

ALKENES

- Structure**
- form a homologous series of **general formula C_nH_{2n}** - *non cyclic alkenes only*
 - contain a **carbon-carbon double bond** somewhere in their structure
 - **unsaturated hydrocarbons** - *they can still have hydrogen atoms added to their formula*

- Naming**
- select the longest chain of C atoms **containing the double bond**; ending is **ENE**
 - number the chain starting from the end nearer the double bond; use a number to indicate the **FIRST** carbon in the double bond.
 - prefix with substituents. Side chain positions are based on the number allocated to the first carbon in the double bond.
 - if geometrical isomerism exists, prefix with *cis* or *trans*.
- e.g. $CH_3 - CH = CH - CH_2 - CH(CH_3) - CH_3$ is called 5-methylhex-2-ene

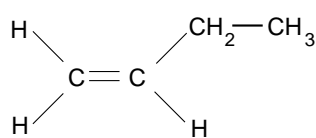
ISOMERISM Two types of isomerism are found in alkenes.

Structural due to

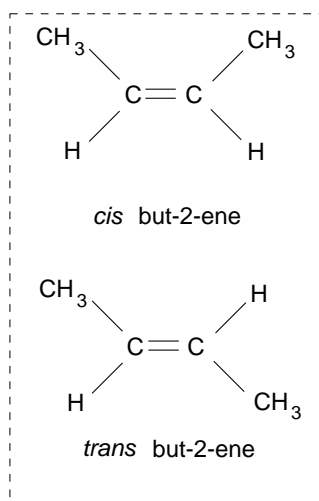
- different positions for the double bond *but-1-ene and but-2-ene*
- branching. *but-1-ene and 2-methylpropene*

Geometrical

- due to **restricted rotation of the carbon-carbon double bond**
- **single bonds can rotate** so the groups around them are not frozen in any position
- **double bonds can't rotate freely**, thus "freezing" groups on either side of the bond
- not all alkenes exhibit this type of isomerism; you need to examine each structure.

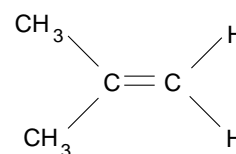


but-1-ene



cis but-2-ene

trans but-2-ene



2-methylpropene

STRUCTURAL ISOMERS

but-1-ene, but-2-ene and 2-methylpropene

GEOMETRICAL ISOMERS

cis and *trans* but-2-ene

Q.1 Draw the structures of all the structural isomers of alkenes of formula C_6H_{12} . Name them and indicate those which exhibit geometrical isomerism.

PHYSICAL PROPERTIES

Boiling point

- increases as molecular mass and size increases - increased van der Waals forces
- for isomeric alkenes the greater the degree of branching, the lower the boiling point
- the lower members of the series are gases at rtp - cyclohexene is a liquid.

Solubility

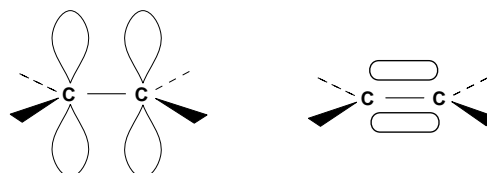
- **non polar** so they are insoluble in water but soluble in organic solvents.

CHEMICAL PROPERTIES

Theory

- spacial arrangement around the C=C is **planar**
- the bond angles are **120°**

Three of the four electrons of carbon are, what is known as, sp^2 hybridised and the remaining electron exists in a 2p orbital at right-angles to the three sp^2 orbitals.



These orbitals overlap to form a new pi (π) orbital; it exists above and below the plane of the carbon-carbon bond.

- the main reaction of alkenes is **ELECTROPHILIC ADDITION**
- electrophiles are attracted to the electron rich carbon-carbon double bond.

