3.4 The Alkenes

Introduction

- General formula: $\mathbf{C_nH_{2n}}$
- Unsaturated hydrocarbons (contains at least one C=C bonds)
- No free rotation around the C=C
- Exhibit E/Z geometric isomerism
- A bond angles of 120^o around each of the double bonded carbons

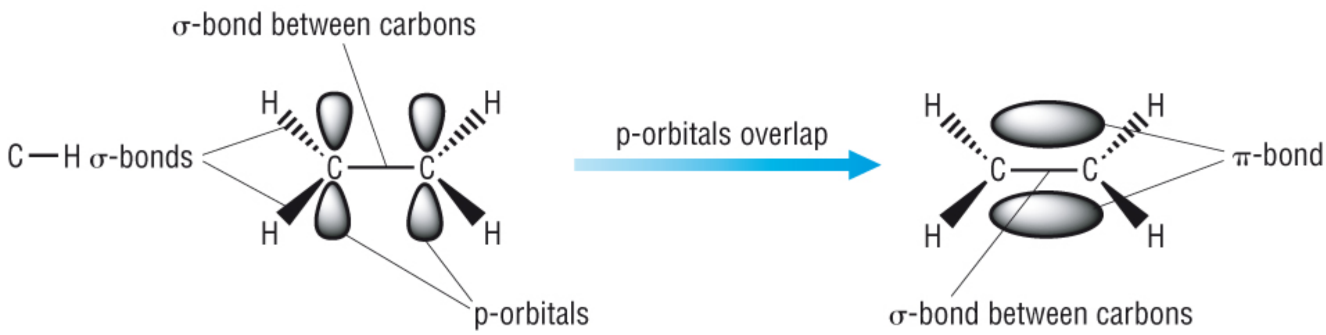
***Saturated**: Contains C – C single bonds only*

***Unsaturated**: Contains at least one C = C double bonds*

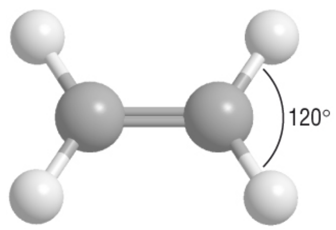
***Hydrocarbon**: Only contains the elements hydrogen and carbon*

The nature of the double bond:

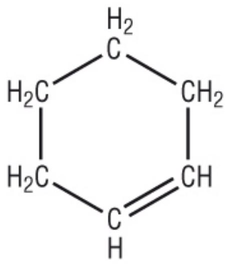
- Alkenes are more reactive than the alkanes due to the high electron dense C=C
- They typically take part in addition reactions (to the C=C).



- The double bond consists of a **sigma bond (σ)** and a **pi bond (π)**.
- The π **bond** is **weaker** than the σ **bond** so breaks first in reactions involving alkenes.
- The π bond changes the shape around the carbon atom to a trigonal planar with a bond angle of 120^o:
- The **planar double bond** locks the molecule around the double bond
- This means that there is **no free rotation** about these bonds.



Cyclic alkenes:



- Cyclic means that the carbon chain is joined at either end forming a ring.
- The reactions of cyclic alkenes is exactly the same as straight chain alkenes
- As there is no 'ends' to the molecule they have 2 H's less in the general formula.

Naming alkenes

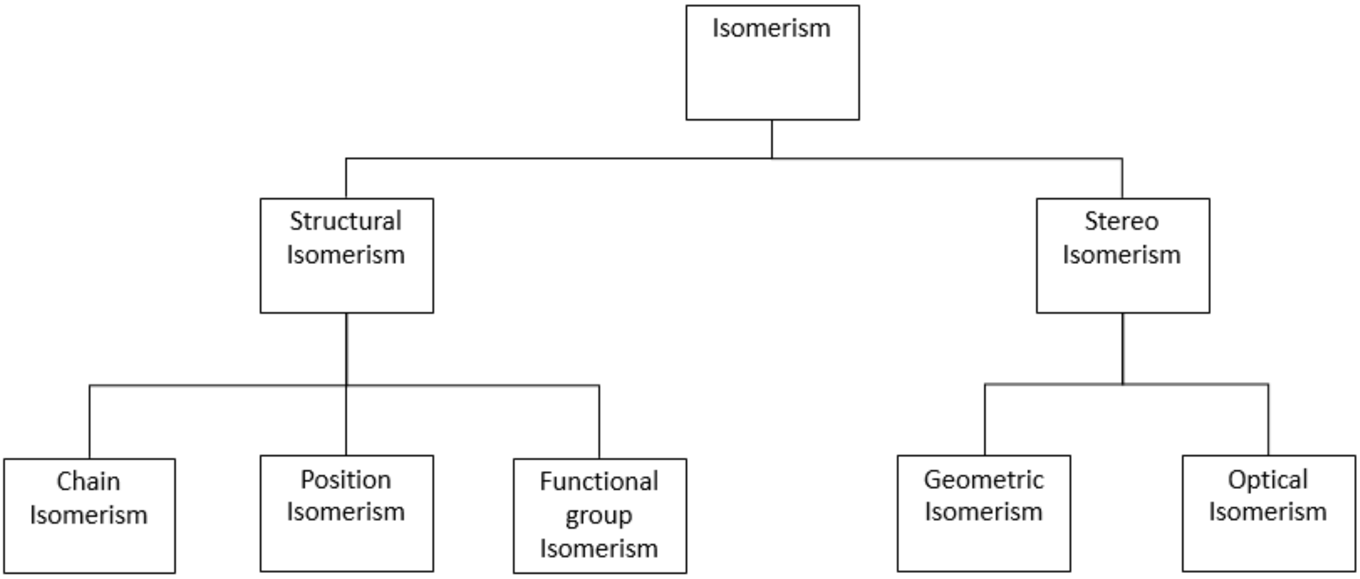
Give the IUPAC name of the following alkenes:

alkene	IUPAC name
$CH_3CH{=}CHCH_3$	
$CH_2{=}CHCH(CH_3)_2$	
$CH_3CH_2CH{=}CHCH{=}CH_2$	

