

Topic 2.9

ALKENES

Structure and bonding in alkenes

E-Z stereoisomerism

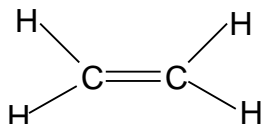
Electrophilic addition reactions of alkenes

Other addition reactions of alkenes

ALKENES

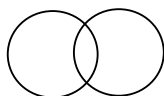
1. Structure and bonding in alkenes

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° .



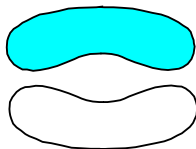
2. E-Z stereoisomerism

In double bonds, the first bond involves an overlap of atomic orbitals directly in between the nuclei of the two atoms:



This is known as a σ -bond. All single covalent bonds are σ -bonds.

The second bond, however, cannot bond in the same place. Instead two p-orbitals overlap above and below the internuclear axis:



This is known as a π -bond. All double covalent bonds consist of one σ -bond and one π -bond.

Since these orbitals overlap in two places, it is not possible to rotate a π -bond about its axis without breaking the bonds. There is thus restricted rotation about the double bond. If both carbon atoms on either side of the bond are attached to different groups, then two different structures arise which cannot be interconverted. This is known as E-Z isomerism

Stereoisomers are molecules with the same molecular formula and the same arrangement of covalent bonds but with different spatial orientations of the groups.

E-Z stereoisomers (also called geometrical isomers) are stereoisomers with different spatial orientations around the carbon-carbon double bond.

It is caused by the restricted rotation about a carbon-carbon double bond.

It arises when the carbon atoms on both sides of the bond are attached two different groups.

Eg but-2-ene has two geometrical isomers:

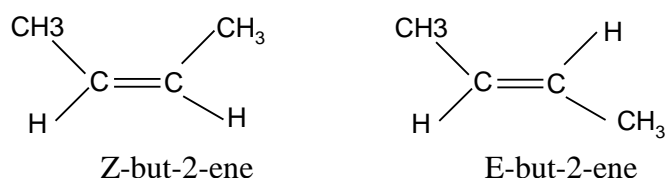


These two isomers cannot be interconverted without breaking the π -bond.

In cases where both C atoms are attached to one hydrogen atom, it is possible to distinguish the isomers by a simple prefix.

If both hydrogen atoms are on the same side of the molecule, the prefix Z is used.

If the hydrogen atoms are on different sides of the molecule, the prefix E is used.

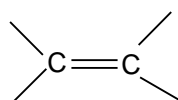


It is only possible to name geometrical isomers using Z and E prefixes if both carbon atoms are attached to a hydrogen atom.

Note that molecules which show geometrical isomerism always have two specific structural features:

- there is a carbon-carbon double bond
- both the carbon atoms are attached to two different groups.

Geometrical isomers should always be drawn using **crab notation**. Crab notation shows the C=C bond as a planar centre with the 4 groups shown as follows:



Using crab notation, it is easy to predict whether geometrical isomerism will exist in molecules.

Ethene	$\begin{array}{c} \text{H} \quad \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \quad \text{H} \end{array}$	No geometrical isomerism
Propene	$\begin{array}{c} \text{H} \quad \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \quad \text{H} \end{array}$	No geometrical isomerism
But-1-ene	$\begin{array}{c} \text{H} \quad \quad \text{C}_2\text{H}_5 \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \quad \text{H} \end{array}$	No geometrical isomerism
But-2-ene	$\begin{array}{c} \text{CH}_3 \quad \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \quad \text{CH}_3 \end{array}$	Geometrical isomerism
2-methylpropene	$\begin{array}{c} \text{CH}_3 \quad \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{CH}_3 \quad \quad \text{H} \end{array}$	No geometrical isomerism

Pent-1-ene	$\begin{array}{c} \text{H} \quad \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \quad \text{CH}_2\text{CH}_2\text{CH}_3 \end{array}$	No geometrical isomerism
Pent-2-ene	$\begin{array}{c} \text{H} \quad \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{C}_2\text{H}_5 \quad \quad \text{CH}_3 \end{array}$	Geometrical isomerism
2-methylbut-1-ene	$\begin{array}{c} \text{CH}_3 \quad \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{C}_2\text{H}_5 \quad \quad \text{H} \end{array}$	No geometrical isomerism
2-methylbut-2-ene	$\begin{array}{c} \text{CH}_3 \quad \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{CH}_3 \quad \quad \text{CH}_3 \end{array}$	No geometrical isomerism
3-methylbut-1-ene	$\begin{array}{c} \text{H} \quad \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \quad \text{CH}(\text{CH}_3)_2 \end{array}$	No geometrical isomerism

3. Chemical properties of alkenes

The presence of the C=C bond gives alkenes a number of chemical properties that are not seen in alkanes.

