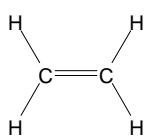


Alkenes

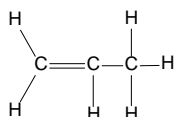
Alkenes are unsaturated hydrocarbons

General formula is C_nH_{2n}

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

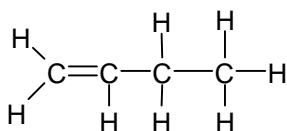


Ethene

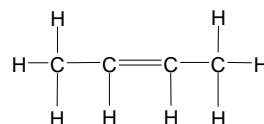


Propene

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

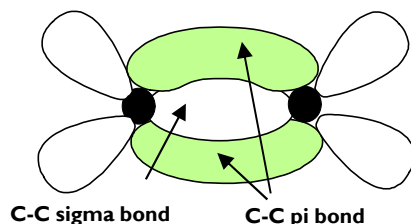


But-1-ene



But-2-ene

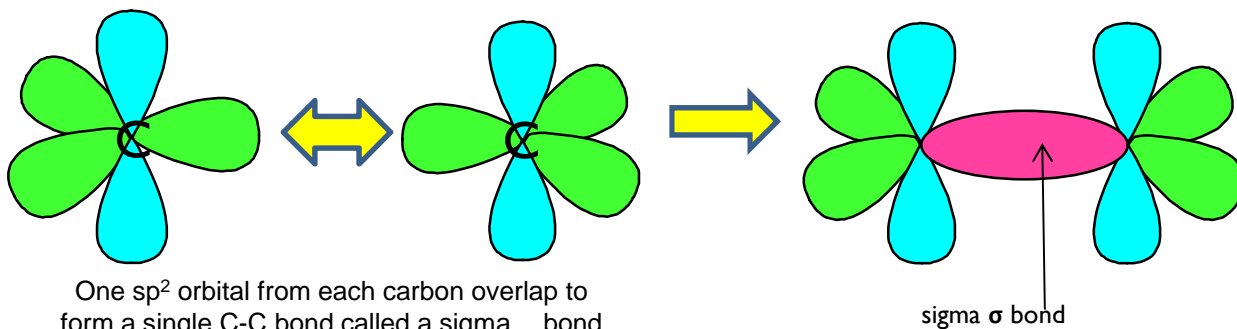
$C=C$ double covalent bond consists of **one sigma (σ) bond and one pi (π) bond.**



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

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

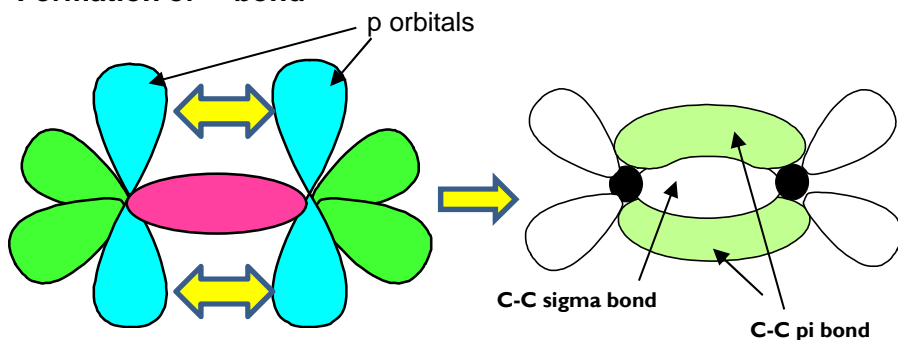
Formation of σ bond



One sp^2 orbital from each carbon overlap to form a single C-C bond called a sigma bond

Rotation can occur around a sigma bond

Formation of π 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

There is Restricted rotation about a π bond

The π bond leads to resultant high electron density above and below the line between the two nuclei

Stereoisomerism

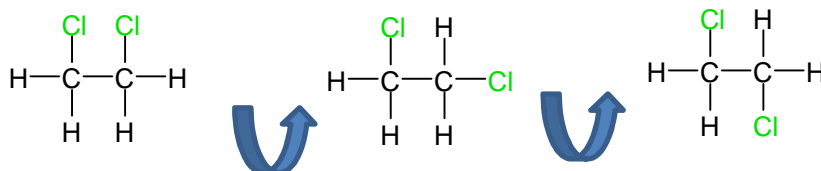
Definition: Stereoisomers have the same structural formulae but have a different spatial arrangement of atoms

There are two types of **stereoisomerism**: geometrical (E-Z isomerism) and optical isomerism

E-Z stereoisomerism

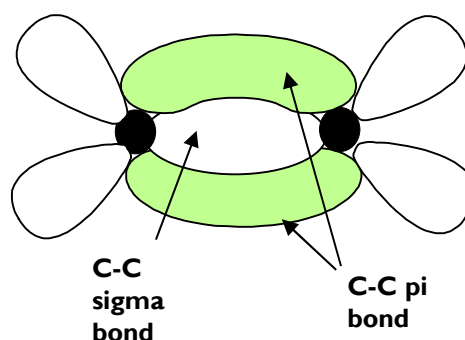
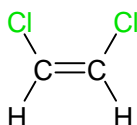
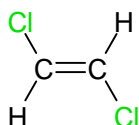
Alkenes can exhibit a type of isomerism called **E-Z stereoisomerism**. This occurs because of restricted rotation that occurs around a double bond

Single carbon-carbon covalent bonds can easily rotate



All three of these structures are the same

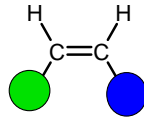
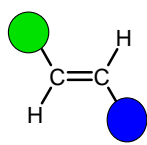
C=C double bonds have restricted rotation, due to position of the pi bond, so the groups on either end of the bond are fixed in one position. It is not easy to flip between the two.



