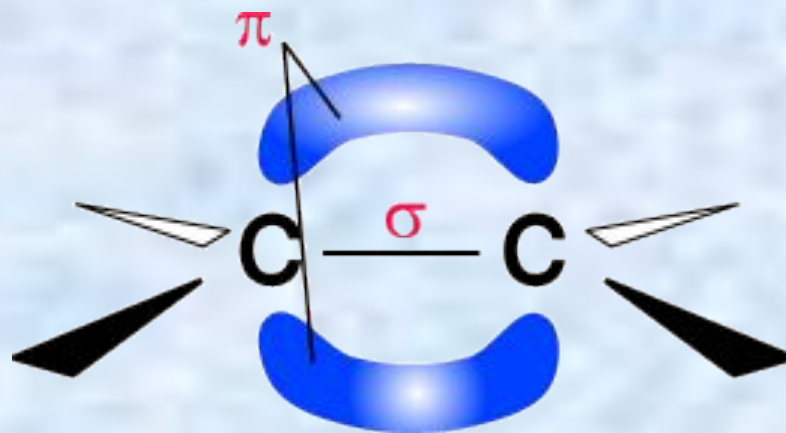


AN INTRODUCTION TO THE CHEMISTRY OF ALKENES



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

- **Structure of alkenes**
- **Nomenclature**
- **Isomerism**
- **Physical properties of alkenes**
- **Electrophilic addition reactions of alkenes**
- **Addition to unsymmetrical alkenes**
- **Other reactions**
- **Polymerisation**
- **Preparation of alkenes**
- **Revision check list**



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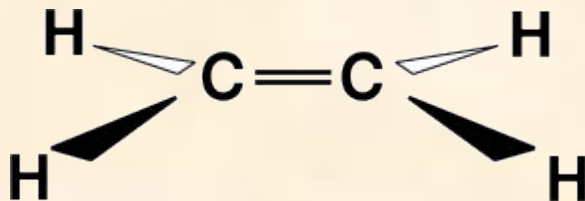
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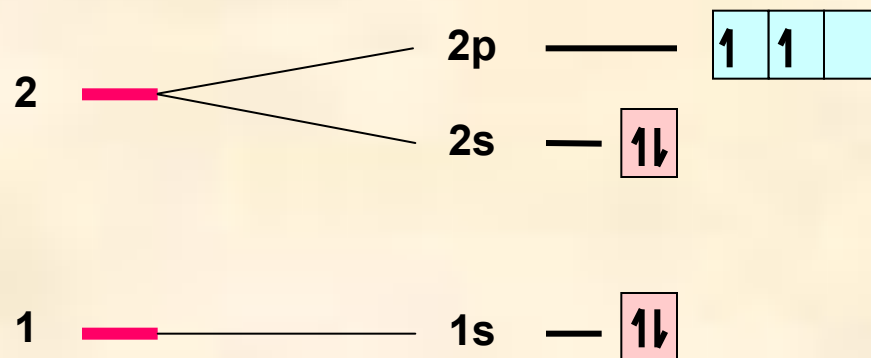
Structure spacial arrangement around the C=C is **planar**

the bond angles are **120°**



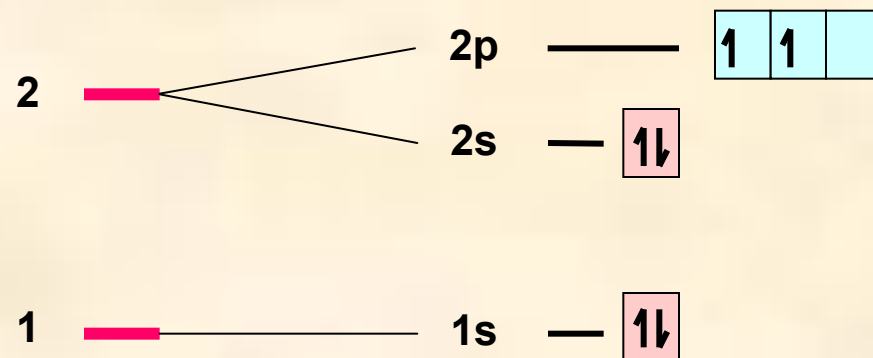
HYBRIDISATION OF ORBITALS

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

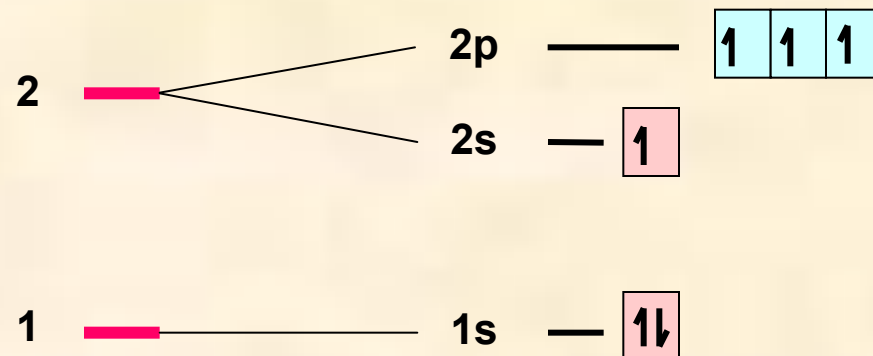


HYBRIDISATION OF ORBITALS

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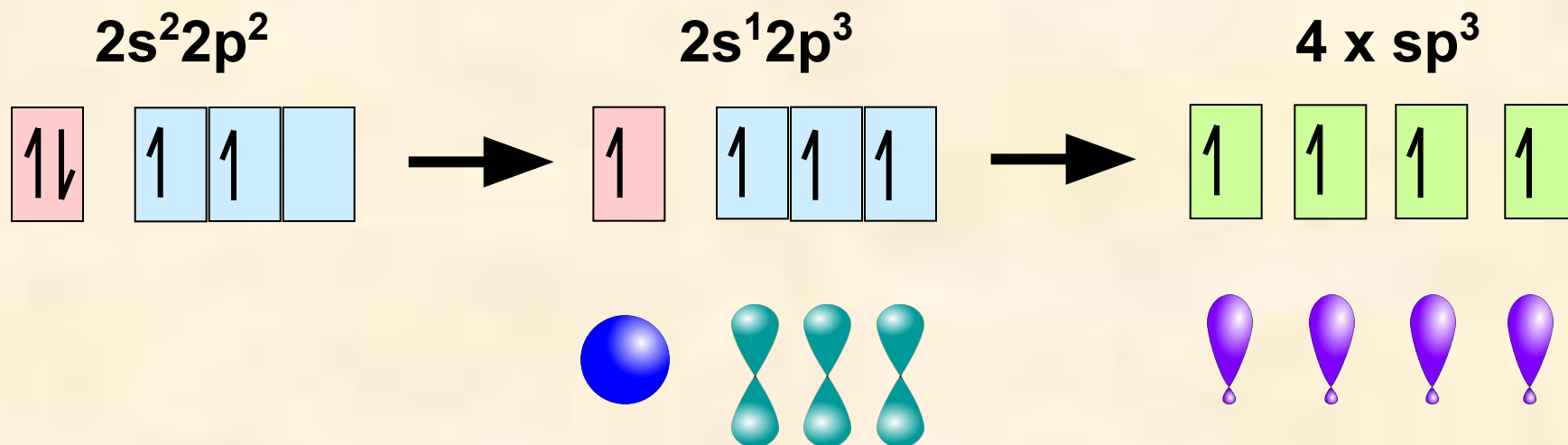
If you provide a bit of energy you can promote (lift) one of the s electrons into a p orbital. The configuration is now $1s^2 2s^1 2p^3$



