

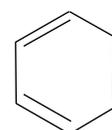
BENZENE

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

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

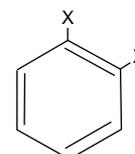
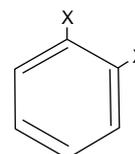
Kekule

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*

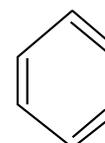
• only **one 1,2 disubstituted product** existed
i.e you didn't get two isomers like these..



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

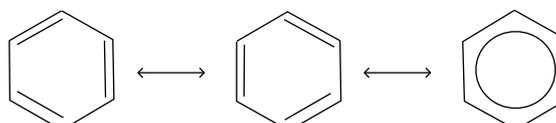


NOT



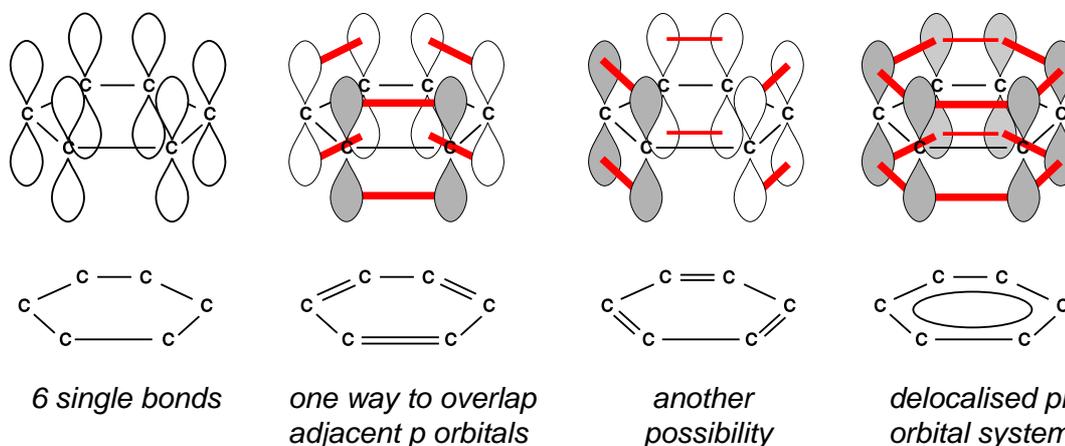
• the ring was **thermodynamically more stable** than expected - *see below*

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

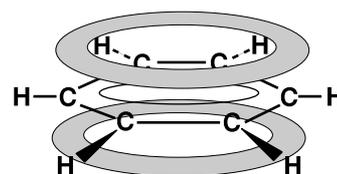


The delocalised system

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.



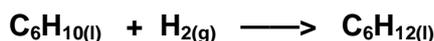
This **structure was particularly stable** and resisted any attempt to break it down through normal electrophilic addition. However, overall substitution of any of the hydrogen atoms would not affect the delocalised system.



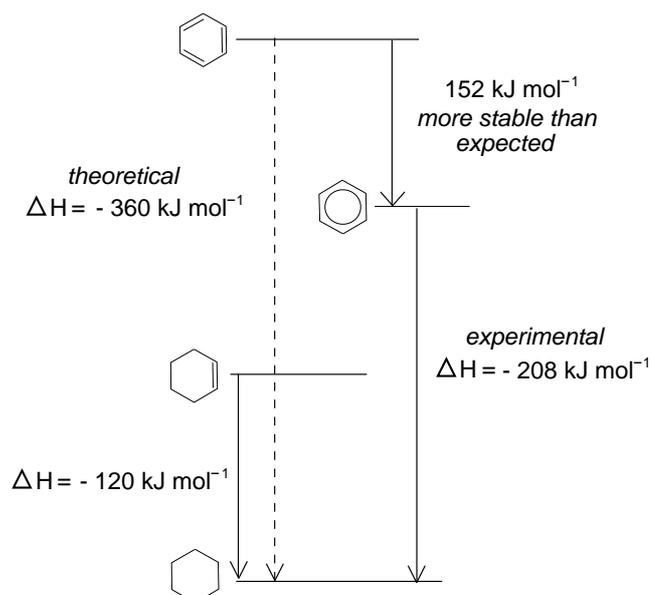
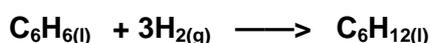
Thermodynamic evidence for stability

