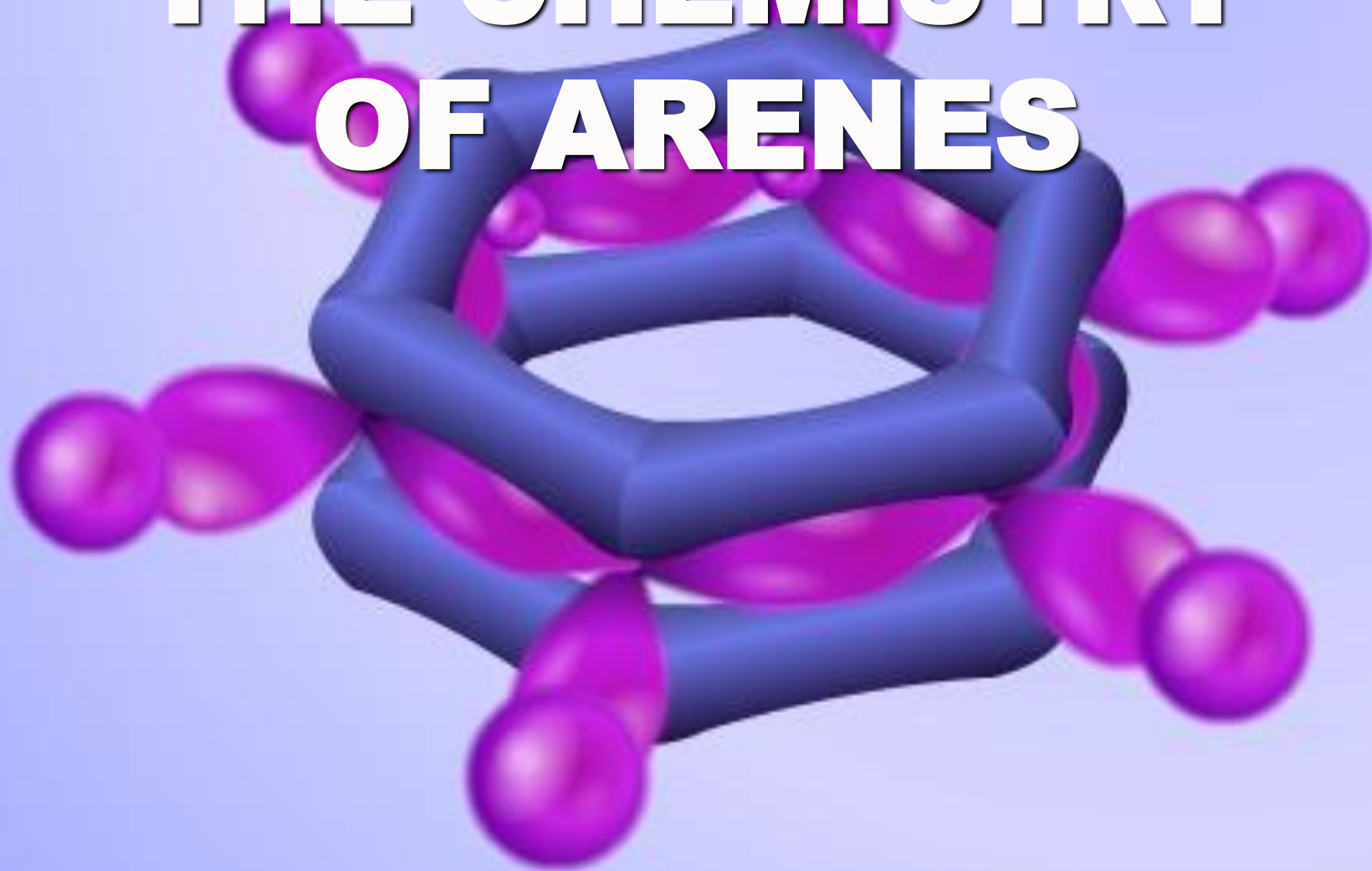


THE CHEMISTRY OF ARENES



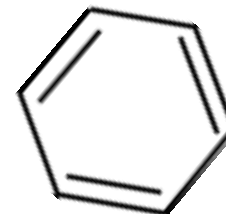
STRUCTURE OF BENZENE

Primary analysis revealed benzene had...

- an **empirical formula of CH** and
- a **molecular mass of 78**
- a **formula of C₆H₆**

Kekulé suggested that benzene was...

PLANAR
CYCLIC and
HAD ALTERNATING DOUBLE AND SINGLE BONDS

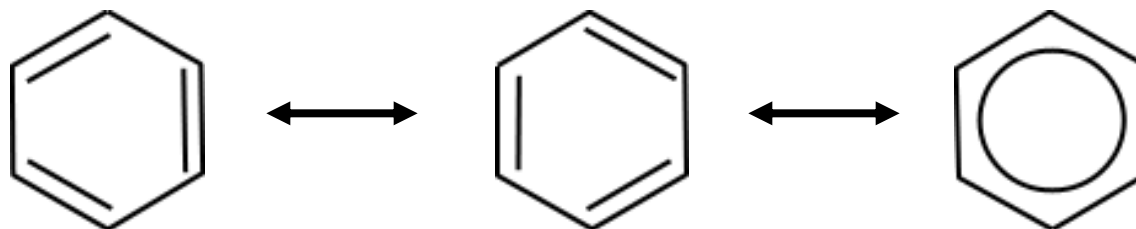


STRUCTURE OF BENZENE

HOWEVER...

- it did not readily undergo electrophilic addition - no true C=C bond
- only one 1,2 disubstituted product existed
- all six C—C bond lengths were similar; C=C bonds are shorter than C-C
- the ring was thermodynamically more stable than expected

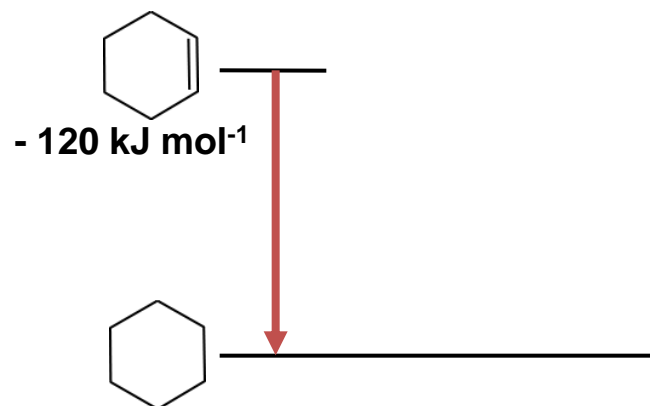
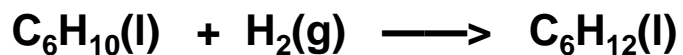
To explain the above, it was suggested that the structure oscillated between the two Kekulé forms but was represented by neither of them. It was a **RESONANCE HYBRID**.



THERMODYNAMIC EVIDENCE FOR STABILITY

When unsaturated hydrocarbons are reduced to the corresponding saturated compound, energy is released. The amount of heat liberated per mole (enthalpy of hydrogenation) can be measured.

When cyclohexene (one C=C bond) is reduced to cyclohexane, 120kJ of energy is released per mole.