Draw the structure of the following alkenes:

alkene	structure
2-methylpropene	
2,3-dimethylbut-1-ene	
2,3-dimethylcyclohexene	

Alkenes exhibit isomerism



Structural Isomer: ***Are compounds with the same molecular formula but a different structural formula***

Stereoisomer: ***A Molecule with the same structural formula but its atoms are arranged differently in space***

Alkanes have **3 types** of structural isomers

Chain Isomerism: ***These have the same molecular formula and functional group but a different arrangement of the carbon skeleton***

Position Isomerism: ***These have the same molecular formula and functional group but the functional group is attached to a different carbon***

Functional group Isomerism: ***These have the same molecular but the atoms are arranged into a different functional group***

Complete the table below for hex - 2 - ene

Chain Isomer	Position Isomer	Functional group Isomer

Stereoisomerism and alkenes

Activity 1:

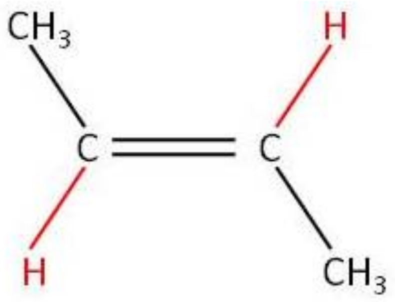
- Build but-2-ene. Look at your neighbours, are they the same?
- There are 2 different structures, draw these below:

Displayed formula		
Structural formula		
Skeletal formula		

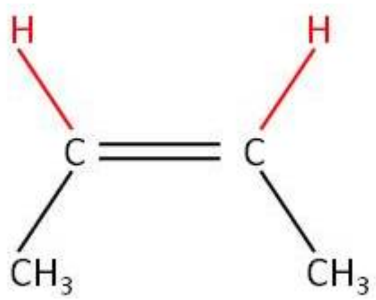
- This type of stereoisomer is called **geometric or E/Z Isomerism:**

<u>Geometric Isomerism (E/Z isomerism)</u>
These have the same molecular formula but different spatial arrangement due to the restricted rotation around the carbon – carbon double bond

Examples:



E-but-2-ene



Z-but-2-ene

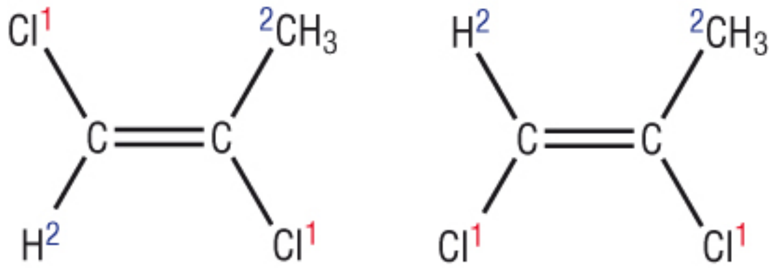
This occurs because:

1) A carbon - carbon double bond, **C=C**
2) Each carbon in the carbon – carbon double bond must be attached to **2 different groups**:

<u>Cahn - Ingold - Prelog nomenclature (CIP):</u>

The rules:

1) Assign a priority to **each atom** attached to each carbon in the double bond using Ar's (assign a **1** or **2**)
2) If the highest priority atoms are on the same side of the C=C assign **Z isomer**
3) If the highest priority atoms are on opposite sides of the C=C assign **E isomer**
4) If two atoms have the same atomic number, move to the next atom along the chain.

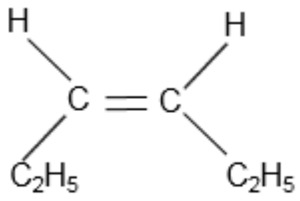
<table>
<tr><td colspan="4">

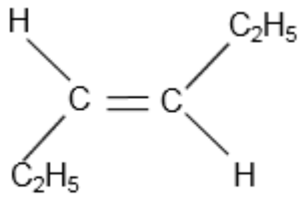
E isomer   *Z* isomer</td></tr>
<tr><td>Cl has highest priority</td><td>Cl has highest priority</td><td>Cl has highest priority</td><td>Cl has highest priority</td></tr>
<tr><td colspan="2">Priority groups on opposite sides, E isomer</td><td colspan="2">Priority groups on same side, Z isomer</td></tr>
</table>

- Chlorine has the highest atomic number so it is given priority.

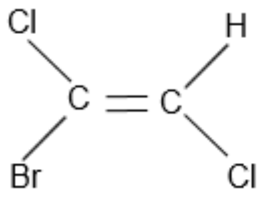
Examples: **Assign or draw and assign** the following as E/Z isomers **followed by the name** of the molecule

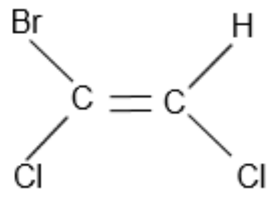
1)



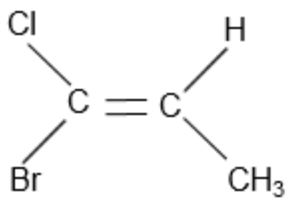


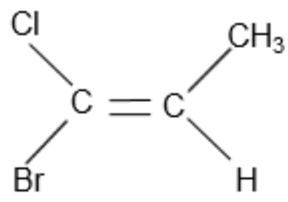
2)



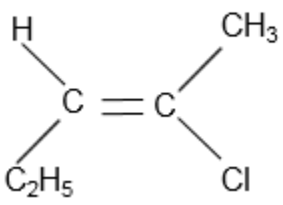


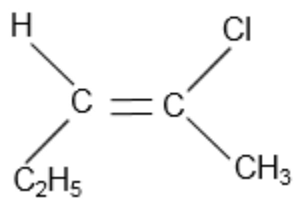
3)





4)





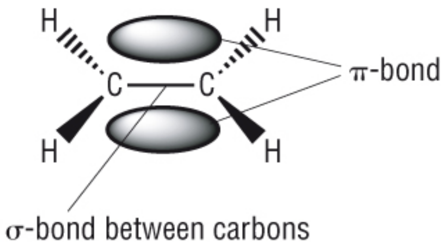
5) 2–bromo–1–iodoropropene

6) 1,3–dibromo–2–methylpropene

Reactions of alkenes:

The reactivity of the C=C double bond:

- Alkenes are more reactive than the alkanes due to the high electron dense C=C
- They typically take part in addition reactions (to the C=C).