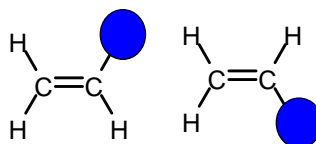
This produces two possibilities. The two structures cannot interchange easily so the atoms in the two molecules occupy different positions in space.

E-Z stereoisomers arise when:

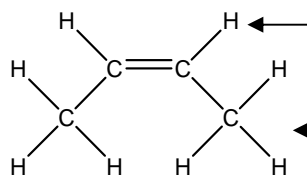
- There is **restricted rotation** around the C=C double bond.
- There are **two different groups/atoms** attached both ends of the restricted double bond



E-Z stereoisomers:
two different groups attached either end of the restricted double bond

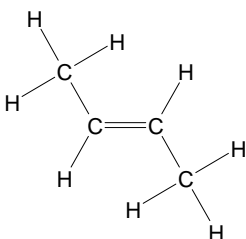


Same structure NOT E-Z stereoisomers: *two identical groups attached to one end of the restricted double bond.*



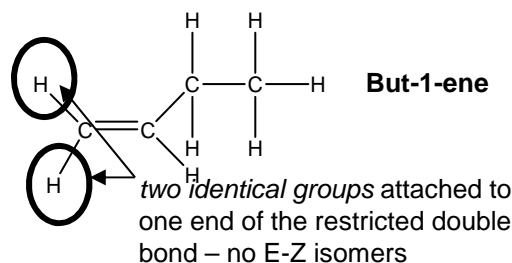
Z-but-2-ene

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



E-but-2-ene

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



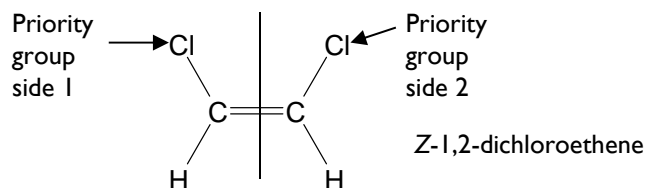
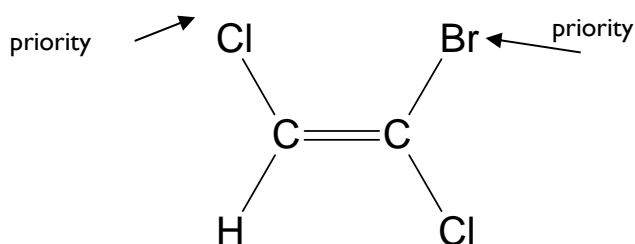
But-1-ene is a structural isomer of But-2-ene but does not show E-Z isomerism

Naming E-Z stereoisomers

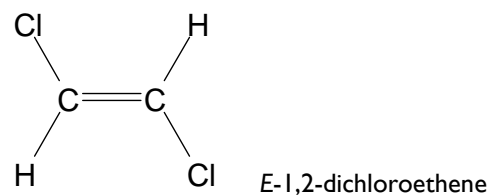
Cahn-Ingold-Prelog (CIP) priority rules.

On both sides of the double bond determine the priority group

1. Compare the atomic number (A_r) of the atoms directly attached to each side of the double bond; the group having the atom of higher atomic number receives higher priority.

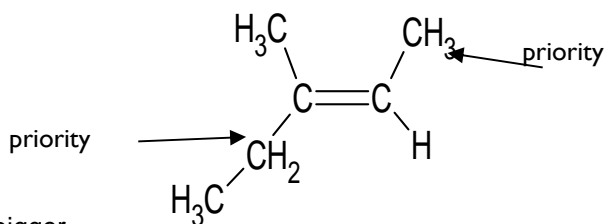


If the priority atom is on the same side of the double bond it is labelled Z from the german zusammen (The Zame Zide!)



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

2. If there are groups of atoms instead of single atoms attached to the carbon of the double bond then consider the sum of the atomic numbers of the entire group. The bigger group is the priority

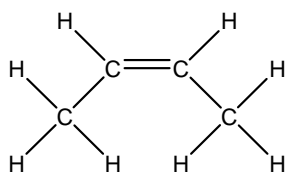


The CH_3CH_2 group is bigger than the CH_3 so it is the priority group

cis-trans isomerism

In some text books you will find this type of E-Z isomerism referred to as geometric isomerism and cis-trans isomerism.

cis-trans isomerism can be considered as a special case of *E/Z isomerism* in which two of the substituent groups are the same. It has been superseded by *E/Z isomerism* because the **Cahn-Ingold-Prelog (CIP) priority rules** allow all alkenes to be considered and not just the ones where the groups are the same.

