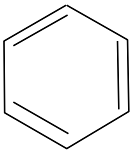
BENZENE

Structure Primary analysis revealed benzene had an... **empirical formula of CH**
and a **molecular formula of C_6H_6**

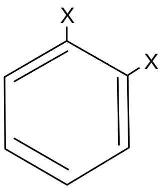
Q.1 *Draw out some suitable structures which fit the molecular formula* C_6H_6

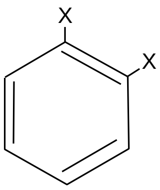
Kekule Kekulé suggested a **PLANAR**, **CYCLIC** structure with **ALTERNATING DOUBLE AND SINGLE BONDS**



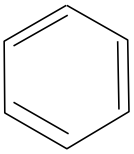
- However it **did not readily undergo electrophilic addition** *- no true C=C bond*

- 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



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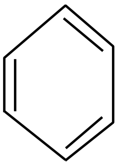
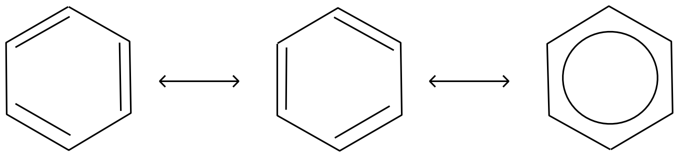
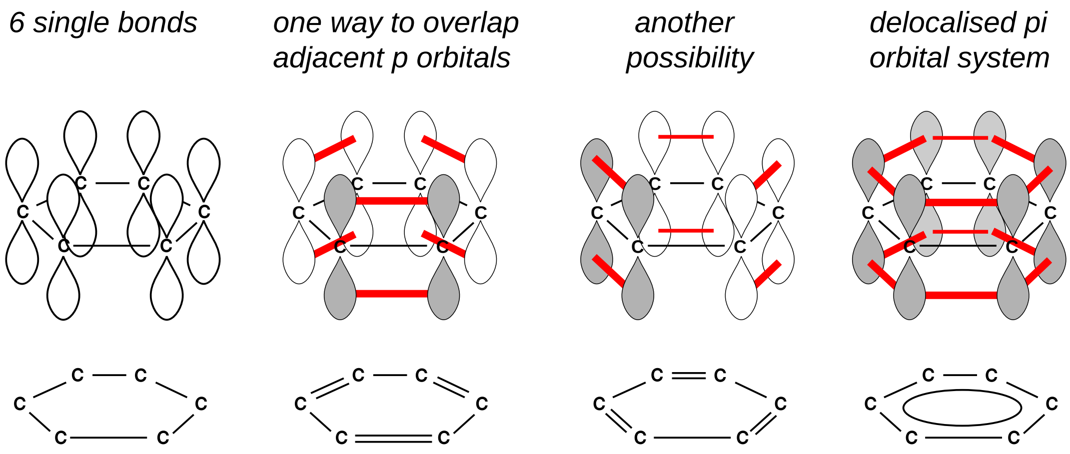


- the ring was **thermodynamically more stable** than expected - *see below*

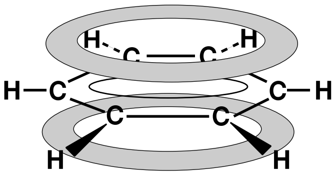
To explain the above, it was suggested that the structure oscillated between the two Kekulé forms but was represented by neither of them - a **resonance hybrid**.



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

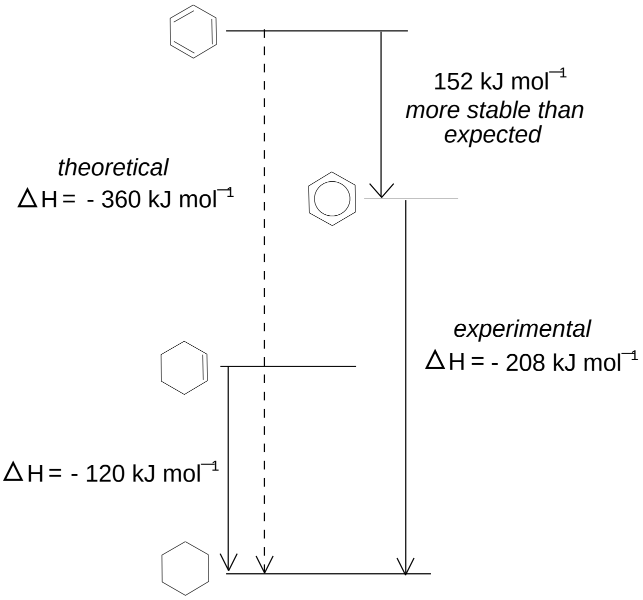
When unsaturated hydrocarbons are reduced to the corresponding saturated compound, energy is released. If the experiment is carried out in a **bomb calorimeter** the amount of heat liberated per mole (enthalpy of hydrogenation) can be measured.