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

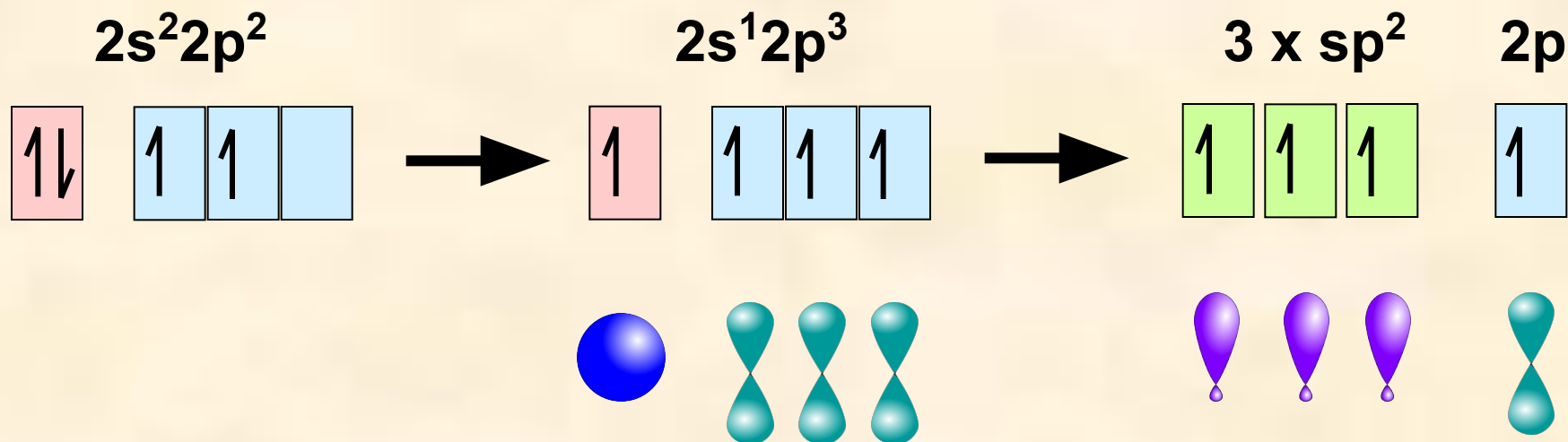
HYBRIDISATION OF ORBITALS - ALKANES

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



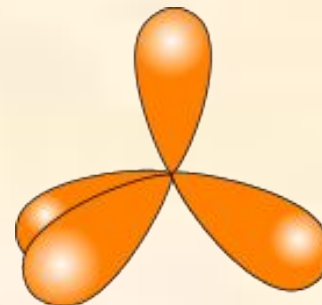
HYBRIDISATION OF ORBITALS - ALKENES

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.



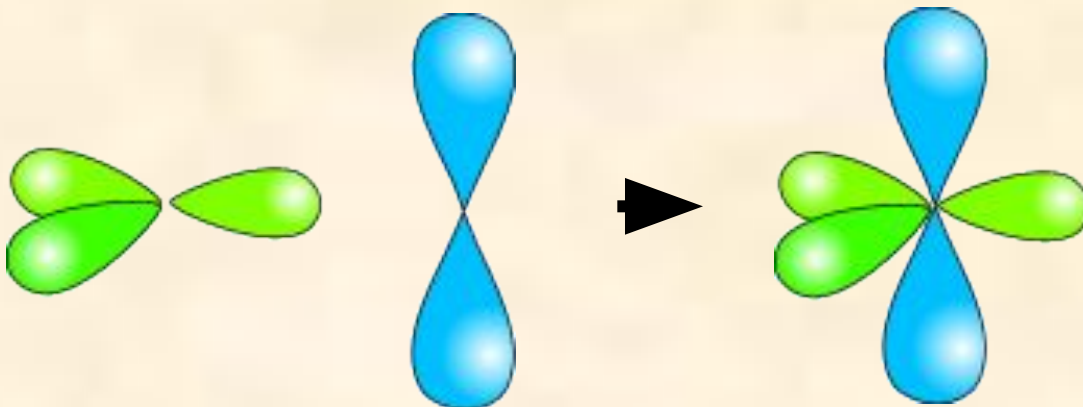
THE STRUCTURE OF ALKENES

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

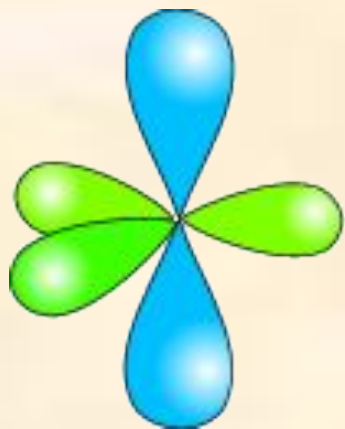


HOWEVER...

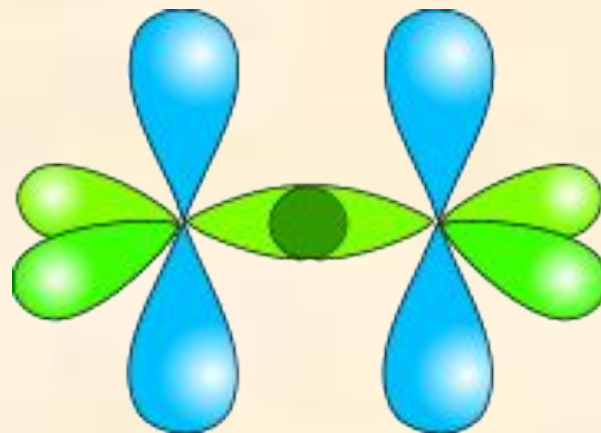
In **ALKENES**, the three sp^2 orbitals repel each other into a planar arrangement and the 2p orbital lies at right angles to them



THE STRUCTURE OF ALKENES

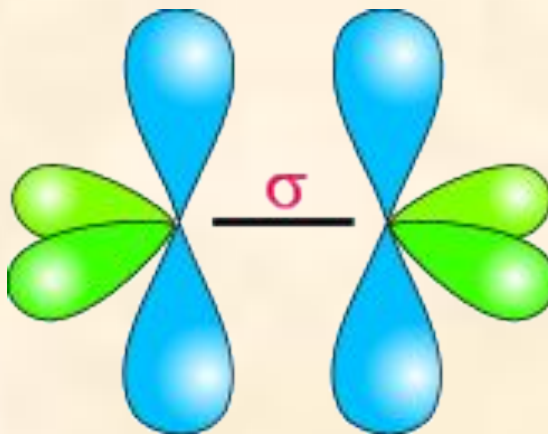


Covalent bonds are formed
by overlap of orbitals.

