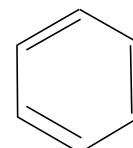


BENZENE

Structure Primary analysis revealed benzene had an... **empirical formula of CH**
and a **molecular formula of C₆H₆**

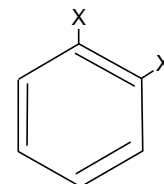
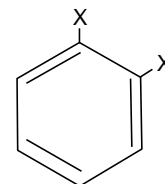
Q.1 Draw out some *suitable* structures which fit the molecular formula C₆H₆

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

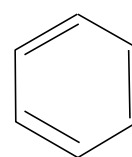


- However it **did not readily undergo electrophilic addition** - *no true C=C bond*

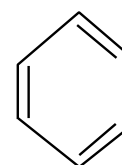
- only **one 1,2 disubstituted product** existed
i.e you didn't get two isomers like these..



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

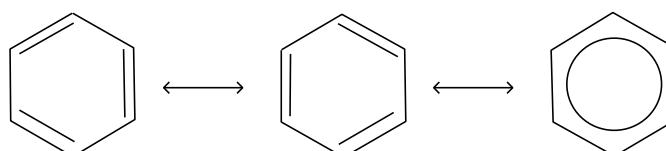


NOT

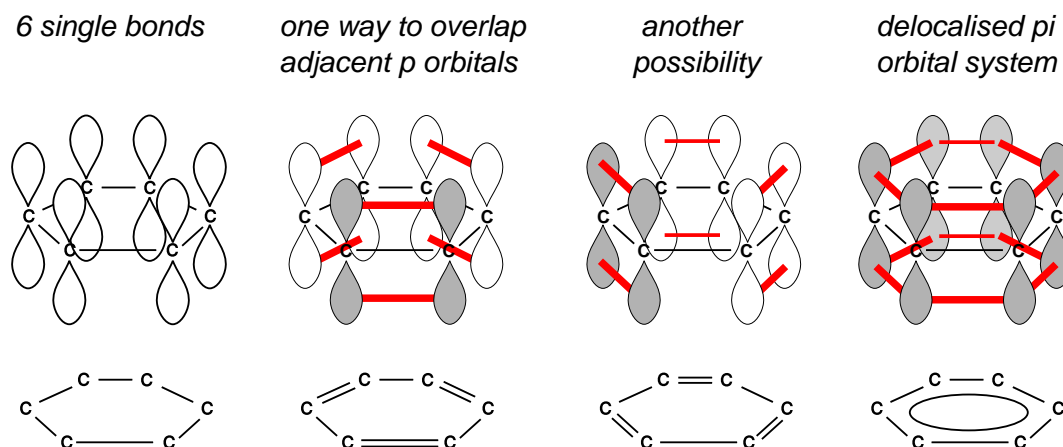


- the ring was **thermodynamically more stable** than expected - *see below*

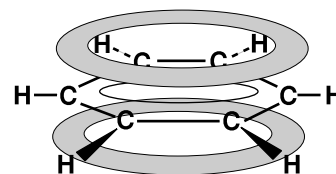
To explain the above, it was suggested that the structure oscillated between the two Kekulé forms but was represented by neither of them - a **resonance hybrid**.



Delocalised system The theory suggested that instead of three localised (in one position) double bonds, the six π (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.



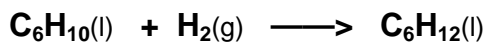
This **structure was particularly stable** and resisted any attempt to break it down through normal electrophilic addition. However, overall substitution of any of the hydrogen atoms would not affect the delocalised system.



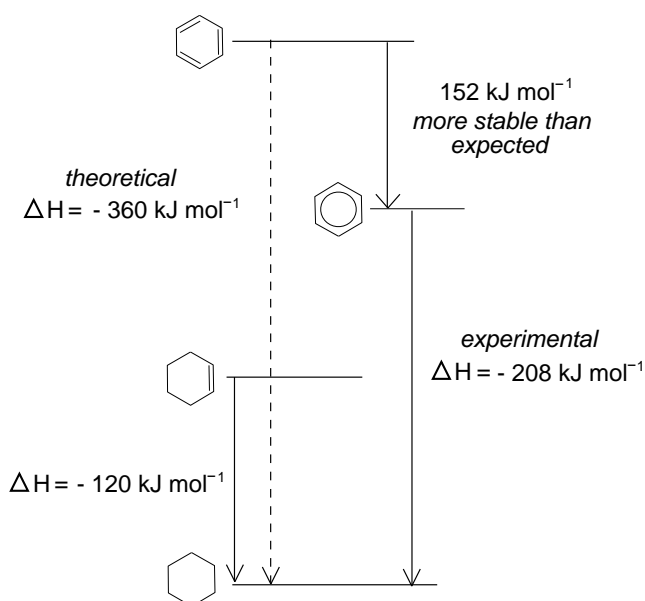
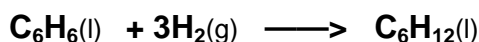
Thermodynamic evidence for stability