ELECTROPHILIC ADDITION REACTIONS OF ALKENES

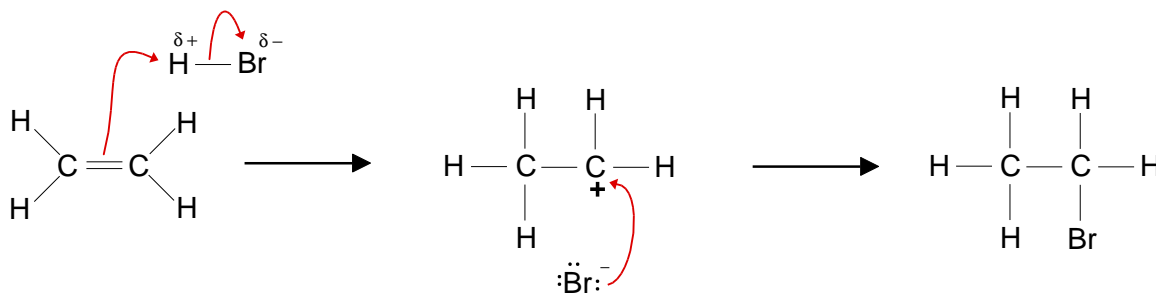
Addition of HBr

Reagent Hydrogen bromide ... it is electrophilic because the H is slightly positive

Condition Room temperature.

Equation $\text{C}_2\text{H}_{4(\text{g})} + \text{HBr}_{(\text{g})} \longrightarrow \text{C}_2\text{H}_5\text{Br}_{(\text{l})}$ *bromoethane*

Mechanism



Step 1 As the HBr nears the alkene, one of the carbon-carbon bonds breaks and the pair of electrons attaches to the slightly positive H end of H-Br. This is an example of **HETEROLYTIC FISSION**. The HBr bond breaks to form a bromide ion. A carbocation (positively charged carbon species) is formed.

Step 2 The bromide ion behaves as a nucleophile and attacks the carbocation.

Overall there has been addition of HBr across the double bond.

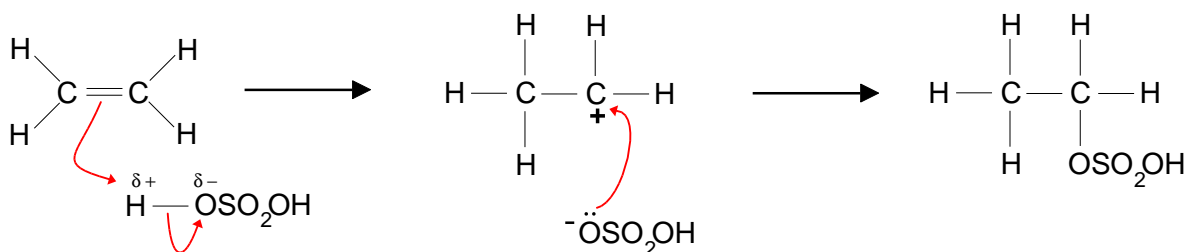
Addition of H₂SO₄

Reagent Concentrated sulphuric acid (85%).

Conditions 0°C

Equation $\text{C}_2\text{H}_{4(\text{g})} + \text{H}_2\text{SO}_{4(\text{conc})} \longrightarrow \text{C}_2\text{H}_5\text{OSO}_2\text{OH}_{(\text{aq})}$ *ethyl hydrogensulphate*

Mechanism



Importance **Hydrolysis** - the product can be converted to ethanol by boiling with water.

$\text{C}_2\text{H}_5\text{OSO}_2\text{OH}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \longrightarrow \text{H}_2\text{SO}_{4(\text{aq})} + \text{C}_2\text{H}_5\text{OH}_{(\text{l})}$ *ethanol*

Industrially **Phosphoric acid** (H₃PO₄) and **steam** are used

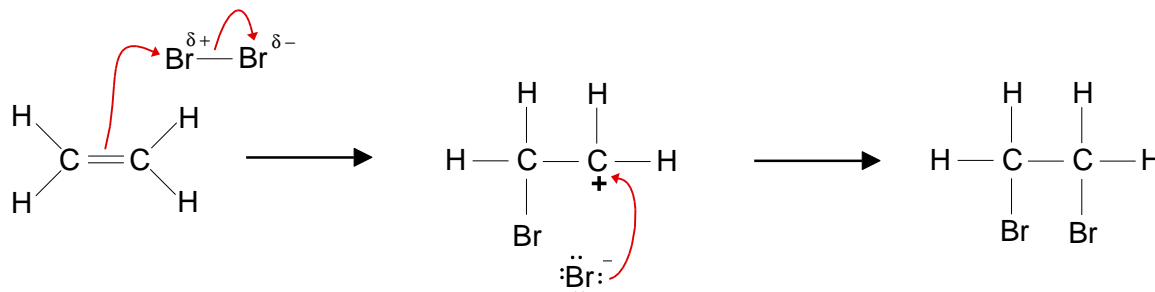
Ethanol can also be made by FERMENTATION

Addition of Br₂

Reagent Bromine. (Neat liquid or dissolved in tetrachloromethane, CCl₄)

Condition Room temperature. No catalyst or UV light required !