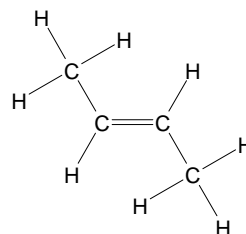


Z- but-2-ene

Can also be called

Cis- but-2-ene

Cis means "on this side of" in latin



E- but-2-ene

Can also be called

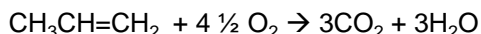
trans- but-2-ene

trans means "across" in latin

Reactions of Alkenes

Combustion

Alkenes will combust in air readily. They do burn with a smokier flame than alkanes. In general the lower the carbon to hydrogen ratio in a hydrocarbon the sootier the flame.



Alkenes are not used as fuels though because their reactivity makes them more valuable for making other chemicals

Reactivity of alkenes

Alkenes are more reactive than alkanes, because of the double bond.

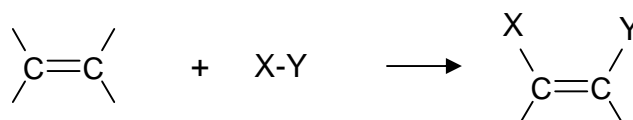
$$E(\text{C}=\text{C}) = +610 \text{ kJ mol}^{-1}.$$

$$E(\text{C}-\text{C}) = +346 \text{ kJ mol}^{-1}.$$

Although the double bond is stronger than a single bond, it is energetically more favourable to form two single bonds than one double bond. The C=C bond energy is less than two times the value of most single bonds. This leads to the double bond undergoing addition reactions.

Addition reactions of alkenes

The double bond in the alkene makes it much more reactive than alkanes. Alkenes undergo a variety of addition reactions where the double bond breaks and a reactant molecule will split and add to the carbons at both ends of the double bond.



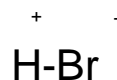
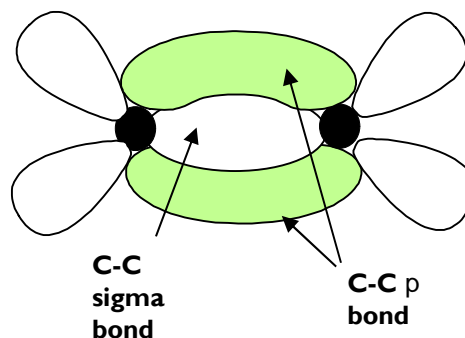
There are a number of different mechanisms by which addition reactions can occur with alkenes. The most common one is called **electrophilic addition**.

Electrophilic Addition

The p (pi) bonds in alkenes are exposed and have high electron density. They are therefore vulnerable to attack by species which are attracted to high electron density. These species are called **electrophiles**.

Electrophiles tend to be molecules where part of the molecule has a slight positive charge. They could be called electron deficient. They attack electron rich parts of molecules. The usual definition of an electrophile is **an acceptor of an electron pair**. This is because during the reaction they will accept the pair of electrons from the double bond to form a bond between the alkene and the electrophile.

H-Br is common electrophile. The molecule has a dipole. The H has a partial positive charge because of the electronegativity difference between the hydrogen and the bromine.



On the next page we will look at the mechanism in detail

Reaction of hydrogen halide with alkenes

Change in functional group:

alkene → halogenoalkane

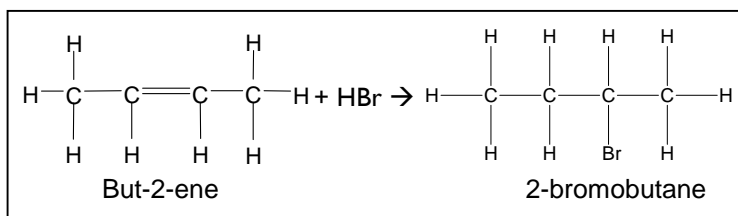
Reagent: HCl or HBr

Conditions: Room temperature

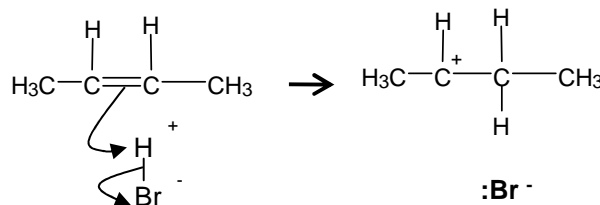
Mechanism: Electrophilic Addition

Type of reagent: Electrophile, $H^{\delta+}$

Type of Bond Fission: Heterolytic



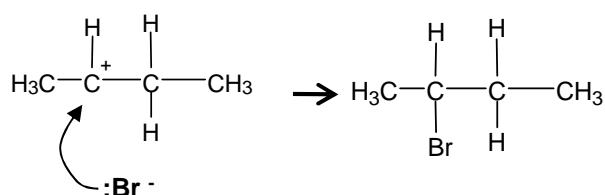
HBr is a polar molecule because Br is more electronegative than H. The $H^{\delta+}$ is attracted to the electron-rich pi bond. The two electrons in the p bond come out to make a covalent bond with the positive hydrogen of the HBr. The H-Br bond breaks heterolytically. The H attaches to one of the carbon atoms and a bromide ion is formed



An intermediate species is formed, which has a positive charge on a carbon atom. This is called a carbocation.

The bromide ion contains a lone pair. It acts as a nucleophile and is attracted to the positive carbon on the carbocation, forming a new covalent bond.

Overall, there is addition of HBr across the alkene.



Reaction of Alkenes with bromine/chlorine

The reaction of alkenes with bromine and chlorine is very similar to the one with hydrogen halides. The difference is the bromine and chlorine molecules are non-polar because of the zero electronegativity difference between the halogen atoms. It may seem unusual how they can act as electrophile. The mechanism below explains how.