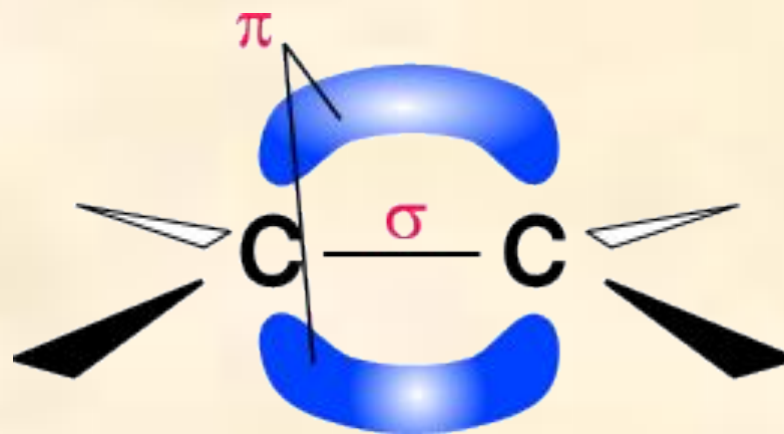
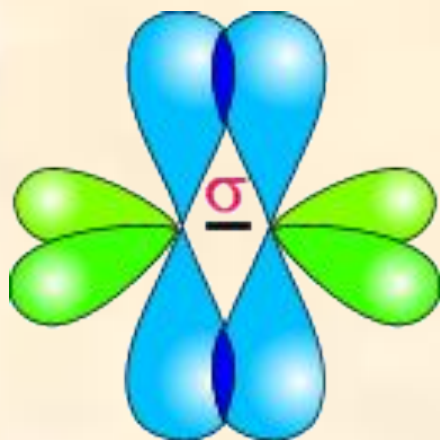


An sp^2 orbital from each carbon
overlaps to form a single C-C bond.

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



THE STRUCTURE OF ALKENES

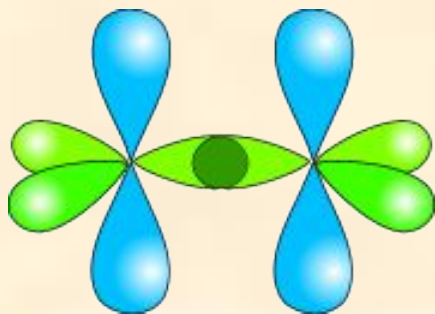


The two 2p orbitals also overlap to form a second bond. This is known as a PI (π) bond.

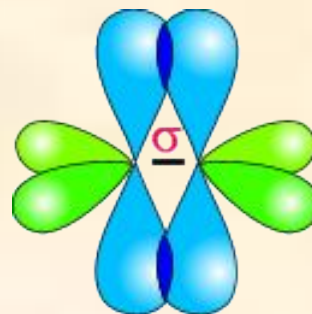
For **maximum overlap** and hence the **strongest bond**, the 2p orbitals are in line.

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

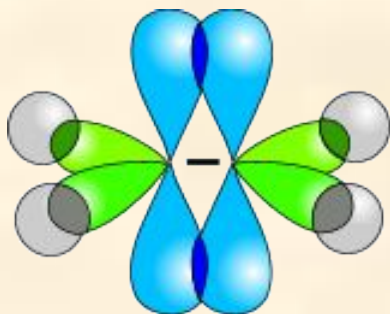
ORBITAL OVERLAP IN ETHENE - REVIEW



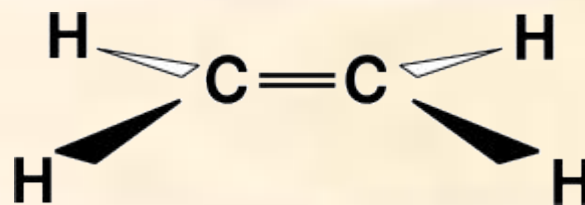
two sp^2 orbitals overlap to form a sigma bond between the two carbon atoms



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 120°

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. $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH}(\text{CH}_3) - \text{CH}_3$ is called **5-methylhex-2-ene**

ISOMERISM IN ALKENES

Two types of isomerism found in alkenes

STRUCTURAL

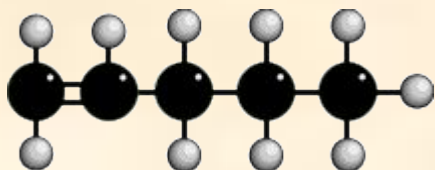
GEOMETRICAL



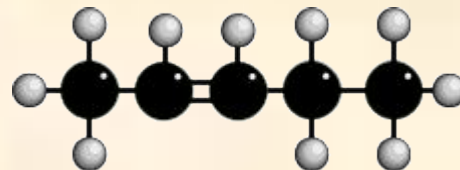
STRUCTURAL ISOMERISM IN ALKENES

Different structures are possible due to...

Different positions for the double bond

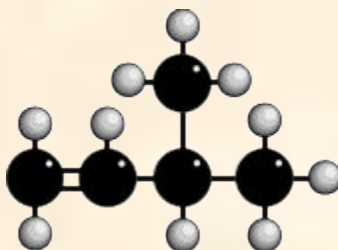


pent-1-ene



pent-2-ene

Branching

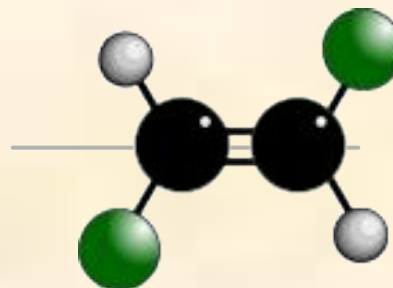
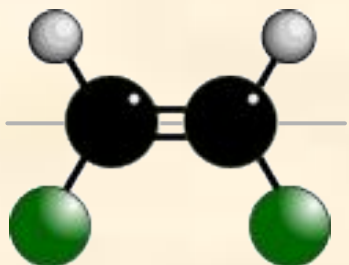


3-methylbut-1-ene

GEOMETRICAL ISOMERISM IN ALKENES

Introduction

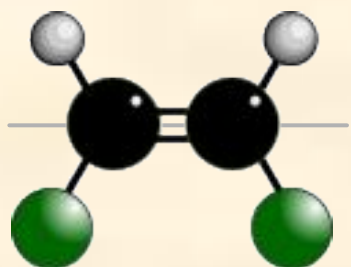
- an example of stereoisomerism
- found in some, but not all, alkenes
- occurs due to the **RESTRICTED ROTATION** OF C=C bonds
- get two forms...



GEOMETRICAL ISOMERISM IN ALKENES

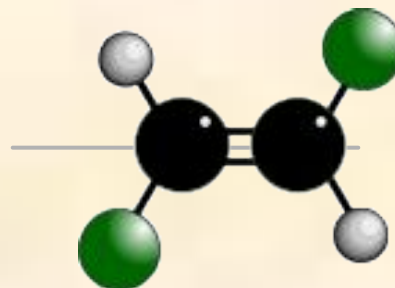
Introduction

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- get two forms...