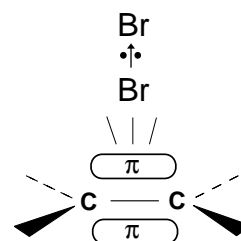
Equation $\text{C}_2\text{H}_{4(g)} + \text{Br}_{2(l)} \longrightarrow \text{CH}_2\text{BrCH}_2\text{Br}_{(l)}$ 1,2 - dibromoethane

Mechanism

It is surprising that bromine should act as an electrophile as it is **non-polar**.

Explanation ...

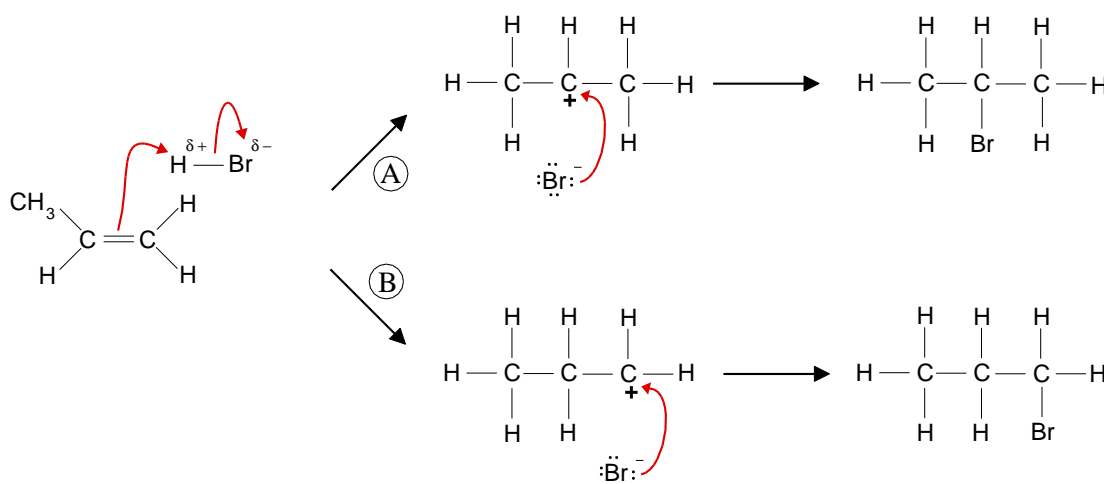
- as a bromine molecule approaches an alkene, electrons in the pi bond of the alkene repel the electron pair in the bromine-bromine bond thus inducing a dipole.

*Importance*

The addition of bromine dissolved in tetrachloromethane (CCl₄) or water (known as **bromine water**) is used as a **test for unsaturation**. If the reddish-brown colour is removed from the bromine solution, the substance possesses a double C=C bond.

Electrophilic addition to propene*Problem*

- addition of HBr to propene gives two isomeric brominated compounds
- HBr is unsymmetrical and can add in two ways
- products are not formed to the same extent
- problem doesn't arise in ethene because it is symmetrical.

