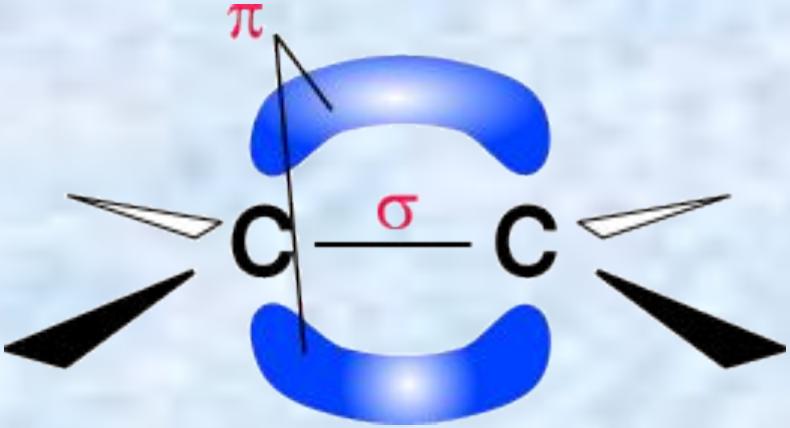
AN INTRODUCTION TO

THE CHEMISTRY OF ALKENES



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THE CHEMISTRY OF ALKENES

INTRODUCTION

This *Powerpoint* show is one of several produced to help students understand selected topics at AS and A2 level Chemistry. It is based on the requirements of the AQA and OCR specifications but is suitable for other examination boards.

Individual students may use the material at home for revision purposes or it may be used for classroom teaching if an interactive white board is available.

Accompanying notes on this, and the full range of AS and A2 topics, are available from the KNOCKHARDY SCIENCE WEBSITE at...

`www.knockhardy.org.uk/sci.htm`

Navigation is achieved by...

either clicking on the grey arrows at the foot of each page

or using the left and right arrow keys on the keyboard

THE CHEMISTRY OF ALKENES

CONTENTS

THE CHEMISTRY OF ALKENES

Before you start it would be helpful to…

- Recall the definition of a covalent bond
- Understand the difference between homolytic and heterolytic fission
- Be able to balance simple equations
- Be able to write out structures for hydrocarbons
- Recall the chemical and physical properties of alkanes

THE STRUCTURE OF ALKENES

General are members of a homologous series

hydrocarbons - contain only C and H

general formula is C_nH_{2n} - for non-cyclic alkenes

unsaturated - atoms can be added to their formula

contain a C=C double bond somewhere in their structure

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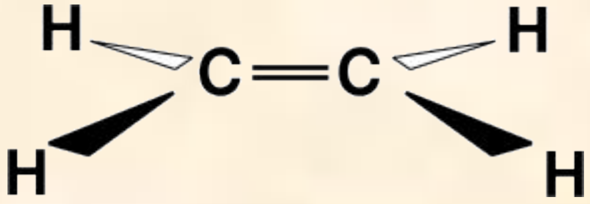
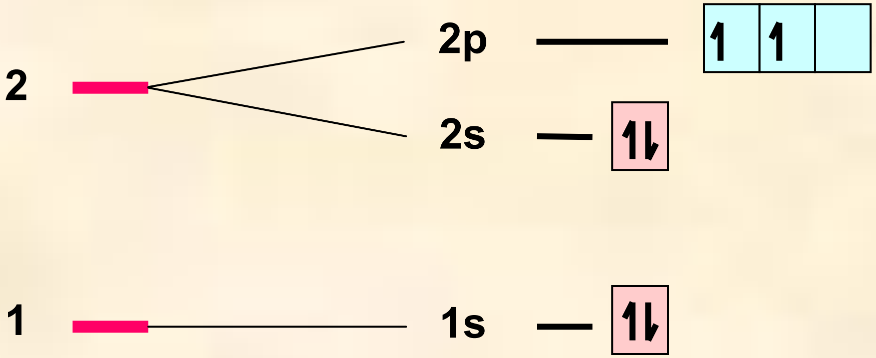
Structure spacial arrangement around the C=C is **planar**

the bond angles are **120°**



HYBRIDISATION OF ORBITALS

The electronic configuration of a carbon atom is **$1s^2 2s^2 2p^2$**



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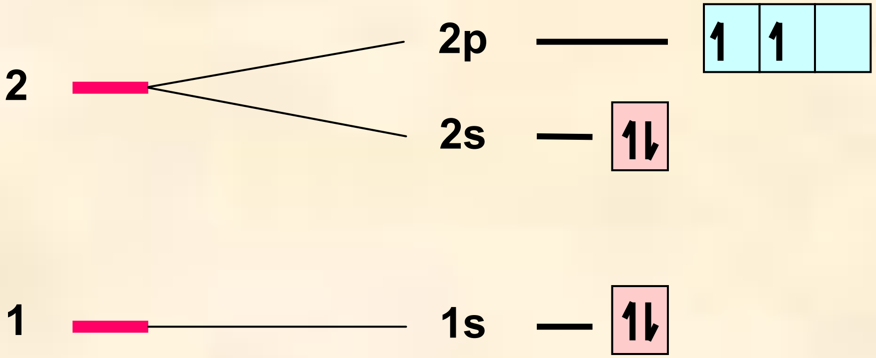
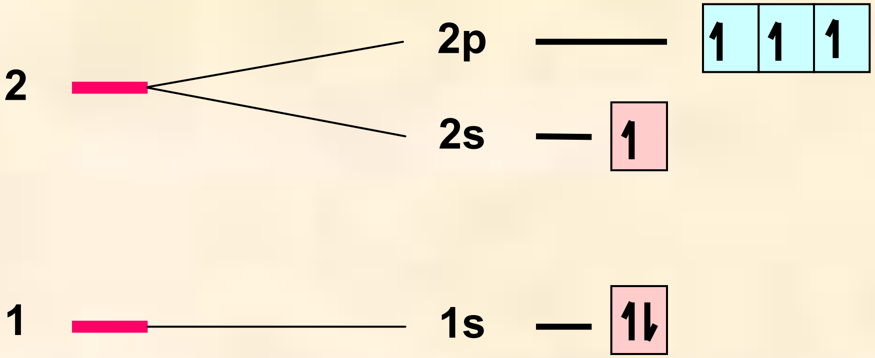


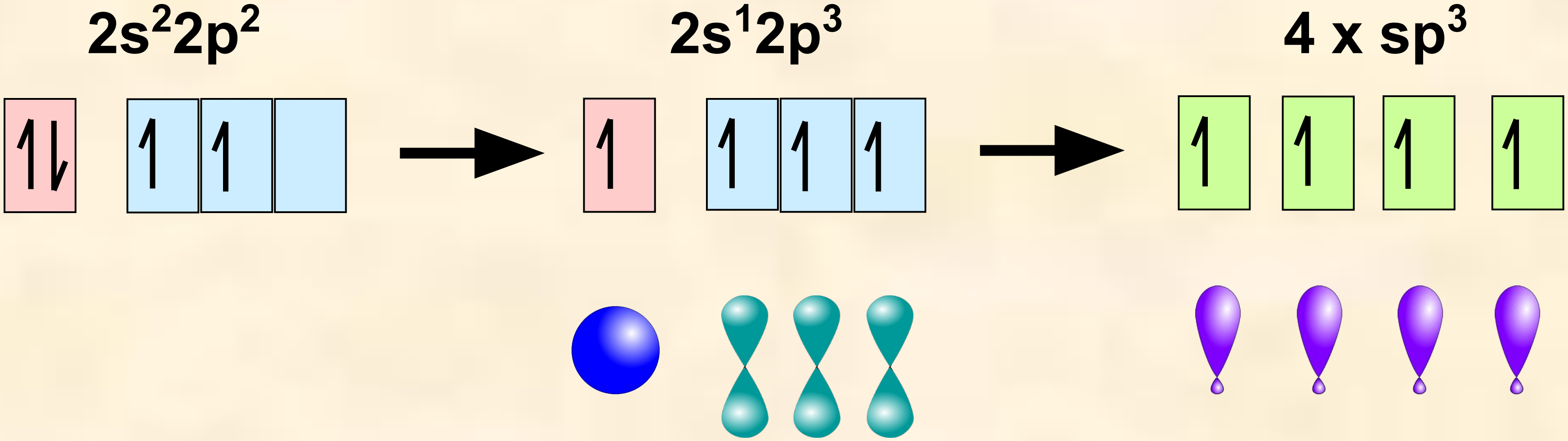
If you provide a bit of energy you can promote (lift) one of the s electrons into a p orbital. The configuration is now **$1s^2 2s^1 2p^3$**



The process is favourable because the of arrangement of electrons; four unpaired and with less repulsion is more stable

HYBRIDISATION OF ORBITALS - ALKANES

The four orbitals (an s and three p’s) combine or **HYBRIDISE** to give **four new orbitals**. All four orbitals are **equivalent**.