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

$$C_6H_{10}(l) + H_2(g) \longrightarrow C_6H_{12}(l)$$

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

$$C_6H_6(l) + 3H_2(g) \longrightarrow C_6H_{12}(l)$$



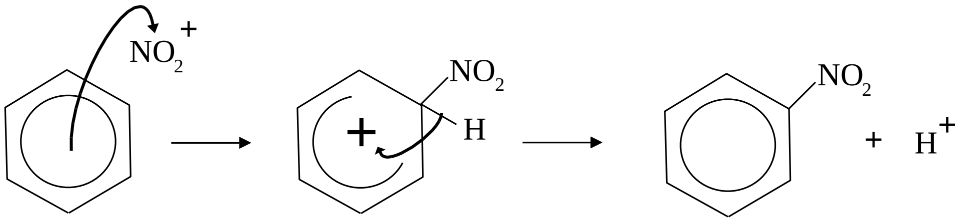
- benzene releases 208kJ per mole when reduced putting it lower down the energy scale
- it is 152kJ per mole more stable than expected.
- this value is known as the **resonance energy.**

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. These lead to the formation of dyes, and explosives.

reagents	**conc**. nitric acid and **conc**. sulphuric acid (catalyst)
conditions	reflux at 55°C
equation	$\mathbf{C_6H_6 \;+\; HNO_3 \;\longrightarrow\; C_6H_5NO_2 \;+\; H_2O}$
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**

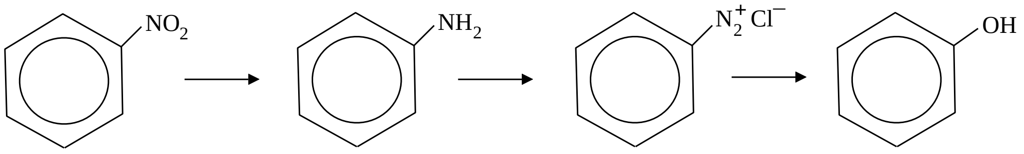
electrophile $\mathbf{NO_2^+}$, **nitronium ion** or nitryl cation

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

$$\mathbf{2H_2SO_4 \;+\; HNO_3 \;\rightleftharpoons\; 2HSO_4^- \;+\; H_3O^+ \;+\; NO_2^+}$$

acid	*base*
proton donor	*proton acceptor*

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



nitrobenzene phenylamine (aniline) benzene diazonium chloride phenol

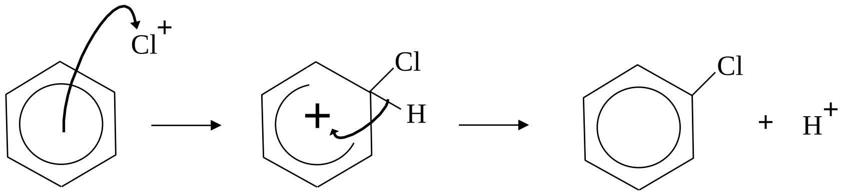
Halogenation Converts benzene into chlorobenzene, C_6H_5Cl

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 $\mathbf{C_6H_6 + Cl_2 \longrightarrow C_6H_5Cl + HCl}$

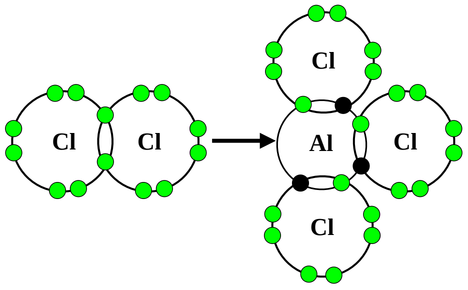
mechanism



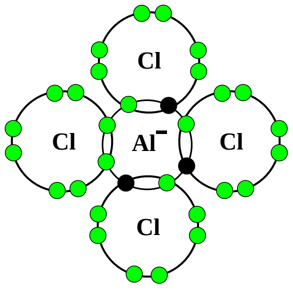
PROBLEM *Chlorine is non polar so is not a good electrophile. A catalyst (HALOGEN CARRIER) is required to polarise the halogen.*