- i) Since the alkene contains π -bonds, it is possible to break the π -bond and form σ -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. Molecules which contain π -bonds and which can hence undergo addition are said to be **unsaturated**. Molecules which do not contain π -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 π -bonds are broken, rather than stronger σ -bonds.
- ii) The π -bond in an alkene is an area of **high electron density**. It can thus attract **electrophiles** and undergo heterolytic fission. **Heterolytic fission is the breaking of a covalent bond which results in both electrons going to the same atom**. This is in contrast to alkanes which can only react with free radicals and undergo homolytic fission. **An electrophile is a species which can accept a pair of electrons from a species with a high electron density**.

The fact that alkenes can react by heterolytic mechanisms, however, does not mean that the π -bond will not undergo homolytic fission as well. On the contrary - since the bond is non-polar it is very likely to undergo homolytic fission.

Alkenes can thus react in two ways:

- by free radical addition
- by electrophilic addition

The ability of alkenes to undergo addition, and their ability to react with electrophiles as well as free radicals, means that they are much more reactive than alkanes.

4. Electrophilic addition reactions of alkenes

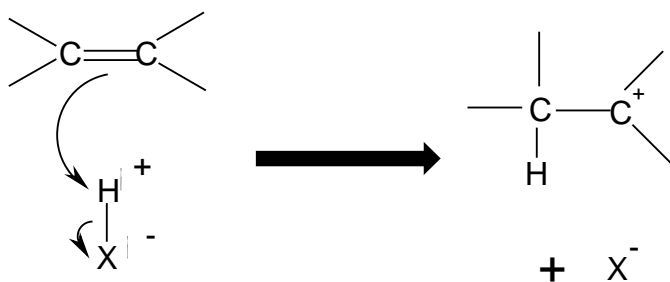
In the presence of electrophiles, the C=C π -bond tends to undergo electrophilic addition.

Possible electrophiles are hydrogen halides (H-Cl, H-Br and H-I) and halogens (Br-Br, Cl-Cl and I-I). Alkenes also undergo an electrophilic addition reaction with H₂SO₄.

i) with hydrogen halides

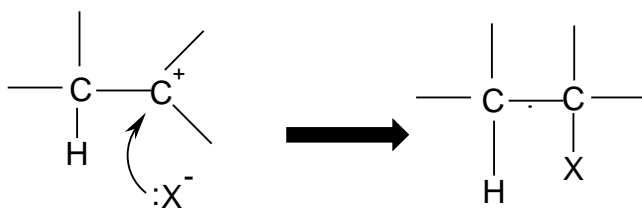


The H in the H-X bond has a positive dipole and is attacked by the pair of electrons on the C=C bond, which undergoes heterolytic fission:



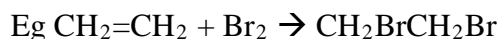
Note that **the curly arrow indicates the movement of a pair of electrons.**

The halide ion then attacks the carbocation to form a haloalkane:

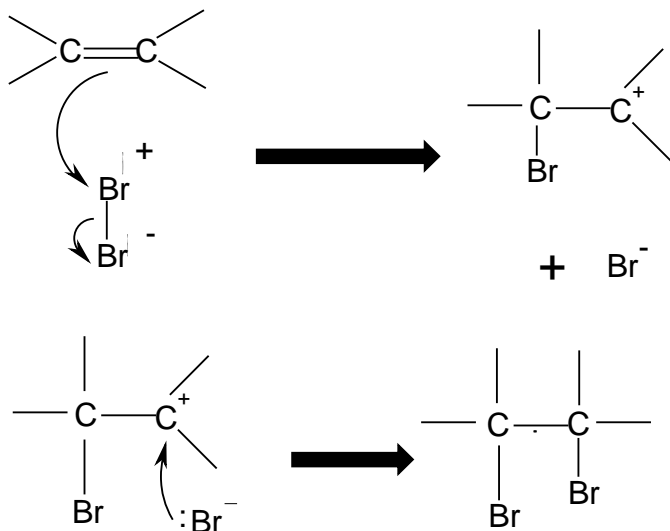


This reaction is fairly quick and takes place readily at room temperature.