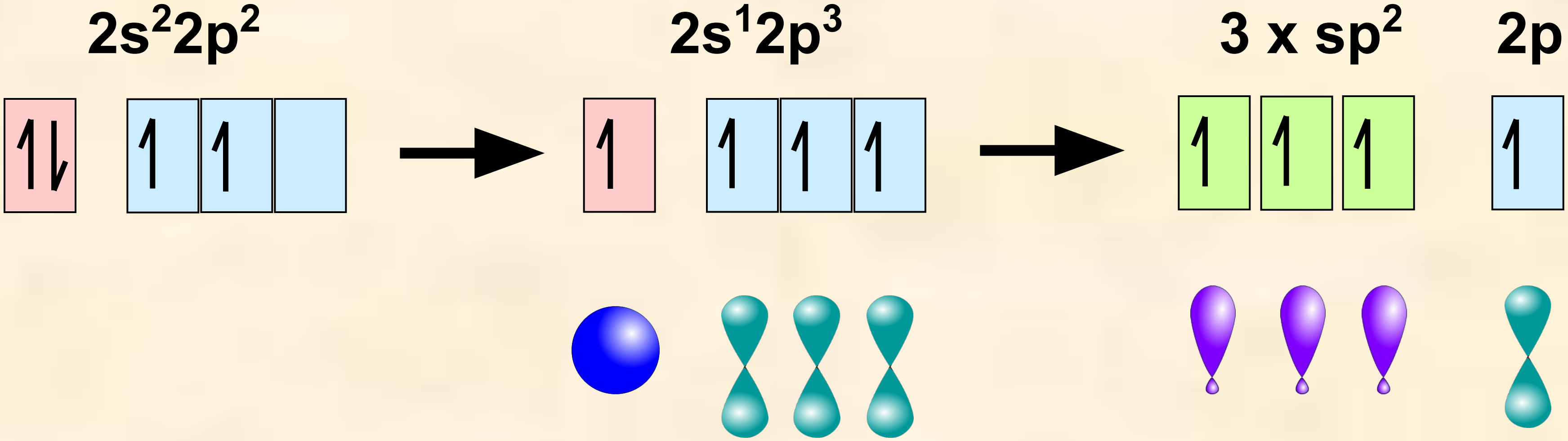
$2s^2 2p^2$

$2s^1 2p^3$

$4 \times sp^3$

HYBRIDISATION OF ORBITALS - ALKENES

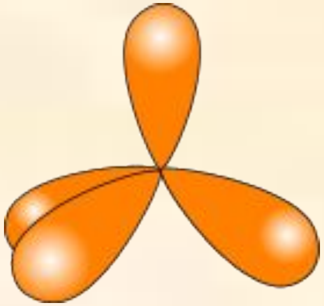
Alternatively, only three orbitals (an s and two p’s) combine or **HYBRIDISE** to give **three new orbitals**. All three orbitals are **equivalent**. The remaining 2p orbital is unchanged.



$2s^2 2p^2$ → **$2s^1 2p^3$** → **$3 \times sp^2$** **2p**

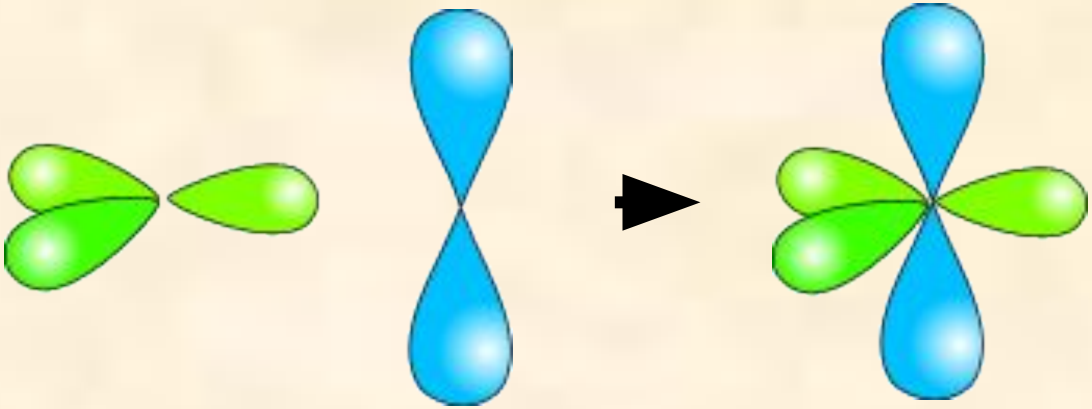
THE STRUCTURE OF ALKENES

In **ALKANES**, the four sp^3 orbitals repel each other into a tetrahedral arrangement.

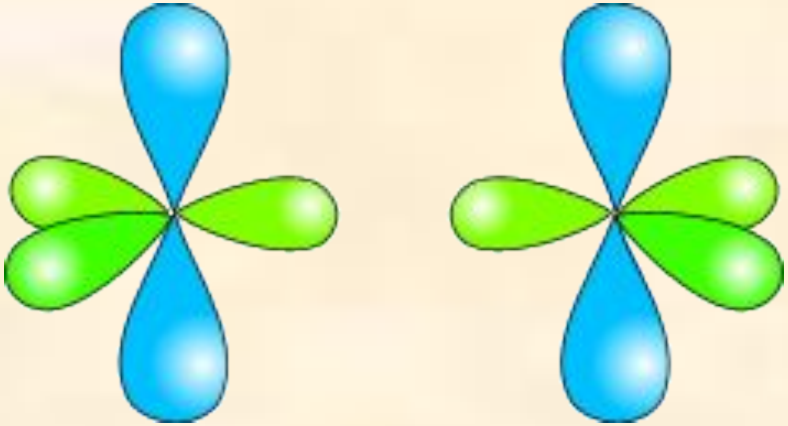


HOWEVER...

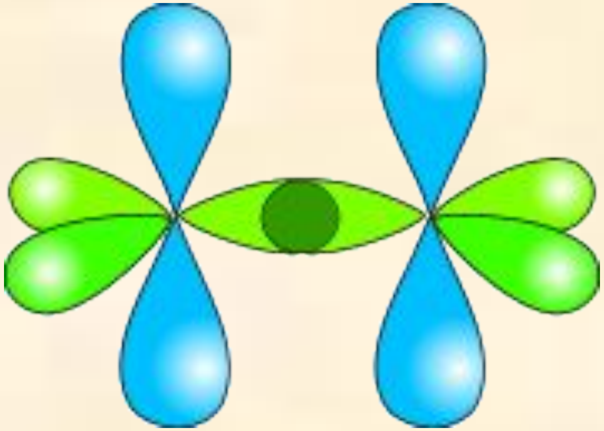
In **ALKENES**, the three sp^2 orbitals repel each other into a planar arrangement and the 2p orbital lies at right angles to them



THE STRUCTURE OF ALKENES

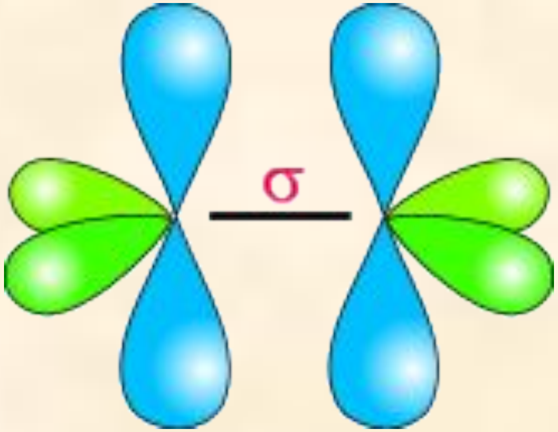


Covalent bonds are formed by overlap of orbitals.