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



GEOMETRICAL ISOMERISM IN ALKENES

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

eg $\text{C}_2\text{H}_5 > \text{CH}_3 > \text{H}$ and $\text{I} > \text{Br} > \text{Cl} > \text{F} > \text{C} > \text{H}$

GEOMETRICAL ISOMERISM IN ALKENES

E/Z or CIS-TRANS

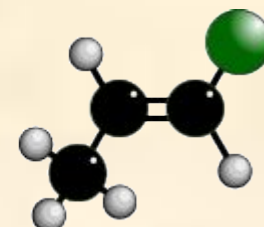
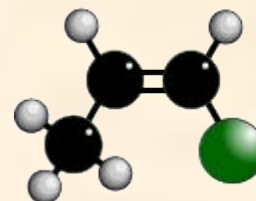
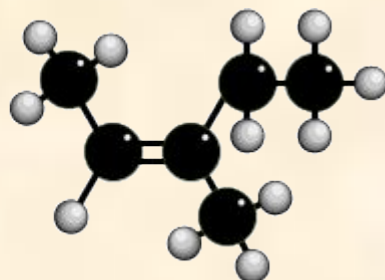
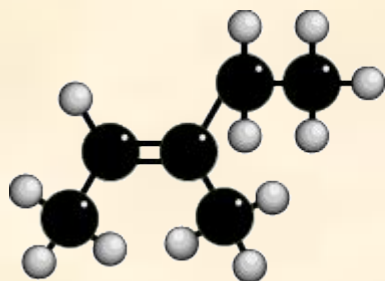
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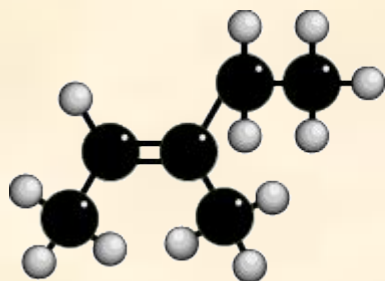
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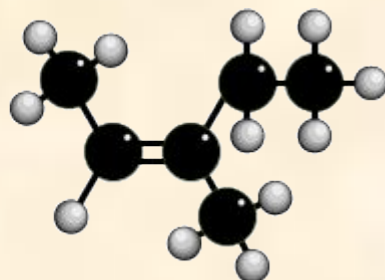
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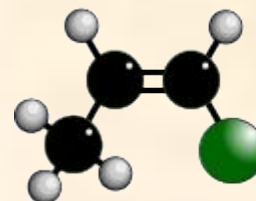
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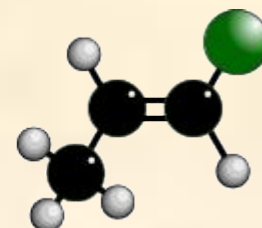
E



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



GEOMETRICAL ISOMERISM IN ALKENES

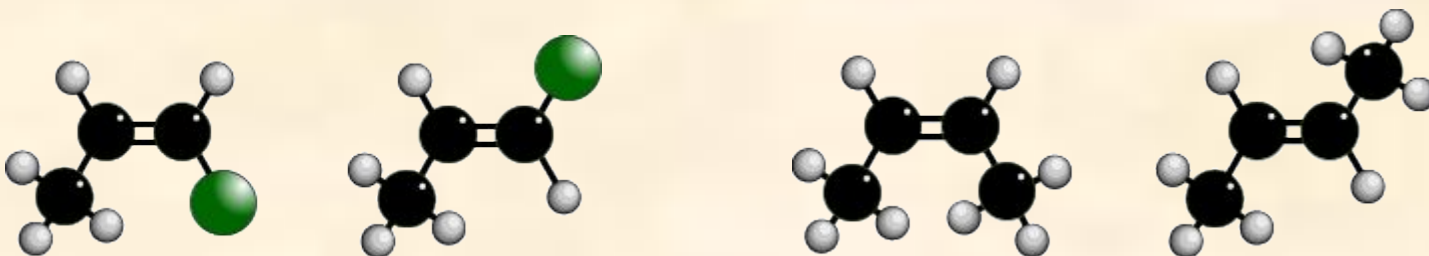
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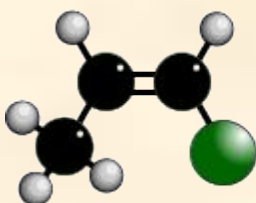
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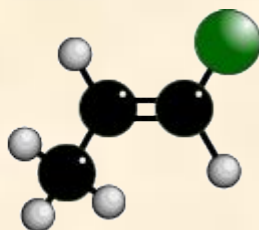
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cis non-hydrogen groups / atoms on the
SAME side of C=C bond

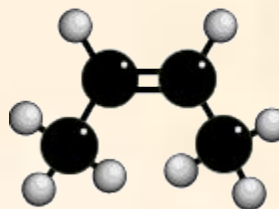
trans non-hydrogen groups / atoms on
OPPOSITE sides of C=C bond



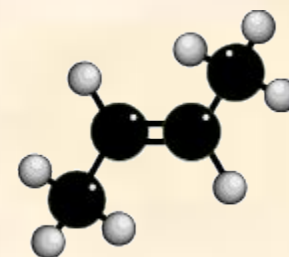
cis



trans



cis

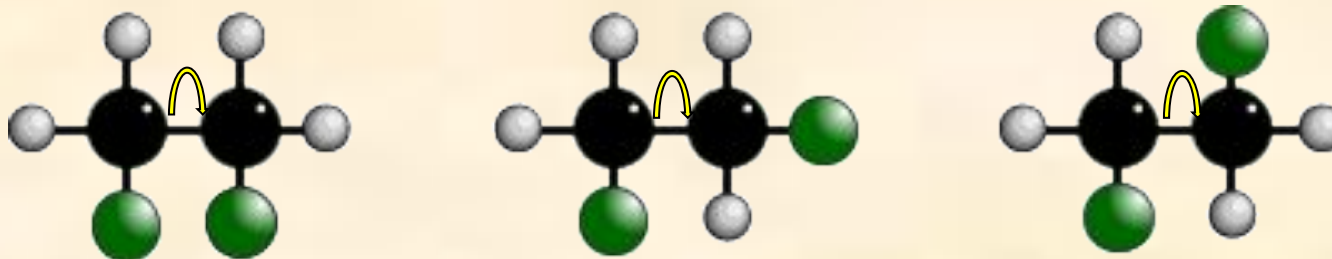


trans

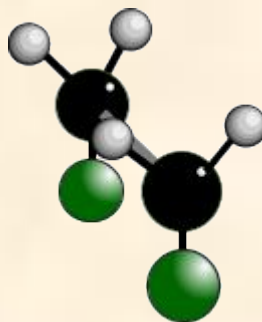
GEOMETRICAL ISOMERISM

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

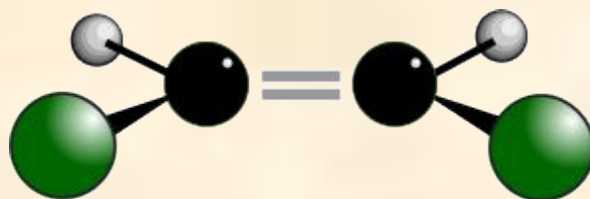


Animation doesn't
work in old
versions of
Powerpoint

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.



Animation doesn't
work in old
versions of
Powerpoint

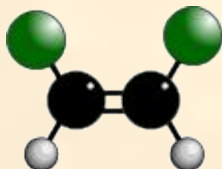
This produces **two possibilities**. The two structures cannot interchange easily so the atoms in the two molecules **occupy different positions in space**.