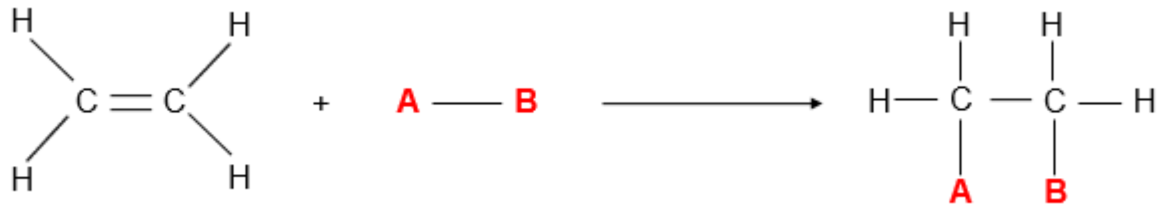


Bond	Bond enthalpy Kj mol^{-1}
σ bond	+347
π bond	+265

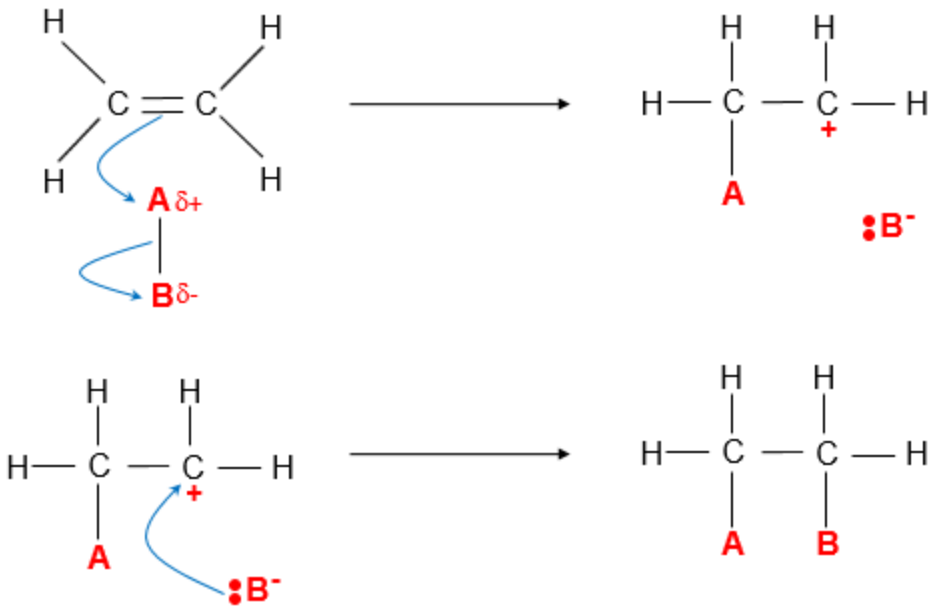
- The C=C requires 612 Kj Mol^{-1} making it a lot stronger than just a C-C.
- The C=C is not however twice as strong
- The **sigma bond (σ)** is a lot stronger than the **pi bond (π)** which means that the **pi bond (π)** breaks leaving the **sigma bond (σ)** intact.

Reactions of the alkanes:

- Alkenes undergo addition reactions as they are **unsaturated**.
- The reactant will add across the C=C forming a **saturated** product:

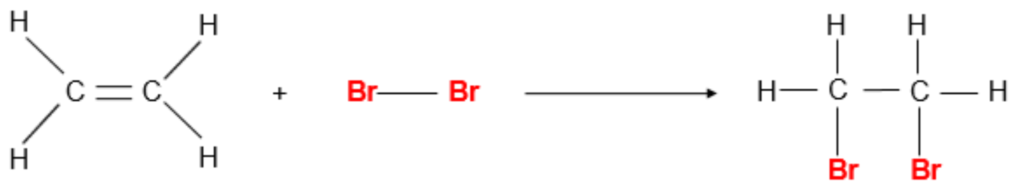


The mechanism

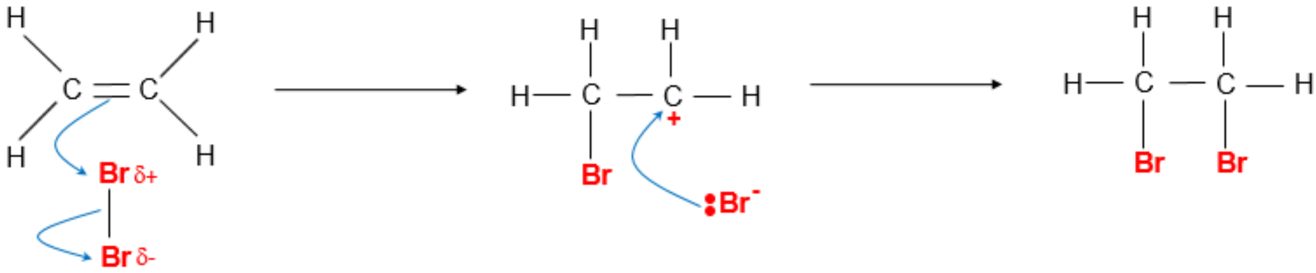


- As **A – B** comes towards the **C = C**, the electrons in the double bond **repels electrons** in the bond, **polarises** the molecule giving a δ- and a δ+ (the molecule may already be polar)
- The δ+ **end** of the molecule is attracted to the **electron rich C = C**.
- The pair of electrons from the **C = C** form a single bond with the δ+ **A atom**. At the same time the electrons from the **A – B** bond breaks **heterolytically** and the pair of electrons go to **atom B**, forming **B**$^-$.
- A **carbocation** (positive) and **negative ion** is formed.
- The electrons from the negative ion, **B**$^-$, donate a pair of electrons to form a bond with the **carbocation**.
- This is an **electrophilic addition** reaction.

