

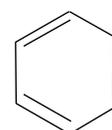
## BENZENE

**Structure** Primary analysis revealed benzene had an... **empirical formula of CH** and a **molecular formula of C<sub>6</sub>H<sub>6</sub>**

**Q.1** Draw out suitable structures which fit the molecular formula C<sub>6</sub>H<sub>6</sub>

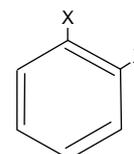
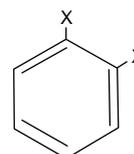
**Kekule**

Kekulé suggested a **PLANAR, CYCLIC** structure with **ALTERNATING DOUBLE AND SINGLE BONDS**



• However it **did not readily undergo electrophilic addition** - *no true C=C bond*

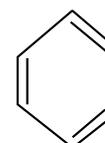
• only **one 1,2 disubstituted product** existed  
*i.e you didn't get two isomers like these..*



• all six C—C **bond lengths were similar**.  
*Double bonds are shorter than single ones*

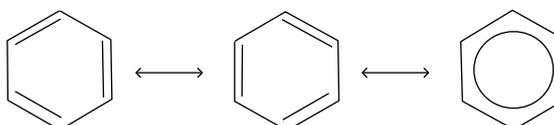


NOT



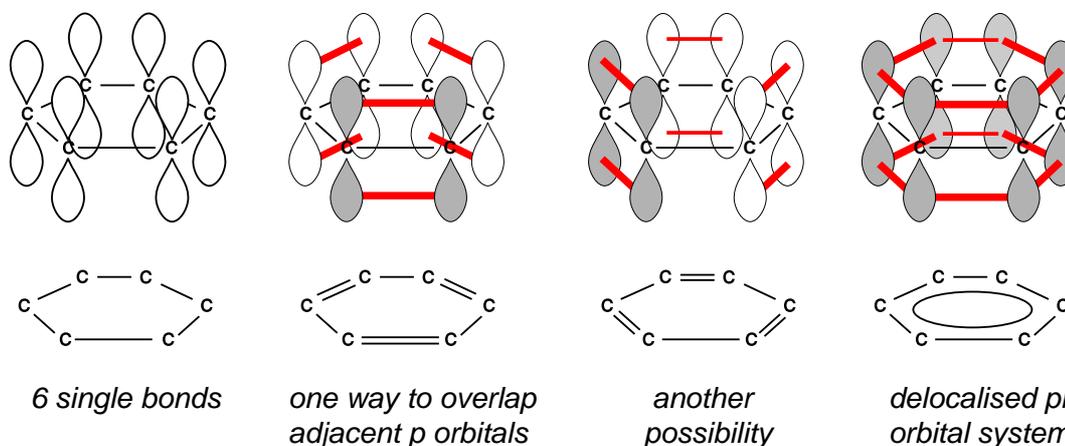
• the ring was **thermodynamically more stable** than expected - *see below*

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**.

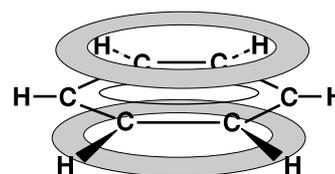


## The delocalised system

The theory suggested that instead of three localised (in one position) double bonds, the six  $\pi$  (pi) 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 to be added to and all bond lengths would be equal. It also gave a **planar** structure.



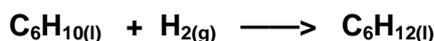
This **structure was particularly stable** and resisted any attempt to break it down through normal electrophilic addition. However, overall substitution of any of the hydrogen atoms would not affect the delocalised system.



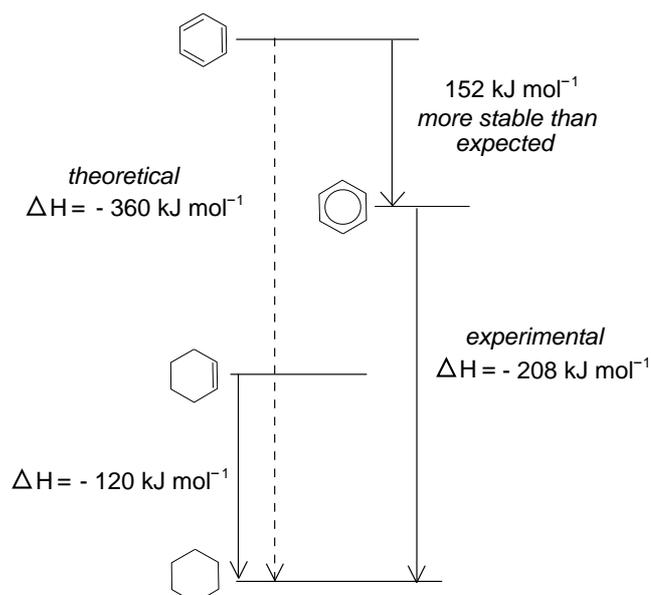
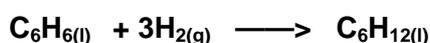
## Thermodynamic evidence for stability

When unsaturated hydrocarbons are reduced to the corresponding saturated compound, energy is released. If the experiment is carried out in a **bomb calorimeter** 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.