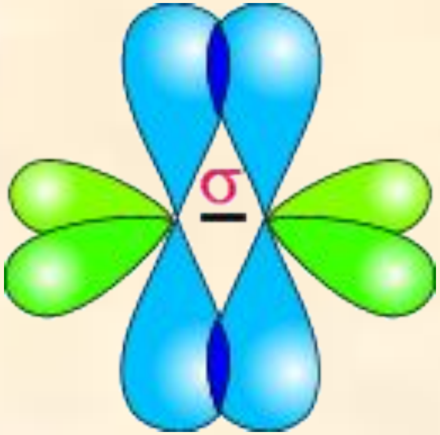


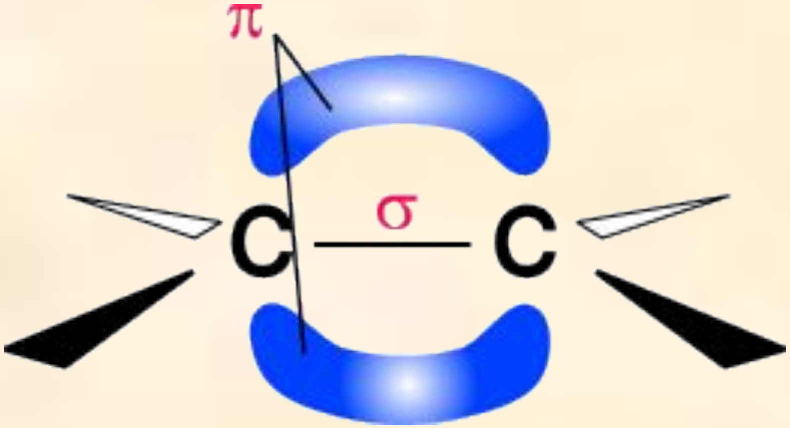
An sp^2 orbital from each carbon overlaps to form a single C-C bond.

The resulting bond is called a SIGMA (δ) bond.



THE STRUCTURE OF ALKENES



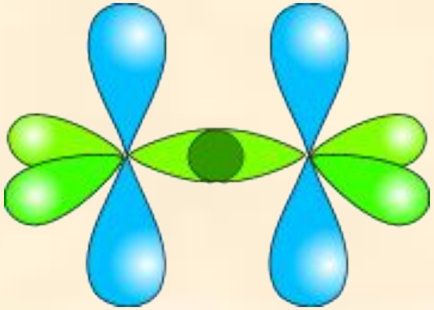


The two 2p orbitals also overlap to form a second bond. This is known as a PI (π) bond.

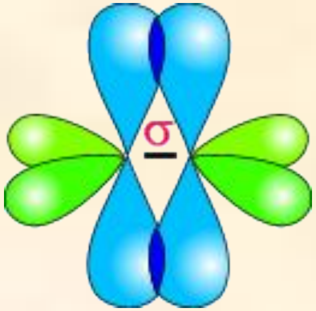
For maximum overlap and hence the strongest bond, the 2p orbitals are in line.

This gives rise to the planar arrangement around C=C bonds.

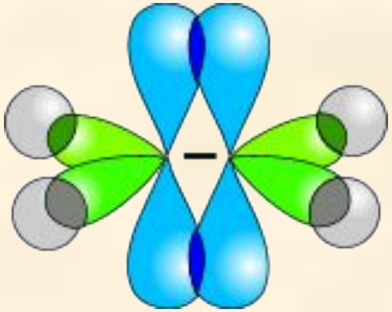
ORBITAL OVERLAP IN ETHENE - REVIEW



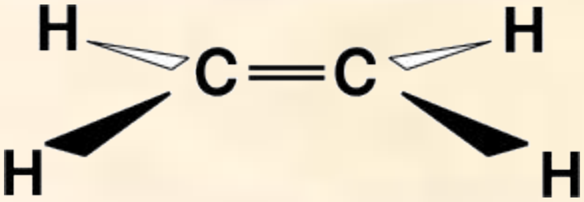
two sp^2 orbitals overlap to form a sigma bond between the two carbon atoms



two 2p orbitals overlap to form a pi bond between the two carbon atoms



s orbitals in hydrogen overlap with the sp^2 orbitals in carbon to form C-H bonds



the resulting shape is planar with bond angles of 120º

NAMING ALKENES

Alkenes are named according to standard IUPAC rules

- select the longest chain of C atoms containing the double bond;
- place the ending ENE on the basic name
- number the chain starting from the end nearer the double bond
- use a number to indicate the lower number carbon of the C=C
- as in alkanes, prefix with substituents
- side chain positions are based on the number allocated to the first C of the C=C
- 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 IN ALKENES

Two types of isomerism found in alkenes

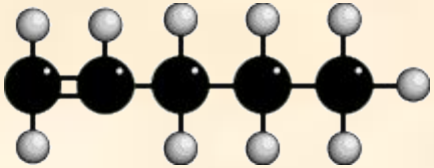
STRUCTURAL

GEOMETRICAL

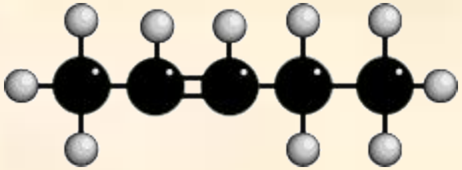
STRUCTURAL ISOMERISM IN ALKENES

Different structures are possible due to...

Different positions for the double bond

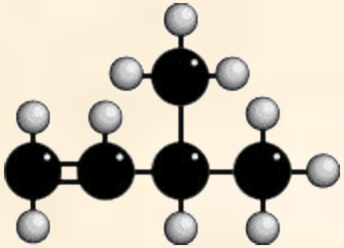


pent-1-ene



pent-2-ene

Branching



3-methybut-1-ene

GEOMETRICAL ISOMERISM IN ALKENES

Introduction

- an example of stereoisomerism
- found in some, but not all, alkenes
- occurs due to the RESTRICTED ROTATION OF C=C bonds
- get two forms...

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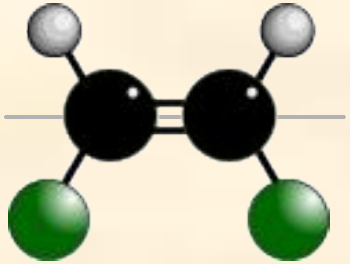
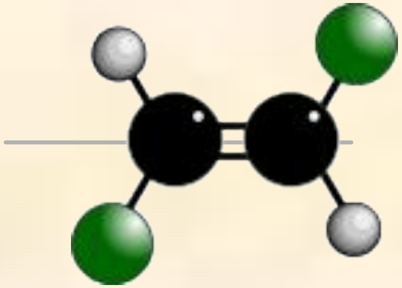


CIS (Z)

Groups/atoms are on the
SAME SIDE of the double bond



TRANS (E)

Groups/atoms are on OPPOSITE
SIDES across the double bond

GEOMETRICAL ISOMERISM IN ALKENES

E/Z or CIS-TRANS

E / Z

Z *(zusammen)* **higher priority groups / atoms on the SAME side of C=C bond**

E *(entgegen)* **higher priority groups / atoms on OPPOSITE sides of C=C bond**

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To determine priority, the Cahn, Ingold and Prelog convention is used.

eg $C_2H_5 > CH_3 > H$ **and** I > Br > C*l* > F > C > H

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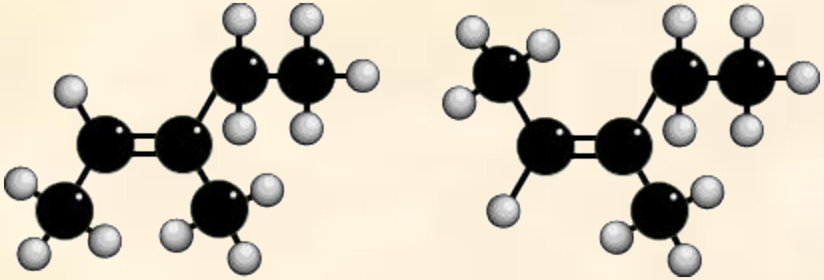

