

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** - *can still have atoms added to their formula*
- Naming**
- select the longest chain of C atoms **containing the double bond**; end in **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 cis-trans 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

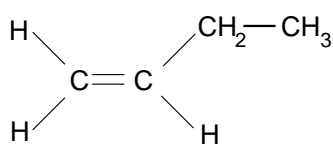
ISOMERISM Two types of isomerism are found in alkenes.

Structural due to

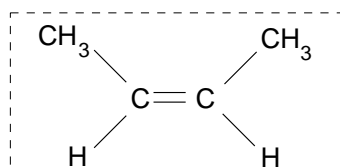
- different positions for the double bond *but-1-ene and but-2-ene*
- branching. *but-1-ene and 2-methylpropene*

E/Z

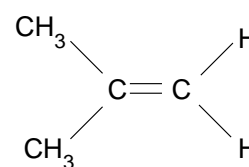
- due to **restricted rotation of the carbon-carbon double bond**
- **single bonds can rotate** so the groups around them are not 'frozen' in position
- **double bonds can't rotate freely**, thus "freezing" groups on either side of C=C
- not all alkenes exhibit this type of isomerism
- eg if there are two H's and two non-hydrogen groups attached to each carbon it is called *cis-trans* isomerism; butene C_4H_8 is a good example



but-1-ene



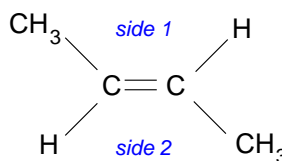
(Z) *cis* but-2-ene



2-methylpropene

Z higher priority groups on the **same side** (NOT END) of the C=C bond.

E higher priority groups on **opposite sides**.



(E) *trans* but-2-ene

Priority of atoms / groups
(higher mass = higher priority)

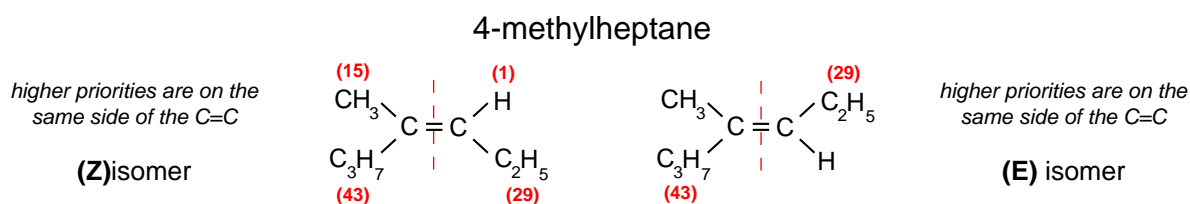
$I > Br > Cl > F > C > H$

$C_3H_7 > C_2H_5 > CH_3 > H$

STRUCTURAL ISOMERS
E/Z or CIS-TRANS ISOMERS

but-1-ene, but-2-ene and 2-methylpropene
cis **(Z)** and trans **(E)** but-2-ene

- CIP RULES**
- they **work out if a geometrical isomer is E or Z**
 - named after the people who developed the system... Cahn-Ingold-Prelog
 - groups/atoms either side of the C=C are prioritised according to their mass
 - **higher mass number = higher priority**



Q.1 Draw the structures of all the structural isomers of alkenes of formula C_6H_{12} . Name them and indicate those which exhibit E/Z (cis-trans) isomerism.

PHYSICAL PROPERTIES

Boiling point

- increases with molecular mass/size - increased induced dipole-dipole attractions
- for isomers 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

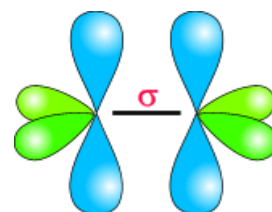
- **non polar** so they are insoluble in water but soluble in organic solvents.

CHEMICAL PROPERTIES

Theory

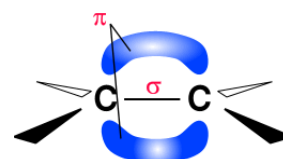
- spacial arrangement around the C=C is **planar**
- the bond angles are **120°**

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



[For more information, see notes on hybridisation]

The 2p 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 electron pair acceptors**
- electrophiles are attracted to the electron rich carbon-carbon double bond.