Change in functional group:

alkene → dihalogenoalkane

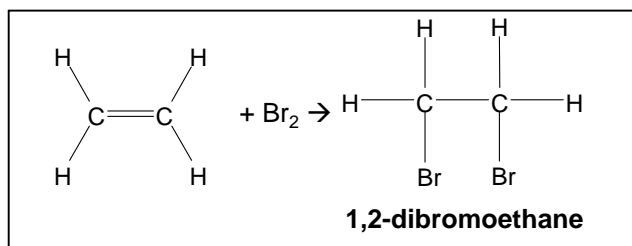
Reagent: Bromine (dissolved in organic solvent)

Conditions: Room temperature (not in UV light)

Mechanism: Electrophilic Addition

Type of reagent: Electrophile, $Br^{\delta+}$

Type of Bond Fission: Heterolytic

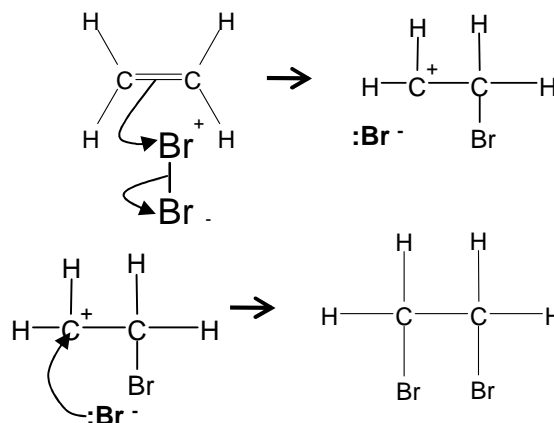


As the Br_2 molecule approaches the alkene, the p bond electrons repel the electron pair in the Br-Br bond. this induces a dipole. Br_2 becomes polar and electrophilic ($Br^{\delta+}$).

The $Br^{\delta+}$ is attracted to the electron-rich pi bond. The two electrons in the p bond come out to make a covalent bond with the positive bromine of the Br_2 . The Br-Br bond breaks heterolytically. One Br attaches to one of the carbon atoms and a bromide ion is formed with the other

The bromide ion contains a lone pair. It acts as a nucleophile and is attracted to the positive carbon on the carbocation, forming a new covalent bond.

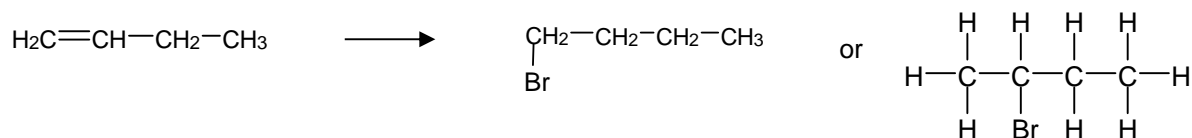
Overall, there is addition of Br_2 across the alkene.



Markownikoff's Addition

If the alkene is unsymmetrical, addition of hydrogen bromide can lead to two isomeric products because there are two different possibilities where the bromine could attach to the alkene- either side of the double bond.

But-1-ene will form a mixture of 1-bromobutane and 2-bromobutane on reaction with hydrogen bromide

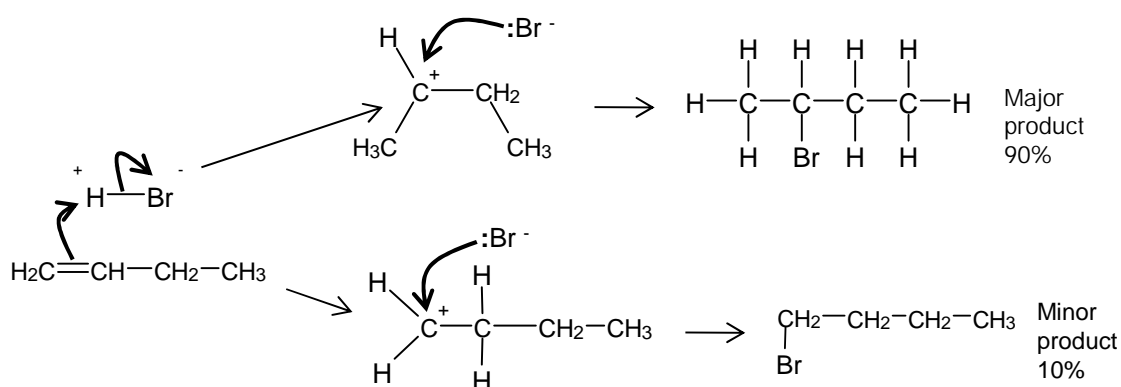


The two products do not, however, form in equal amounts. The 2-Bromobutane forms much more often (90%) and is called the **major product**. The other possibility 1-bromobutane is called the minor product and forms much less (10%)

We can use Markownikoff's rule to identify which is the major product but it is not an explanation about why it happens. We need to look at the mechanism to understand why.

'Markownikoff's Rule'

In most cases, bromine will be added to the carbon with the fewest hydrogens attached to it

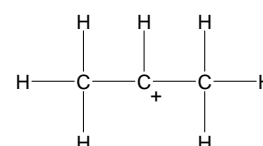


If we look at the mechanism, the major product forms via a secondary carbocation and the minor product forms via a primary carbocation. The secondary carbocation is much more stable than a primary carbocation. This is because in a secondary carbocation the alkyl (e.g. methyl, ethyl) groups on either side of the positive carbon are electron releasing and reduce the charge on the positive carbon which stabilises it. In a primary carbocation there is only one electron releasing alkyl group so the carbocation is less stabilised and less likely to form.