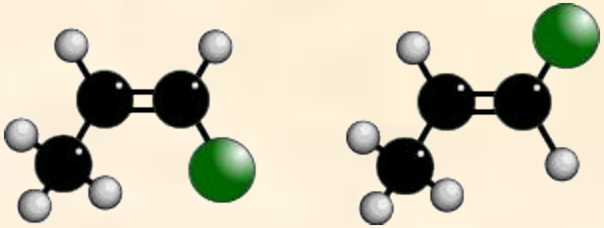

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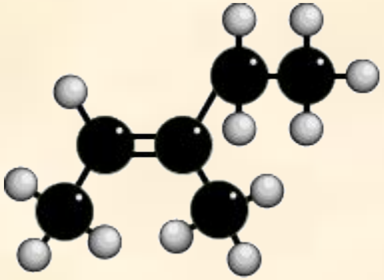
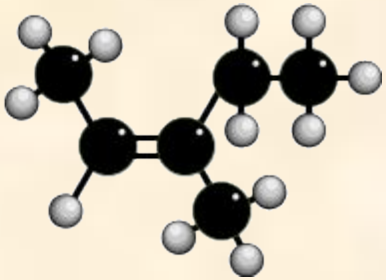
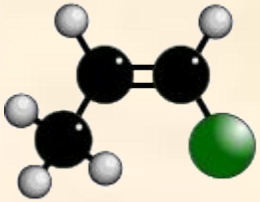


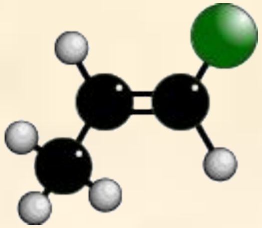
E



Z



Z



E

GEOMETRICAL ISOMERISM IN ALKENES

E/Z or CIS-TRANS

CIS / TRANS Should only be used when there are two H’s and two non-hydrogen groups attached to each carbon.

cis non-hydrogen groups / atoms on the **SAME** side of C=C bond

trans non-hydrogen groups / atoms on **OPPOSITE** sides of C=C bond

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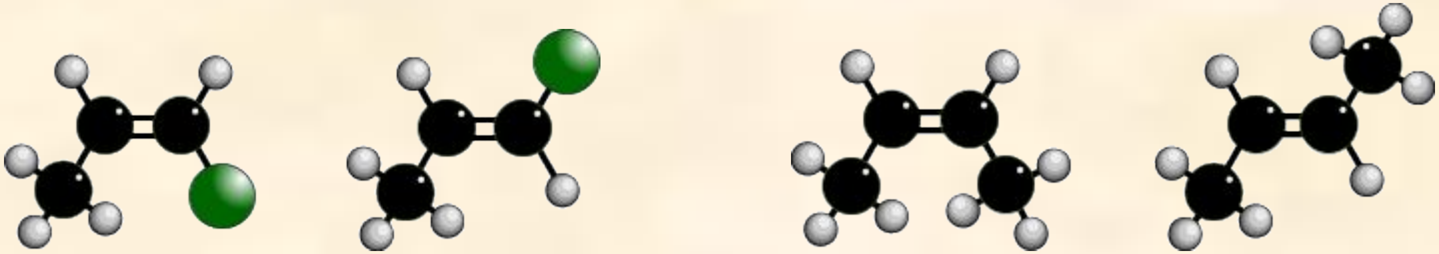

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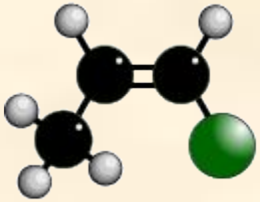
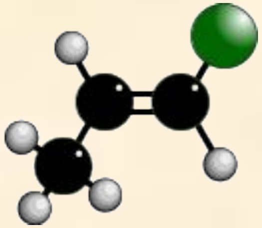
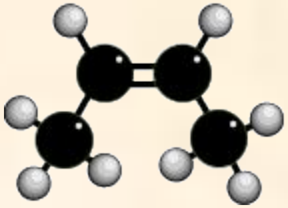


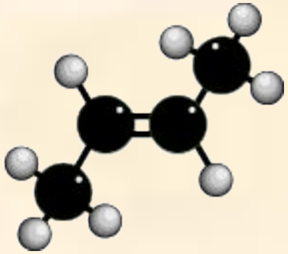
cis



trans



cis

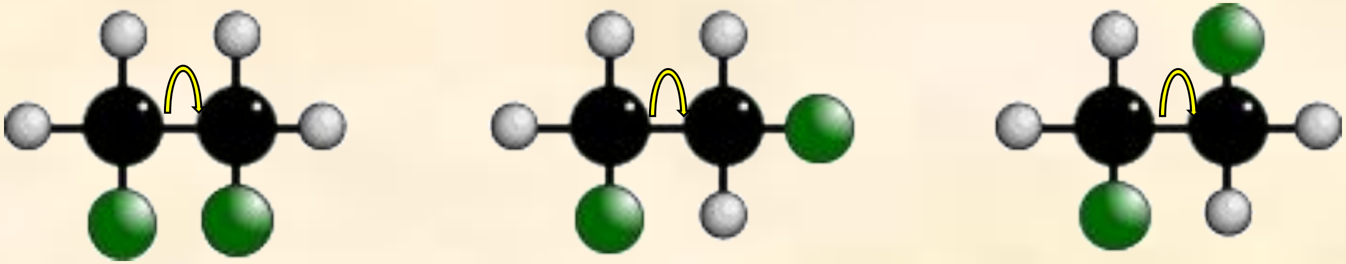


trans

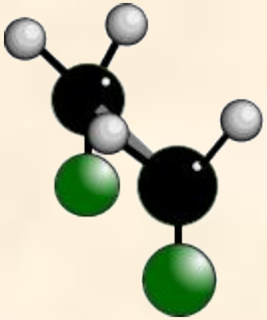
GEOMETRICAL ISOMERISM

RESTRICTED ROTATION OF C=C BONDS

Single covalent bonds can easily rotate. What appears to be a different structure is not. It looks like it but, due to the way structures are written out, they are the same.



ALL THESE STRUCTURES ARE THE SAME BECAUSE C-C BONDS HAVE ‘FREE’ ROTATION

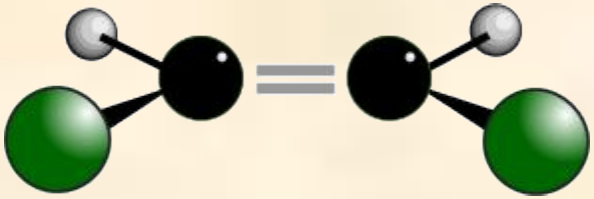


Animation doesn’t
work in old
versions of
Powerpoint

GEOMETRICAL ISOMERISM

RESTRICTED ROTATION OF C=C BONDS

C=C bonds have restricted rotation so the groups on either end of the bond are 'frozen' in one position; it isn't easy to flip between the two.



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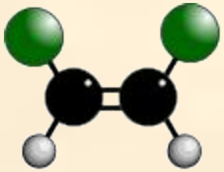
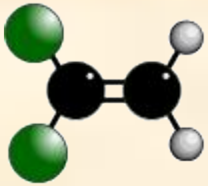
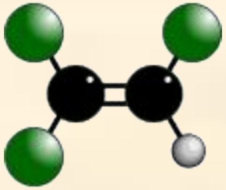
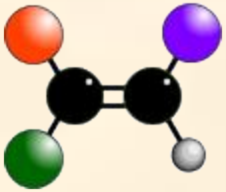
This produces two possibilities. The two structures cannot interchange easily so the atoms in the two molecules occupy different positions in space.