ELECTROPHILIC ADDITION REACTIONS OF ALKENES

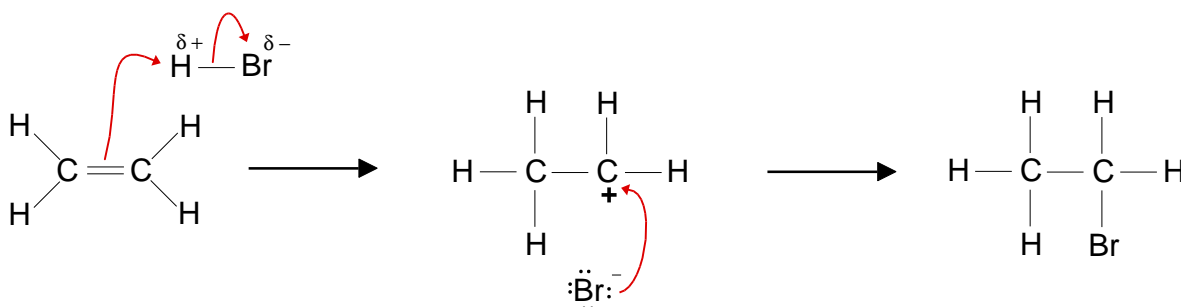
Addition of HBr

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 H_2SO_4

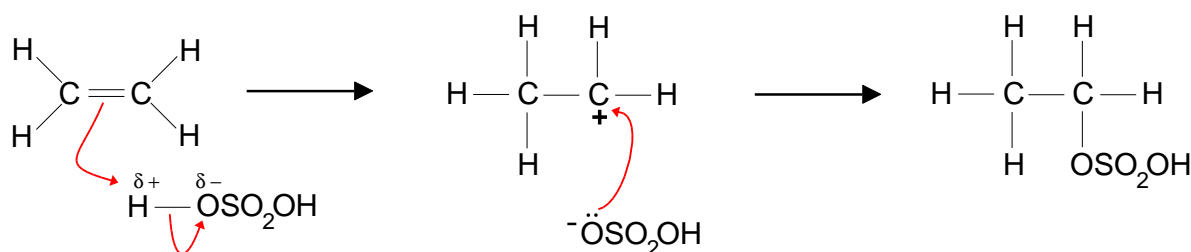
Reagent Concentrated sulphuric acid (85%).

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 is made into ethanol by boiling with water.

$\text{C}_2\text{H}_5\text{OSO}_2\text{OH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{SO}_4(\text{aq}) + \text{C}_2\text{H}_5\text{OH}(\text{g})$ *ethanol*

Industrially

Phosphoric acid (H_3PO_4) and **steam** are used
Ethanol can also be made by **FERMENTATION**

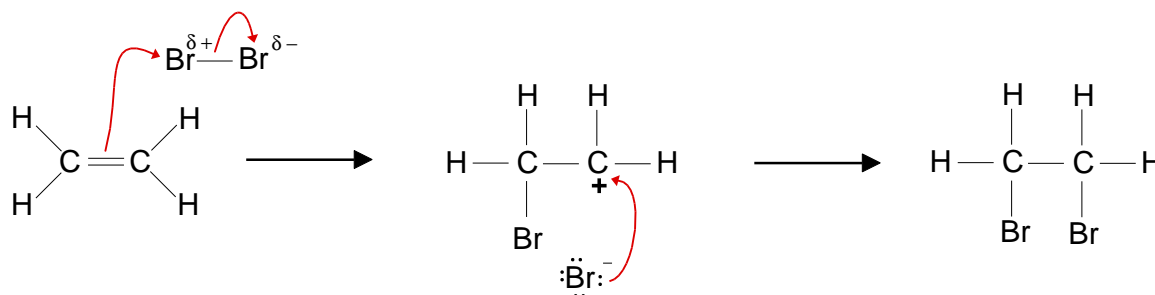
Addition of Br₂

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

Condition Room temperature. No catalyst or UV light required !

Equation $\text{C}_2\text{H}_4(\text{g}) + \text{Br}_2(\text{g}) \longrightarrow \text{CH}_2\text{BrCH}_2\text{Br}(\text{l})$ 1,2 - dibromoethane

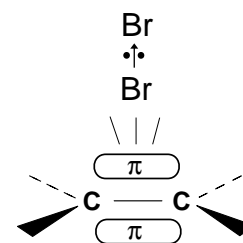
Mechanism



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.