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**

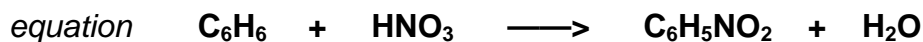
REACTIONS OF THE BENZENE (AROMATIC) RING

Nitration Converts benzene into nitrobenzene, $C_6H_5NO_2$

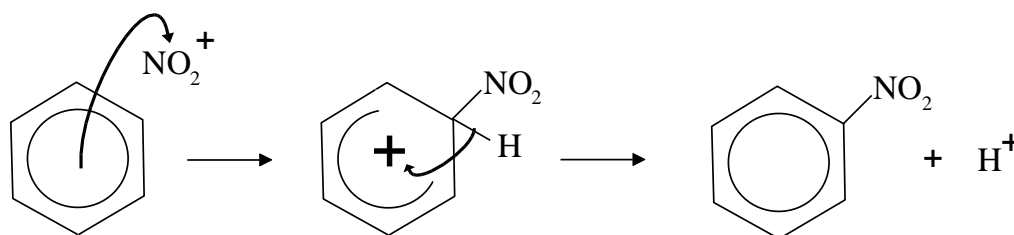
The nitration of benzene is the first step in an historically important chain of reactions (see below). These lead to the formation of dyes, and explosives.

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

conditions reflux at $55^\circ C$



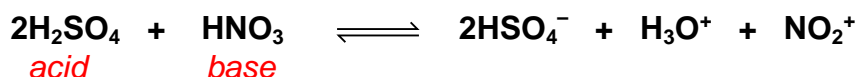
mechanism



- 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**

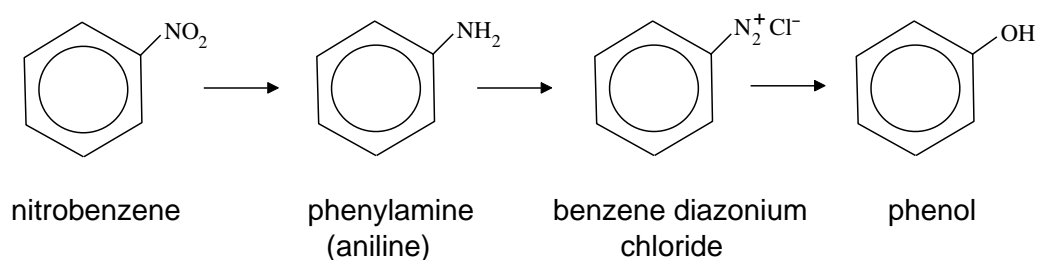
electrophile NO_2^+ , **nitronium ion** or nitryl cation

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.



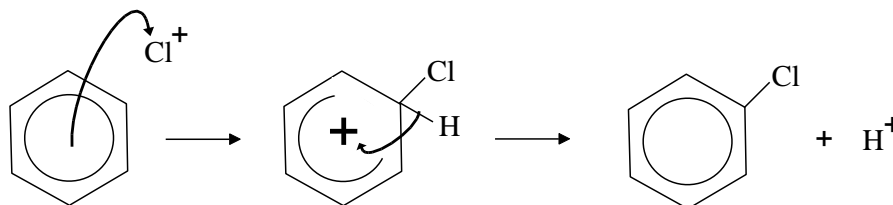
Halogenation Converts benzene into chlorobenzene, C_6H_5Cl

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 $C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$

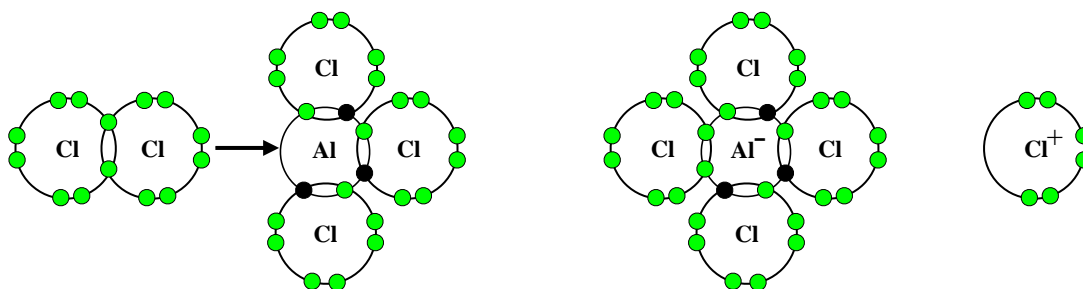
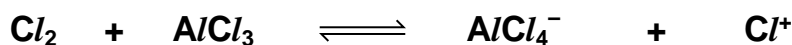
mechanism



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

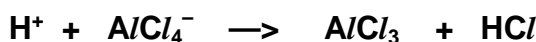


The aluminium chloride acts as a **LEWIS ACID** as the aluminium atom has only 6 electrons in its outer shell. It accepts a pair of electrons from one of the atoms in the chlorine molecule.

