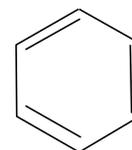


## BENZENE

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

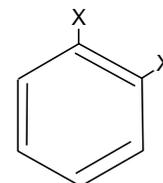
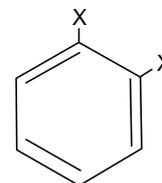
**Q.1** Draw out some *suitable* structures which fit the molecular formula C<sub>6</sub>H<sub>6</sub>

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

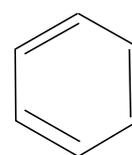


- However it **did not readily undergo electrophilic addition** - *no true C=C bond*

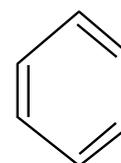
- only **one 1,2 disubstituted product** existed  
*i.e you didn't get two isomers like these..*



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

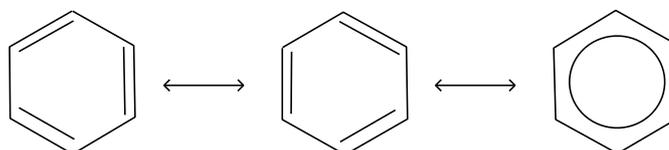


NOT

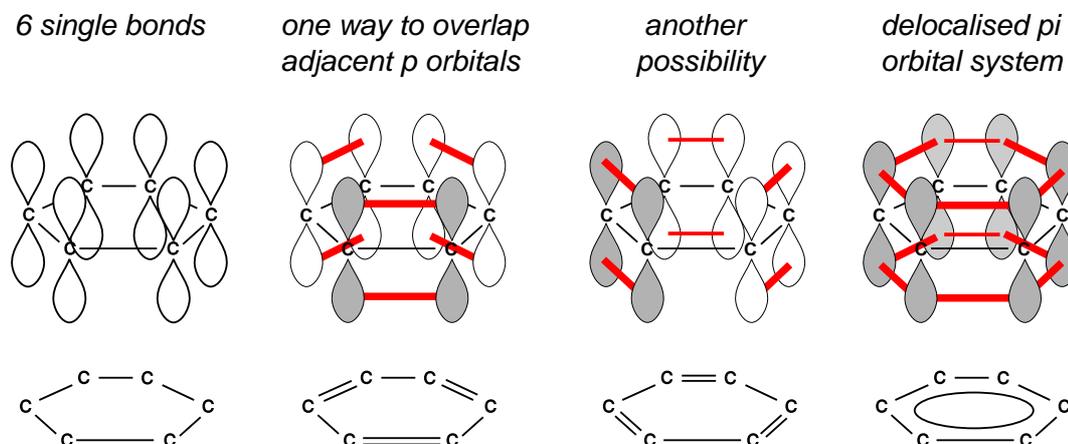


- the ring was **thermodynamically more stable** than expected - *see below*

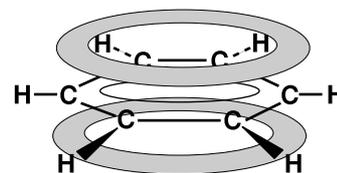
To explain the above, it was suggested that the structure oscillated between the two Kekulé forms but was represented by neither of them - a **resonance hybrid**.



**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.



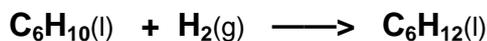
This **structure was particularly stable** and resisted any attempt to break it down through normal electrophilic addition. However, overall substitution of any of the hydrogen atoms would not affect the delocalised system.



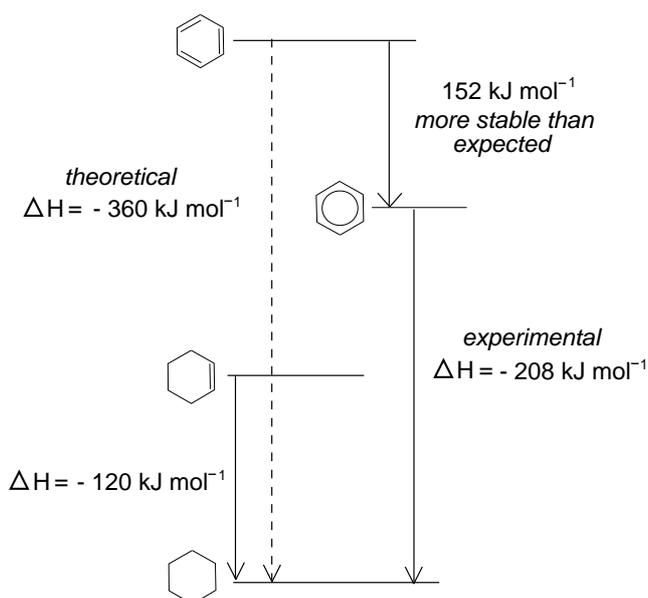
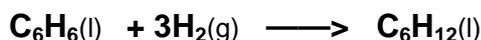
### Thermodynamic evidence for stability