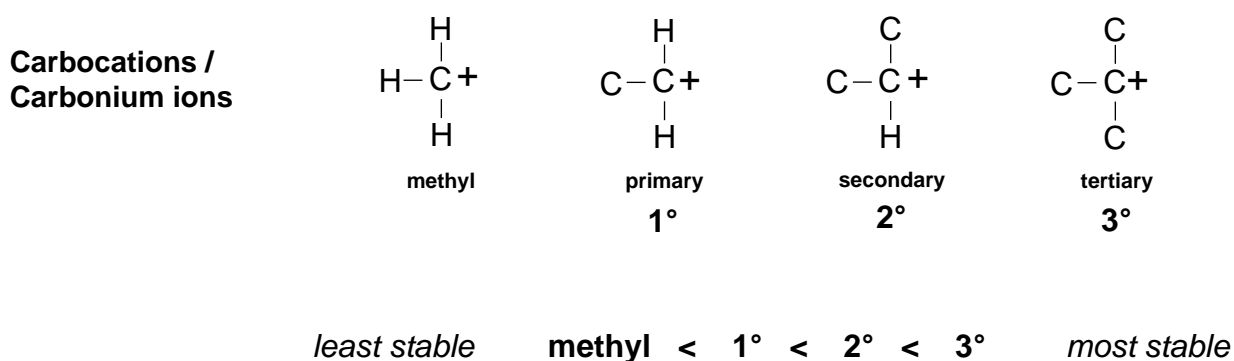
Mechanism

Markownikoff's Rule

Background The Russian scientist, Markownikoff, investigated the products of the addition of hydrogen halides to alkenes. He found that, when two products were formed, one was formed in a larger quantity. His original rule was based only on this reaction. The up-to-date version of Markownikoff's Rule uses carbocation stability as a criterion for predicting the products.

It states that **“In electrophilic addition to alkenes the major product is formed via the more stable carbocation (carbonium ion).”**

In the above reaction, path **A** involves a 2° carbocation, path **B** a 1° carbocation. As the 2° ion is more stable, the major product (i.e. 2-bromopropane) is formed via that route.



Theory Build up of charge in one place leads to instability. However, if it can be spread around or neutralised in some way, the stability is increased. Alkyl groups are electron releasing and can “push” electrons towards the carbocations thus reducing the charge density.

Q.2 Draw the structures of the product(s) formed when HBr reacts with each of the isomers of C₄H₈. If two products are formed, state which is the major product.

Q.3 Outline the mechanism for the reaction between propene and conc. H₂SO₄. Which alcohols are produced by hydrolysing the products ?

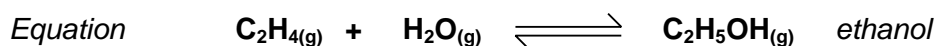
OTHER ADDITION REACTIONS

Direct Hydration

<i>Reagent</i>	steam (330°C)
<i>Conditions</i>	High Pressure (6MPa) Catalyst - phosphoric acid

Bond enthalpies (kJ mol^{-1})

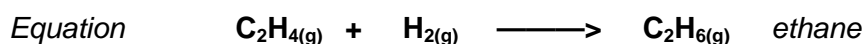
O-H 463 H-Br 366

Product alcohol*Use* ethanol manufacture

Note O-H bonds are more polar than H-Br bonds yet the addition of H_2O requires a catalyst. An explanation is that O-H bonds are stronger so more energy is needed to break them.

Hydrogenation

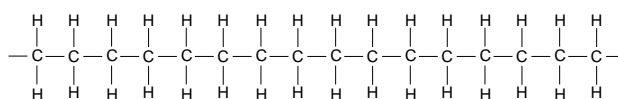
<i>Reagent</i>	hydrogen
<i>Conditions</i>	nickel catalyst - finely divided

Product alkanes*Use* margarine manufacture

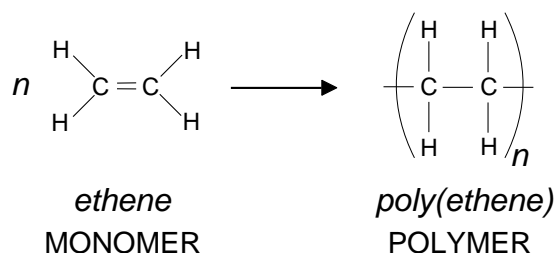
POLYMERISATION

Process

- during polymerisation, an alkene undergoes an **addition reaction with itself**
- all the atoms in the original alkenes are used to form the polymer
- long hydrocarbon chains are formed



- the equation shows the original monomer and the repeating unit in the polymer



Preparation Many are prepared by a free radical process involving high pressure, high temperature and a catalyst. The catalyst is usually a substance (e.g. an organic peroxide) which readily breaks up to form radicals which, in turn, initiate a chain reaction.