1) Addition of halogens - Br_2: *Forming a dihalogenoalkane*

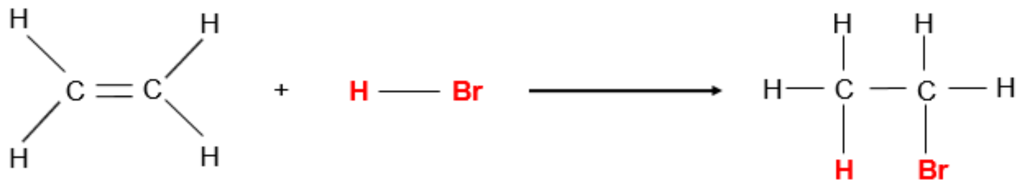


The mechanism:

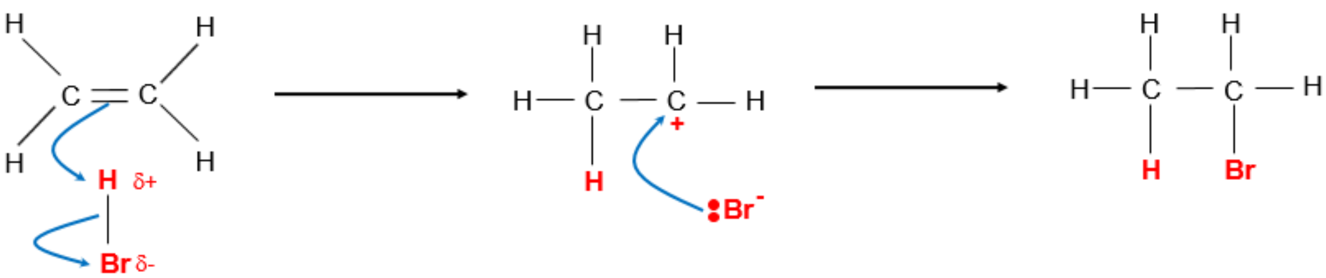


Chemical test for C=C / unsaturation: • Bromine water • Orange to clear and colourless

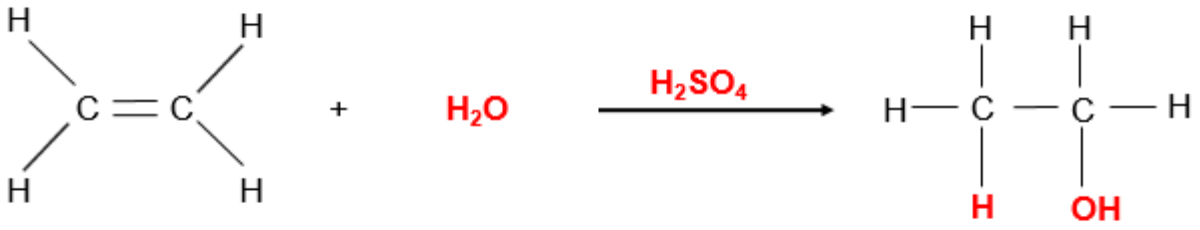
2) Addition of hydrogen halides - HBr: *Forming a halogenoalkane*



The mechanism:

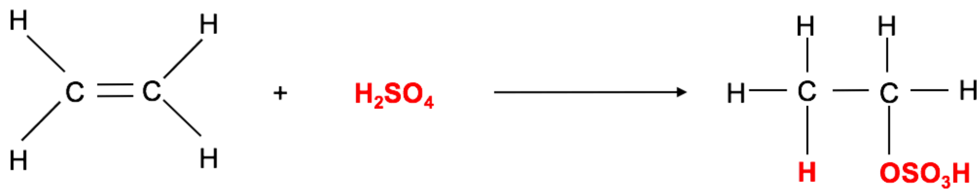


3) Heating with H_2O / H_2SO_4: *Forming an alcohol (in 2 steps)*

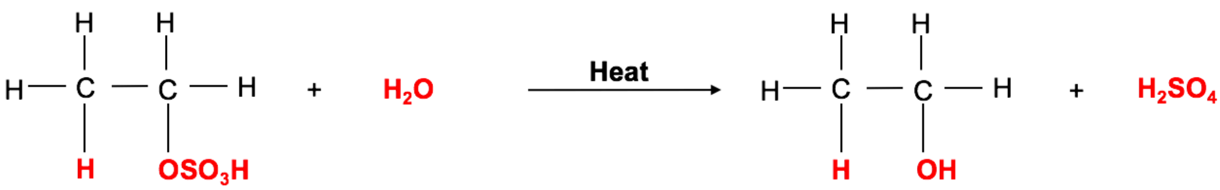


- However this happens in 2 stages with the sulphuric acid behaving as a **catalyst:**

Step 1:

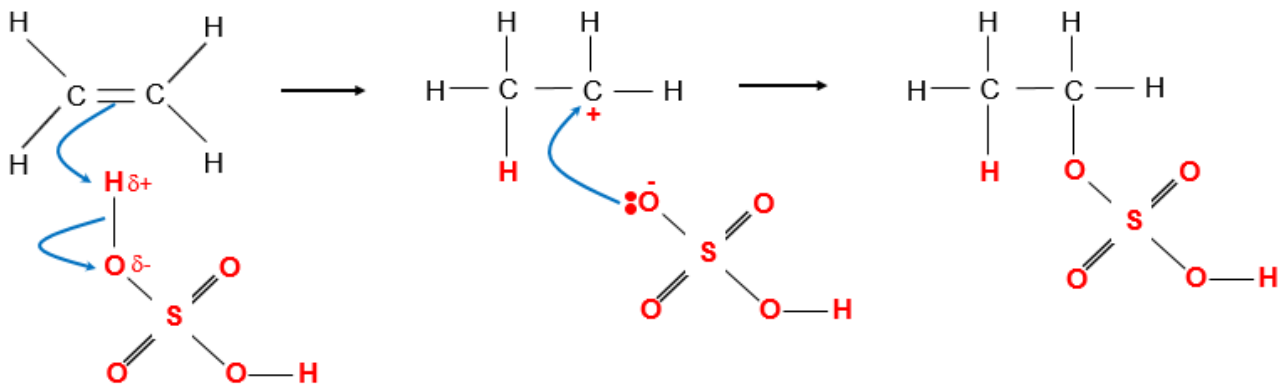


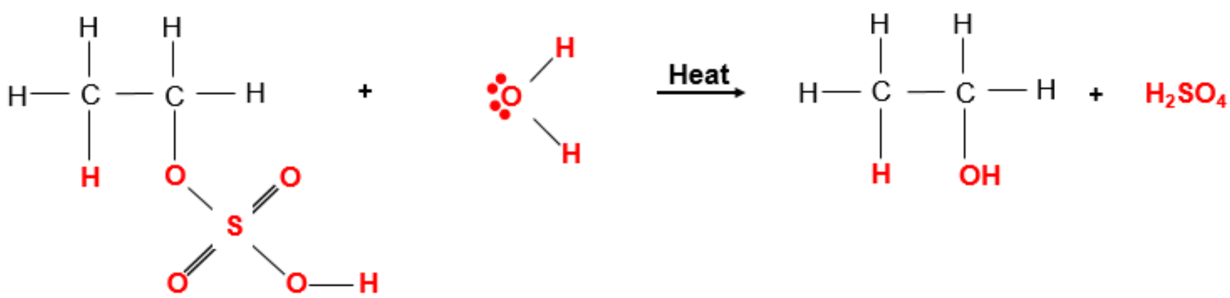
Step 2:



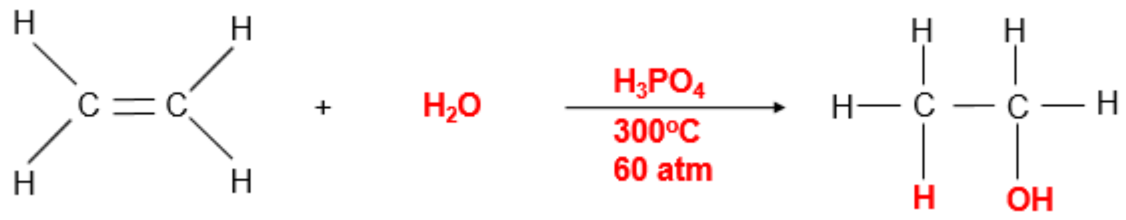
- The sulphuric acid is used up in step 1 but regenerated in step 2

The mechanism:

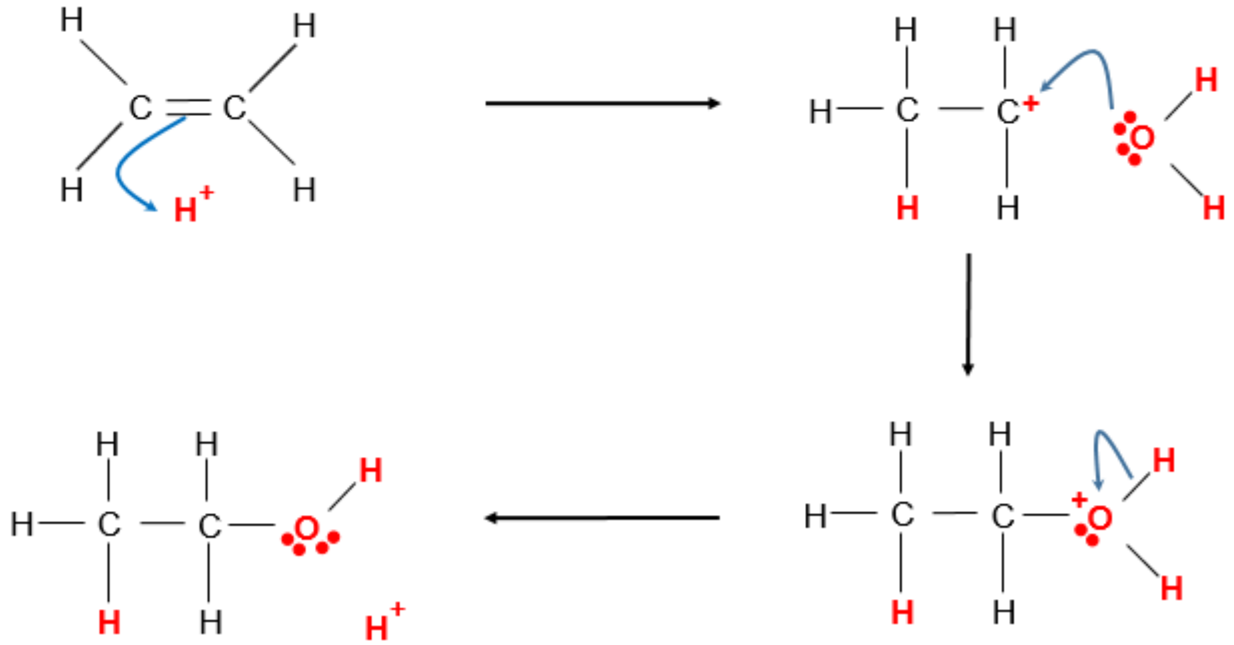




4) Hydration of alkenes with H_2O / H_3PO_4 catalyst / 300°C / 60atm: ***Forming an alcohol***

