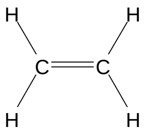
4.1.3 Alkenes

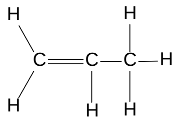
Alkenes are unsaturated hydrocarbons

General formula is **C_nH_{2n}**

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

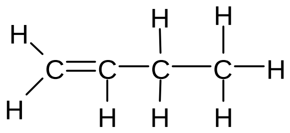


Ethene

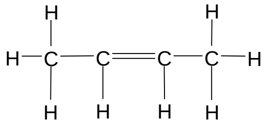


Propene

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

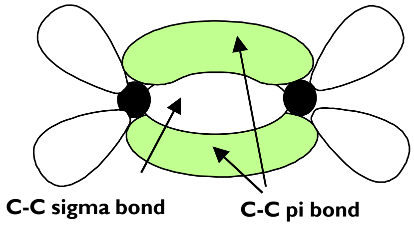


But-1-ene



But-2-ene

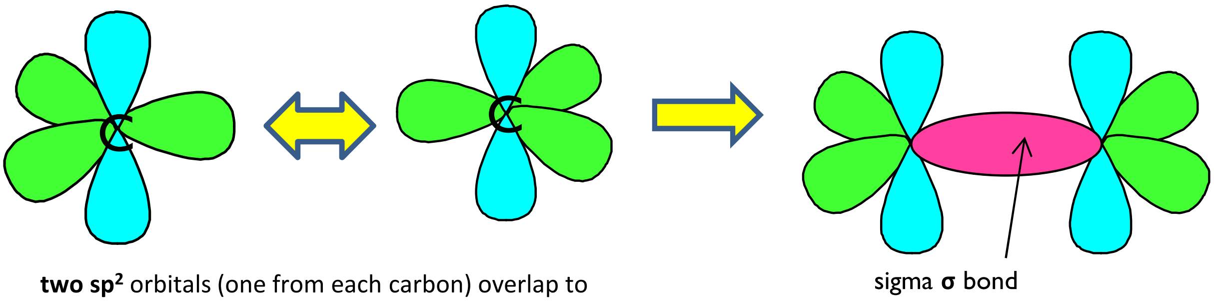
C=C double covalent bond consists of **one sigma (σ) bond *and* one pi (π) bond.**



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

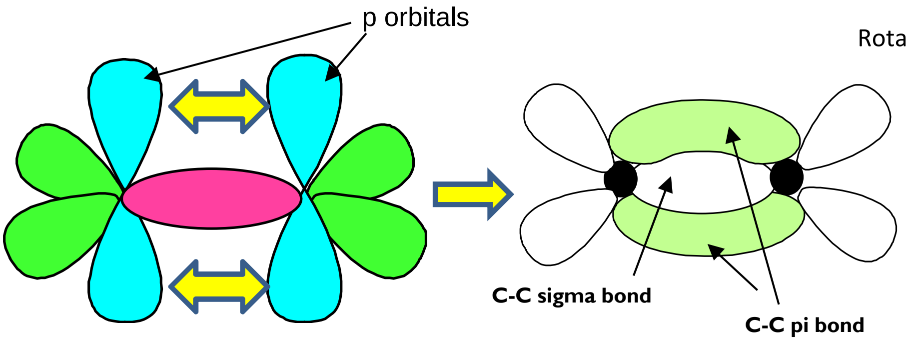
They are therefore vulnerable to attack by species which 'like' electrons: these species are called **electrophiles**.

Formation of σ bond in alkenes



two sp^2 orbitals (one from each carbon) overlap to form a single C-C bond called a sigma **σ** bond

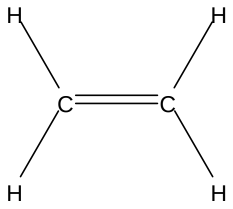
Formation of π bond in alkenes

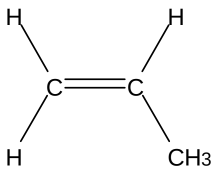


Rotation can occur around a sigma bond

The π **bond** is formed by sideways overlap of two p orbitals on each carbon atom forming a π-bond above and below the plane of molecule.

The π bond is weaker than the σ bond.





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

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**

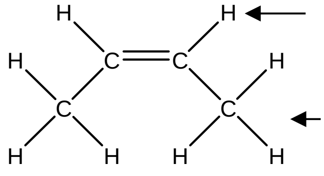
E-Z isomers exist due to restricted rotation about the C=C bond

Single carbon-carbon covalent bonds can easily rotate

E-Z stereoisomers arise when:

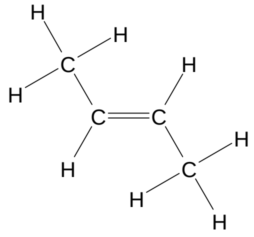
(a) There is **restricted rotation** around the C=C double bond.