Another famous type of catalyst is a Ziegler-Natta catalyst (named after the scientists who developed it). Such catalysts are based on the compound TiCl_4 .

Properties

Physical These can be varied by changing the reaction conditions (pressure, temperature etc).

Chemical Polymers have chemical properties based on the functional groups within their structure.

e.g. poly(ethene) is typical; it is fairly inert as it is basically a very large alkane.
This means it is resistant to chemical attack and non-biodegradable.

Problems Although polymers derived from alkenes are invaluable to modern society, their disposal creates widespread problems.

- they are unreactive to most chemicals and bacteria (**non-biodegradable**)
- if they are just discarded they add to the landfill problem

recycling • high cost of collection and re-processing

burn waste • saves on landfill sites and produces energy
• toxic fumes (HCl) can be removed by 'scrubbing' from burning chlorinated polymers such as poly(chloroethene)

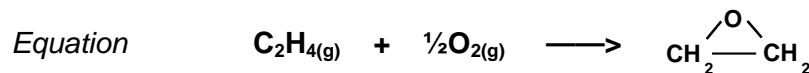
feedstock • use the waste for the production of useful organic compounds
• new technology can convert waste into hydrocarbons
• hydrocarbons can then be turned back into polymers.

Q.4 Complete the details showing the formation and use of different polymers.

<i>Polymer</i>	<i>Formula of monomer</i>	<i>Formula of polymer</i>	<i>Use(s)</i>
poly(ethene)	$n \text{ CH}_2=\text{CH}_2$	\longrightarrow $-(\text{CH}_2 - \text{CH}_2)_n-$	
poly(propene)			
poly(chloroethene)			
poly(phenylethene)			
poly(tetrafluoroethene)			
poly(ethenyl ethanoate)			

EPOXYETHANE (Ethylene oxide)

Preparation *Reagent* Ethene + oxygen + a **silver catalyst** on an alumina support
Conditions 250-300°C and 1-2 MPa pressure



Hazards

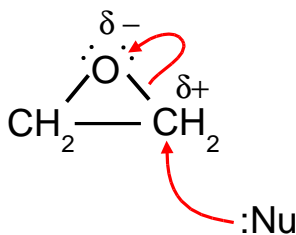
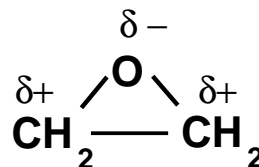
- highly exothermic reaction
- epoxyethane is ... flammable
explosive
very toxic

Properties

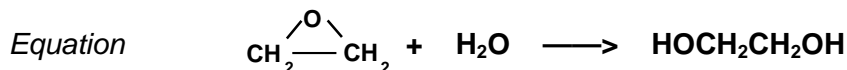
- colourless gas (b.p. 10°C)
- flammable and explosive
- toxic - causes respiratory system irritation and neurological effects

Reactivity

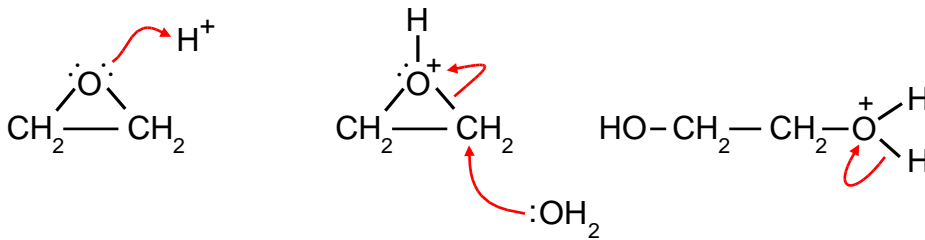
- 3-membered epoxide ring is very strained
- polar C-O-C bond = readily attacked by nucleophiles
- ring breaks open to relieve the strain.