GEOMETRICAL ISOMERISM

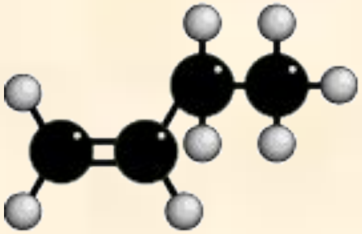
How to tell if it exists

Two different atoms/groups attached		Two different atoms/groups attached	✔	**GEOMETRICAL ISOMERISM**
Two similar atoms/groups attached		Two similar atoms/groups attached	▯	Once you get two similar atoms/groups attached to one end of a C=C, you cannot have geometrical isomerism
Two similar atoms/groups attached		Two different atoms/groups attached	▯	
Two different atoms/groups attached		Two different atoms/groups attached	✔	**GEOMETRICAL ISOMERISM**

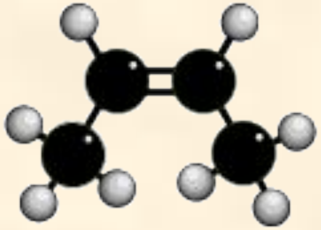
GEOMETRICAL ISOMERISM

Isomerism in butene

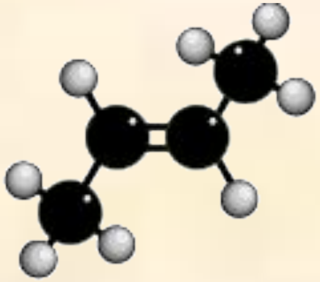
There are 3 structural isomers of C_4H_8 that are alkenes*. Of these ONLY ONE exhibits geometrical isomerism.



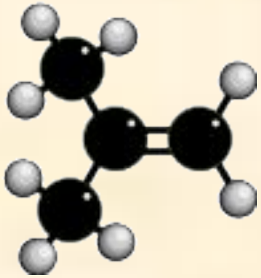
but-1-ene



cis but-2-ene
(Z) but-2-ene



trans but-2-ene
(E) but-2-ene



2-methylpropene

* YOU CAN GET ALKANES WITH FORMULA C_4H_8 IF THE CARBON ATOMS ARE IN A RING

PHYSICAL PROPERTIES OF ALKENES

Boiling point trends are similar to those shown in alkanes
increases as they get more carbon atoms in their formula
more atoms = greater induced dipole-dipole interactions
greater intermolecular force = more energy to separate molecules
greater energy required = higher boiling point
the lower members are gases at room temperature and pressure
cyclohexene C_6H_{10} is a liquid
for isomers, greater branching = lower boiling point

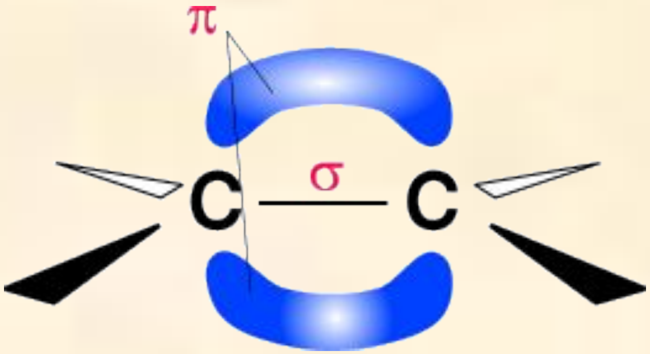
C_2H_4 (- 104 °C) C_3H_6 (- 48°C) .... C_6H_{10} (83°C)

Melting point general increase with molecular mass
the trend is not as regular as that for boiling point.

Solubility alkenes are non-polar so are immiscible (don't mix with) with water
miscible with most organic solvents.

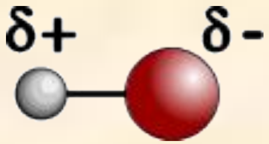
CHEMICAL PROPERTIES OF ALKENES

ELECTROPHILIC ADDITION MECHANISM



The main reaction of alkenes is addition

Because of the extra electron density in a C=C double bond, alkenes are attacked by species which ‘like’ electrons.



These species are called electrophiles; they possess a positive or partial positive charge somewhere in their structure.

Examples include... hydrogen halides
concentrated H_2SO_4

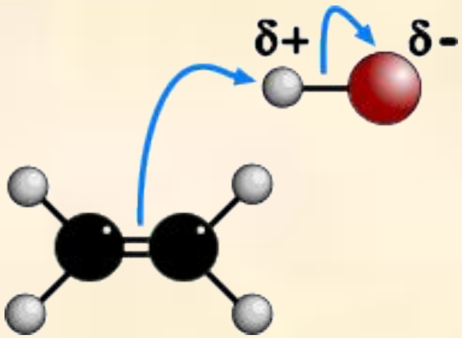
CHEMICAL PROPERTIES OF ALKENES

ELECTROPHILIC ADDITION MECHANISM

The electrophile, having some positive character, is attracted to the alkene.

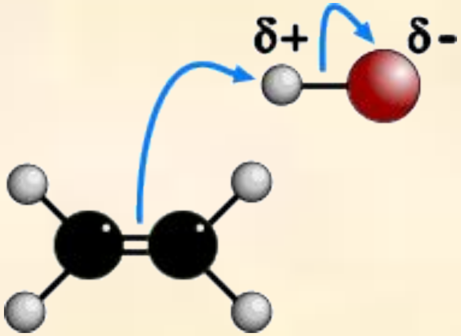
The electrons in the pi bond come out to form a bond to the positive end.

Because hydrogen can only have two electrons in its orbital, its other bond breaks heterolytically. The H attaches to one of the carbon atoms.



CHEMICAL PROPERTIES OF ALKENES

ELECTROPHILIC ADDITION MECHANISM



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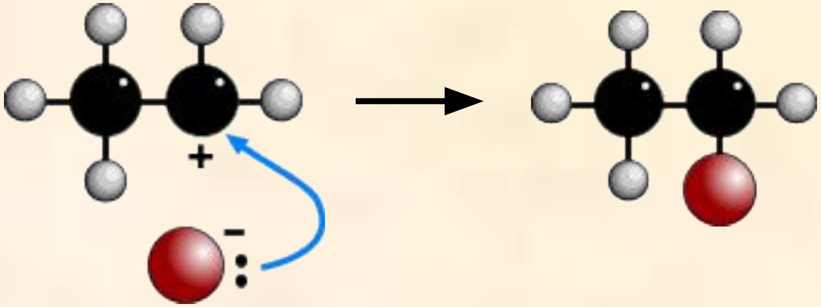


A carbocation is formed. The species that left now has a lone pair.

It acts as nucleophile and attacks the carbocation using its lone pair to form a covalent bond. Overall, there is ADDITION

CHEMICAL PROPERTIES OF ALKENES

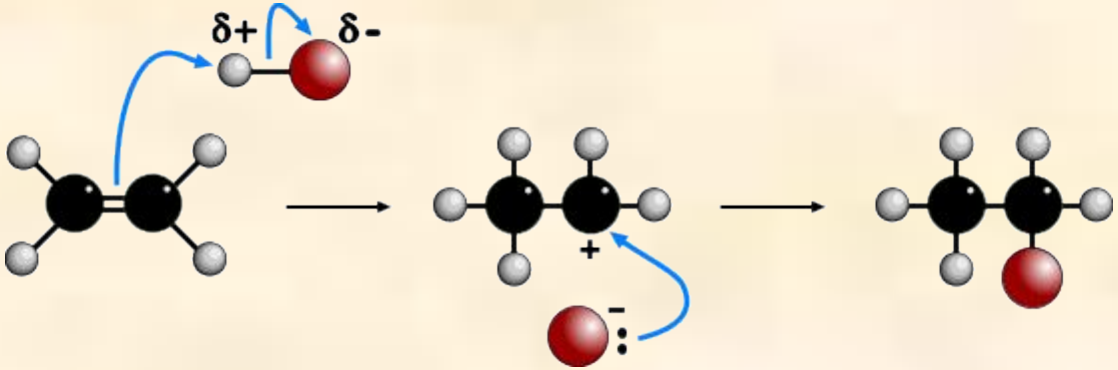
ELECTROPHILIC ADDITION OF HYDROGEN BROMIDE

Reagent **Hydrogen bromide... it is electrophilic as the H is slightly positive**

Condition **Room temperature.**

Equation $C_2H_4(g) + HBr(g) \longrightarrow C_2H_5Br(l)$ bromoethane

Mechanism



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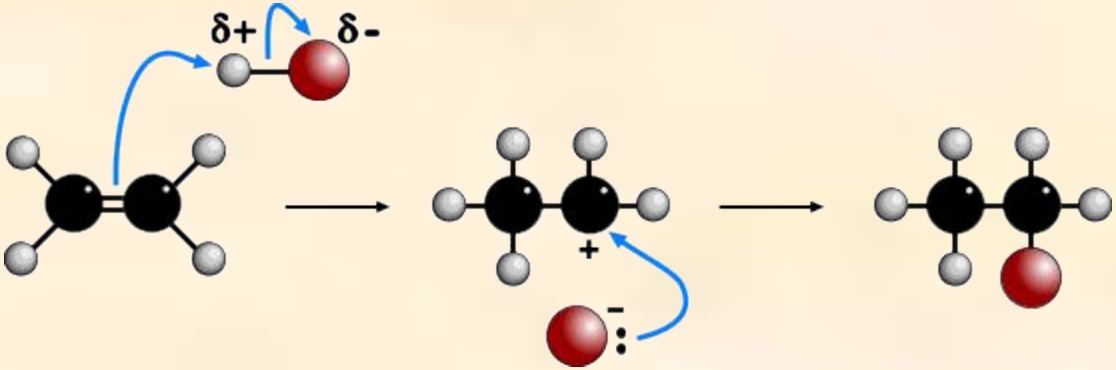

Step 1 As the HBr nears the alkene, one of the carbon-carbon bonds breaks
The pair of electrons attaches to the slightly positive H end of H-Br.
The HBr bond breaks to form a bromide ion.
A carbocation (positively charged carbon species) is formed.