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 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**

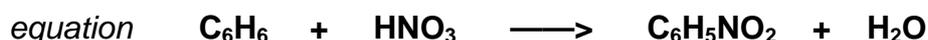
## REACTIONS OF THE BENZENE (AROMATIC) RING

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

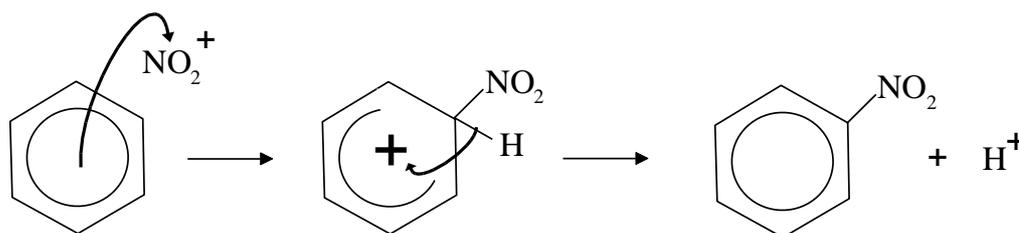
The nitration of benzene is the first step in an historically important chain of reactions (see below). These lead to the formation of dyes, and explosives.

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

conditions reflux at  $55^\circ C$



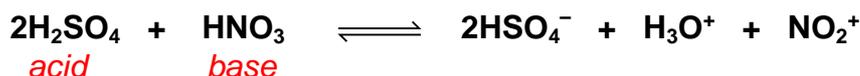
mechanism



- an electron pair 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**

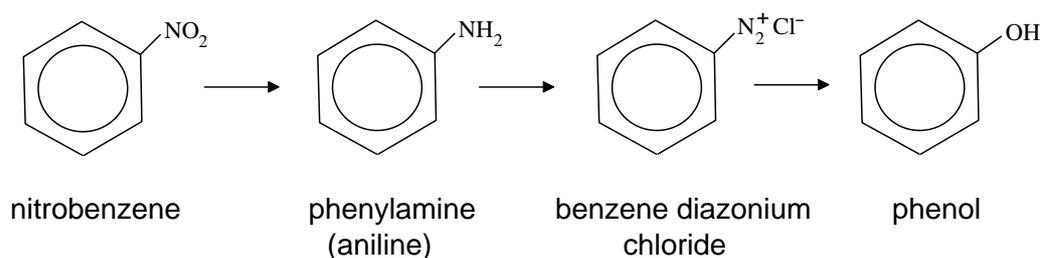
electrophile  $NO_2^+$ , **nitronium ion** or nitryl cation

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



*proton donor*                      *proton acceptor*

**Importance** Nitrobenzene is the start of an important chain of reactions.



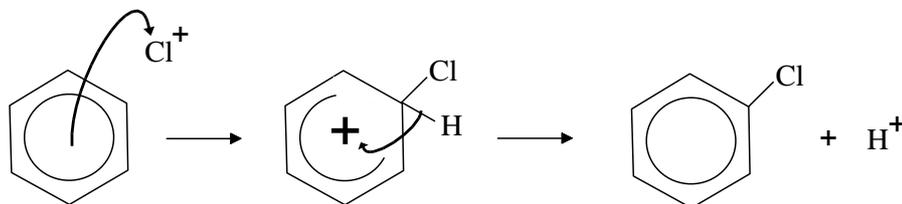
**Halogenation** Converts benzene into chlorobenzene,  $C_6H_5Cl$

*reagents* chlorine and a halogen carrier (the catalyst)