GEOMETRICAL ISOMERISM

How to tell if it exists

Two **different**
atoms/group
s attached

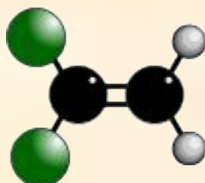


Two **different**
atoms/group
s attached



GEOMETRICAL ISOMERISM

Two **similar**
atoms/group
s attached

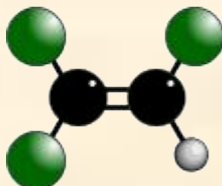


Two **similar**
atoms/group
s attached



Once you get two similar
atoms/groups attached to
one end of a C=C, you
cannot have geometrical
isomerism

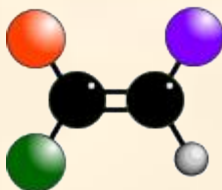
Two **similar**
atoms/group
s attached



Two **different**
atoms/group
s attached



Two **different**
atoms/group
s attached



Two **different**
atoms/group
s attached

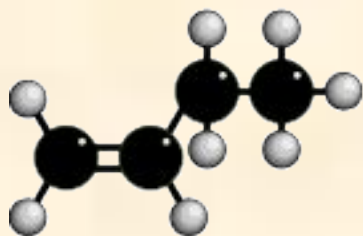


GEOMETRICAL ISOMERISM

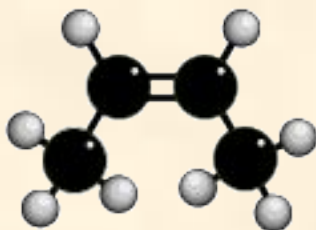
GEOMETRICAL ISOMERISM

Isomerism in butene

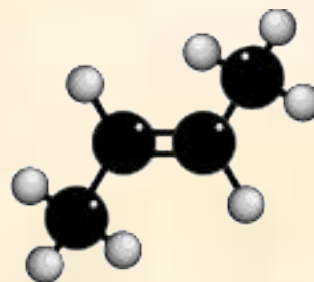
There are 3 structural isomers of C_4H_8 that are alkenes*. Of these ONLY ONE exhibits geometrical isomerism.



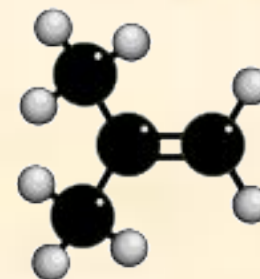
but-1-ene



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



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

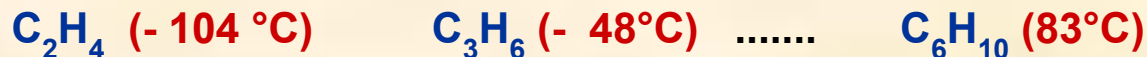


2-methylpropene

* 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



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

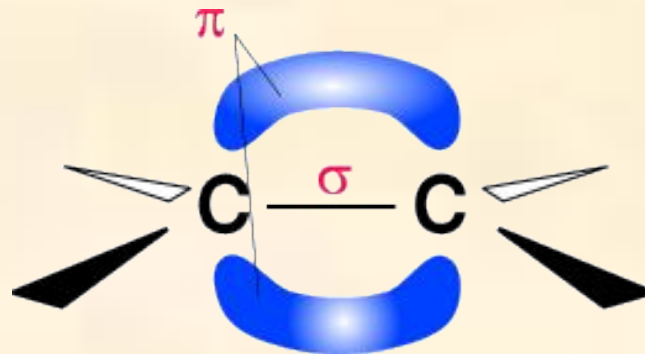
Solubility alkenes are **non-polar** so are immiscible (don't mix with) with water
miscible with most organic solvents.

CHEMICAL PROPERTIES OF ALKENES

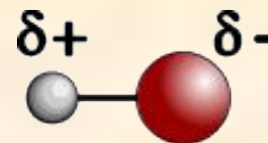
ELECTROPHILIC ADDITION MECHANISM

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

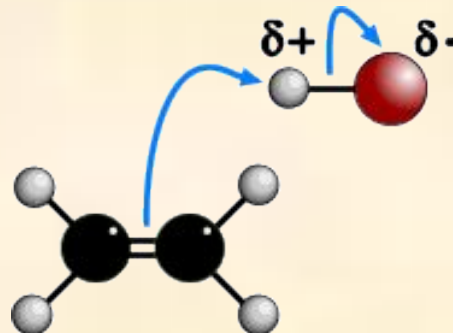
CHEMICAL PROPERTIES OF ALKENES

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

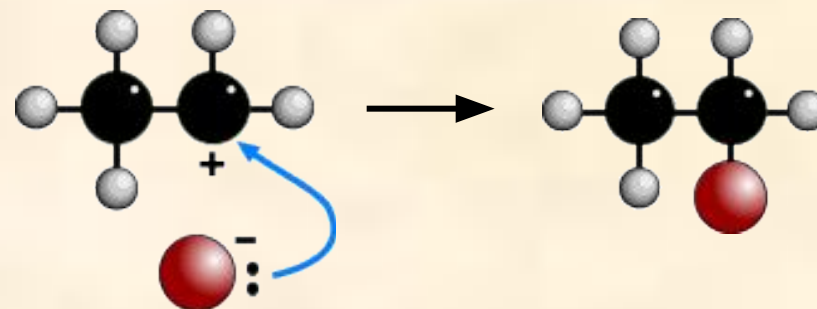
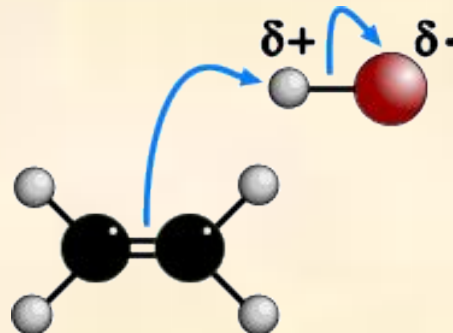
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A **carbocation** is formed. The species that left now has a lone pair.

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

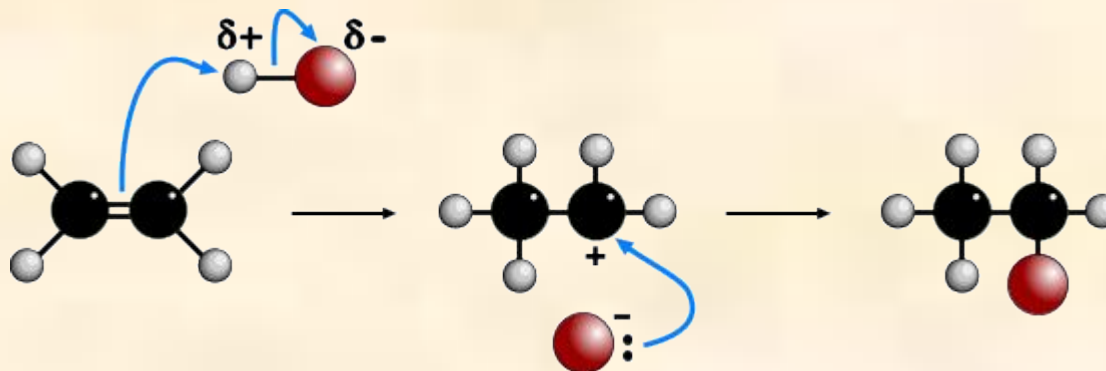
Reagent
Condition

Hydrogen bromide... it is electrophilic as the H is slightly positive
Room temperature.