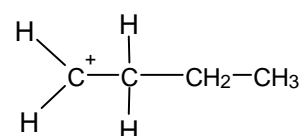
The overall rule is in **electrophilic addition** to alkenes, the **major product** is formed **via the more stable carbocation** intermediate.

The order of stability for carbocations is
tertiary > secondary > primary

It is possible for an unsymmetrical alkene (e.g. pent-2-ene) to react with HBr and give two secondary carbocations. In this case then both will be equally stable and a 50/50 split will be achieved (2-bromopentane and 3-bromopentane)



A secondary carbocation has two carbons attached to the carbon with a positive charge



A primary carbocation has one carbon attached to the carbon with a positive charge

Reaction of Sulfuric acid with Alkenes

Concentrated sulfuric acid can also react with alkenes in an electrophilic addition reaction. This reaction is usually done as the first part of a 2 stage reaction to product an alcohol from an alkene. Only the first stage is an electrophilic addition. It produces an alkyl hydrogensulfate molecule. In the second stage the hydrogensulfate is warmed with water to produce the alcohol in a hydrolysis reaction.

Stage 1

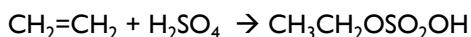
Change in functional group
alkene → alkyl hydrogensulfate

Reagents: concentrated H_2SO_4

Conditions: room temperature

Mechanism: Electrophilic Addition

Type of reagent: Electrophile, H_2SO_4



Stage 2

Change in functional group
alkyl hydrogensulfate → alcohol

Reagents: water

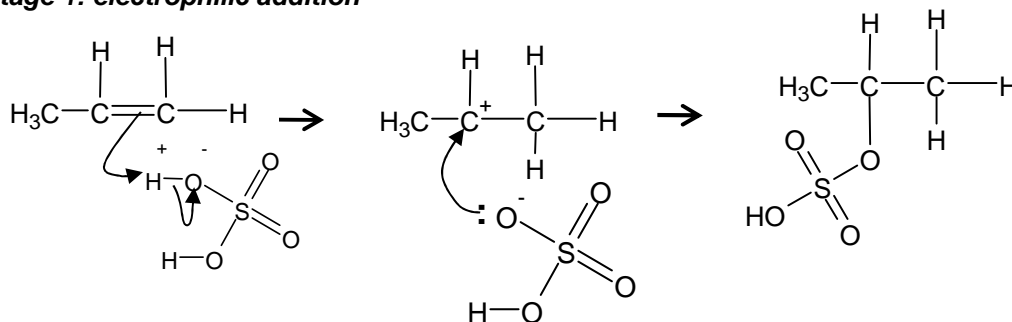
Conditions: warm mixture

Type of reaction: hydrolysis

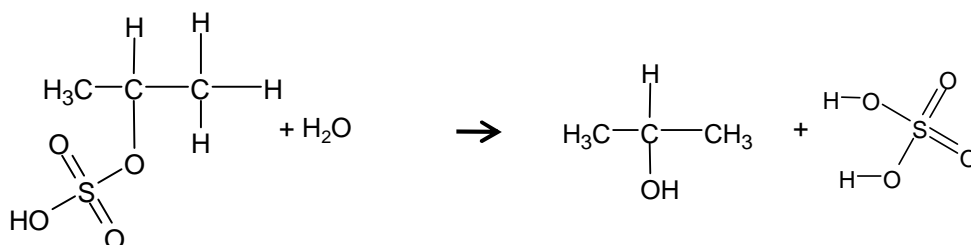


Definition: Hydrolysis – a reaction where the molecule is **split** by the addition of water

Stage 1: electrophilic addition



Stage 2: hydrolysis



This reaction is a laboratory method for making an alcohol from an alkene. It does not work well on large industrial scale

industrial formation from of ethanol from ethene

Ethanol can be made by reacting ethene with steam at high temperatures in the presence of an acid catalyst. This process is used industrially to produce ethanol. It is an addition reaction but is not the same sort of electrophilic addition reaction as the previous cases. The mechanism is a different because of the role of a phosphoric acid catalyst

This reaction is sometimes called a **Hydration reaction** $\text{CH}_2=\text{CH}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CH}_3\text{CH}_2\text{OH}(\text{l}) \quad \Delta H = -45 \text{ kJ mol}^{-1}$

Ethene → ethanol

Reagents: steam

Conditions: high temperature 300 °C, high pressure 70 atm and strong acidic catalyst of **concentrated H_3PO_4**

Mechanism: acid catalysed addition

A low temperature would produce a high yield because the forward reaction is exothermic. A low temperature would give a slow rate.

Therefore a compromise temperature of 300°C is used that gives a fast reaction without giving a very small percentage yield.