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

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

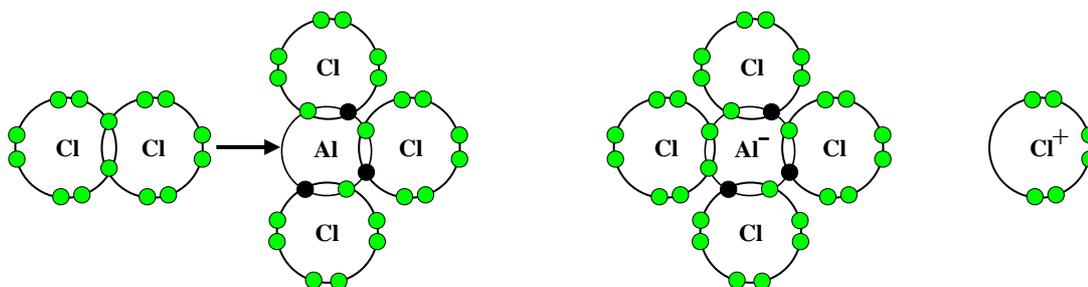
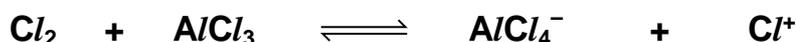
*mechanism*



*mechanism*  $Cl^+$  a positive chlorine ion

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

- **anhydrous aluminium chloride** can act as the catalyst
- the Al in  $AlCl_3$  has only 6 electrons in its outer shell; - **LEWIS ACID**
- it **increases the polarisation of the Cl-Cl bond**
- this makes the charge on C more positive and the following occurs

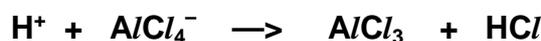


The aluminium chloride acts as a **LEWIS ACID** as the aluminium atom has only 6 electrons in its outer shell. It accepts a pair of electrons from one of the atoms in the chlorine molecule.

All the atoms in the new species have complete outer shells

The new species has 6 electrons in its outer shell. It has one less electron than a chlorine atom so has a + charge.

- the  $H^+$  ion removed from the benzene ring reacts with the  $AlCl_4^-$  ion to regenerate the  $AlCl_3$



*Comparison with alkenes*

The conditions are much tougher than with alkenes because the delocalised system makes benzene more stable and less reactive.

## Friedel Crafts Reactions

### General

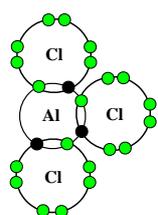
- involve **electrophilic substitution** of benzene rings
- there are two types - **Alkylation** and **Acylation**
  - Alkylation** involves the substitution of alkyl groups such as  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$  and  $\text{C}_3\text{H}_7$
  - Acylation** involves the substitution of acyl groups such as  $\text{CH}_3\text{C}=\text{O}$
- in both cases a **catalyst is needed**
- this is because the attacking species isn't a strong enough electrophile
- it hasn't enough positive character to persuade benzene to react
- haloalkanes and acyl chlorides have polar bonds but the C isn't positive enough



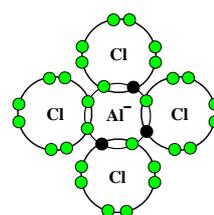
- a **catalyst** makes the attacking species more positive
- **anhydrous aluminium chloride** is the catalyst
- it works because it is a **Lewis acid**
- in  $\text{AlCl}_3$  the aluminium is **electron deficient** - it has 6 electrons in its outer shell
- in both cases the reagent has a polar C-Cl bond
- the carbon atom has a  $\delta+$  charge but it isn't enough to tempt the benzene
- the aluminium chloride increases the charge so that benzene become interested

### Action of $\text{AlCl}_3$

- acts as a Lewis acid as it can accept a lone pair to make up its octet



BEFORE  
incomplete octet  
**trigonal planar shape**



AFTER  
complete octet  
**tetrahedral shape**

- it can do this by attracting a chlorine atom away from a C-Cl bond  
(see above for explanation of the action of  $\text{AlCl}_3$ )
- the more the Cl is attracted by the  $\text{AlCl}_3$  the more polar the C-Cl bond gets
- in the extreme case it pulls the chlorine right off leaving a  $\text{C}^+$  behind