CHEMICAL PROPERTIES OF ALKENES

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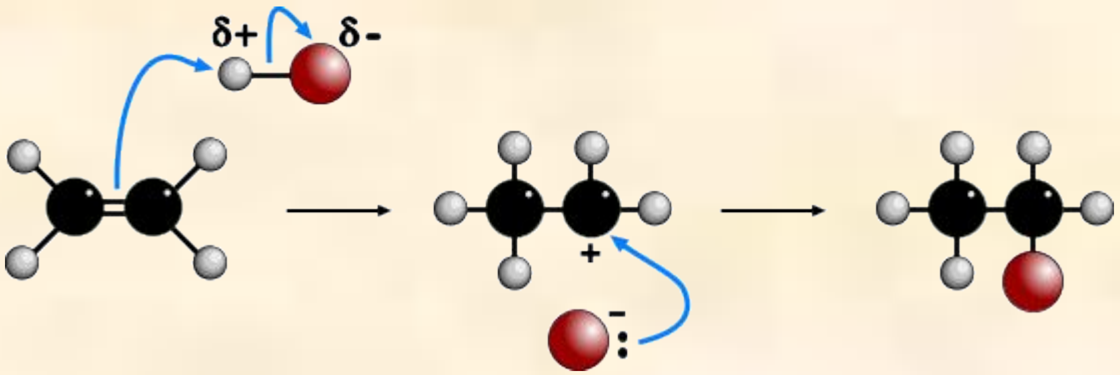

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Step 2 The bromide ion behaves as a nucleophile and attacks the carbocation.
Overall there has been addition of HBr across the double bond.

CHEMICAL PROPERTIES OF ALKENES

ELECTROPHILIC ADDITION OF HYDROGEN BROMIDE

ANIMATED MECHANISM

ELECTROPHILIC
ADDITION

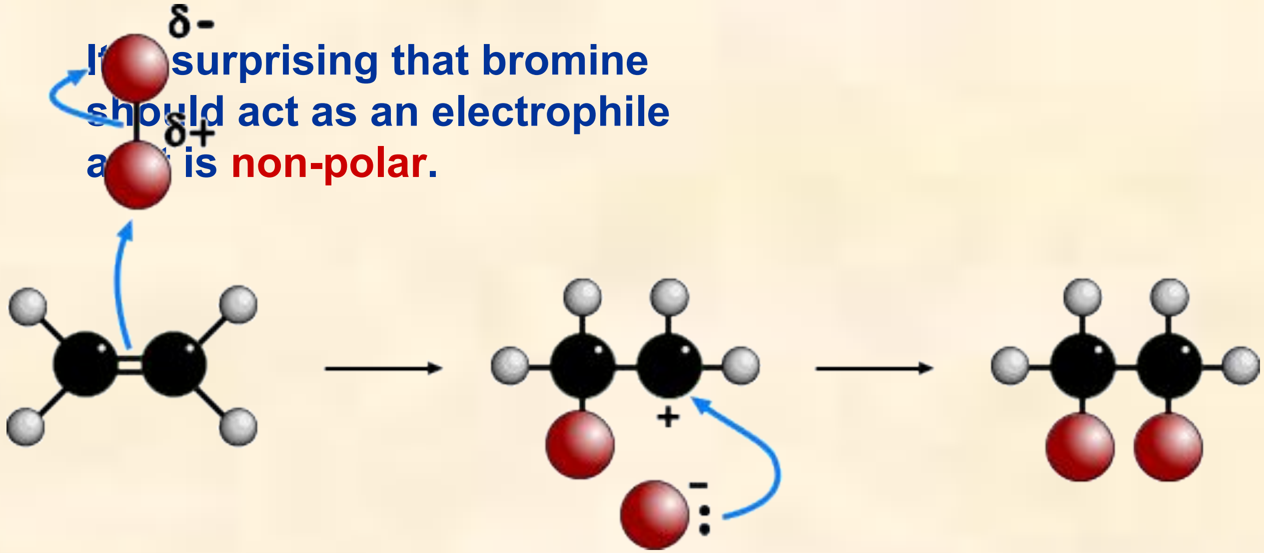
Animation repeats continuously after every 10 seconds

CHEMICAL PROPERTIES OF ALKENES

ELECTROPHILIC ADDITION OF BROMINE

Reagent	**Bromine.** (Neat liquid or dissolved in tetrachloromethane, CCl_4)
Condition	**Room temperature. No catalyst or UV light required!**
Equation	$C_2H_4(g) + Br_2(l) \longrightarrow CH_2BrCH_2Br(l)$ **1,2 - dibromoethane**

Mechanism



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

SEE NEXT SLIDE FOR AN EXPLANATION OF THE BEHAVIOUR OF BROMINE

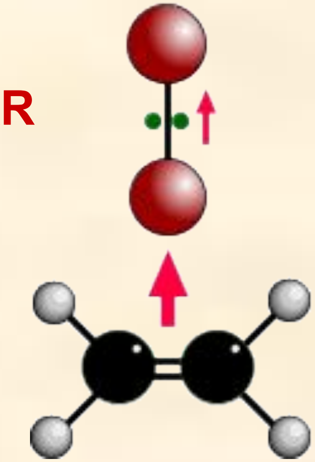
CHEMICAL PROPERTIES OF ALKENES

ELECTROPHILIC ADDITION OF BROMINE

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.**

NON-POLAR



AS A NON-POLAR BROMINE MOLECULE APPROACHES AN ALKENE, ELECTRONS IN THE PI ORBITAL OF THE ALKENE REPEL THE SHARED PAIR OF ELECTRONS IN THE Br-Br BOND

CHEMICAL PROPERTIES OF ALKENES

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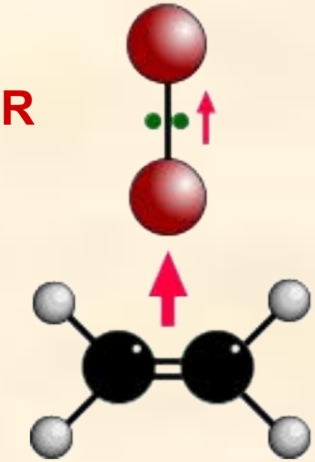
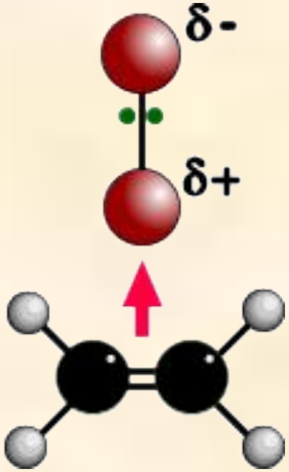




POLAR

AS A NON-POLAR BROMINE MOLECULE APPROACHES AN ALKENE, ELECTRONS IN THE PI ORBITAL OF THE ALKENE REPEL THE SHARED PAIR OF ELECTRONS IN THE Br-Br BOND

THE ELECTRON PAIR IS NOW NEARER ONE END SO THE BROMINE MOLECULE IS POLAR AND BECOMES ELECTROPHILIC.