(b) There are **two different groups/atoms** attached both ends of the double bond.



two different groups attached either end of the restricted double bond- leads to EZ isomers

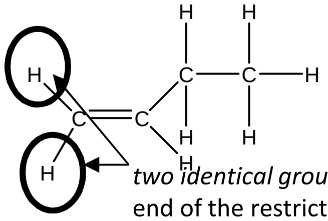
***Z*- but-2-ene**



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

***E* -but-2-ene**

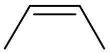
But-1-ene is a structural isomer of But-2-ene but does not show E-Z isomerism.



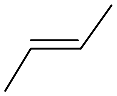
But-1-ene

two identical groups attached to one end of the restricted double bond – no E-Z isomers

Skeletal formulae can also represent E-Z isomerism



Z-but-2-ene



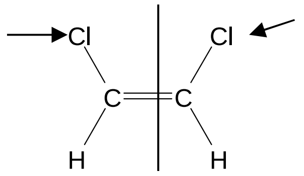
E-but-2-ene

Naming E-Z stereoisomers

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

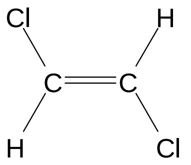
Priority Group: The atom with the bigger atomic number is classed as the priority atom

Priority group side 1



Priority group side 2

Z-1,2-dichloroethene



E-1,2-dichloroethene

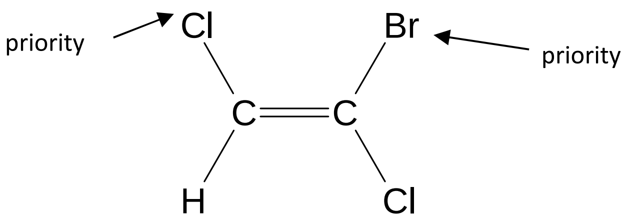
If the priority atom is on the same side of the double bond it is labelled Z from the german zusammen (The Zame Zide!)

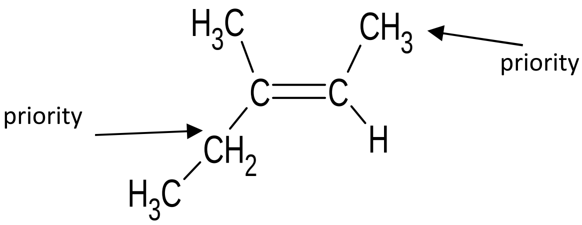
If the priority atom is on the opposite side of the double bond it is labelled E from the german entgegen (The Epposite side!)

Cahn–Ingold–Prelog (CIP) priority rules.

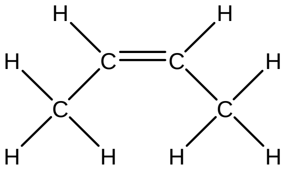
1. Compare the atomic number of the atoms directly attached to each side of the double bond; the atom of higher atomic number is given priority.

2. If the atoms are the same, consider the atoms at distance 2 from the double bond. Make a list of each atom bonded to the one directly attached to the double bond. Arrange list in order of decreasing atomic number. Compare the lists atom by atom; at the earliest difference, the group containing the atom of higher atomic number is given priority





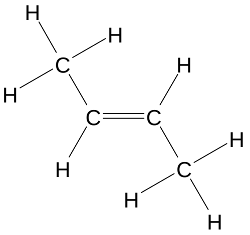
cis-trans isomerism is a special case of *EIZ* isomerism in which two of the substituent groups are the same.



***Z-* but-2-ene**

Can also be called

Cis- but-2-ene



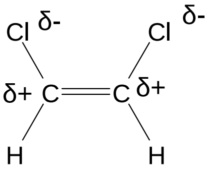
***E-* but-2-ene**

Can also be called

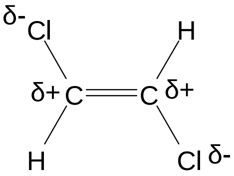
trans- but-2-ene

The effect of EZ stereoisomerism on physical properties

E-Z stereoisomers can have differing melting and boiling points.



Z-1,2-dichloroethene
Boiling point =60^{o}C
This molecule is **polar**. The polar C-Cl bonds are on the same side of the molecule. One side of the molecule is slightly negative.
The intermolecular forces are both London forces and permanent dipole-dipole attractions.



E-1,2-dichloroethene
Boiling point =48^{o}C
This molecule is non- **polar**. The polar C-Cl bonds are on opposite sides of the molecule. The dipoles cancel out.
The intermolecular forces are is only London forces so lower boiling point.