- The aromatic ring will now attack and electrophilic substitution takes place

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

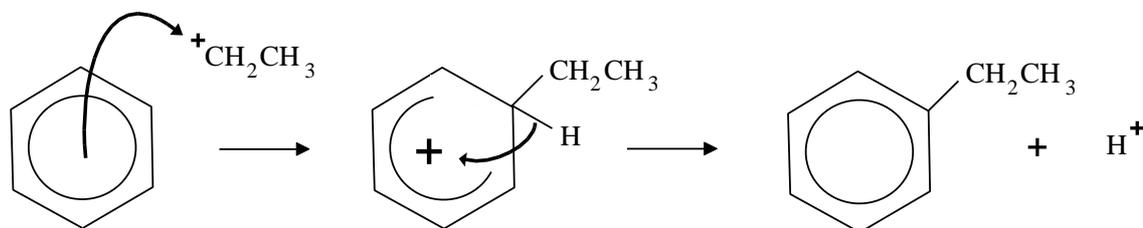
*reagents* a haloalkane (RX) and anhydrous aluminium chloride  $AlCl_3$

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

*electrophile* a carbocation  $R^+$  (e.g.  $CH_3^+$ )

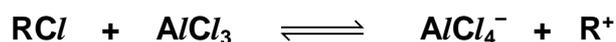
*equation*  $C_6H_6 + C_2H_5Cl \longrightarrow C_6H_5C_2H_5 + HCl$

*mechanism*



*catalyst* **anhydrous aluminium chloride**

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
- $C_6H_5CH_3$

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

**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  $AlCl_3$

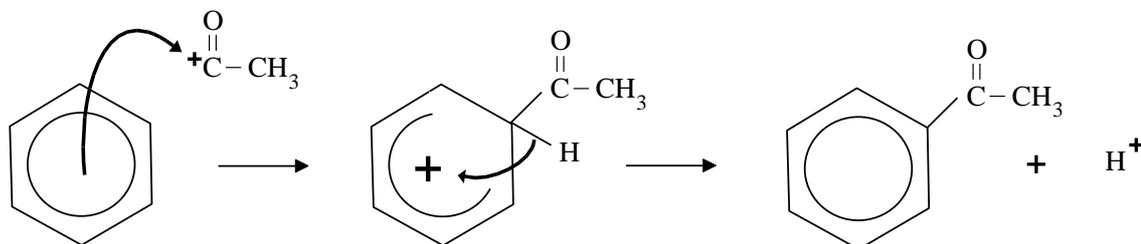
*conditions* reflux  $50^\circ C$ ; dry inert solvent (ether)

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

*product* carbonyl compound (aldehyde or ketone)

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

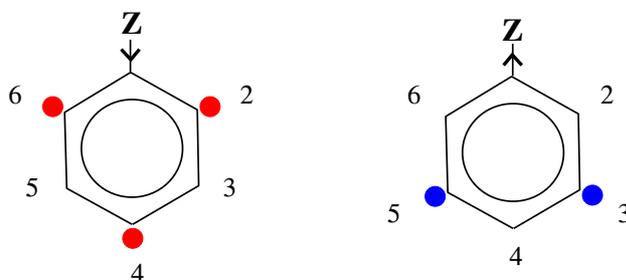
*catalyst*  $RCOCl + AlCl_3 \rightleftharpoons AlCl_4^- + RC^+=O$



## FURTHER SUBSTITUTION OF BENZENE

*Theory* It is possible to substitute more than one functional group.  
But, **the functional group already on the ring** affects...

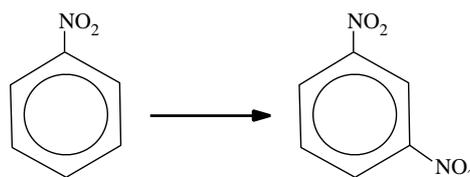
- **how easy it can be done**
- **where the next substituent goes**



Group		<b>ELECTRON RELEASING</b>	<b>ELECTRON WITHDRAWING</b>
<i>Example(s)</i>	Z =	OH, NH <sub>2</sub> , CH <sub>3</sub>	NO <sub>2</sub>
<i>Electron density of ring</i>		Increases	Decreases
<i>Ease of substitution</i>		Easier	Harder
<i>Position of substitution</i>		2,4, and 6	3 and 5