Theoretically, if benzene contained three separate C=C bonds it would release 360kJ per mole when reduced to cyclohexane



- benzene releases only 208kJ per mole when reduced putting it lower down the energy scale
- it is 152kJ per mole more stable than expected.
- this value is known as the **resonance energy**.

## REACTIONS OF THE BENZENE (AROMATIC) RING

**Nitration** Converts benzene into nitrobenzene,  $C_6H_5NO_2$

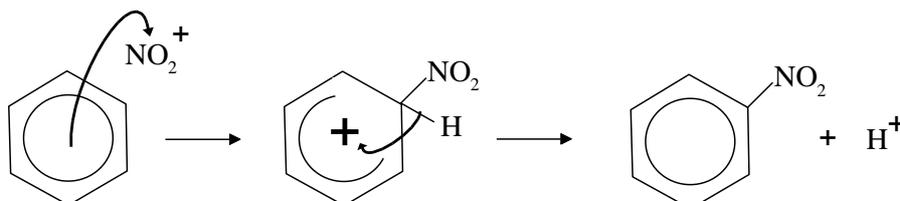
*The nitration of benzene is the first step in an historically important chain of reactions. These lead to the formation of dyes, and explosives.*

*reagents* **conc.** nitric acid and **conc.** sulphuric acid (catalyst)

*conditions* reflux at  $55^\circ C$

*equation*  $C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + H_2O$

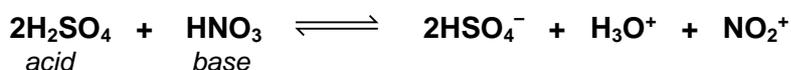
*mechanism*



- a pair of electrons leaves the delocalised system to form a bond to the electrophile  $NO_2^+$
- 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**

*electrophile*  $NO_2^+$ , **nitronium ion** or nityl cation

it is generated in an **acid-base** reaction as follows...



**Halogenation** Converts benzene into chlorobenzene,  $C_6H_5Cl$

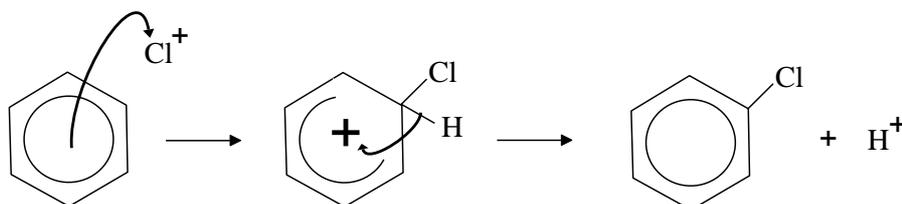
*Chlorine is non polar so is not a good electrophile. A catalyst (HALOGEN CARRIER) is required to polarise the halogen.*

*reagents* chlorine and a halogen carrier (catalyst)

*conditions* reflux in the presence of a **halogen carrier** such as iron, iron(III) chloride, iron(III) bromide

*equation*  $C_6H_6 + Cl_2 \longrightarrow C_6H_5Cl + HCl$

*mechanism*



## Friedel Crafts Reactions

*General* A catalyst is used to increase the positive nature of the electrophile and make it better at attacking benzene rings. **AlCl<sub>3</sub> acts as a Lewis Acid** and helps break the C—Cl bond.