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 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, $C_6H_5NO_2$

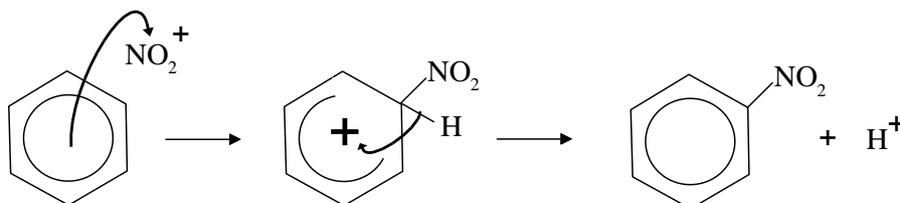
The nitration of benzene is the first step in an historically important chain of reactions. These lead to the formation of dyes, and explosives.

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

conditions reflux at $55^\circ C$

equation $C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + H_2O$

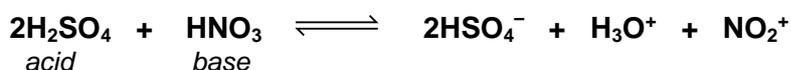
mechanism



- 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

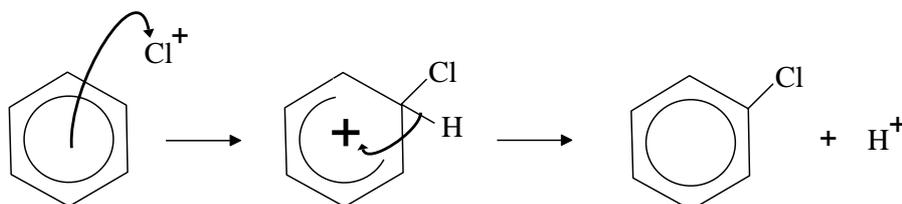
Chlorine is non polar so is not a good electrophile. A catalyst (HALOGEN CARRIER) is required to polarise the halogen.

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. **AlCl₃ acts as a Lewis Acid** and helps break the C—Cl bond.

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

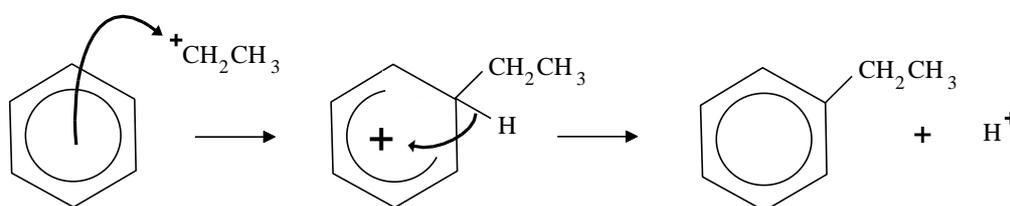
reagents a haloalkane (RX) and anhydrous aluminium chloride AlCl₃

conditions room temperature; dry inert solvent (ether)

electrophile a carbocation ion R⁺ (e.g. CH₃⁺)



mechanism



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

the Al in AlCl₃ 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
- C₆H₅CH₃

Industrial

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

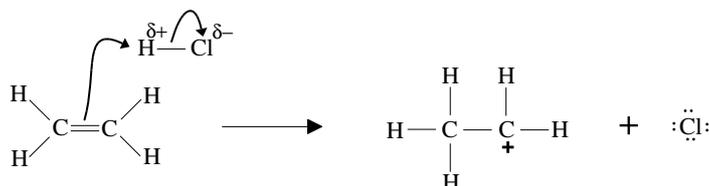
Phenylethane, $C_6H_5C_2H_5$ is made by this method

reagents ethene, anhydrous $AlCl_3$, conc. HCl

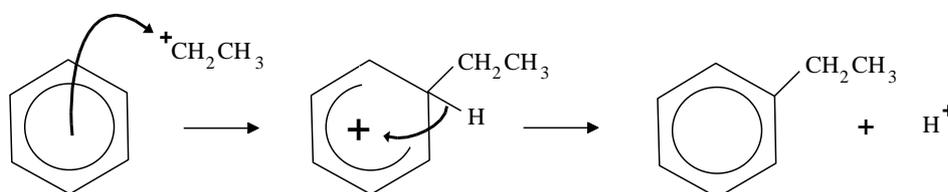
electrophile $C_2H_5^+$ (an ethyl carbocation)