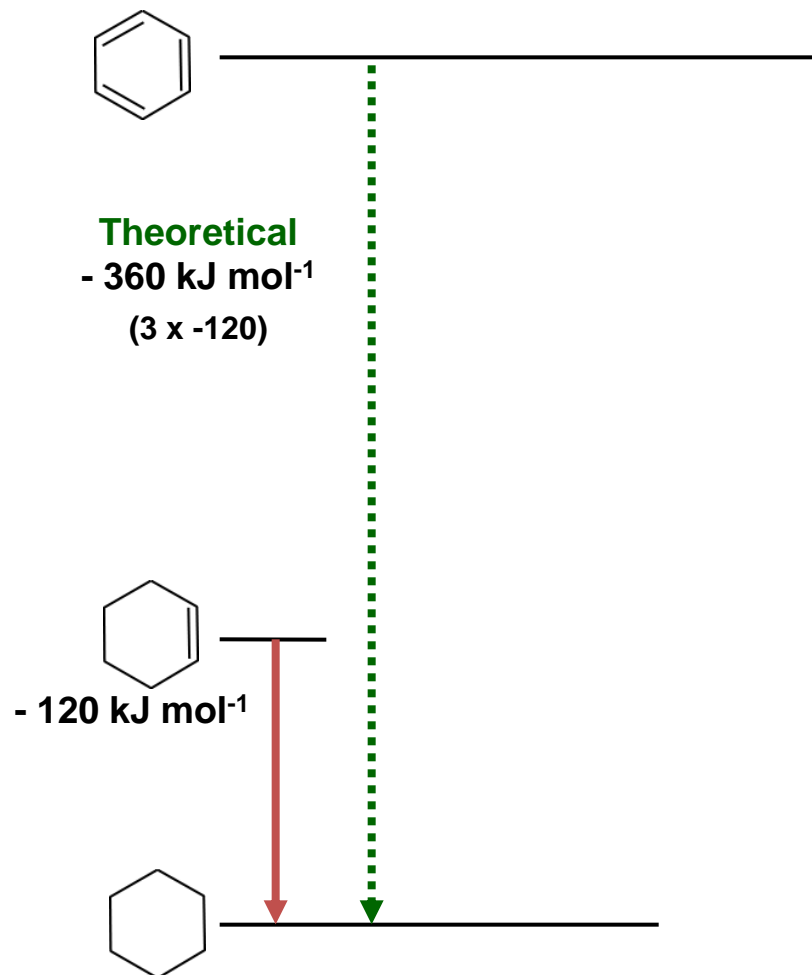
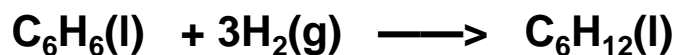
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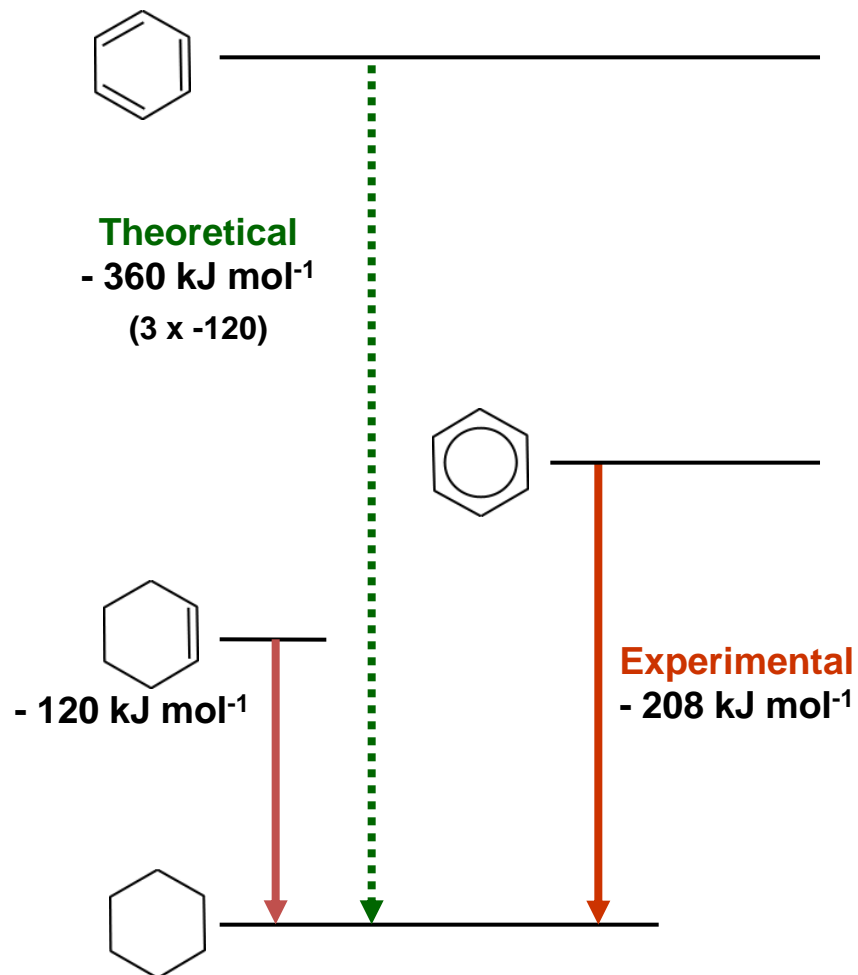
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Actual benzene releases only 208kJ per mole when reduced, putting it lower down the energy scale



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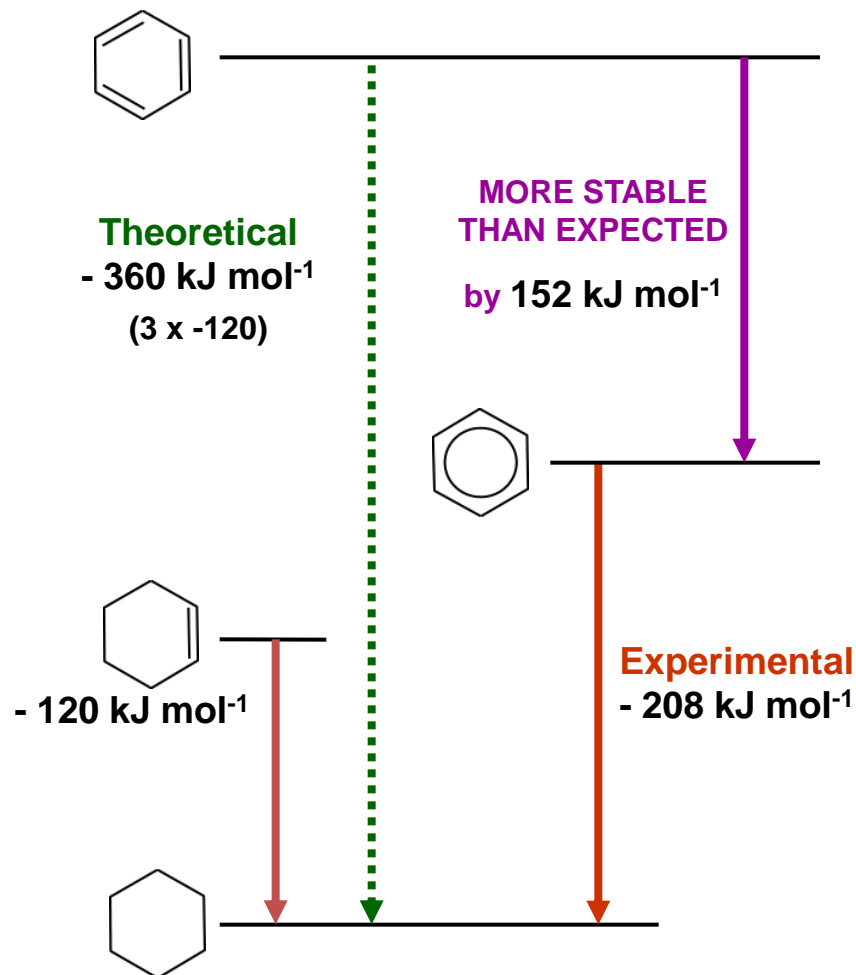