ii) with halogens



The Br-Br molecule is non-polar but in the presence of alkenes the electrons move to one side of the molecule and it acquires a temporary dipole (in other words a dipole is induced by the alkene). The δ^+ ve Br is then attacked by the alkene:



A dibromoalkane is formed. The Br₂ should be dissolved in water or an organic solvent, and is decolorised during the reaction. (orange → colourless).

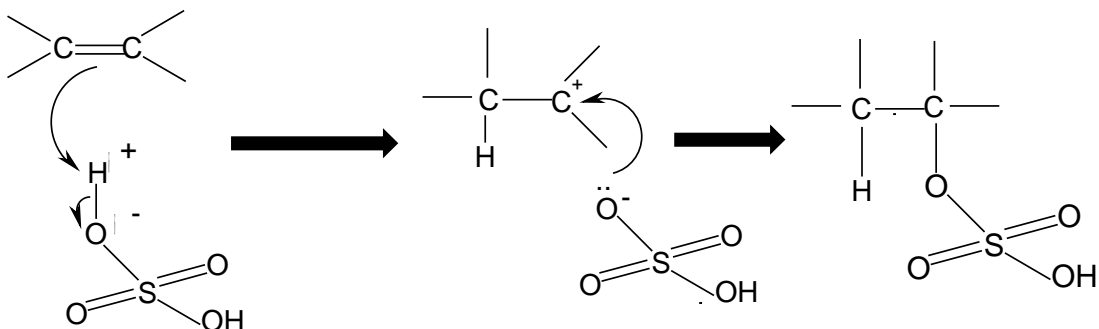
The reaction is fairly quick and takes place readily at room temperature.

If bromine solution is added to an alkene and the mixture shaken, it will thus decolorise and this is a good test for an alkene.

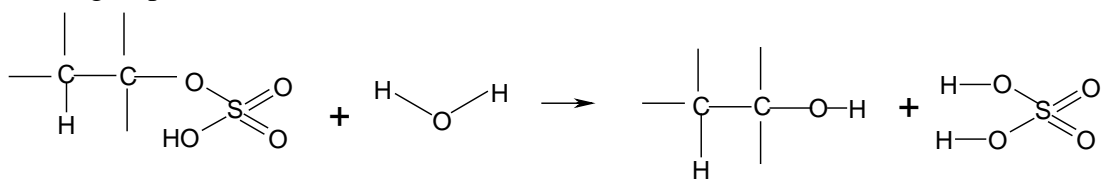
iii) with H₂SO₄



Alkenes will undergo an electrophilic addition reaction with cold concentrated sulphuric acid:

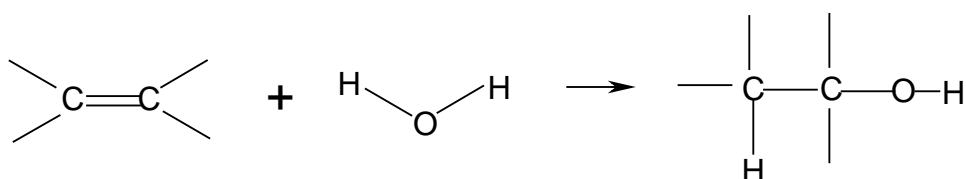


If the mixture is then warmed and water added, the H_2SO_4 group will be replaced by an OH group and an alcohol will be formed:



This is known as a **hydrolysis** reaction. Hydrolysis means using water to break covalent bonds.

The overall reaction is thus:



This is a two step reaction:

Step 1: cold concentrated H_2SO_4

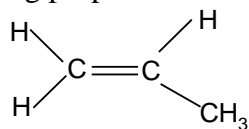
Step 2: warm and add H_2O

It is a useful way of converting alkenes into alcohols in the laboratory.

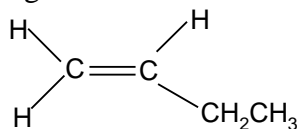
5. Unsymmetrical alkenes

Unsymmetrical alkenes are those in which the two carbon atoms in the double bond are not attached to the same groups.

