn as

H-OSO₂OH

in exams. Its real structure is



Overall role of sulfuric acid is that of a **catalyst** (as it is regenerated)

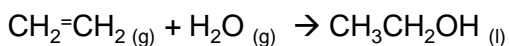
With unsymmetrical alkenes a minor and major product can also be formed similar to the addition of HBr. The same explanation applies.

Definition: Hydrolysis – a reaction where the molecule is **split** by the addition of water

Direct industrial hydration of alkenes to form alcohols

Industrially alkenes are converted to alcohols in one step rather than the two in the above sulfuric acid reaction. They are reacted with water in the presence of an acid catalyst.

This reaction can be called **hydration**: a reaction where water is **added** to a molecule



Essential Conditions

High temperature 300 to 600°C

High pressure 70 atm

Catalyst of **concentrated H₃PO₄**

The high pressures needed mean this cannot be done in the laboratory. It is preferred industrially, however, as there are no waste products and so has a high atom economy. It would also mean separation of products is easier (and cheaper) to carry out. See equilibrium chapter for more on the industrial conditions for this reaction.

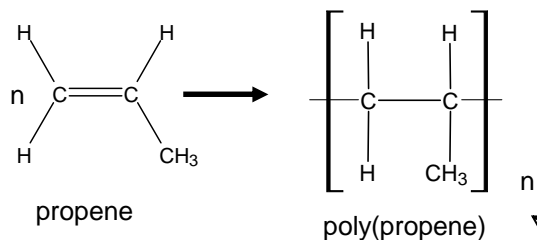
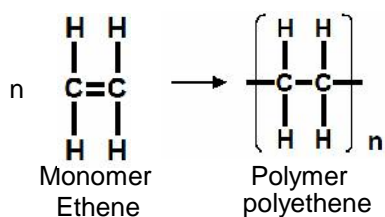
Testing for Alkenes with Bromine water

Bromine water decolourises in the presence of a double bond. This can be used as a test for the presence of a double bond in a molecule. It can be used quantitatively to show the presence of multiple double bonds in compounds like polyunsaturated oils.

Addition Polymers

Addition polymers are formed from alkenes

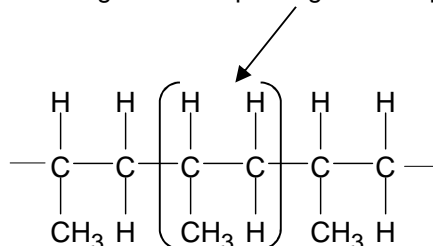
This is called **addition polymerisation**



Poly(propene) is recycled

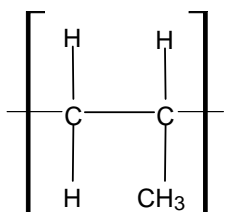
Poly(alkenes) like alkanes are unreactive due to the strong C-C and C-H bonds

be able to recognise the repeating unit in a poly(alkene)

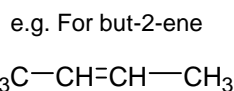


Add the **n's** if writing an equation showing the reaction where 'n' monomers become 'n' repeating units

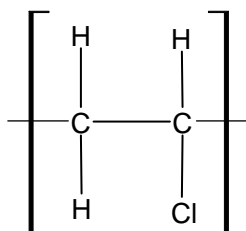
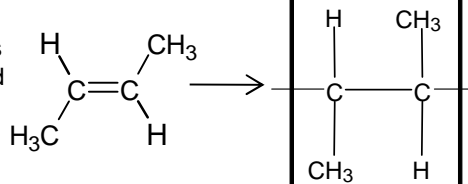
If asked to draw **one repeating unit**, don't add the **n** on to your diagram, because n represents a large number



You should be able to draw the polymer repeating unit for any alkene



It is best to first draw out the monomer with groups of atoms arranged around the double bond



Poly(chloroethene) is a polymer that is water proof, an electrical insulator and doesn't react with acids.

In its pure form it is a rigid plastic due to the strong intermolecular bonding between polymer chains prevents them moving over each other. In this un-plasticised form it is used make uPVC window frame coverings and guttering.

If a plasticiser is added the intermolecular forces are weakened which allows the chains to move more easily, resulting in more flexibility in the polymer. In this form PVC is used to make insulation on electrical wires, and waterproof clothing.