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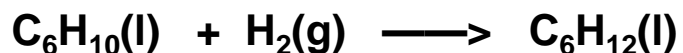
It is 152kJ per mole more stable than expected. This value is known as the RESONANCE ENERGY.



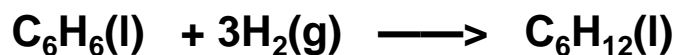
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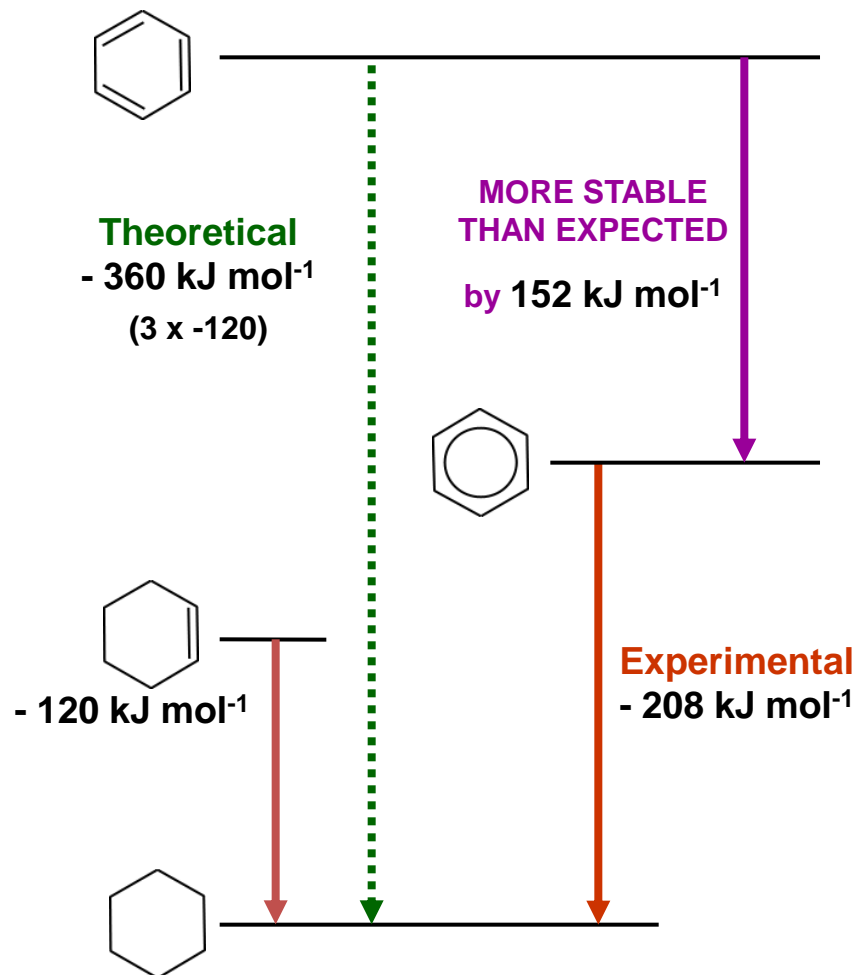


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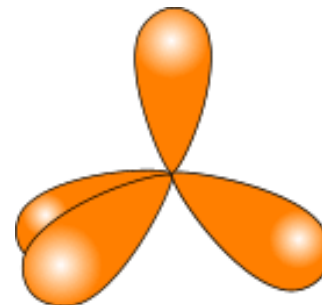
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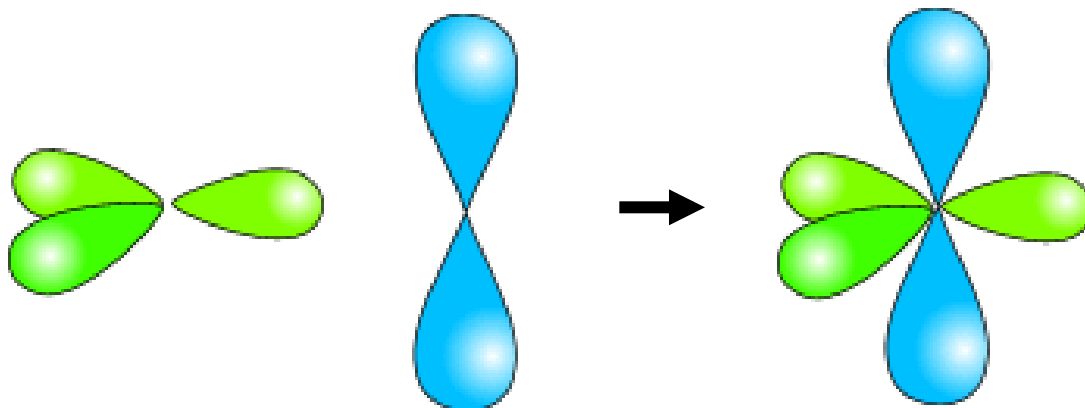


STRUCTURE OF ALKENES - REVISION

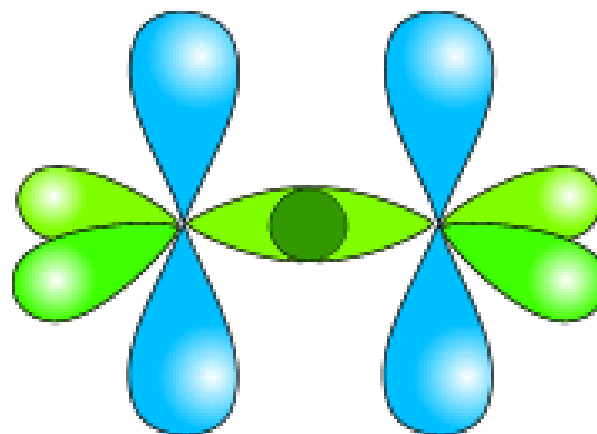
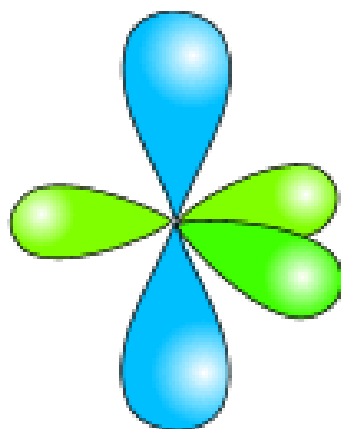
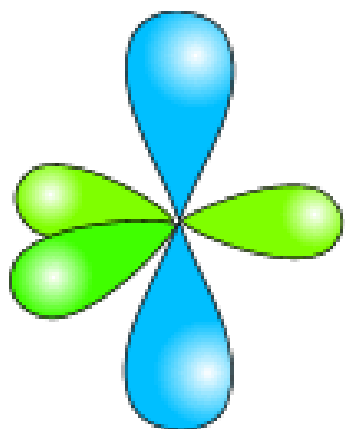
In ALKANES, the four sp^3 orbitals repel each other into a tetrahedral arrangement.