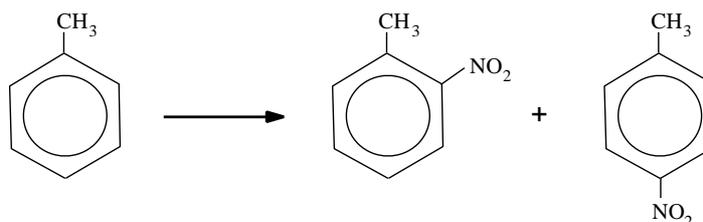
*Examples* **Substitution of nitrobenzene is...**

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

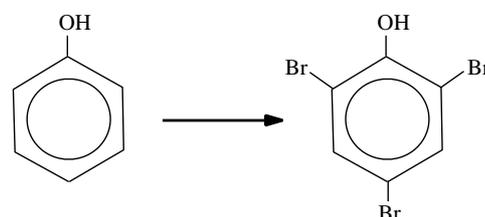


**Substitution of methylbenzene is...**

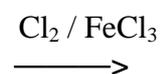
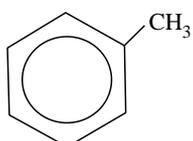
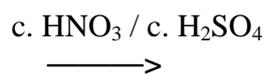
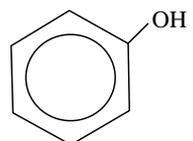
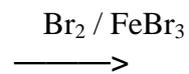
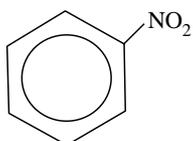
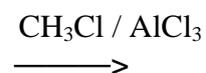
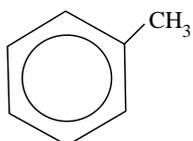
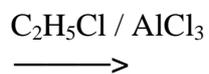
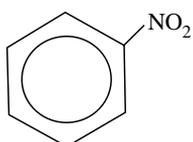
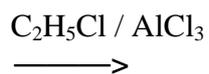
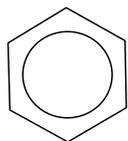
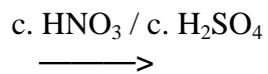
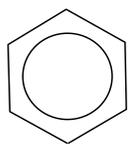
- **easier** than with benzene - CH<sub>3</sub> is electron releasing
- produces a mixture of isomers - CH<sub>3</sub> directs to 2 (*ortho*) and 4 (*para*) positions



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

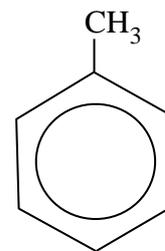


**Q.4** Draw structures for the *monosubstituted* organic product(s) of the following reactions.



## METHYLBENZENE

- Introduction**
- methylbenzene used to be called toluene
  - it has a methyl group attached directly to the benzene ring
  - it has the formula  $\text{C}_6\text{H}_5\text{CH}_3$



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

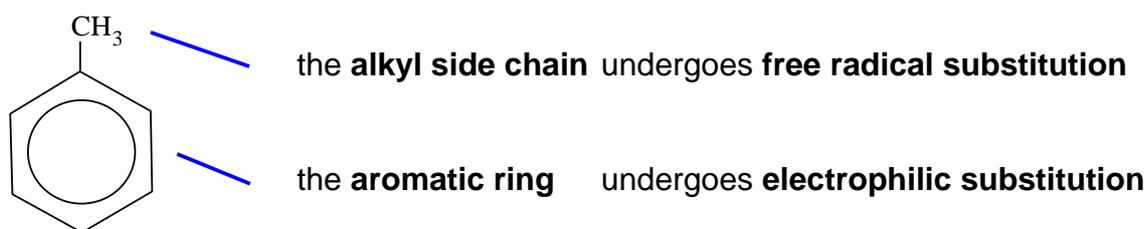
**reagents** chloromethane and anhydrous aluminium chloride  $\text{AlCl}_3$

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

**electrophile**  $\text{CH}_3^+$

**equation**  $\text{C}_6\text{H}_6 + \text{CH}_3\text{Cl} \longrightarrow \text{C}_6\text{H}_5\text{CH}_3 + \text{HCl}$

**Reactions** • there are two parts to the methylbenzene molecule



**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  $\text{NaOH}(\text{aq})$