**Alkylation** substitutes an alkyl (e.g. methyl, ethyl) group

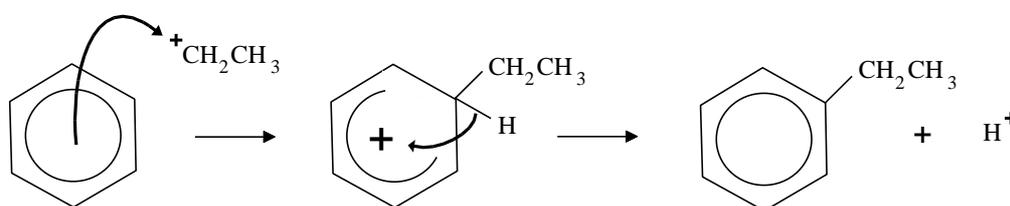
*reagents* a haloalkane (RX) and anhydrous aluminium chloride AlCl<sub>3</sub>

*conditions* room temperature; dry inert solvent (ether)

*electrophile* a carbocation ion R<sup>+</sup> (e.g. CH<sub>3</sub><sup>+</sup>)



*mechanism*

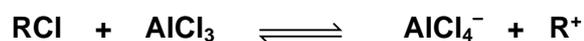


*catalyst* **anhydrous aluminium chloride** acts as the catalyst

the Al in AlCl<sub>3</sub> has only 6 electrons in its outer shell; it is a **LEWIS ACID**

it **increases the polarisation of the C-Cl bond** in the haloalkane

this makes the charge on C more positive and the following occurs



**Q.2** Which haloalkane would you use to make...

- propylbenzene
- C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>

**Industrial**

Alkenes are used instead of haloalkanes but an acid must also be present

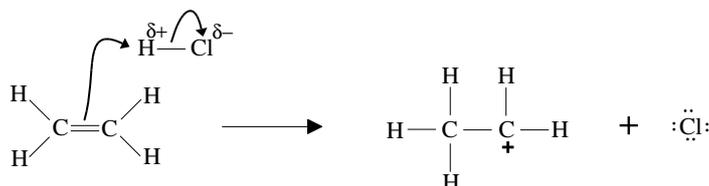
**Phenylethane,  $C_6H_5C_2H_5$**  is made by this method

*reagents* ethene, anhydrous  $AlCl_3$ , conc. HCl

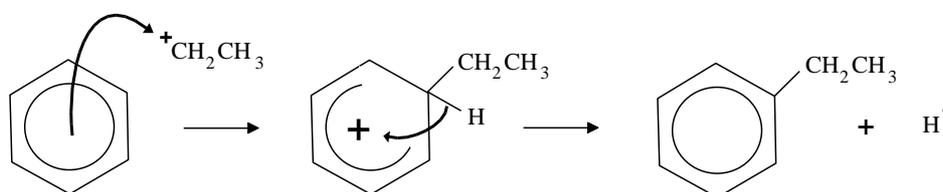
*electrophile*  $C_2H_5^+$  (an ethyl carbocation)

*equation*  $C_6H_6 + C_2H_4 \longrightarrow C_6H_5C_2H_5$  (ethyl benzene)

*mechanism* a) the HCl reacts with the alkene to generate a carbocation



b) electrophilic substitution then takes place as the  $C_2H_5^+$  attacks the ring



*use* ethyl benzene is dehydrogenated to produce phenylethene (styrene); this is then used to make poly(phenylethene) - also known as polystyrene

**Q.3** Why is ethene used industrially rather than chloroethane ?

**Acylation**

substitutes an acyl (e.g. ethanoyl) group

the aluminium chloride catalyst acts in the same way as with alkylation

*reagents* an acyl chloride ( $RCOCl$ ) and anhydrous  $AlCl_3$

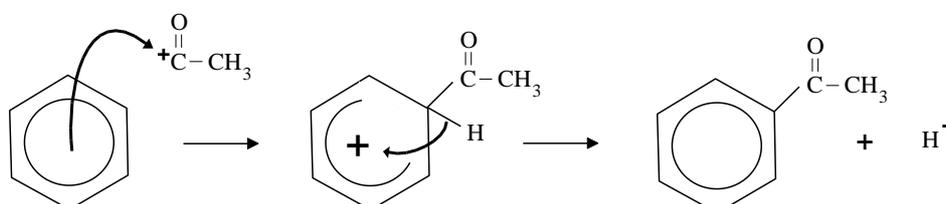
*conditions* reflux  $50^\circ\text{C}$ ; dry inert solvent (ether)

*electrophile*  $RC^+=O$  (e.g.  $CH_3C^+=O$ )

*product* carbonyl compound (aldehyde or ketone)

*equation*  $C_6H_6 + CH_3COCl \longrightarrow C_6H_5COCH_3 + HCl$

*mechanism*



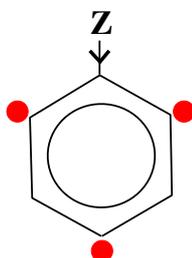
## FURTHER SUBSTITUTION OF BENZENE

### Theory

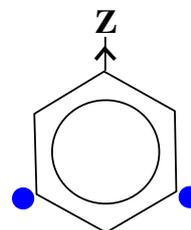
It is possible to substitute more than one functional group.