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



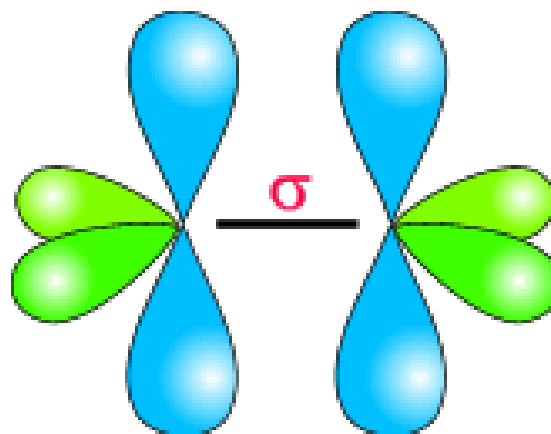
STRUCTURE OF ALKENES - REVISION



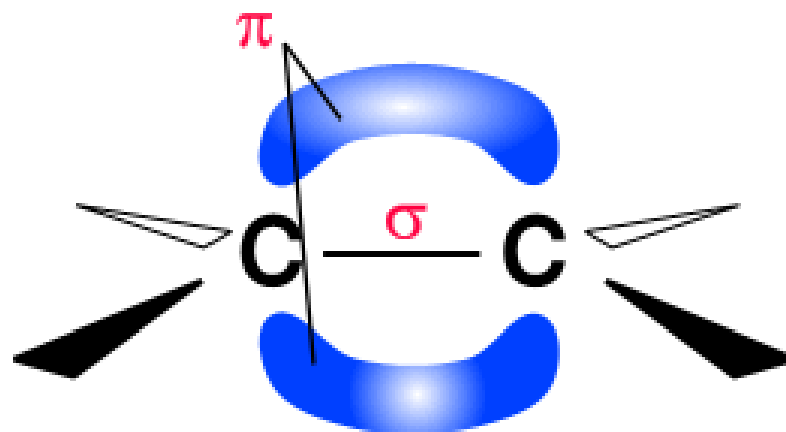
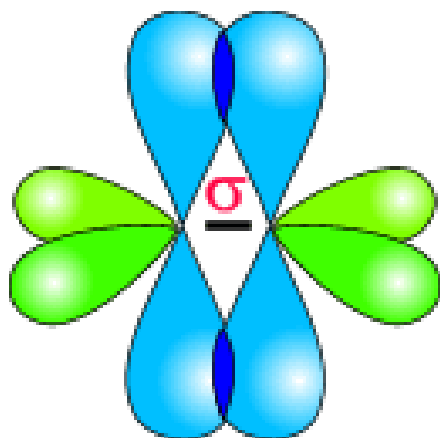
Covalent bonds are formed by overlap of orbitals.

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

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



STRUCTURE OF ALKENES - REVISION

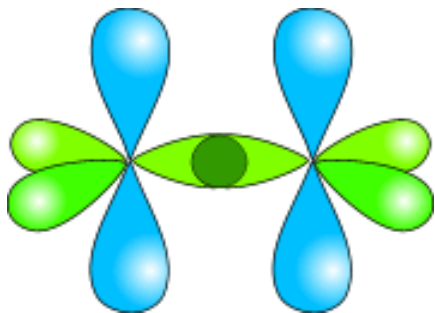


The two 2p orbitals also overlap. This forms a second bond; it is known as a PI (π) bond.

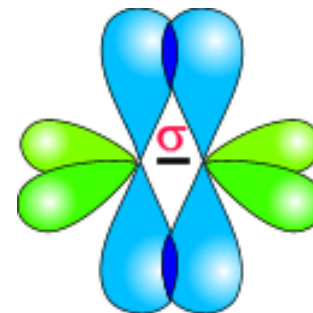
For **maximum overlap** and hence the **strongest bond**, the 2p orbitals are in line.

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

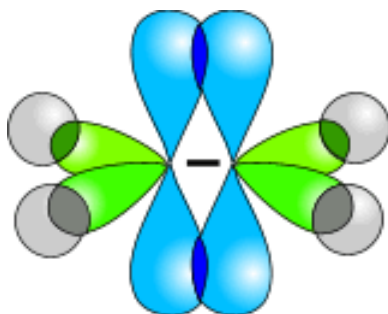
ORBITAL OVERLAP IN ETHENE - REVIEW



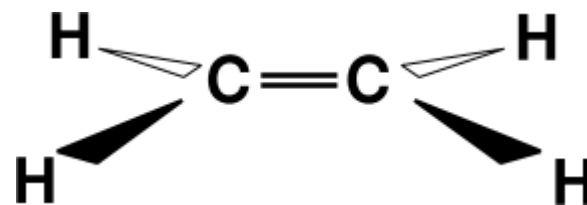
two sp^2 orbitals overlap to form a sigma bond between the two carbon atoms



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



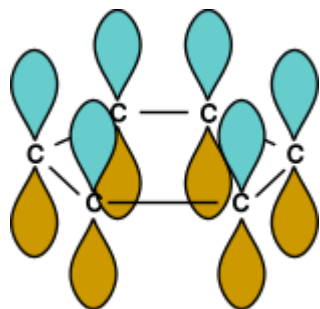
s orbitals in hydrogen overlap with the sp^2 orbitals in carbon to form C-H bonds



the resulting shape is planar with bond angles of 120°

STRUCTURE OF BENZENE - DELOCALISATION

The theory suggested that instead of three localised (in one position) double bonds, the six p (π) electrons making up those bonds were **delocalised** (not in any one particular position) around the ring by overlapping the p orbitals. There would be no double bonds and all bond lengths would be equal. It also gave a **planar structure**.