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 $AlCl_3$

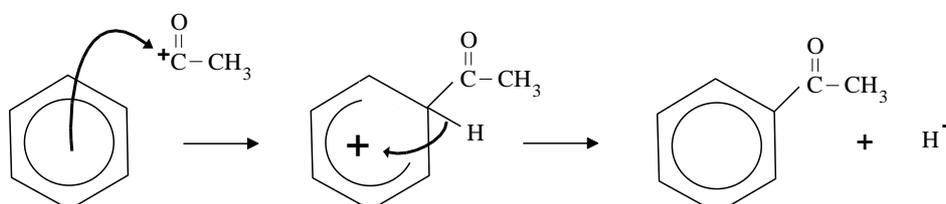
conditions reflux 50°C ; dry inert solvent (ether)

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



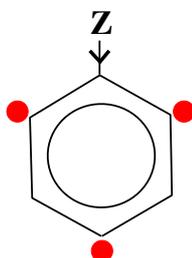
FURTHER SUBSTITUTION OF BENZENE

Theory

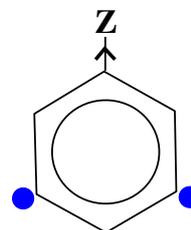
It is possible to substitute more than one functional group.

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, CH₃

Increases

Easier

2,4, and 6

NO₂

Decreases

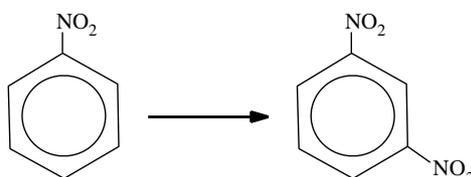
Harder

3 and 5

Examples

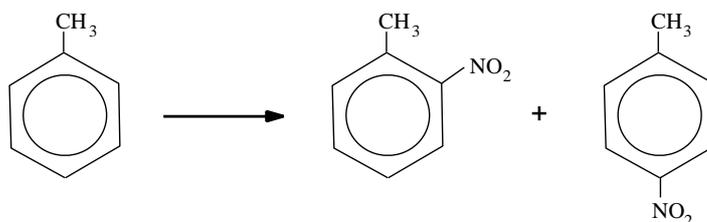
Substitution of nitrobenzene is...

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

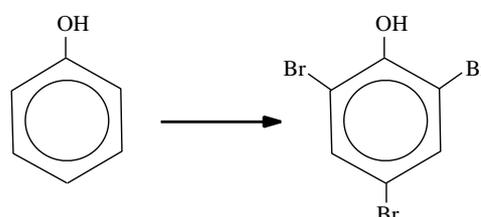


Substitution of methylbenzene is...

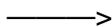
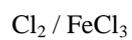
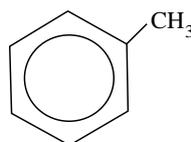
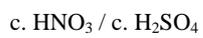
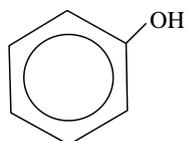
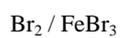
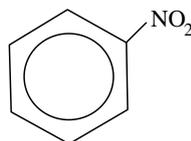
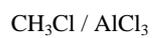
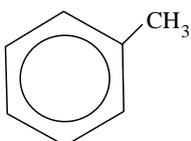
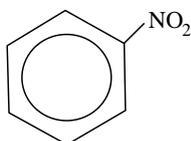
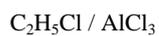
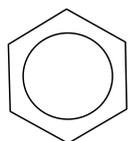
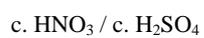
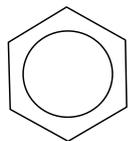
- easier than with benzene
- produces a mixture of isomers
- CH₃ is electron releasing
- CH₃ directs to the 2 (*ortho*) and 4 (*para*) position



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

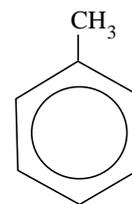


Q.4 Draw structures for the *monosubstituted* organic product(s) of the following reactions.



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 $AlCl_3$

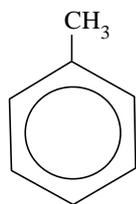
conditions room temperature; dry inert solvent (ether)

electrophile CH_3^+



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 $NaOH(aq)$