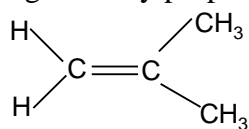
Eg propene



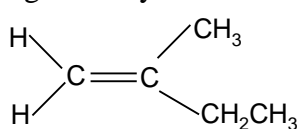
Eg but-1-ene



Eg 2-methylpropene

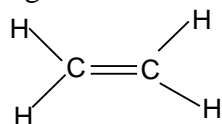


Eg 2-methylbut-1-ene

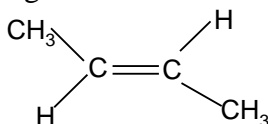


Alkenes in which both carbon atoms are attached to the same groups are known as symmetrical alkenes.

Eg ethene



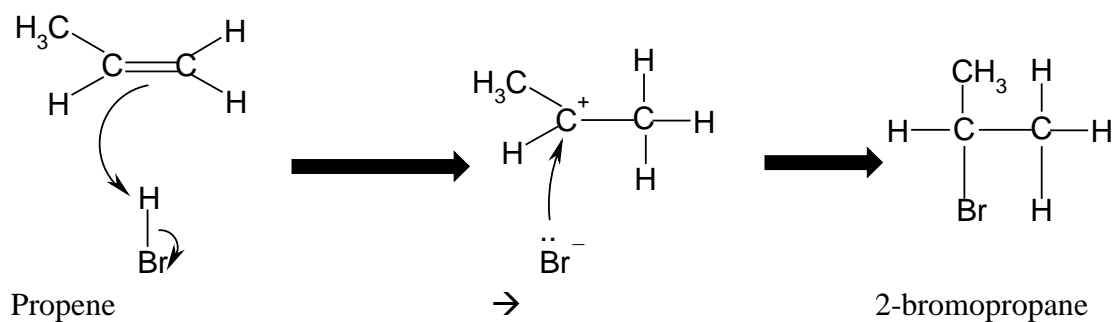
Eg but-2-ene



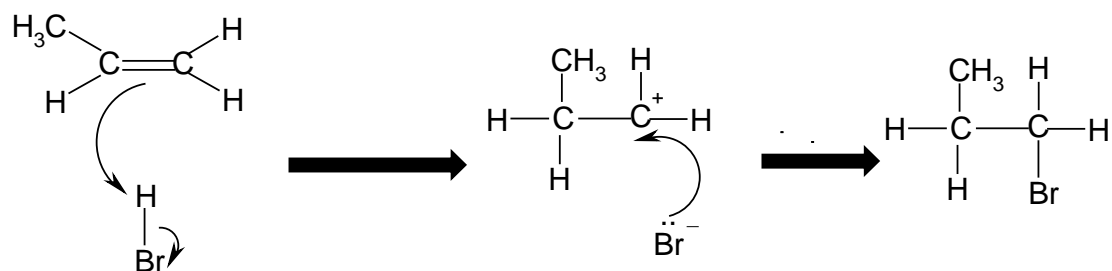
If unsymmetrical alkenes react with unsymmetrical electrophiles such as H-X or H₂SO₄, there are two possible products:

Eg propene with hydrogen bromide

Route 1:



Route 2:



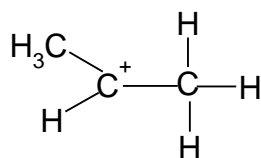
Propene

→

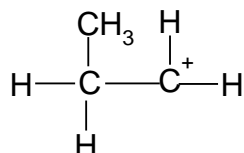
1-bromopropane

The two products are not formed in equal quantities. The likelihood of one product being formed over the other depends on the stability of the **carbocation intermediate**.

In route 1, the intermediate is a **secondary carbocation**, as the carbon holding the positive charge is attached to **two** other carbon atoms:



In route 2, the intermediate is a **primary carbocation**, as the carbon holding the positive charge is attached to **one** other carbon atom:



Secondary carbocations are more stable than primary carbocations. Tertiary carbocations are even more stable than secondary cations. Therefore the product of route 1 (2-bromopropane) is a more likely product than the product of route 2 (1-bromopropane).