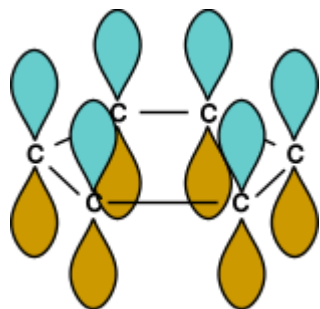


6 single bonds

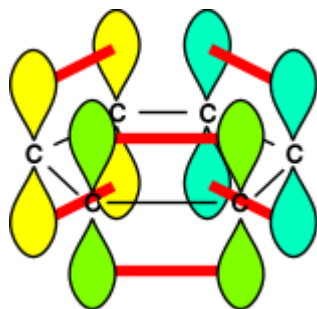


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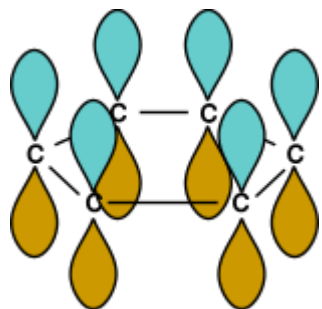
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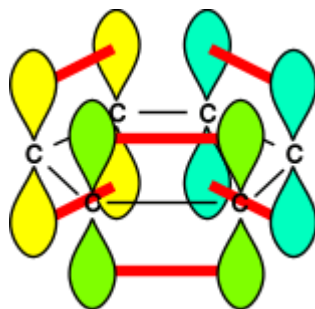
one way to overlap adjacent p orbitals

STRUCTURE OF BENZENE - DELOCALISATION

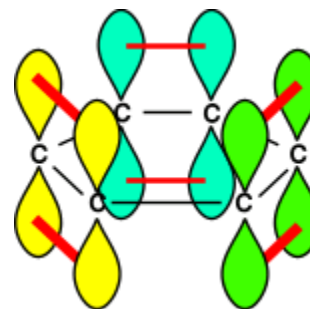
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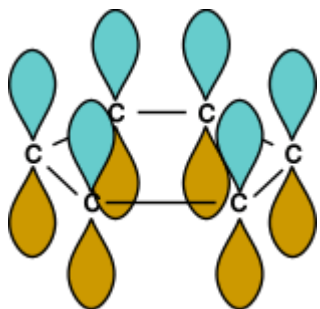
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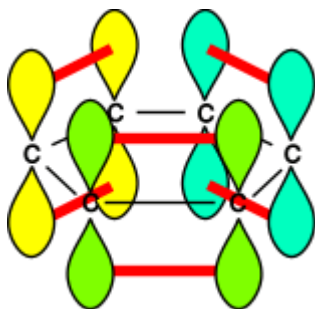
another possibility

STRUCTURE OF BENZENE - DELOCALISATION

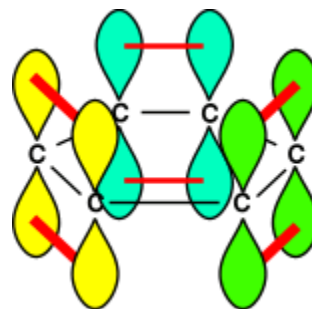
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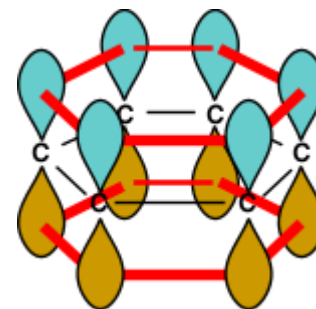
6 single bonds



one way to overlap adjacent p orbitals



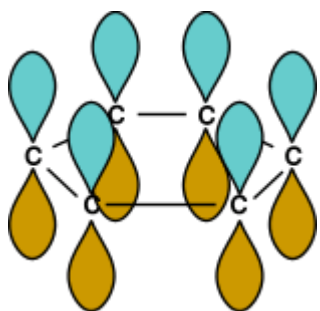
another possibility



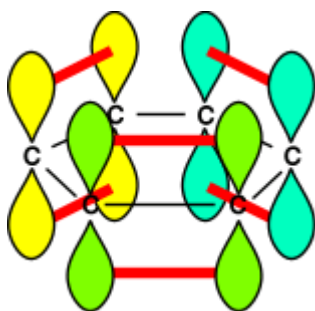
delocalised pi orbital system

STRUCTURE OF BENZENE - DELOCALISATION

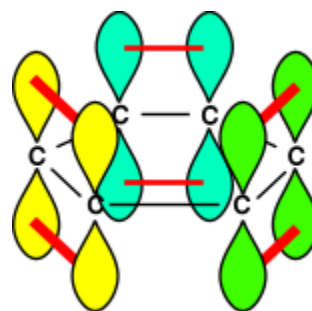
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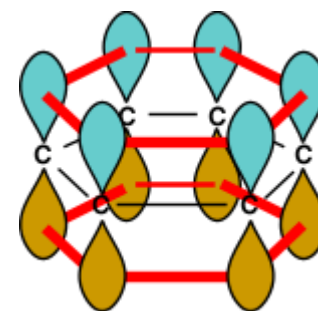
6 single bonds



one way to overlap adjacent p orbitals

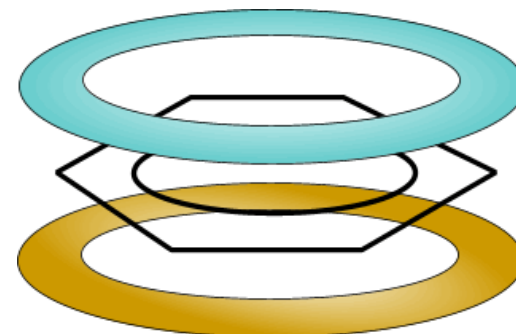


another possibility

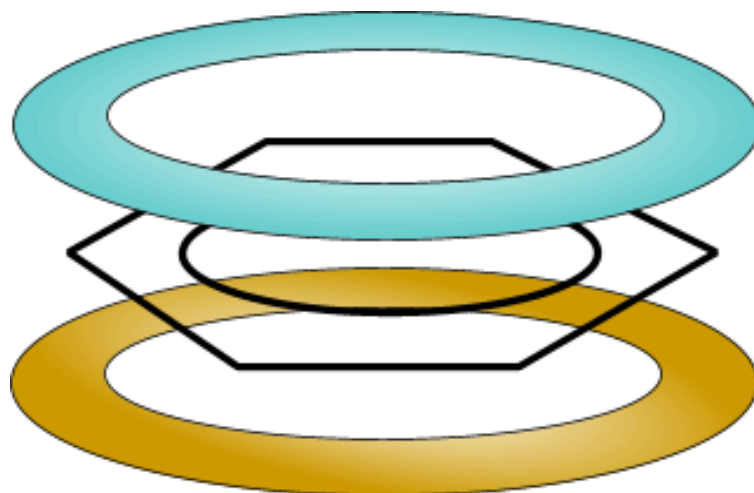
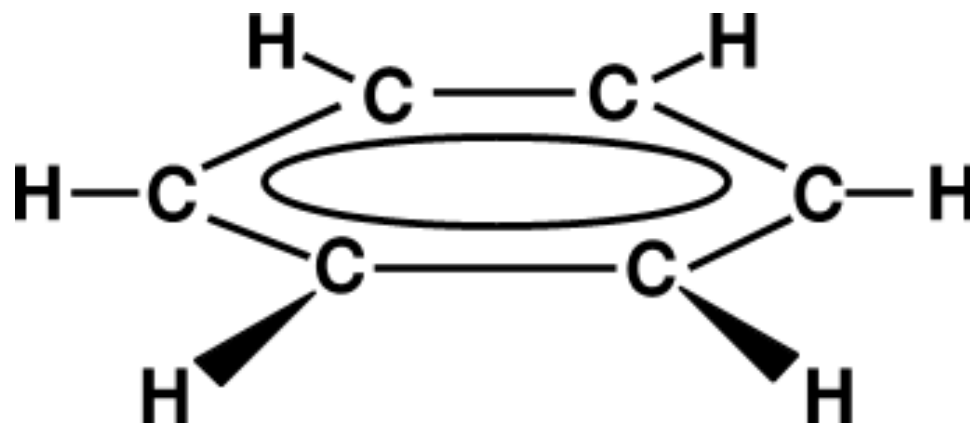


delocalised pi orbital system

This final structure was particularly stable and resisted attempts to break it down through normal electrophilic addition. However, substitution of any hydrogen atoms would not affect the delocalisation.