Choosing pressure conditions

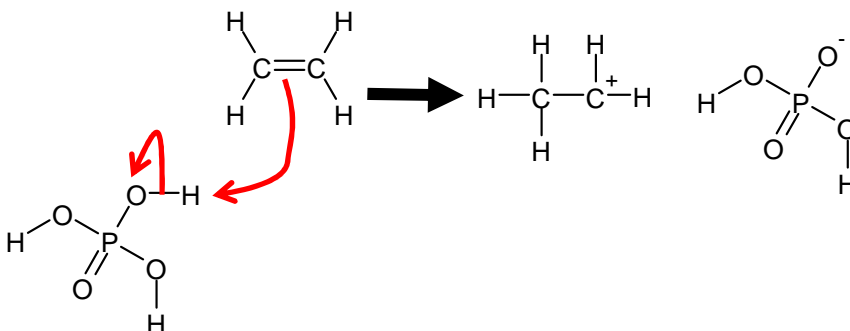
A higher pressure is used to push the position of equilibrium to the right as two moles of gas will go to one.

The high pressures needed mean this cannot be done in the laboratory. Too high pressure can lead to unwanted polymerisation of ethene to poly(ethene), and would also lead to too high electrical energy costs for pumps to produce the pressure.

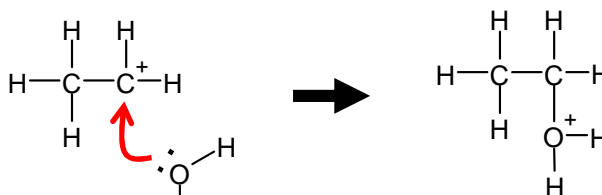
At chosen conditions only 5% conversion occurs, but a recycle is used to recycle the unreacted ethene.

Mechanism for acid catalysed addition of steam to ethene

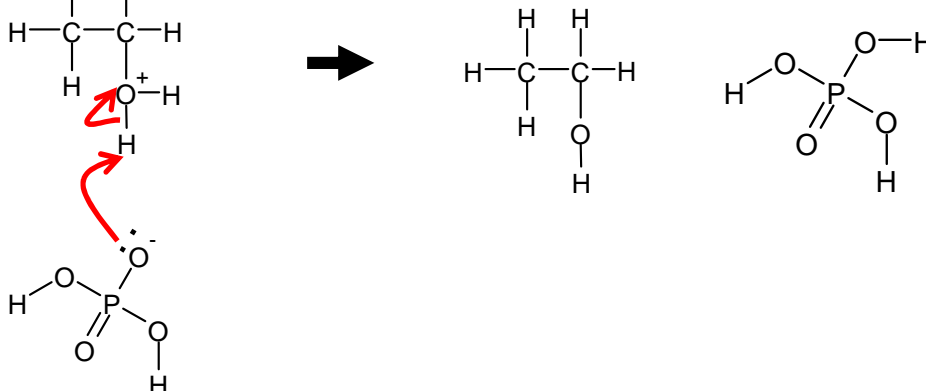
Step 1: A pair of electrons from the double bond in the alkene forms a bond with a proton from the phosphoric acid forming a carbocation intermediate.



Step 2: The lone pair of electrons on the water form a bond to the carbocation forming a protonated alcohol.



Step 3: The protonated alcohol loses a proton to the phosphate ion regenerating the phosphoric acid catalyst in the process.



Reaction of alkenes with hydrogen

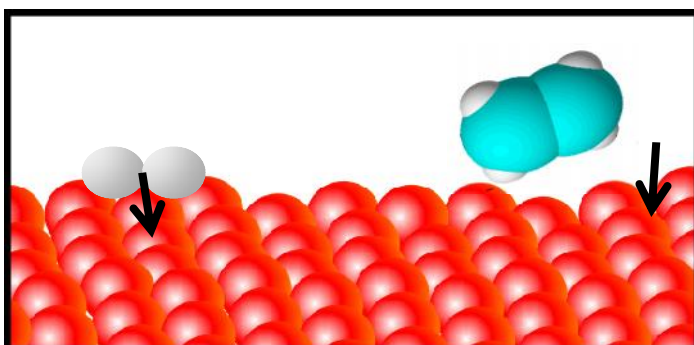
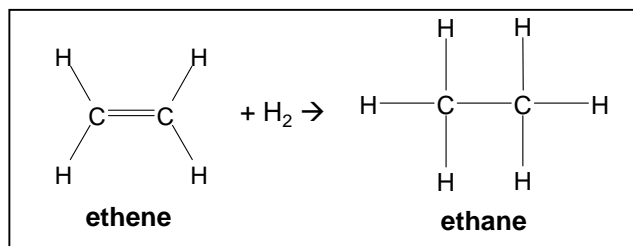
Another addition reaction of alkenes is that with hydrogen gas using a nickel catalyst. This reaction is used industrially to add hydrogen to unsaturated vegetable oils to increase their melting points and make them margarine in a process called hardening. This is another type of mechanism involving a solid heterogeneous nickel catalyst. The diagrams below illustrate how the reaction occurs.