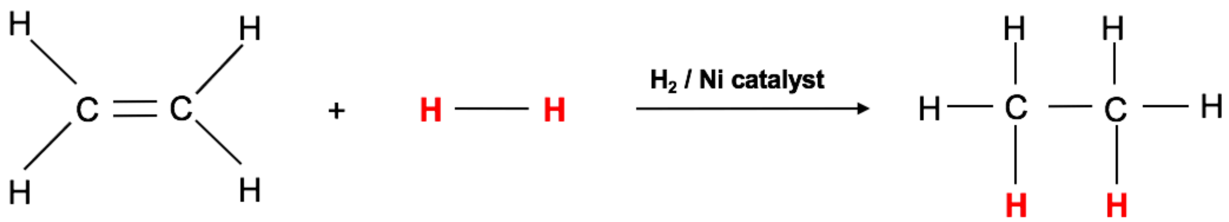


The mechanism:

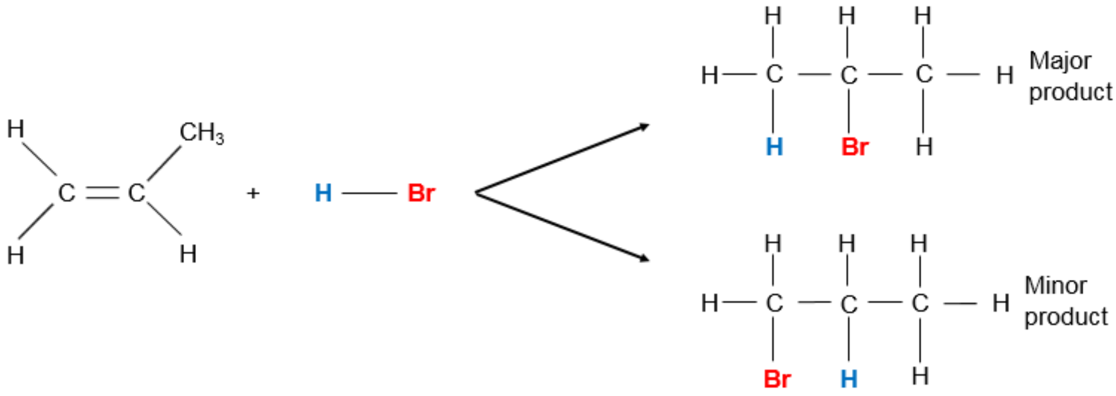


- A pair of electrons from the C=C forms a bond with the H^+ from the acid.
- A lone pair of electrons from water form a bond with the carbocation.
- An O – H bond breaks moving the pair of electrons back to the oxygen.
- The alcohol is formed.
- The acid is a catalyst as it is used up in the first step / regenerated in the final step.

5) Hydrogenation – H_2: ***Forming alkanes*** **– H_2 / Ni Catalyst / Heat**

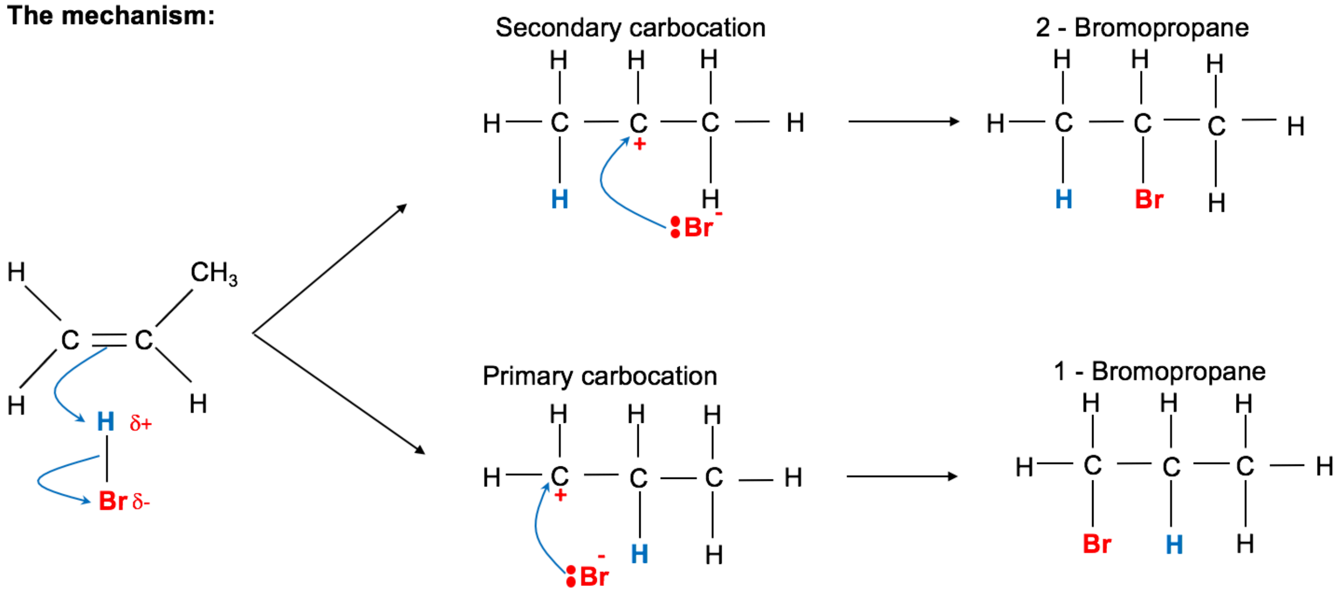


Addition to unsymmetrical alkenes: Markovnikov addition

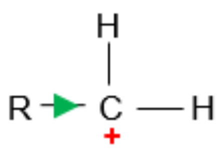
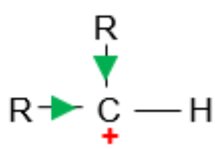
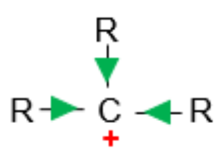


- In this reaction the hydrogen and the halogen could add either way round across the C=C.
- This will give you a mixture of products of both halogenoalkanes.
- At first glance it would appear that both would be equally as likely.