STRUCTURE OF BENZENE



WHY ELECTROPHILIC ATTACK?

Theory The high electron density of the ring makes it open to attack by electrophiles

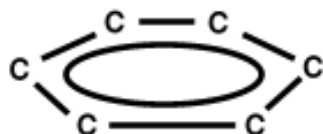
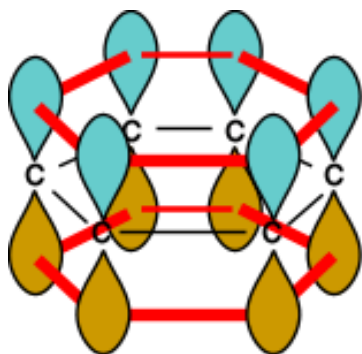
HOWEVER...

Because the mechanism involves an initial disruption to the ring electrophiles will have to be more powerful than those which react with alkenes.

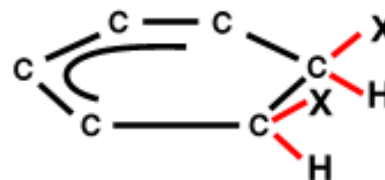
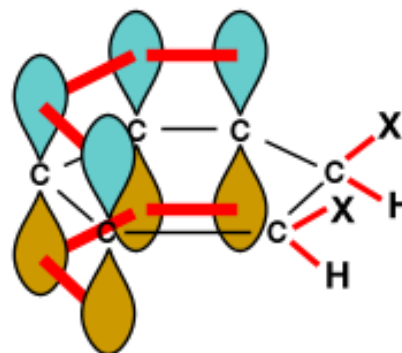
A fully delocalised ring is stable so will resist attack.

WHY SUBSTITUTION?

Theory Addition to the ring would upset the delocalised electron system



STABLE DELOCALISED SYSTEM



ELECTRONS ARE NOT DELOCALISED AROUND THE WHOLE RING - **LESS STABLE**

Substitution of hydrogen atoms on the ring does not affect the delocalisation

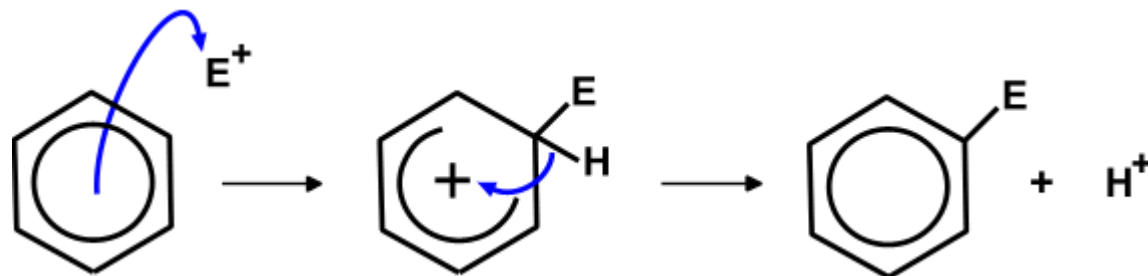
Overall there is **ELECTROPHILIC SUBSTITUTION**



ELECTROPHILIC SUBSTITUTION

Theory The high electron density of the ring makes it open to attack by electrophiles
Addition to the ring would upset the delocalised electron system
Substitution of hydrogen atoms on the ring does not affect the delocalisation
Because the mechanism involves an initial disruption to the ring,
electrophiles must be more powerful than those which react with alkenes
Overall there is **ELECTROPHILIC SUBSTITUTION**

Mechanism



- a **pair of electrons leaves the delocalised system** to form a bond to the electrophile
- this **disrupts the stable delocalised system** and forms an unstable intermediate
- to restore stability, the **pair of electrons in the C-H bond moves back** into the ring
- overall there is substitution of hydrogen ... **ELECTROPHILIC SUBSTITUTION**

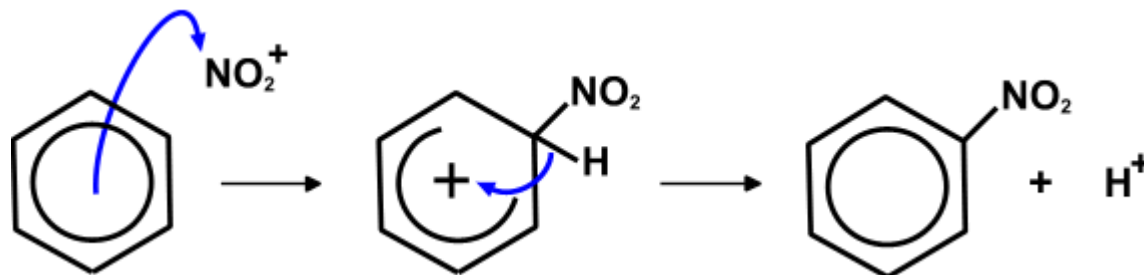
ELECTROPHILIC SUBSTITUTION REACTIONS - NITRATION

Reagents conc. nitric acid and conc. sulphuric acid (catalyst)

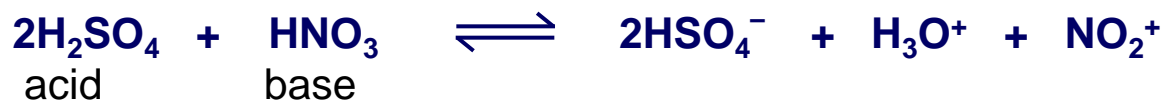
Conditions reflux at 55°C



Mechanism



Electrophile NO₂⁺, **nitronium ion** or **nitryl cation**; it is generated in an acid-base reaction...



Use The nitration of benzene is the first step in an historically important chain of reactions. These lead to the **formation of dyes, and explosives.**



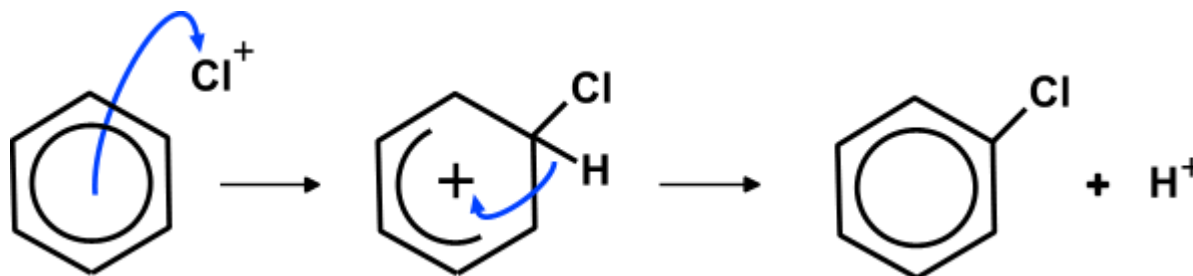
ELECTROPHILIC SUBSTITUTION REACTIONS - HALOGENATION

Reagents chlorine and a **halogen carrier** (catalyst)

Conditions reflux in the presence of a halogen carrier (Fe, FeCl₃, AlCl₃)
chlorine is non polar so is not a good electrophile
the halogen carrier is required to polarise the halogen



Mechanism



Electrophile Cl⁺ it is generated as follows...



a
Lewis Acid



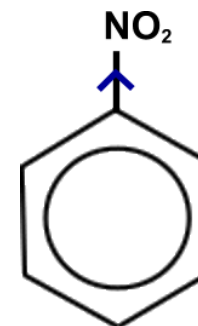
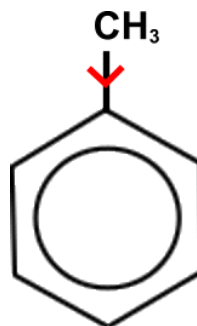
FURTHER SUBSTITUTION OF ARENES

Theory

It is possible to substitute more than one functional group.