CHEMICAL PROPERTIES OF ALKENES

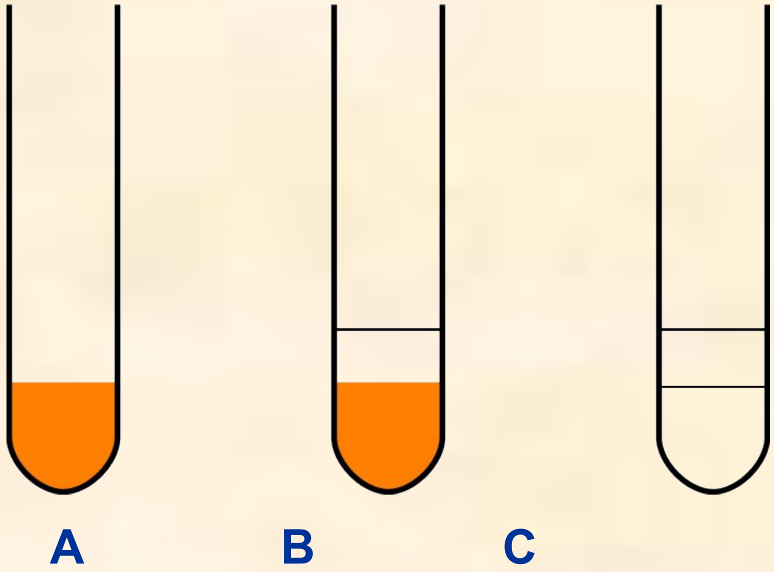
ELECTROPHILIC ADDITION OF BROMINE
TEST FOR UNSATURATION

The addition of bromine dissolved in tetrachloromethane (CCl_4) 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 C=C bond.

A **PLACE A SOLUTION OF BROMINE IN A TEST TUBE**

B **ADD THE HYDROCARBON TO BE TESTED AND SHAKE**

C **IF THE BROWN COLOUR DISAPPEARS THEN THE HYDROCARBON IS AN ALKENE**



Because the bromine adds to the alkene, it no longer exists as molecular bromine and the typical red-brown colour disappears

CHEMICAL PROPERTIES OF ALKENES

ELECTROPHILIC ADDITION OF SULPHURIC ACID

Reagent	Concentrated sulphuric acid (85%)
Conditions	0°C
Equation	$C_2H_4(g) + H_2SO_4(conc) \longrightarrow C_2H_5OSO_2OH(aq)$ ethyl hydrogensulphate

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

$$C_2H_5OSO_2OH(aq) + H_2O(l) \longrightarrow H_2SO_4(aq) + C_2H_5OH(l)$$

Industrial method(s) Phosphoric acid (H_3PO_4) and steam are used - see later

Ethanol can also be made by FERMENTATION

ADDITION TO UNSYMMETRICAL ALKENES

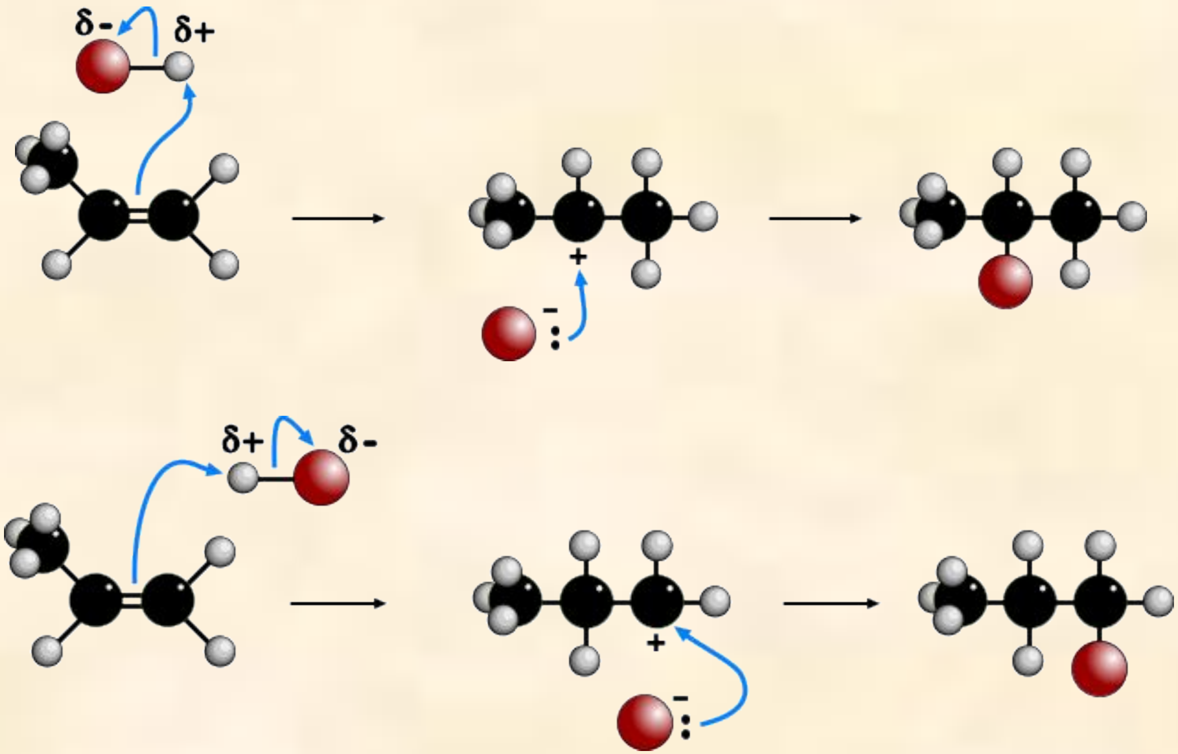
ELECTROPHILIC ADDITION TO PROPENE

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
- the problem doesn't arise in ethene because it is symmetrical.

Mechanism

Two possibilities



ADDITION TO UNSYMMETRICAL ALKENES

MARKOWNIKOFF’S RULE

A 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 modern version uses carbocation stability as a criterion for predicting the products.

In the electrophilic addition to alkenes the major product is formed via the more stable carbocation (carbonium ion)

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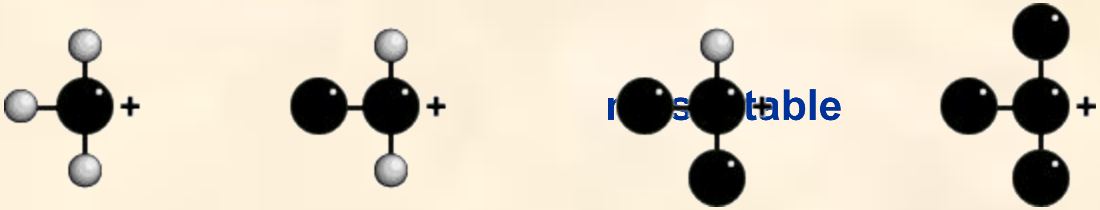
Carbocation Stability

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

least stable



most stable

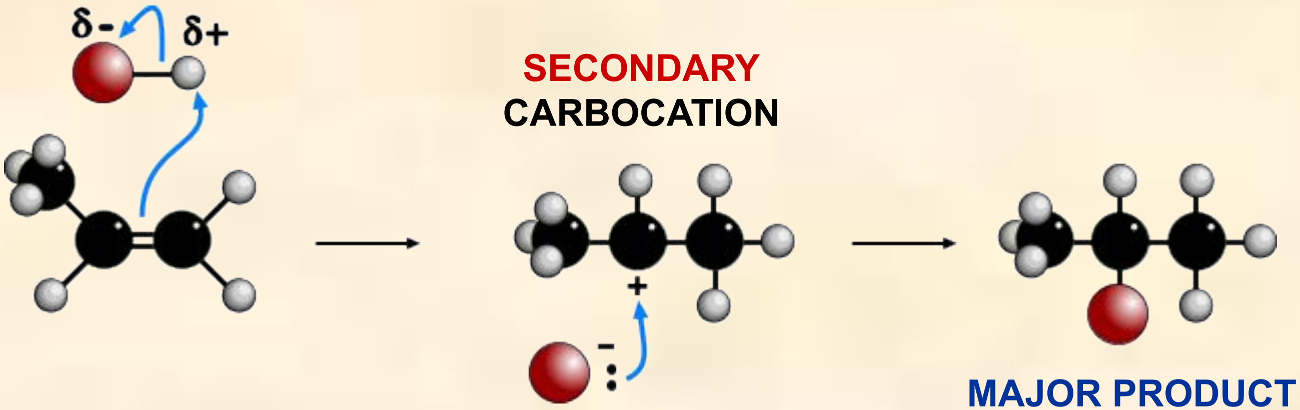
methyl < primary (1°) < secondary (2°) < tertiary (3°)

ADDITION TO UNSYMMETRICAL ALKENES

MARKOWNIKOFF’S RULE

In the addition to propene, 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 this way.