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

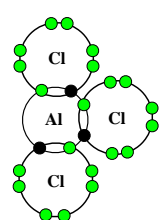
- involve **electrophilic substitution** of benzene rings
- there are two types - **Alkylation** and **Acylation**
 - Alkylation** involves the substitution of alkyl groups such as CH_3 , C_2H_5 and C_3H_7
 - Acylation** involves the substitution of acyl groups such as $\text{CH}_3\text{C}=\text{O}$
- 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



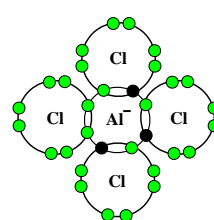
- a **catalyst** makes the attacking species more positive
- **anhydrous aluminium chloride** is the catalyst
- it works because it is a **Lewis acid**
- in AlCl_3 the aluminium is **electron deficient** - it has 6 electrons in its outer shell
- in both cases the reagent has a polar C-Cl bond
- the carbon 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 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 AlCl_3)
- the more the Cl is attracted by the AlCl_3 the more polar the C-Cl bond gets
- in the extreme case it pulls the chlorine right off leaving a C^+ behind



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

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

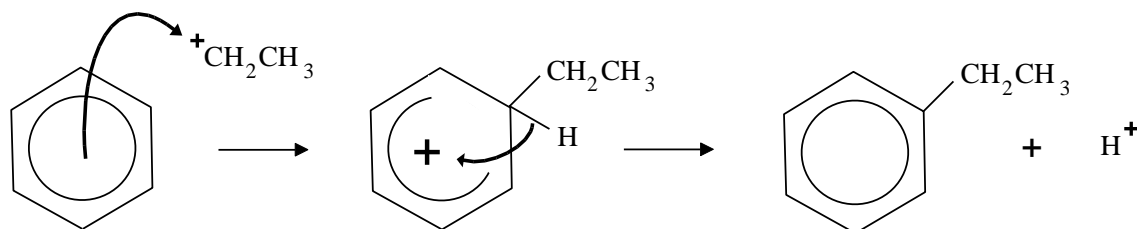
reagents a haloalkane (RX) and anhydrous aluminium chloride $AlCl_3$

conditions room temperature; dry inert solvent (ether)

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

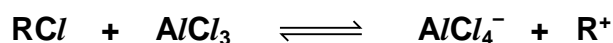
equation $C_6H_6 + C_2H_5Cl \longrightarrow C_6H_5C_2H_5 + HCl$

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 $AlCl_3$

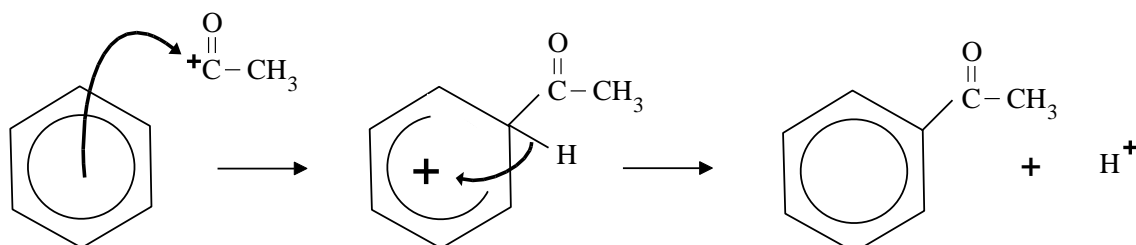
conditions reflux $50^\circ C$; dry inert solvent (ether)

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

product carbonyl compound (aldehyde or ketone)

equation $C_6H_6 + CH_3COCl \longrightarrow C_6H_5COCH_3 + HCl$

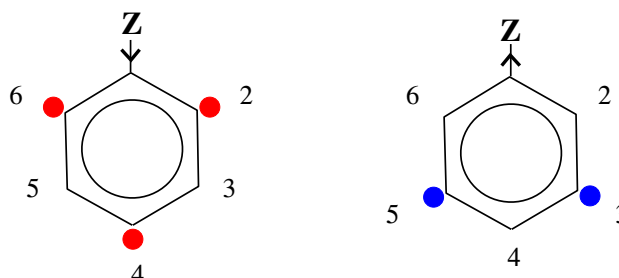
catalyst $RCOCl + AlCl_3 \rightleftharpoons AlCl_4^- + RC^+=O$