Equation



Mechanism



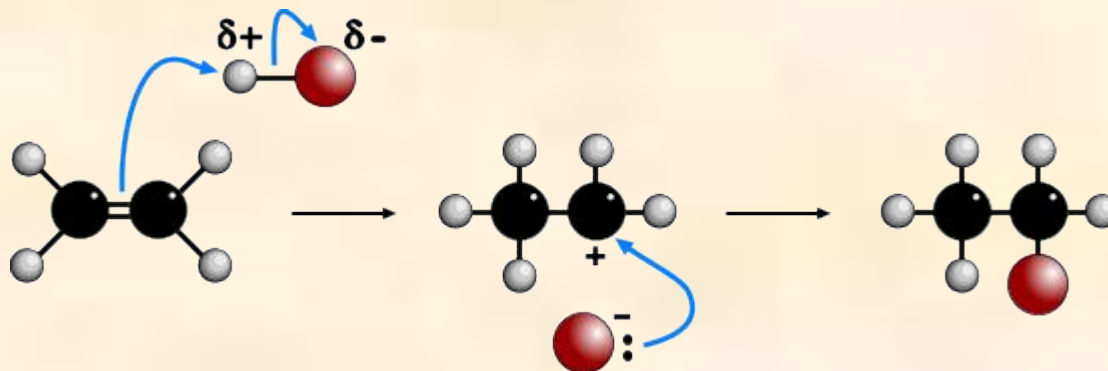
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Mechanism



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.

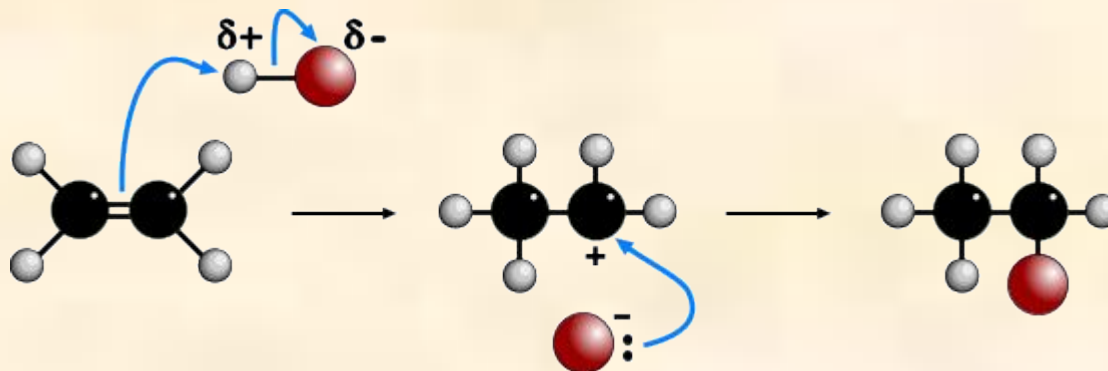
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Step 2 The bromide ion behaves as a nucleophile and attacks the carbocation. Overall there has been addition of HBr across the double bond.

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

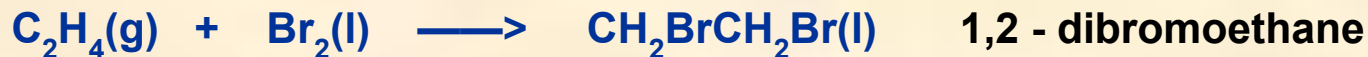
Reagent

Bromine. (Neat liquid or dissolved in tetrachloromethane, CCl_4)

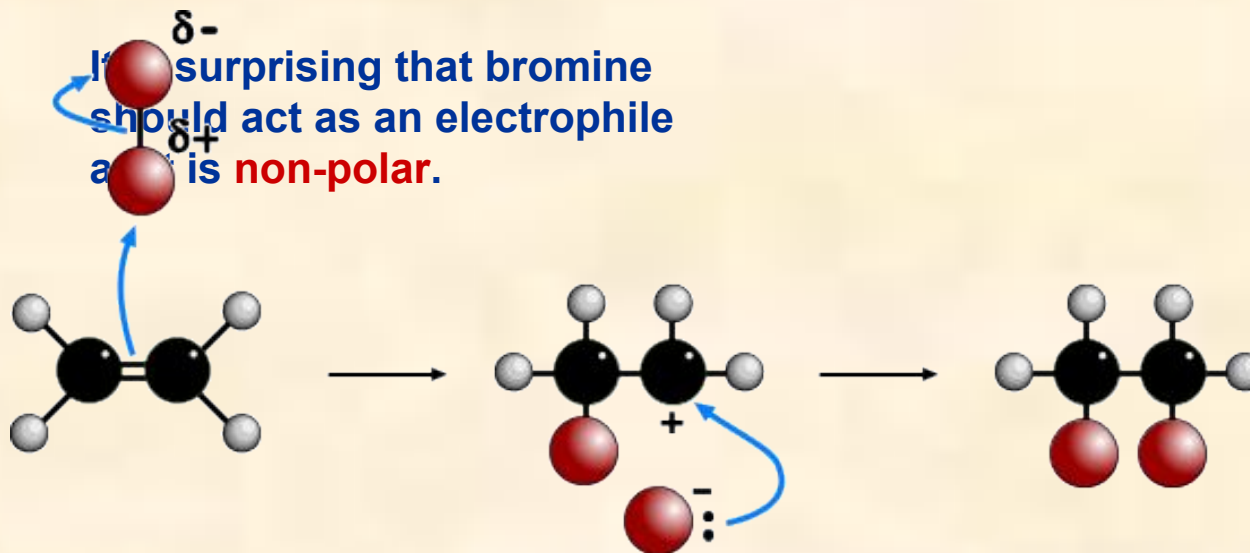
Condition

Room temperature. No catalyst or UV light required!

Equation



Mechanism



SEE NEXT SLIDE FOR AN EXPLANATION OF THE BEHAVIOUR OF BROMINE

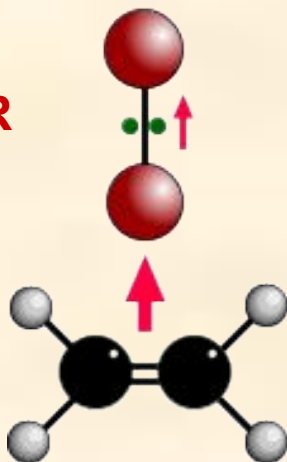
CHEMICAL PROPERTIES OF ALKENES

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

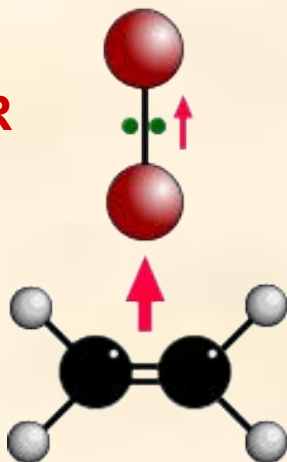
CHEMICAL PROPERTIES OF ALKENES

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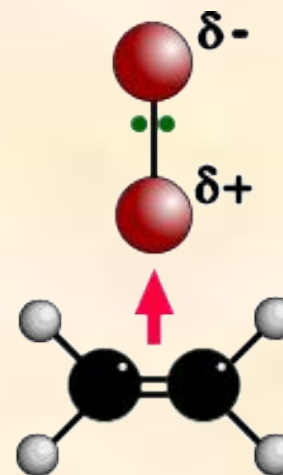
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POLAR