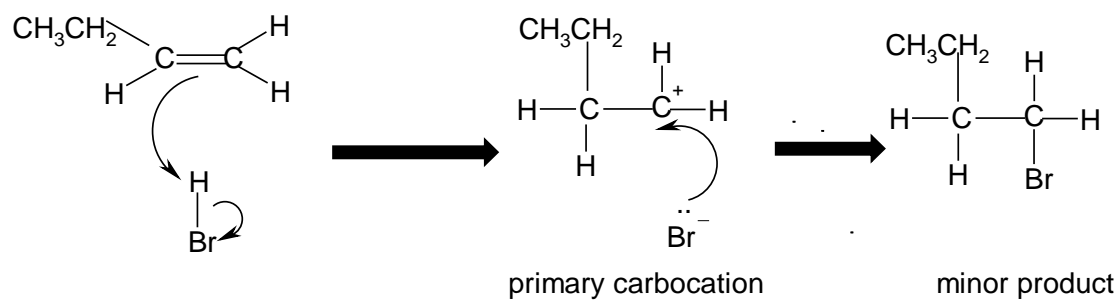
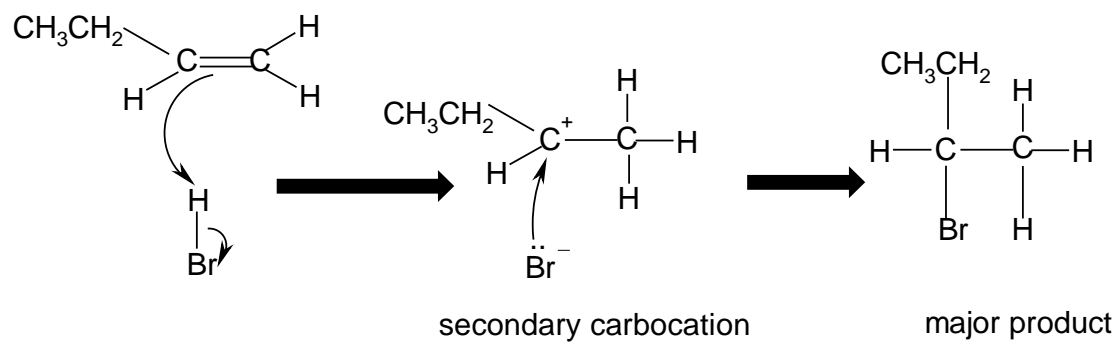
Thus 2-bromopropane will be the major product and 1-bromopropane will be the minor product.

In general, the more stable carbocation will be the one which is more highly substituted. The more electronegative part of the electrophile will thus always attach itself to the more highly substituted carbon atom.

This is known as Markownikoff's rule: "The more electronegative part of the electrophile will usually attach itself to the more highly substituted carbon atom".

The major product of the addition reaction is known as the Markownikoff product. The minor product of the addition reaction is known as the anti-Markownikoff product.

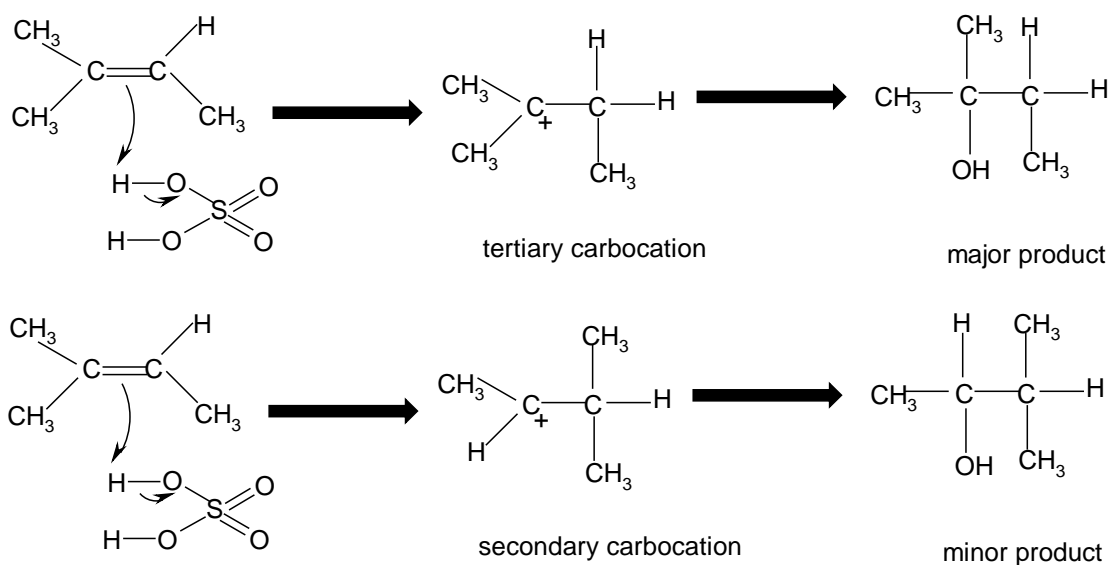
Eg but-1-ene + HBr



The major product is 2-bromobutane.