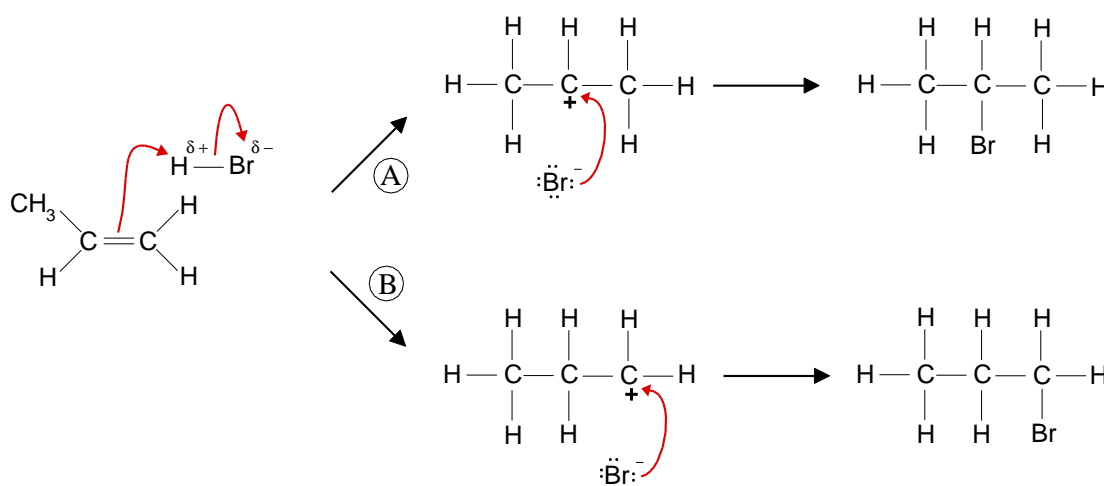
Importance The addition of bromine dissolved in tetrachloromethane (CCl₄) or water (known as **bromine water**) is used as a **test for unsaturation**. If the reddish-brown colour is removed from the bromine solution, the substance possesses a double C=C bond.

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



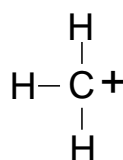
Markownikoff's Rule

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.

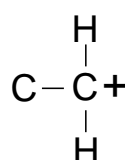
It states that **“In electrophilic addition to alkenes the major product is formed via the more stable carbocation (carbonium ion).”**

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.

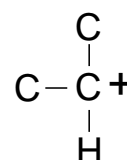
**Carbocations /
Carbonium ions**



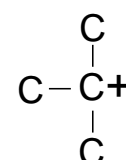
methyl



primary
1°



secondary
2°



tertiary
3°

least stable methyl < 1° < 2° < 3° *most stable*

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
<i>Product</i>	alcohol
<i>Equation</i>	$\text{C}_2\text{H}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{C}_2\text{H}_5\text{OH}(\text{g})$ ethanol
<i>Use</i>	ethanol manufacture

<i>Bond enthalpies (kJ mol⁻¹)</i>	
O-H 463	H-Br 366

Note O-H bonds are more polar than H-Br bonds yet the addition of H₂O requires a catalyst. An explanation is that O-H bonds are stronger so more energy is needed to break them.

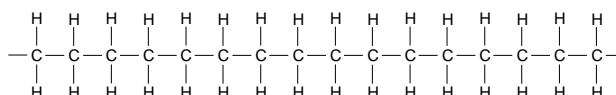
Hydrogenation

<i>Reagent</i>	hydrogen
<i>Conditions</i>	nickel catalyst - <i>finely divided</i>
<i>Product</i>	alkanes
<i>Equation</i>	$\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_6(\text{g})$ ethane
<i>Use</i>	margarine manufacture

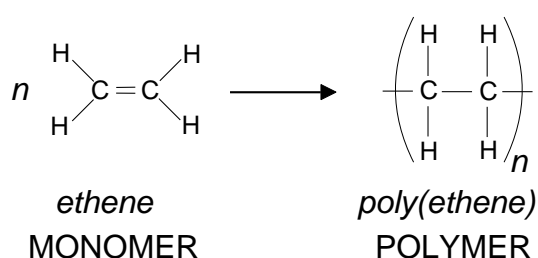
POLYMERISATION

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



POLYMERS

Preparation Many are prepared by a free radical process involving high pressure, high temperature and a catalyst. The catalyst is usually a substance (an organic peroxide) which readily breaks up to form radicals which 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 Can be varied by changing the reaction conditions (pressure, temperature etc).

Chemical Chemical properties are 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
- the different types of polymer have to be separated

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.

Polymer	Formula of monomer	Formula of polymer	Use(s)
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)			

Q.5 Identify the monomer units in the following addition polymers.