FURTHER SUBSTITUTION OF BENZENE

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

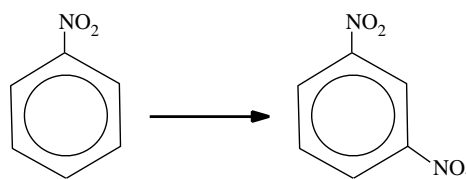
- **how easy it can be done**
- **where the next substituent goes**



Group	ELECTRON RELEASING	ELECTRON WITHDRAWING
<i>Example(s)</i> Z =	OH, NH ₂ , CH ₃	NO ₂
<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

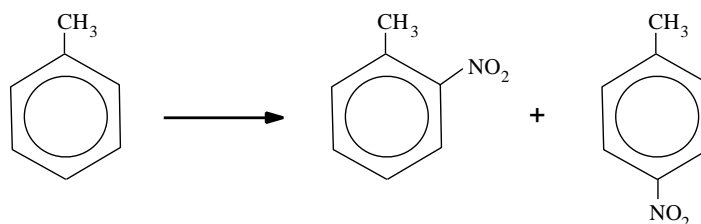
Examples **Substitution of nitrobenzene** is...

- **more difficult** than with benzene - NO₂ is electron withdrawing
- produces a 1,3 disubstituted product - NO₂ directs to the 3 (*meta*) position

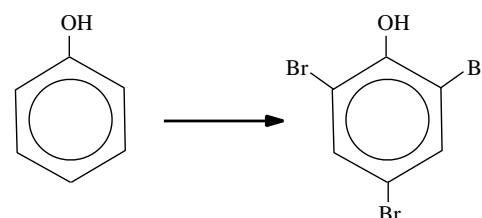


Substitution of methylbenzene is...

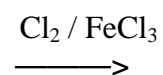
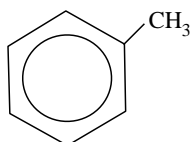
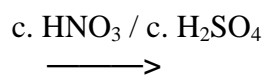
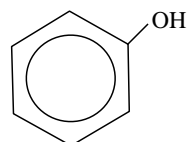
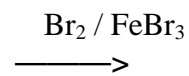
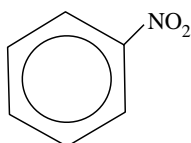
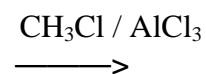
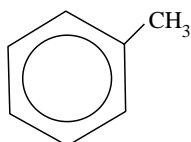
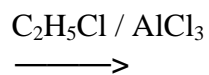
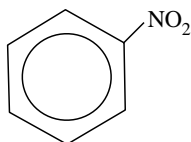
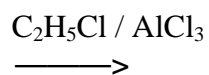
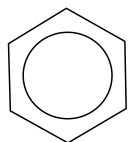
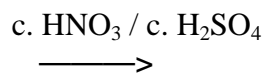
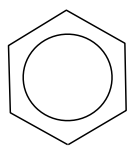
- **easier** than with benzene - CH₃ is electron releasing
- produces a mixture of isomers - CH₃ directs to 2 (*ortho*) and 4 (*para*) positions



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

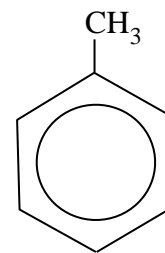


Q.4 Draw structures for the *monosubstituted* organic product(s) of the following reactions.



METHYLBENZENE

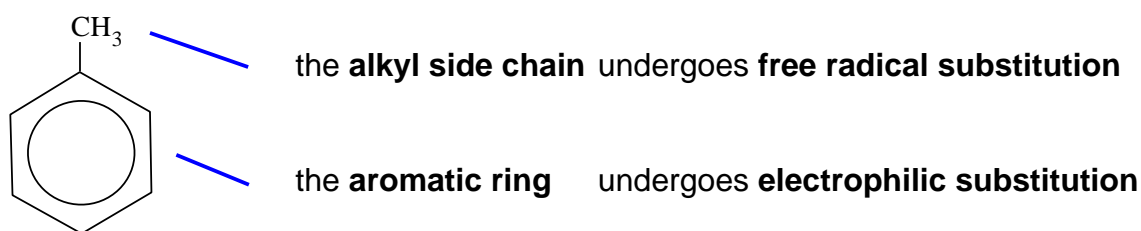
- Introduction**
- methylbenzene used to be called toluene
 - it has a methyl group attached directly to the benzene ring
 - it has the formula $\text{C}_6\text{H}_5\text{CH}_3$



Preparation formed from benzene using Friedel-Crafts alkylation

<i>reagents</i>	chloromethane and anhydrous aluminium chloride AlCl_3
<i>conditions</i>	room temperature; dry inert solvent (ether)
<i>electrophile</i>	CH_3^+
<i>equation</i>	$\text{C}_6\text{H}_6 + \text{CH}_3\text{Cl} \longrightarrow \text{C}_6\text{H}_5\text{CH}_3 + \text{HCl}$

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