But, the **functional group already on the ring** affects...

- how easy it can be done
- where the next substituent goes



Group

ELECTRON DONATING

ELECTRON WITHDRAWING

Example(s)

OH, CH₃

NO₂

Electron density of ring

Increases

Decreases

Ease of substitution

Easier

Harder

Position of substitution

2,4,and 6

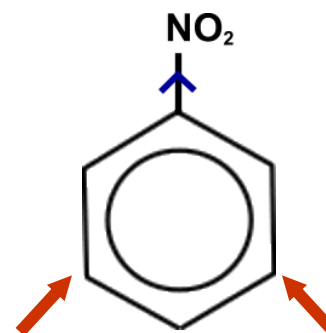
3 and 5

FURTHER SUBSTITUTION OF ARENES

Examples

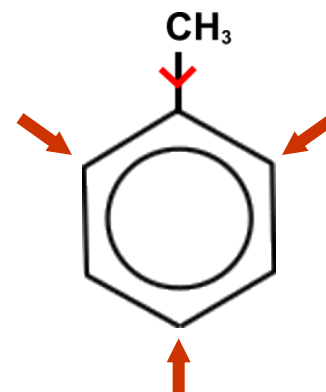
Substitution of nitrobenzene is...

- **more difficult** than with benzene
- produces a 1,3 disubstituted product



Substitution of methylbenzene is...

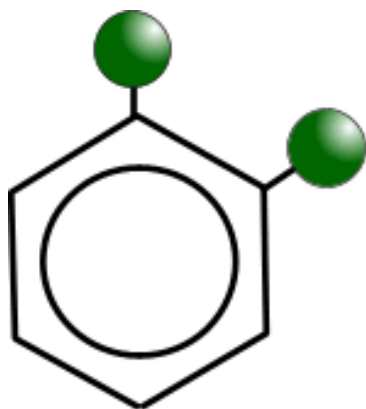
- **easier** than with benzene
- produces a mixture of 1,2 and 1,4 isomeric products



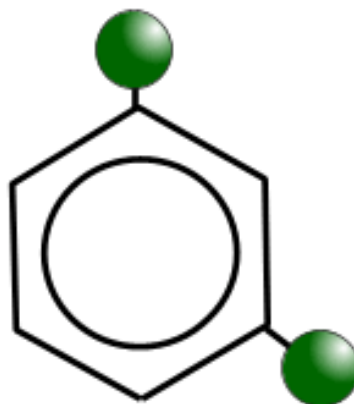
Some groups (OH) make substitution so much easier that multiple substitution takes place

STRUCTURAL ISOMERISM

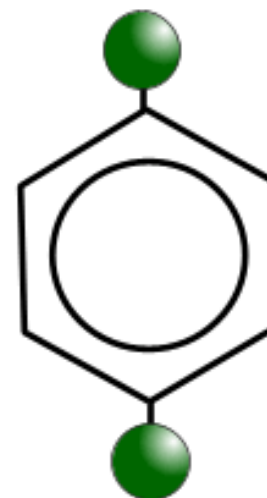
RELATIVE POSITIONS ON A BENZENE RING



1,2-DICHLOROBENZENE
ortho dichlorobenzene



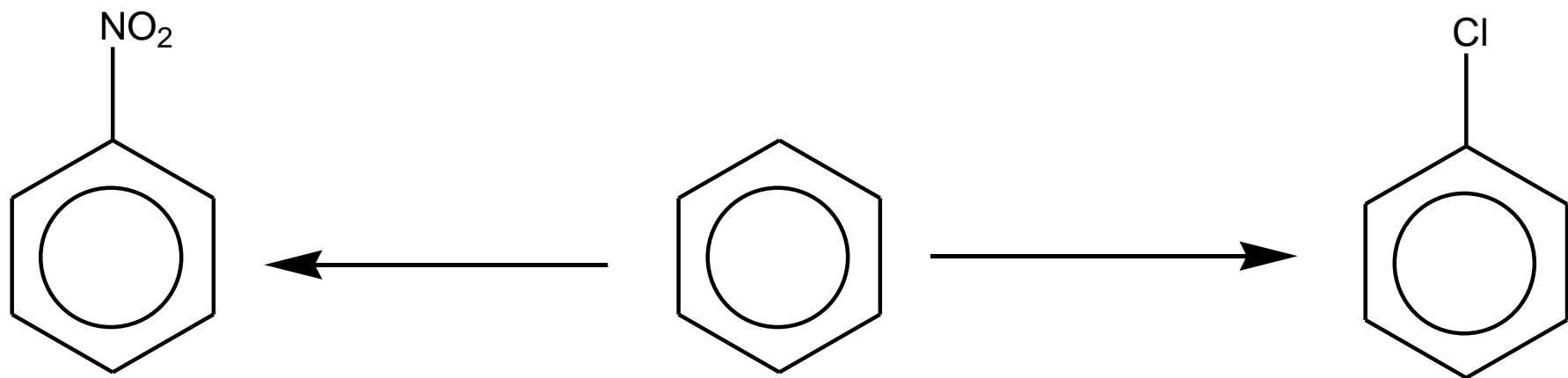
1,3-DICHLOROBENZENE
meta dichlorobenzene



1,4-DICHLOROBENZENE
para dichlorobenzene

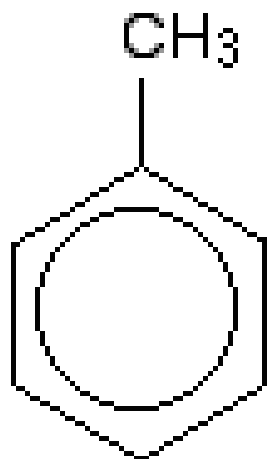
Compounds have similar chemical properties but different physical properties

THE CHEMISTRY OF ARENES



Methylbenzene

The reactions of the CH_3 group and how they are modified by the ring



The reactions of the ring and how they are modified by the CH_3 group

The tendency of the CH_3 group to "push" electrons away from itself also has an effect on the ring, making methylbenzene react more quickly than benzene itself.