The minor product is 1-bromobutane.

Eg 2-methylbut-2-ene + H₂SO₄, then warm and dilute



The major product is 2-methylbutan-2-ol

The minor product is 3-methylbutan-2-ol

Symmetrical alkenes only give one product when electrophiles are added.

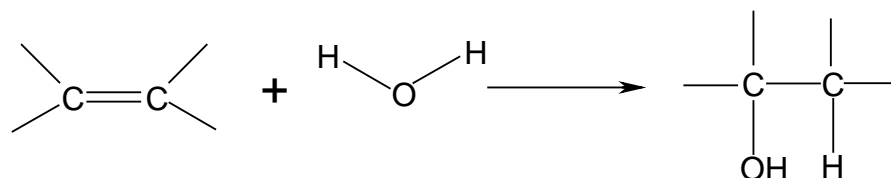
Unsymmetrical alkenes only give one product if the electrophile is symmetrical (Eg propene Br₂).

Thus two products are only obtained when both the alkene and the electrophile are unsymmetrical. In such cases the identity of the major and minor products can be predicted by Markownikoff's rule.

6. Other addition reactions of alkenes

a) addition of steam (hydration)

When alkenes are treated with steam at 300 °C, a pressure of 60 atmospheres and a phosphoric acid (H₃PO₄) catalyst, the H₂O is added across the double bond and an alcohol is formed in a reaction known as **hydration**:

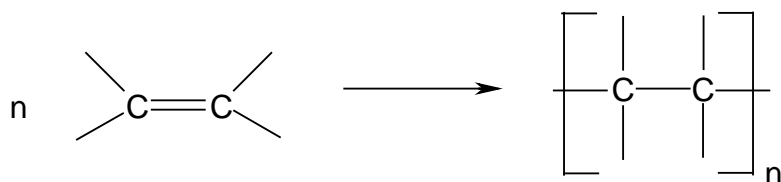


Eg $\text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH}$

This is a common industrial method for the production of pure ethanol.

b) addition polymerisation

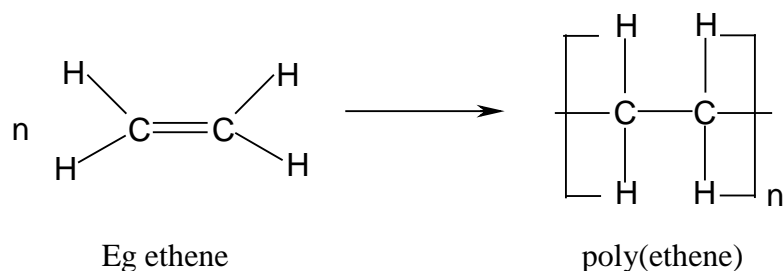
Alkenes can be made to join together in the presence of high pressure and a suitable catalyst. This is known as **addition polymerisation**.



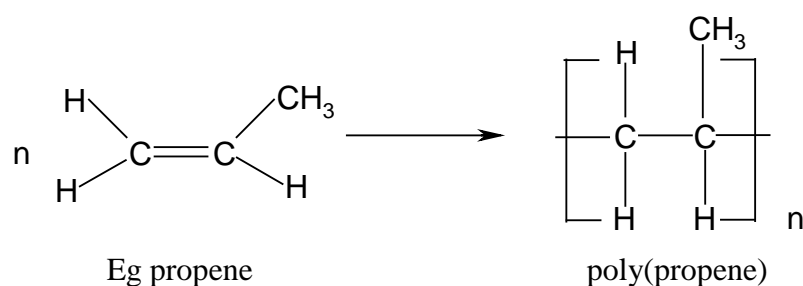
The product of this addition process is a very long hydrocarbon chain. This is known as a polymer. Since it is a product of an addition reaction (unlike some other polymers) it is known as an **addition polymer**. Since it is made from an alkene it is known as a polyalkene.