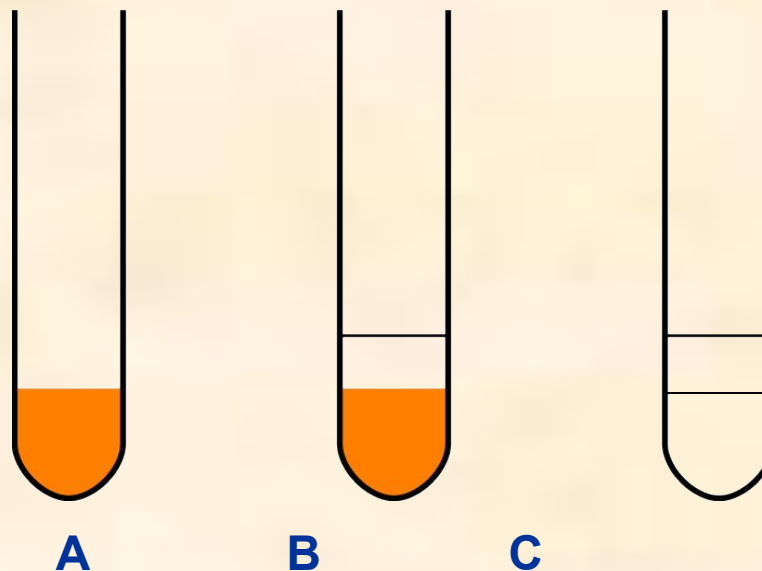
THE ELECTRON PAIR IS NOW NEARER ONE END SO THE BROMINE MOLECULE IS POLAR AND BECOMES ELECTROPHILIC.

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 $\text{C}=\text{C}$ 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
$$\text{C}_2\text{H}_4(\text{g}) + \text{H}_2\text{SO}_4(\text{conc}) \longrightarrow \text{C}_2\text{H}_5\text{OSO}_2\text{OH}(\text{aq})$$

ethyl hydrogensulphate

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



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

Ethanol can also be made by FERMENTATION

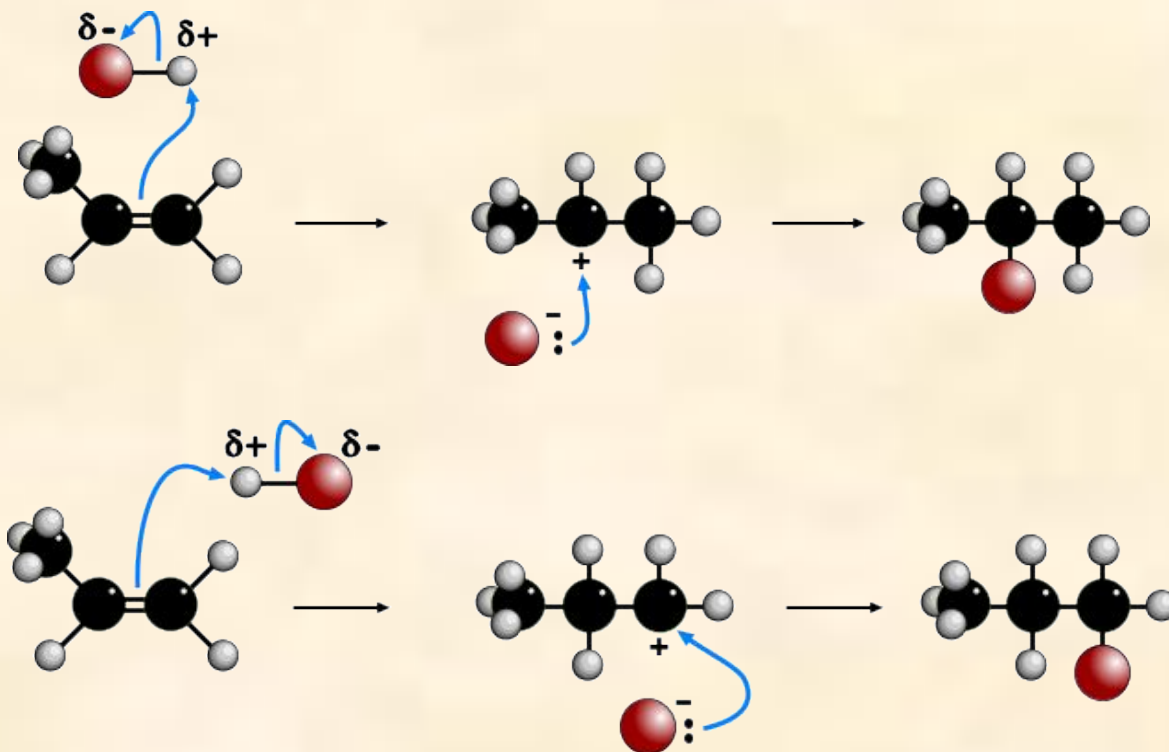
ADDITION TO UNSYMMETRICAL ALKENES

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)



ADDITION TO UNSYMMETRICAL ALKENES

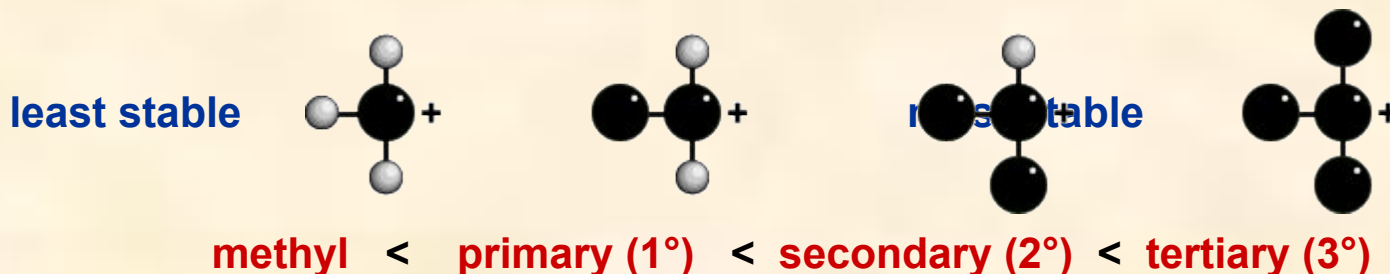
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Carbocation Stability

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.