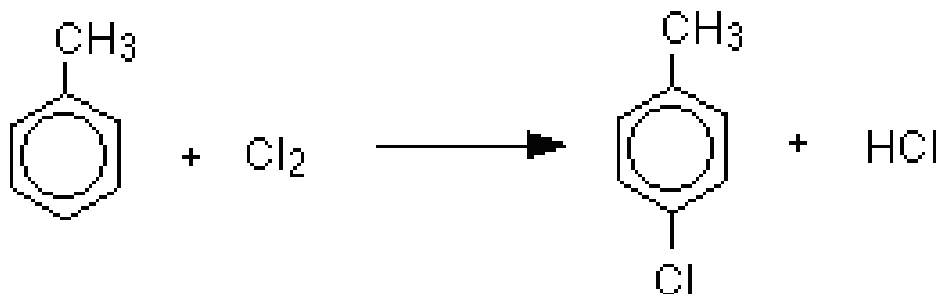
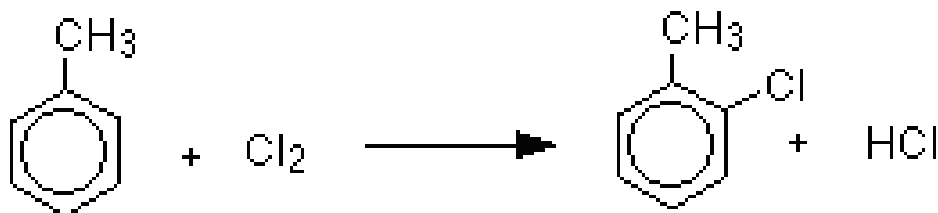
The reactivity of a benzene ring is governed by the electron density around the ring. Methyl groups tend to "push" electrons towards the ring - increasing the density, and so making the ring more attractive to attacking reagents.

The halogenation of methylbenzene

It is possible to get two quite different substitution reactions between methylbenzene and chlorine

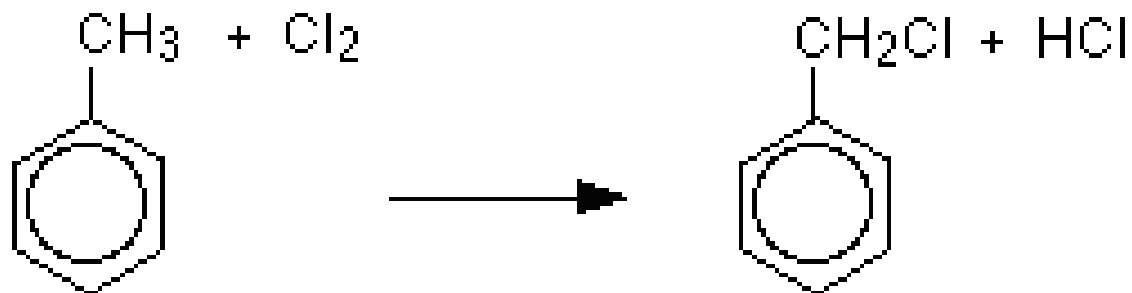
Substitution into the ring

Substitution in the ring happens in the presence of aluminium chloride . The reactions happen at room temperature.



Methyl groups are *2,4-directing*

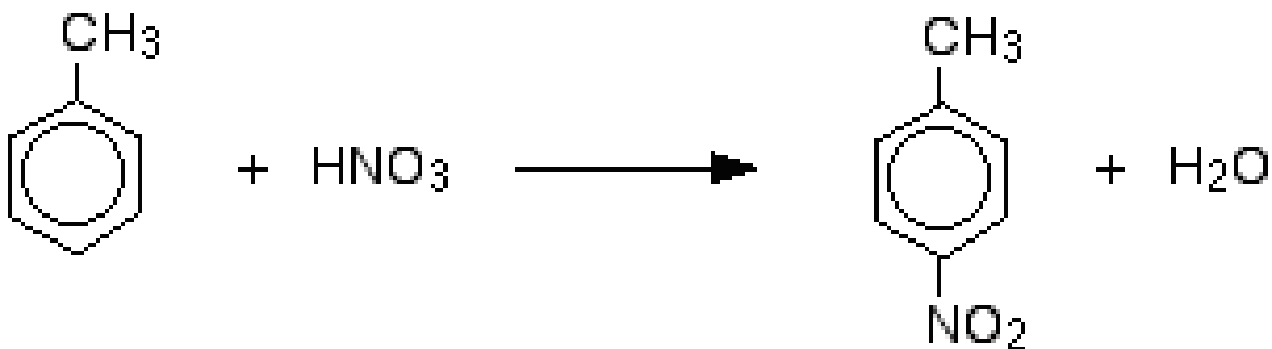
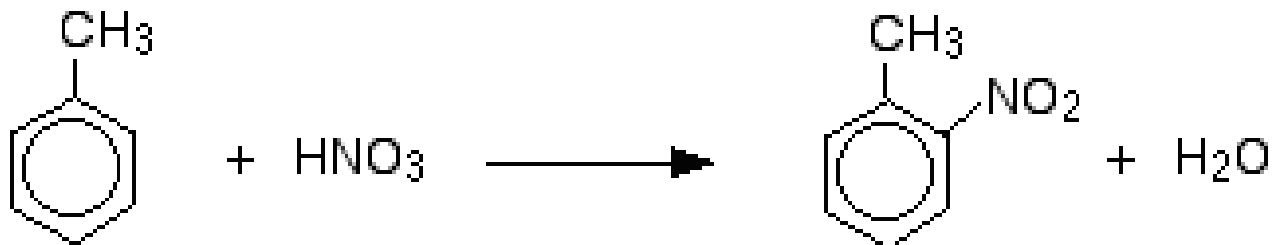
Substitution into the methyl group



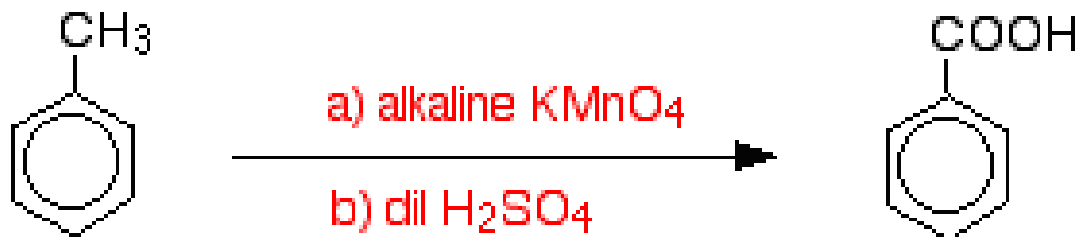
If chlorine or bromine react with boiling methylbenzene in the absence of a catalyst but in the presence of UV light, substitution happens in the methyl group rather than the ring

The nitration of methylbenzene (toluene)

Methylbenzene reacts rather faster than benzene - in nitration, the reaction is about 25 times faster. That means that you would use a lower temperature to prevent more than one nitro group being substituted - in this case, 30°C rather than 50°C



Side chain oxidation in alkylbenzenes



An alkylbenzene is simply a benzene ring with an alkyl group attached to it. Methylbenzene is the simplest alkylbenzene. Alkyl groups are usually fairly resistant to oxidation. However, when they are attached to a benzene ring, they are easily oxidised by an alkaline solution of potassium manganate(VII) (potassium permanganate). Methylbenzene is heated under reflux with a solution of potassium manganate(VII) made alkaline with sodium carbonate. The purple colour of the potassium manganate(VII) is eventually replaced by a dark brown precipitate of manganese(IV) oxide. The mixture is finally acidified with dilute sulphuric acid