The mechanism:



2-bromopropane is the major product as it is formed from the **2° carbocation** which is more stable than the **1° carbocation.**

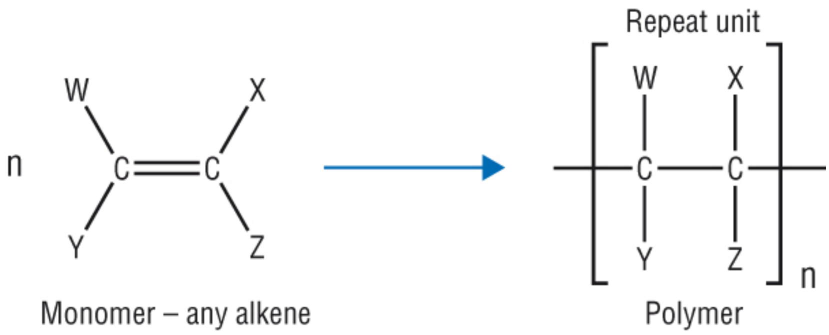
		
1° as it has 1 alkyl group attached	2° as it has 2 alkyl group attached	3° as it has 3 alkyl group attached
1° Primary carbocation	**2° Secondary carbocation**	**3° Tertiary carbocation**
1 alkyl group	**2 alkyl groups**	**3 alkyl groups**
Alkyl groups are slightly electron releasing		

- As the number of alkyl groups increase there is a decrease in the positive charge.
- This increases the stability of the carbocation

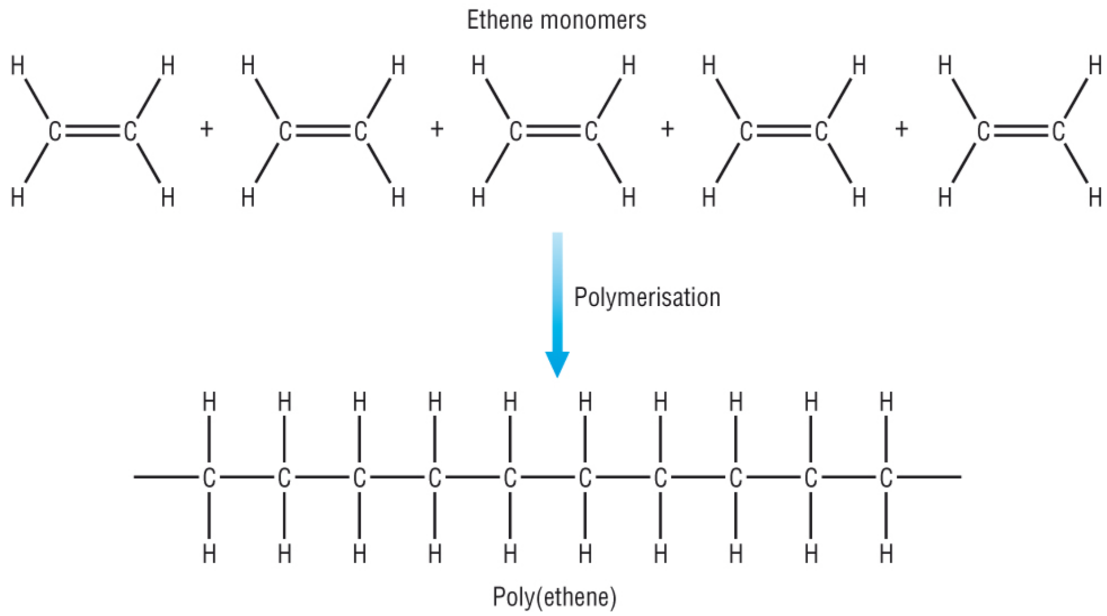
Addition polymerisation:

Polymers

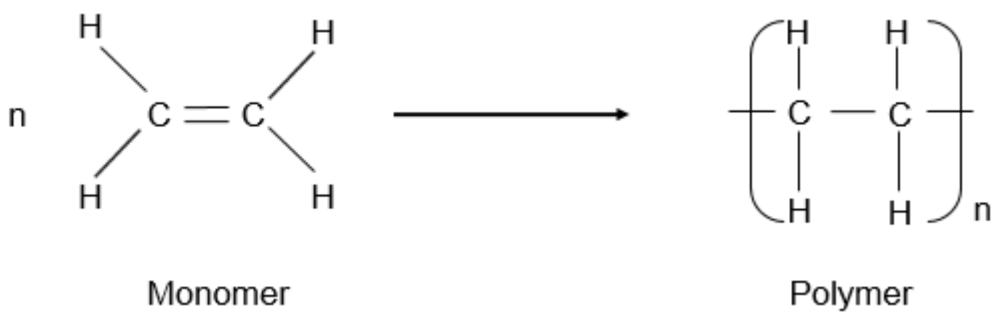
- Polymerisation is when an alkene undergoes an addition reaction to itself.
- The short starting alkenes are referred to as **monomers**
- A long molecule, **polymer** is formed with high Mr's.
- The type of reaction is **addition polymerisation**.
- Different polymers arise from different alkenes.
- A common equation for addition polymerisation is:



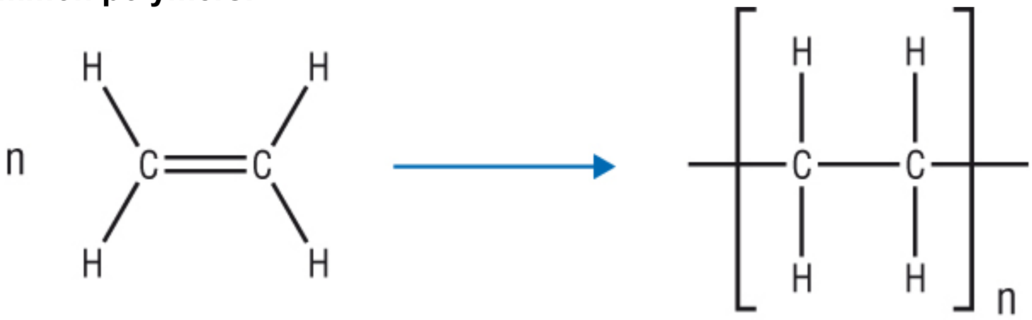
Poly(ethane) is the simplest:



Overall:



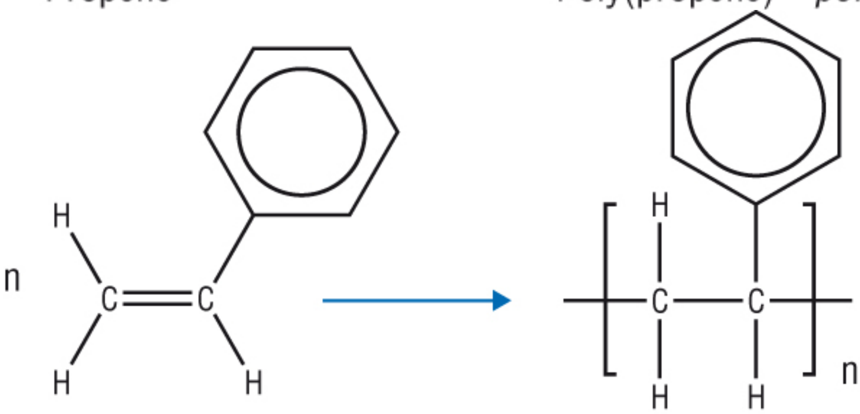
Some common polymers:



Ethene → Poly(ethene) – *polythene*

Chloroethene → Poly(chloroethene) – *PVC*

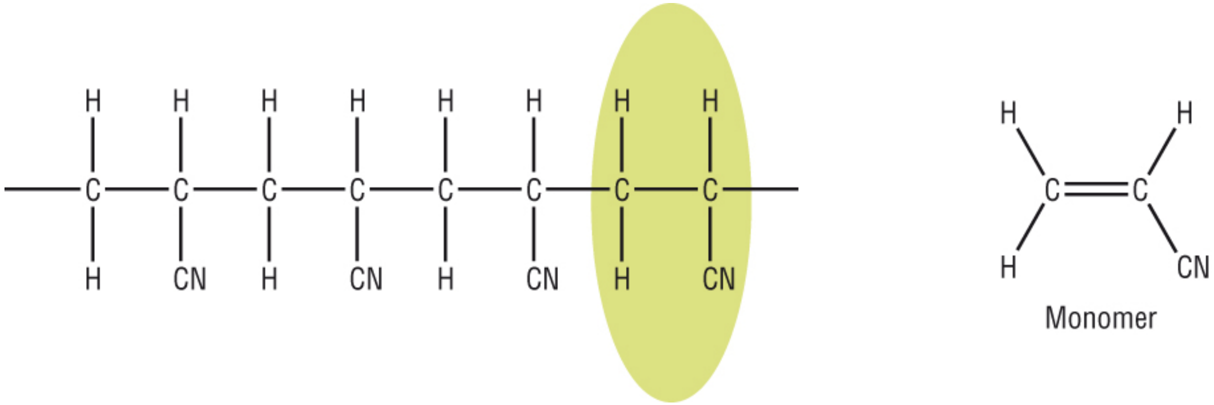
Propene → Poly(propene) – *polypropylene*



Phenylethene → Poly(phenylethene) – *polystyrene*

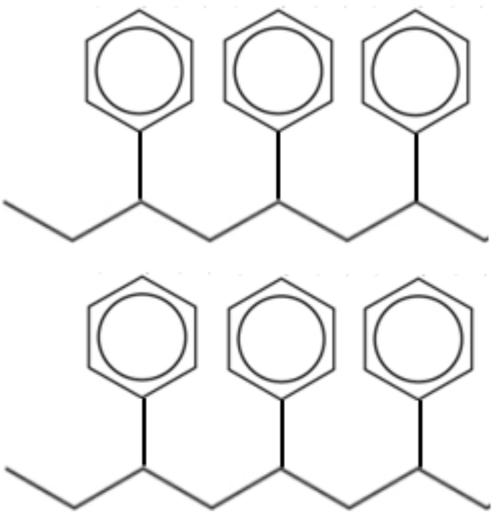
Identifying the monomer:

- The monomer is always identified by looking for the **repeat unit**.
- Once the repeat unit is found add a double bond between the carbons of the repeat unit.
- Then remove the 'branch' bonds linking it to the rest of the polymer:

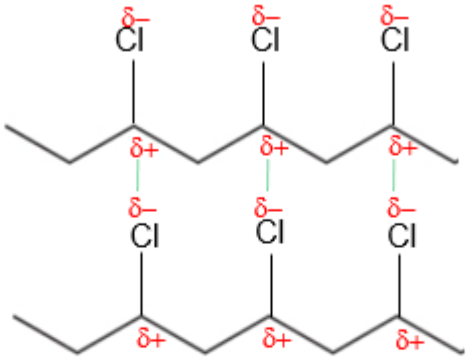


Properties of Polymers

a) Effect of branching / packing

	• Polymers with no branching can pack closely together. • This makes the Van der Waals forces of attraction strong and hold the polymer molecules in place. • A strong rigid material is formed – Poly(ethane)
	• Polymers with large branches cannot pack closely together. • This makes the Van der Waals forces of attraction weaker and the polymer molecules can move past each other slightly. • A flexible material is formed – Poly(phenylethene) / Poly(styrene)

b) Effect of electronegative side groups

	• As chlorine is more electronegative than carbon, a permanent dipole is formed. • The δ- chlorine is attracted to the δ+ carbon in the next polymer molecule. • The material is therefore hard but brittle. • PVC – window frames.

c) Effect of plasticisers

- Plasticisers are chemicals you add to polymers.
- They get between the polymer molecules pushing them further apart.
- This weakens the intermolecular forces of attraction.
- The material is more flexible as they can slide past each other more easily.
- Electrical cable insulation.