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

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



**ELECTRON  
RELEASING**



**ELECTRON  
WITHDRAWING**

Group

Example(s)

Electron density of ring

Ease of substitution

Position of substitution

OH, CH<sub>3</sub>

Increases

Easier

2,4, and 6

NO<sub>2</sub>

Decreases

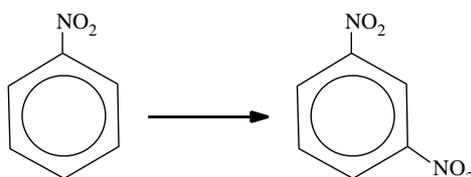
Harder

3 and 5

### Examples

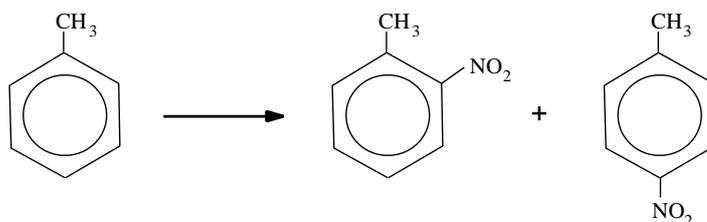
**Substitution of nitrobenzene** is...

- more difficult than with benzene
- produces a 1,3 disubstituted product
- NO<sub>2</sub> is electron withdrawing
- NO<sub>2</sub> directs to the 3 (*meta*) position

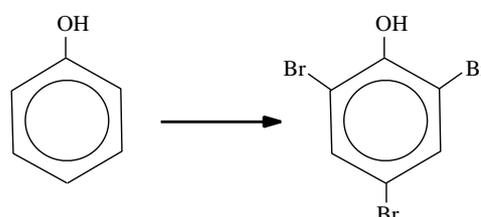


**Substitution of methylbenzene** is...

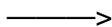
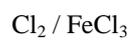
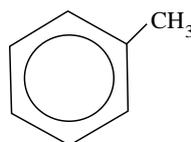
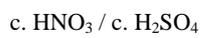
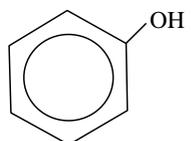
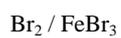
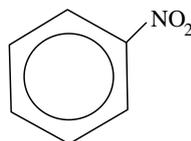
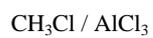
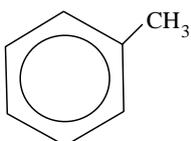
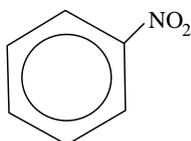
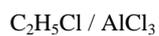
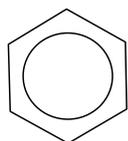
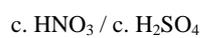
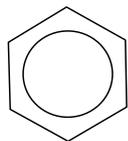
- easier than with benzene
- produces a mixture of isomers
- CH<sub>3</sub> is electron releasing
- CH<sub>3</sub> directs to the 2 (*ortho*) and 4 (*para*) position



Some groups make substitution so much easier that multiple substitution takes place

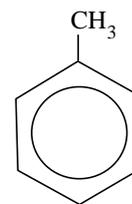


**Q.4** Draw structures for the *monosubstituted* organic product(s) of the following reactions.



## METHYLBENZENE

- Introduction**
- methylbenzene used to be called toluene
  - it has a methyl group attached directly to the benzene ring
  - it has the formula  $C_6H_5CH_3$



**Preparation** formed from benzene using Friedel-Crafts alkylation

**reagents** chloromethane and anhydrous aluminium chloride  $AlCl_3$

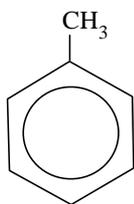
**conditions** room temperature; dry inert solvent (ether)

**electrophile**  $CH_3^+$

**equation**  $C_6H_6 + CH_3Cl \longrightarrow C_6H_5CH_3 + HCl$

**Reactions**

- there are two parts to the methylbenzene molecule



the **alkyl side chain** undergoes **free radical substitution**

the **aromatic ring** undergoes **electrophilic substitution**

**Q.5** For each of the reactions below...

- state the reagents and conditions required
- state the type of mechanism taking place
- write a balanced equation
- state any other possible organic products, giving brief reasons for their formation
- explain how the chlorinated product responds to treatment with  $NaOH(aq)$