Change in functional group: alkene → alkane

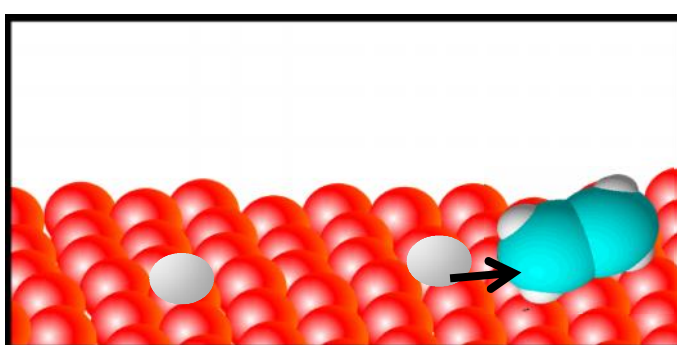
Reagent: hydrogen

Conditions: Nickel catalyst

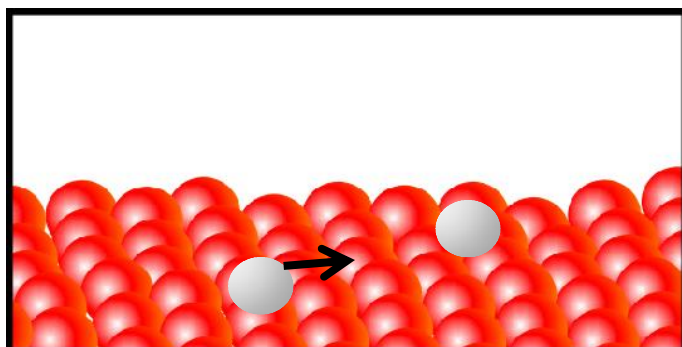
Type of reaction: Addition/Reduction



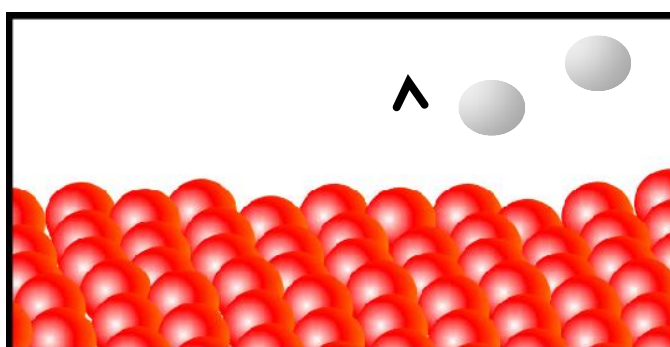
Ethene and hydrogen adsorb on to atoms on the surface of the catalyst by donating electron density into empty d-orbitals in the nickel atoms.



The bonds within the hydrogen molecules break and produce hydrogen radicals. A hydrogen radical interacts with the electron density in the ethene double bond producing an ethyl radical



The second hydrogen radical forms a bond with the ethyl radical



The ethane desorbs from the surface of the catalyst

Testing for alkenes

The following two reactions can be used as functional group tests for alkene double bonds.

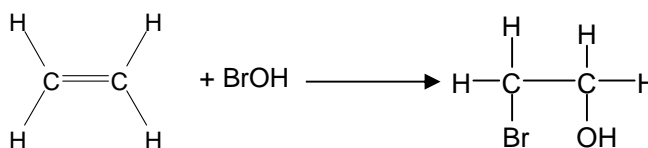
Reaction of Bromine Water with Alkenes

Reagent: Bromine dissolved in water

Conditions: Room temperature

Type of reaction: Addition

Observation: Orange colour of bromine water will decolourise to colourless



This reaction with its colour change is used as a test for the alkene functional group.

Reaction of Potassium Manganate(VII) with Alkenes

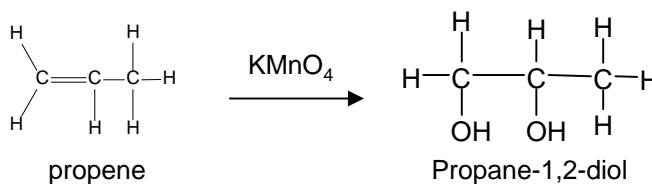
Change in functional group: alkene \rightarrow diol

Reagent: KMnO_4 in an acidified solution

Conditions: Room temperature

Type of reaction: Oxidation

Observation: purple colour of MnO_4^- ion will decolourise to colourless



This reaction with its colour change can be used as a test for the alkene functional group. It would not change colour with alkanes

Addition polymerisation

An important reaction industrially for alkenes is their conversion to addition polymers. This is dealt in detail in the polymer chapter

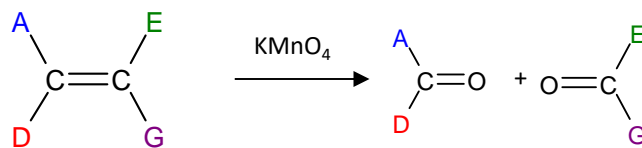
Reaction of hot concentrated Potassium Manganate(VII) with Alkenes

Change in functional group: alkene → carbonyls (mostly)