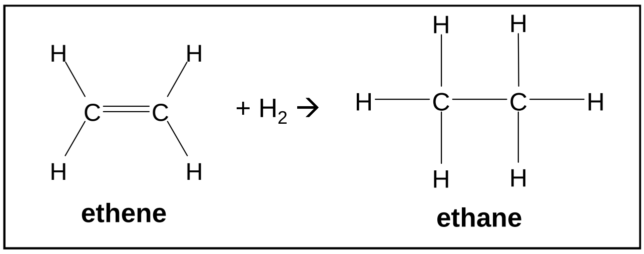
Addition reactions of alkenes

The alkenes are relatively reactive because of the relatively low bond enthalpy of the π-bond.

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

1. Reaction of Alkenes with Hydrogen

Change in functional group: alkene → alkane
Reagent: hydrogen
Conditions: nickel catalyst
Type of reaction: Addition/reduction



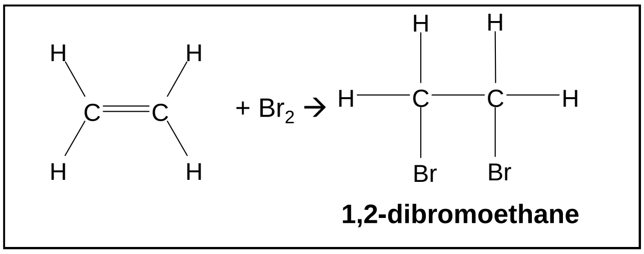
Electrophilic Addition Reactions of Alkenes

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

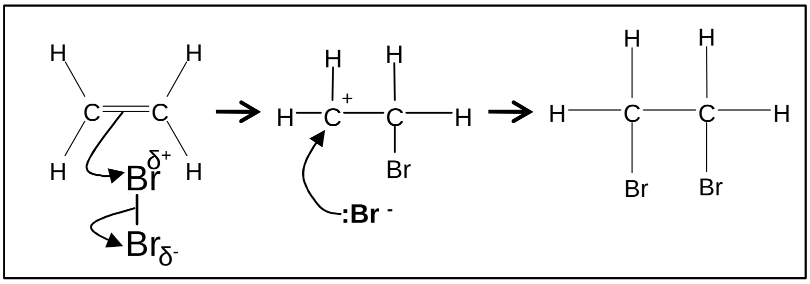
Definition Electrophile: an **electron pair acceptor**

2. Reaction of alkenes with bromine/chlorine

Change in functional group: alkene → dihaloalkane
Reagent: Bromine
Conditions: Room temperature (not in UV light)
Mechanism: Electrophilic Addition
Type of reagent: Electrophile, $Br^{\delta+}$
Type of Bond Fission: Heterolytic



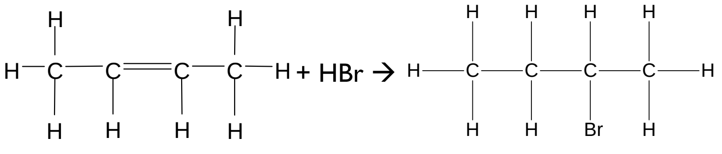
As the Br_2 molecule approaches the alkene, the pi bond electrons repel the electron pair in the Br-Br bond. This **INDUCES** a **DIPOLE**. Br_2 becomes **polar** and **ELECTROPHILIC** (**$Br^{\delta+}$**).



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

3. Reaction of Hydrogen Bromide with Alkenes

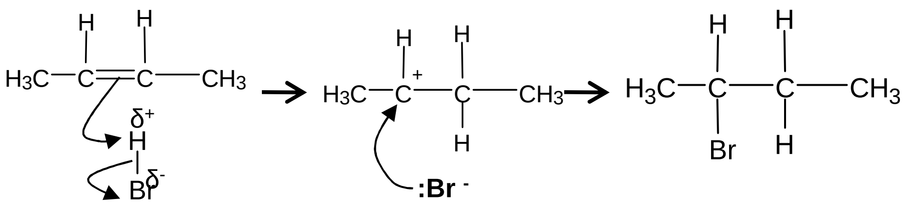
Change in functional group: alkene→haloalkane
Reagent: HCl or HBr
Conditions: Room temperature
Mechanism: Electrophilic Addition
Type of reagent: Electrophile, $H^{\delta+}$