Water *Reagent* water + acid catalyst (e.g. sulphuric acid)
Conditions 60°C , **excess water** (stops polymerisation occurring)
Product ethane-1,2-diol (ethylene glycol)



Mechanism



Uses

- raw material for making Terylene :- poly(ethyleneterephthalate)
- antifreeze . . . due to m.pt. of -12°C and miscibility with water

Alcohols	<i>Reagent</i>	alcohols <i>e.g. methanol</i>
	<i>Conditions</i>	180°C and 1MPa pressure
	<i>Product</i>	poly alkoxyalcohols . . . see equation



Mechanism

- Uses*
- solvents in the paint industry
 - printing inks
 - plasticisers
 - non-ionic detergents

ALKENES (2)

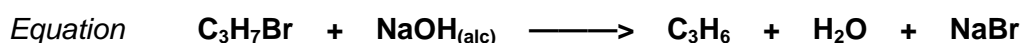
PREPARATION

1. From haloalkanes - Elimination

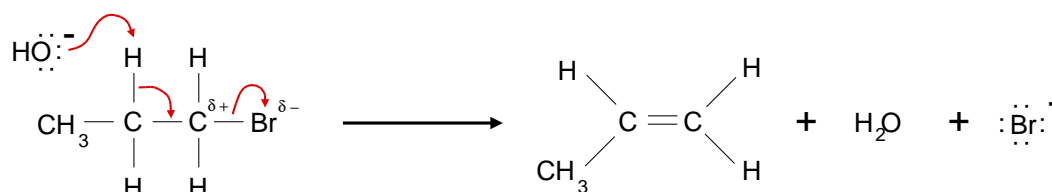
Problem The products of reactions between haloalkanes and OH^- are influenced by the solvent. Both mechanisms take place simultaneously but the choice of solvent favours one route.

Solvent	Product	Action of OH^-	Mechanism
WATER	ALCOHOL	NUCLEOPHILE	SUBSTITUTION
ALCOHOL	ALKENE	BASE	ELIMINATION

Reaction **Reagent** Alcoholic sodium (or potassium) hydroxide
Conditions Reflux in alcoholic solution
Product Alkene
Mechanism Elimination



Mechanism



The hydroxide ion acts as a base and picks up a proton from a carbon atom next to the one bonded to the halogen. The electron pair left moves to form a second bond between the carbon atoms and the halogen is displaced. Overall there is ELIMINATION of HBr.

Complication The OH^- removes a proton from a carbon atom adjacent the C bearing the halogen. In the above example there was only one possible choice. However, if there had been another carbon atom on the other side of the C-Halogen bond, its hydrogen(s) would also be open to attack. If the haloalkane is symmetrical (e.g. 2-bromopropane) it doesn't matter where the attack takes place but if it is unsymmetrical (e.g. 2-bromobutane) there are two different sites of attack and a mixture of isomeric alkene products is obtained.

2. From alcohols - Dehydration

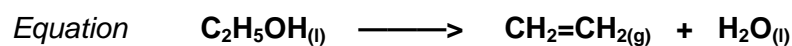
Theory Lone pairs on the oxygen atom make alcohols behave as Lewis Bases (lone pair donors)
They can use a lone pair to

- pick up protons or
- behave as nucleophiles.

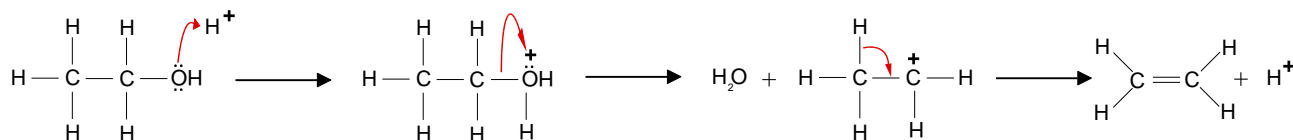
When refluxed with conc. H_2SO_4 or H_3PO_4 , alcohols lose water and are converted to alkenes.

Reaction

<i>Reagent</i>	Conc. sulphuric acid or conc. phosphoric acid (H_3PO_4)
<i>Conditions</i>	Reflux
<i>Product</i>	Alkene
<i>Mechanism</i>	Dehydration (elimination)



Mechanism Occurs in 3 stages



- **protonation of the alcohol** using a lone pair on oxygen (alcohol acts as a Lewis base) .
- **loss of a water molecule** to generate a carbonium ion.
- **loss of a proton (H^+)** to give the alkene.

PREPARATION

- From haloalkanes by elimination.
- From alcohols by elimination. *(see relevant sections for more detail)*