Reagent: KMnO_4 in an acidified solution

Conditions: hot concentrated

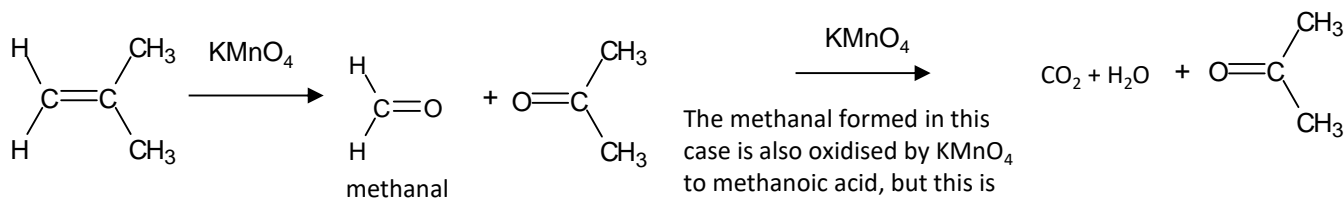
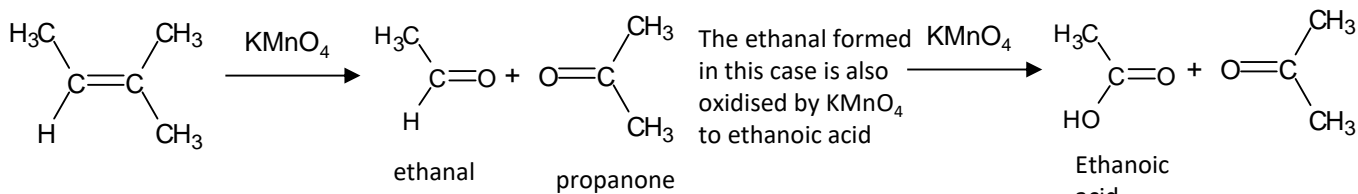
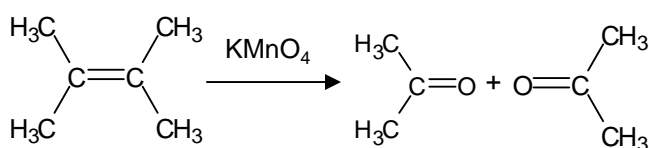
Type of reaction: Oxidation



General reaction – double bond breaks and two carbonyls are formed. The products formed can be used to work out which alkene was the reactant

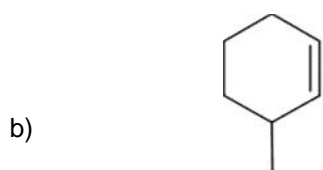
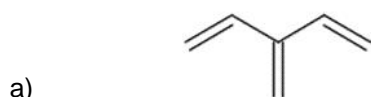
This reaction splits an alkene in two at the double bond and oxidises the products to carbonyl or carboxylic acids

Different alkenes will lead to different types of products.



Alkene Questions

- State what is meant by the term *unsaturated* as applied to an alkene.
 - Draw the skeletal formulae and name all the chain and position isomers of C_5H_{10}
 - Draw a functional group isomer of C_5H_{10}
 - But-2-ene can exist as a pair of stereoisomers.
 - State what is meant by the term *stereoisomers*.
 - Draw the structure of (*E*)-but-2-ene.
 - Draw and name the geometrical *EZ* isomers of pent-2-ene
- What are the molecular formulae of the following molecules and calculate the M_r of them?



3) Draw the displayed formulae of the products of the following reactions

- But-2-ene + HBr
- Propene + Br_2
- cyclohexene + HCl
- 2-methylbut-1-ene + Cl_2

4) Organic reaction mechanisms help to develop an understanding of how and why reactions occur.

Name the mechanism for the reaction of bromine with but-2-ene. Draw the mechanism out with curly arrows. Add a written description to your mechanism covering the following points.

- Describe what happens initially to a bromine molecule as it approaches an ethene double bond.
- Describe the interaction in an electrophilic attack between electrons of the double bond and bromine.
- Describe the species formed when a bromine atom has been added to ethene and a bromide ion has formed.
- Describe how the bromide ion then reacts with the electron-deficient carbon atom.

5) Propene reacts with hydrogen bromide by an electrophilic addition mechanism forming 2-bromopropane as the major product.

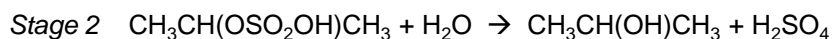
(a) Outline the mechanism for this reaction using curly arrows, showing clearly the structure of the intermediate carbocation formed.

(b) Give the structure of the alternative carbocation which could be formed in the reaction between propene and hydrogen bromide. Explain why this carbocation leads to the minor product compared to the carbocation drawn in part a)

6) Choose an alkene with molecular formula C_4H_8 which reacts with HBr to form two structural isomers. Give the structures of these two isomers and name the type of structural isomerism shown. Identify which of the isomers would be the major and minor product. Outline a mechanism for the formation of the major product

Explain why the major product forms in preference to the minor product.

7) Alkenes can be converted into alcohols in a two stage reaction.



(a) Name and outline a mechanism using curly arrows for Stage 1 using concentrated sulfuric acid.

(b) Stage 2 can be called a hydrolysis reaction. What does this mean?

(c) State the overall role of the sulfuric acid for overall reaction of the two stages.

8) Compound A has the molecular formula C_4H_8 . It shows E-Z Stereoisomerism. Compound A reacts with Br_2 to form compound B. Compound B is then reacted with aqueous KOH to form compound C. Draw skeletal formulae of compound A, B and C.

9) Propene can undergo an electrophilic addition reaction with a molecule of $I-Br$ to form two isomeric products.

- Deduce what the dipole would be on a molecule of $I-Br$.
- Draw the structures of the two products and say which would be the major and minor product.
- Draw out the mechanism for the formation of the major product
- Explain why the major product forms in preference to the minor product.

10) Cyclohexa-1,3-diene also displays reactivity typical of alkenes. Its structure is shown.

Draw the skeletal formulae of all possible products of the reaction when one molecule of cyclohexa-1,3-diene completely reacts with two molecules of hydrogen bromide. Ignore any stereochemistry