Polyalkenes are saturated, like alkanes. They are therefore unreactive.

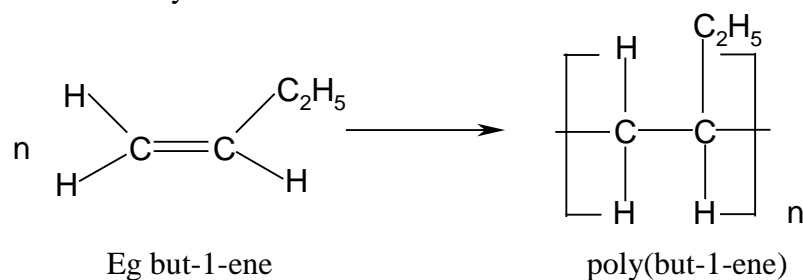
Addition polymers can be made from any alkene:

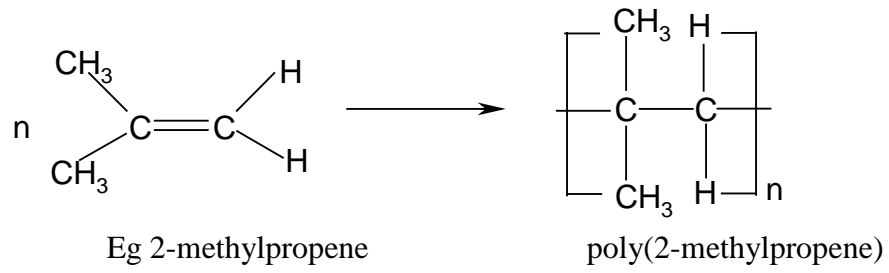
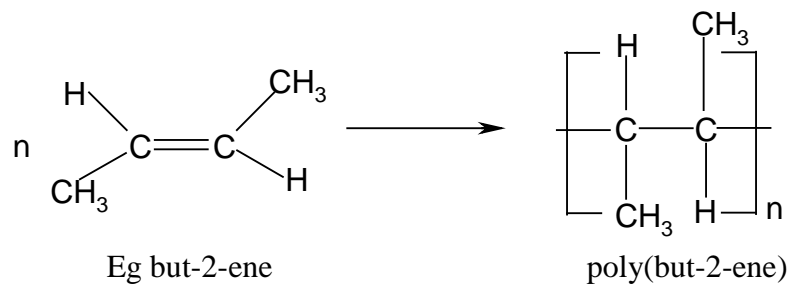


Polyethene is most widely used in plastic shopping bags.



Polypropene is used in birros, straws and plastic food containers. It can be recycled commercially.





7. Summary of addition reactions of alkenes

a) Alkene \rightarrow polyalkene

Conditions: high p.

Equation:



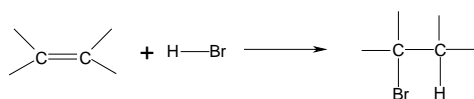
Type of reaction: addition polymerisation

b) Alkene \rightarrow halogenoalkane

Reagent: HX(g)

Conditions: room T

Equation:



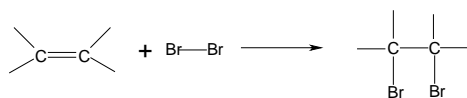
Mechanism: electrophilic addition

c) Alkene \rightarrow dihalogenoalkane

Reagent: X₂ in water or in an organic solvent

Conditions: room T

Equation:



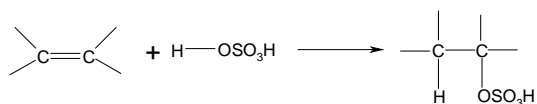
Mechanism: electrophilic addition

d) Alkene \rightarrow alkylhydrogensulphate

Reagent: concentrated sulphuric acid

Conditions: cold

Equation:



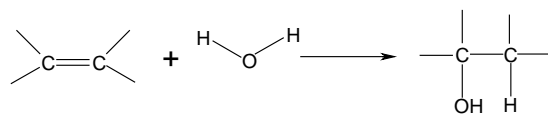
Mechanism: electrophilic addition

f) Alkene \rightarrow alcohol

Reagent: steam

Conditions: 300 °C, 60 atm, H₃PO₄ catalyst

Equation:



Type of reaction: hydration