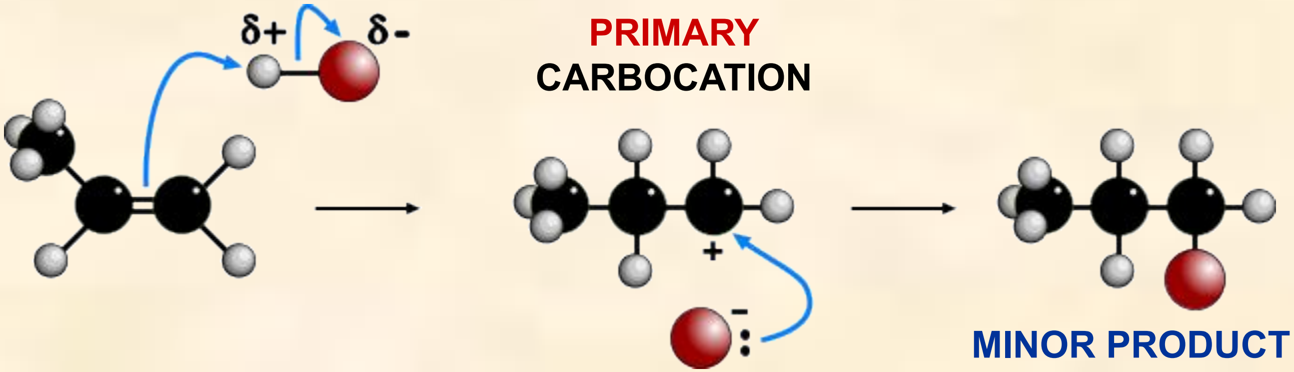
PATH A



SECONDARY CARBOCATION

MAJOR PRODUCT

PATH B



PRIMARY CARBOCATION

MINOR PRODUCT

ADDITION TO UNSYMMETRICAL ALKENES

ELECTROPHILIC ADDITION TO PROPENE

ANIMATED MECHANISM

ELECTROPHILIC
ADDITION TO
PROPENE

Animation repeats continuously after every 10 seconds

CHEMICAL PROPERTIES OF ALKENES

OTHER ADDITION REACTIONS

DIRECT HYDRATION

Reagent	steam
Conditions	high pressure
Catalyst	phosphoric acid
Product	alcohol
Equation	$C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g)$ ethanol

Use ethanol manufacture

Comments It may be surprising that water needs such vigorous conditions to react with ethene. It is a highly polar molecule and you would expect it to be a good electrophile.

However, the O-H bonds are very strong so require a great deal of energy to be broken. This necessitates the need for a catalyst.

CHEMICAL PROPERTIES OF ALKENES

OTHER ADDITION REACTIONS

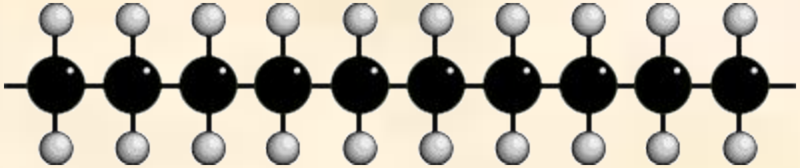
HYDROGENATION

Reagent	**hydrogen**
Conditions	**nickel catalyst** - finely divided
Product	**alkanes**
Equation	$C_2H_4(g) \quad + \quad H_2(g) \longrightarrow C_2H_6(g)$ **ethane**
Use	**margarine manufacture**

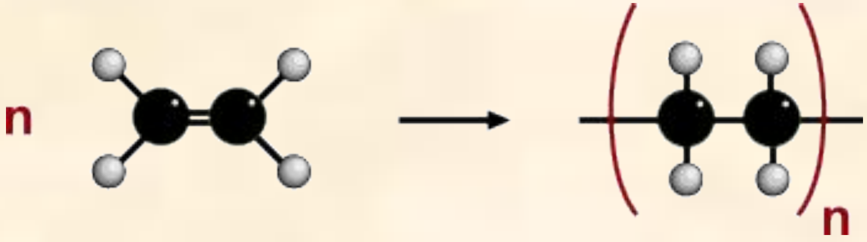
POLYMERISATION OF ALKENES

ADDITION 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



n represents a large number

ethene
MONOMER

poly(ethene)
POLYMER

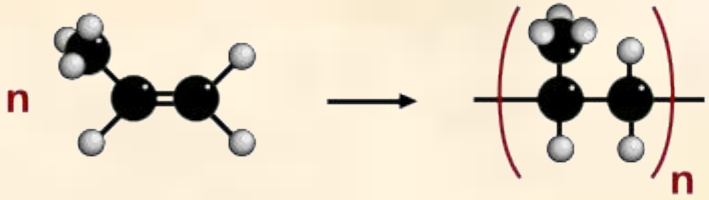
POLYMERISATION OF ALKENES

EXAMPLES OF ADDITION POLYMERISATION

ETHENE

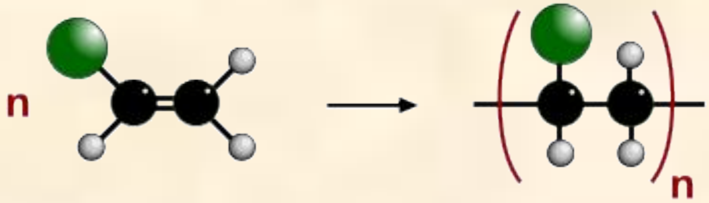
POLY(ETHENE)

PROPENE



POLY(PROPENE)

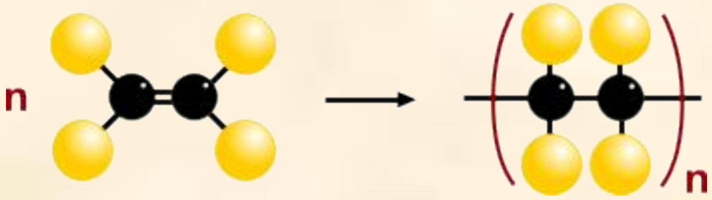
CHLOROETHENE



POLY(CHLOROETHENE)

POLYVINYLCHLORIDE PVC

TETRAFLUOROETHENE



POLY(TETRAFLUOROETHENE)

PTFE “Teflon”

POLYMERISATION OF ALKENES

ADDITION POLYMERISATION

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 whichinitiate 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 varied by changing the reaction conditions (pressure, temperature etc).

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

POLYMERISATION OF ALKENES

PROBLEMS WITH POLYMERS

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 from burning chlorinated polymers**
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.**

PREPARATION OF ALKENES

FROM HALOGENOALKANES - Elimination

Reagent	**Alcoholic sodium (or potassium) hydroxide**
Conditions	**Reflux in alcoholic solution**
Product	**Alkene**
Mechanism	**Elimination**
Equation	$C_3H_7Br + NaOH(alc) \longrightarrow C_3H_6 + H_2O + NaBr$

FROM ALCOHOLS - Dehydration

Reagent	**Conc. sulphuric acid or conc. phosphoric acid** (H_3PO_4)
Conditions	**Reflux**
Product	**Alkene**
Mechanism	**Dehydration** (elimination of water)
Equation	$C_2H_5OH(l) \longrightarrow CH_2{=}CH_2(g) + H_2O(l)$

REVISION CHECK

What should you be able to do?

Recall and explain the physical properties of alkenes

Recall and explain the types of isomerism found in alkenes

Recall and explain why alkenes undergo electrophilic addition

Write balanced equations representing the reactions taking place in this section

Understand why, in some addition reactions, a mixture of isomeric products is obtained

Recall the importance of addition polymerisation, including examples

CAN YOU DO ALL OF THESE?

YES **NO**

You need to go over the relevant topic(s) again

Click on the button to return to the menu

WELL DONE!

Try some past paper questions

AN INTRODUCTION TO

THE CHEMISTRY OF ALKENES

THE END