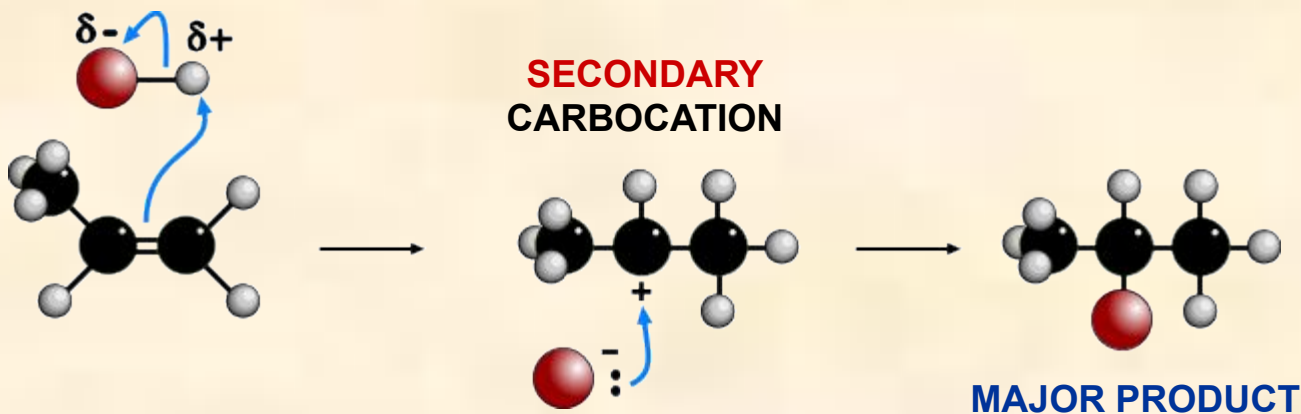


ADDITION TO UNSYMMETRICAL ALKENES

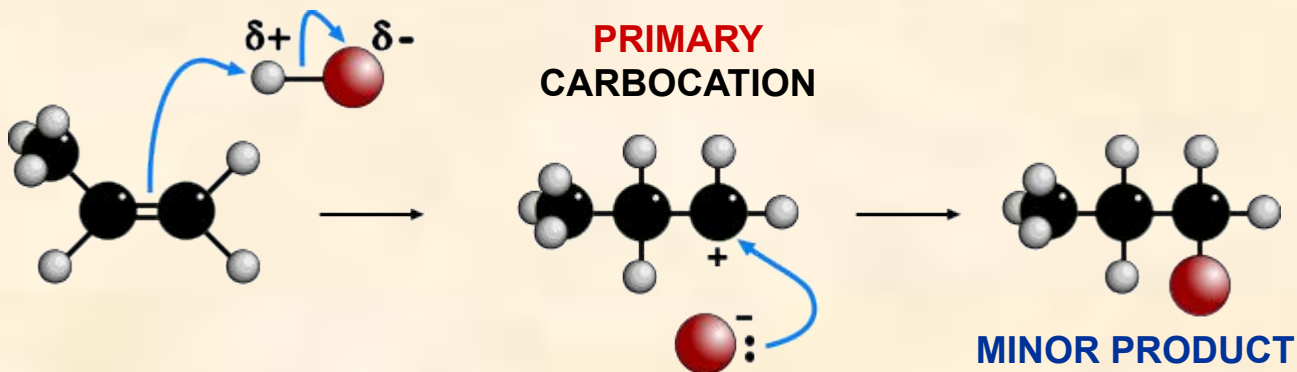
MARKOWNIKOFF'S RULE

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



PATH B



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 $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{C}_2\text{H}_5\text{OH}(\text{g})$ ethanol

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

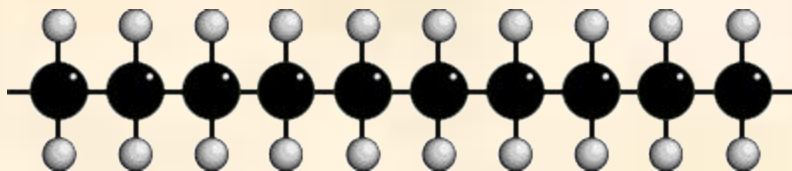
Equation $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_6(\text{g})$ ethane

Use margarine manufacture

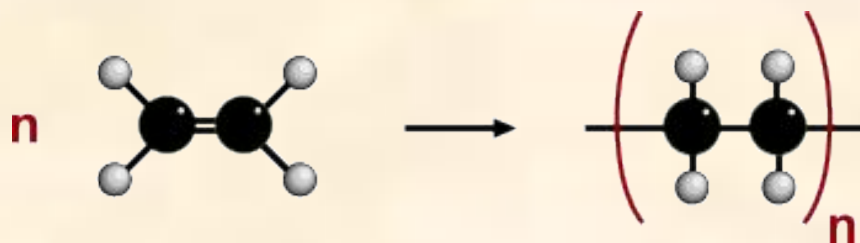
POLYMERISATION OF ALKENES

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

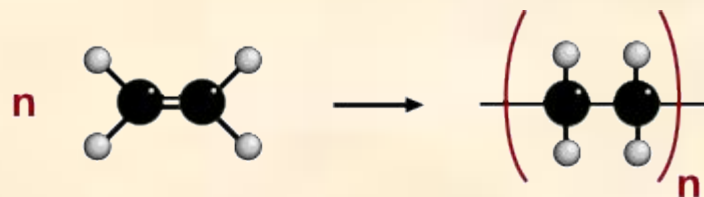
ethene
MONOMER

poly(ethene)
POLYMER

POLYMERISATION OF ALKENES

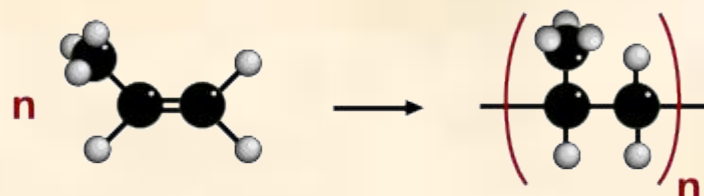
EXAMPLES OF ADDITION POLYMERISATION

ETHENE



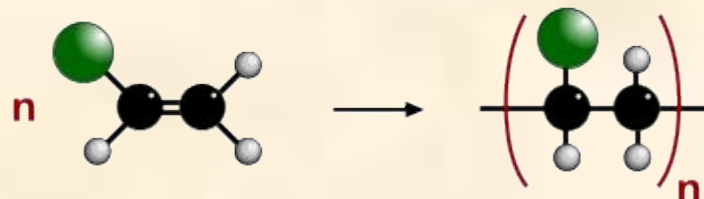
POLY(ETHENE)

PROPENE



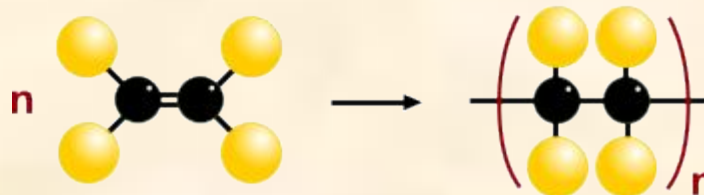
POLY(PROPENE)

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 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 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 $\text{C}_3\text{H}_7\text{Br} + \text{NaOH(alc)} \longrightarrow \text{C}_3\text{H}_6 + \text{H}_2\text{O} + \text{NaBr}$

FROM ALCOHOLS - Dehydration

Reagent Conc. sulphuric acid or conc. phosphoric acid (H_3PO_4)

Conditions Reflux

Product Alkene

Mechanism Dehydration (elimination of water)

Equation $\text{C}_2\text{H}_5\text{OH(l)} \longrightarrow \text{CH}_2=\text{CH}_2\text{(g)} + \text{H}_2\text{O(l)}$

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