But-2-ene

2-bromobutane

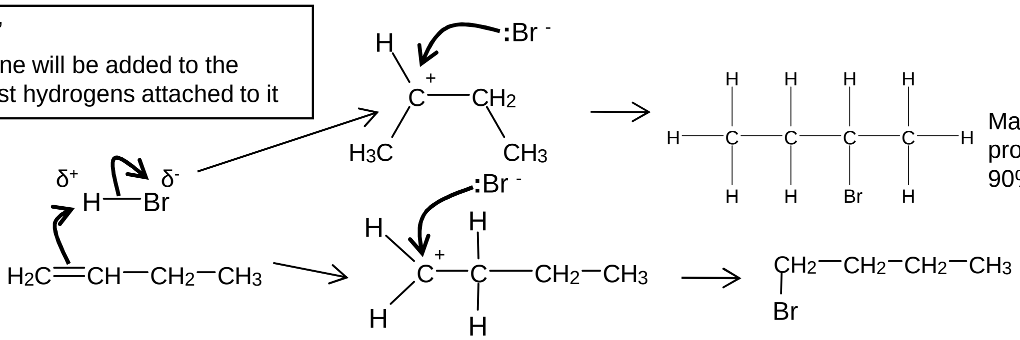
HBr is a polar molecule because Br is more electronegative than H. The H $^{\delta+}$ is attracted to the electron-rich pi bond.



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

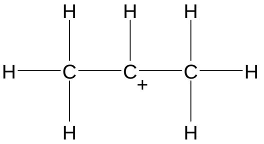
If the alkene is unsymmetrical, addition of hydrogen bromide can lead to two isomeric products.



Major product 90%

Minor product 10%

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.

The order of stability for carbocations is

tertiary > secondary >primary

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)

4. Reaction of alkenes with steam to form alcohols

Industrially alkenes are converted to alcohols in one step. They are reacted with steam in the presence of an acid catalyst.

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

$CH_2{=}CH_{2\,(g)} + H_2O_{(g)} \rightarrow CH_3CH_2OH_{(l)}$

Reagent : steam

Essential Conditions

High temperature 300 to 600°C

High pressure 70 atm

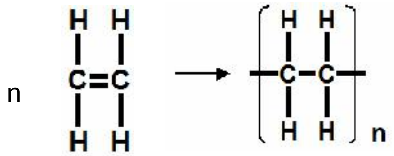
Catalyst of **concentrated H_3PO_4**

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.

Addition Polymers

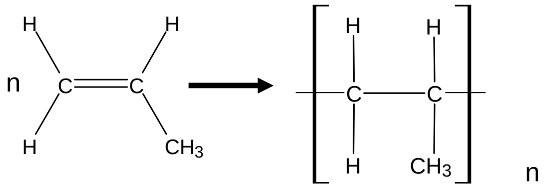
Addition polymers are formed from alkenes

This is called **addition polymerisation**



Monomer
Ethene

Polymer
polyethene



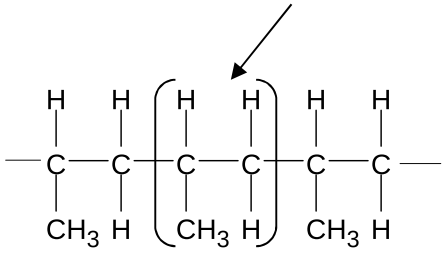
propene

poly(propene)

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)



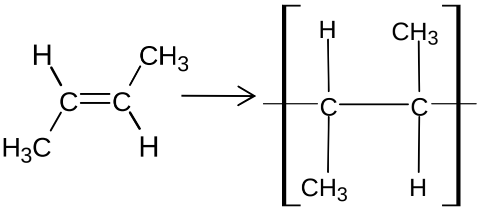
Add the **n's** if writing an equation showing the reaction where 'n' monomers become 'n' repeating units

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

e.g. For but-2-ene

$H_3C—CH{=}CH—CH_3$

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



Industrial importance of alkenes
The formation of polymers from ethene based monomers is a major use of alkenes.
The manufacture of margarine by catalytic hydrogenation of unsaturated vegetable oils using hydrogen and a nickel catalyst is another important industrial process.

Liquid vegetable oils are generally polyunsaturated alkenes. Hydrogenation by the reaction of hydrogen using a nickel catalyst converts the double bonds to saturated single bonds. This increases the melting point of the oil making it harder and more solid.

Dealing with waste polymers

Waste polymers can be processed in several ways.

Separation and recycling
The waste is sorted into each different type of polymer (ie PTFE, PVC, PET) and then each type can be recycled by melting and remoulding.

Feedstock for Cracking
Waste polymers can be used as a feedstock for the cracking process allowing for the new production of plastics and other chemicals.

Combustion for energy production
Waste polymers can be incinerated and the heat released can be used to generate electricity.
Combustion of halogenated plastics (ie PVC) can lead to the formation of toxic, acidic waste products such as HCl.
Chemists can minimise the environmental damage of this by removing the HCl fumes formed from the combustion process.

Chemists have also been developing a range of biodegradable polymers, compostable polymers, soluble polymers and photodegradable polymers.

Polymers formed from isoprene (2-methyl-1,3-butadiene), maize and starch are biodegradable