- **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

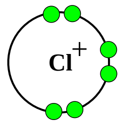
$$\mathbf{Cl_2 + AlCl_3 \rightleftharpoons AlCl_4^- + Cl^+}$$



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 $AlCl_3$

$$H^+ + AlCl_4^- \longrightarrow AlCl_3 + HCl$$

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

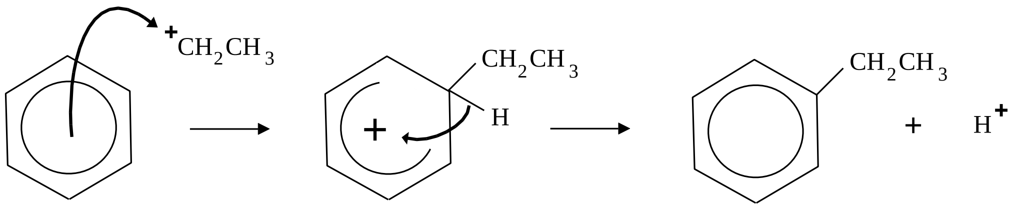
Friedel Crafts Reactions

General A catalyst is used to increase the positive nature of the electrophile and make it better at attacking benzene rings. **$AlCl_3$ 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 $AlCl_3$
conditions	room temperature; dry inert solvent (ether)
electrophile	a carbocation ion R^+ (e.g. CH_3^+)
equation	$C_6H_6 + C_2H_5Cl \longrightarrow C_6H_5C_2H_5 + HCl$

mechanism



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

the Al in $AlCl_3$ has only 6 electrons in its outer shell; - **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

$$RCl + AlCl_3 \rightleftharpoons AlCl_4^- + R^+$$

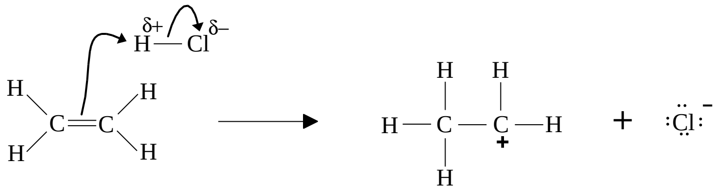
Q.2 *Which haloalkane would you use to make...*

- *propylbenzene*
- $C_6H_5CH_3$

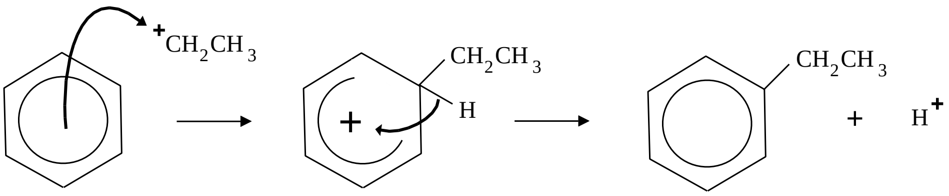
Industrial Alkenes are used instead of haloalkanes but an acid must also be present
Phenylethane, $C_6H_5C_2H_5$ is made by this method

reagents	ethene, anhydrous A*l*C*l*$_3$, conc. HC*l*
electrophile	$C_2H_5^+$ (an ethyl carbocation)
equation	**C_6H_6 + C_2H_4 ———> $C_6H_5C_2H_5$** *(ethyl benzene)*

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



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



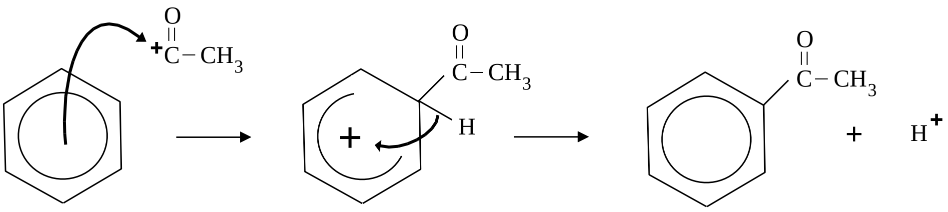
use ethyl benzene is dehydrogenated to produce phenylethene (styrene);
this is then used to make poly(phenylethene) - *also known as polystyrene*

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 was as with alkylation

reagents	an acyl chloride (RCOC*l*) and anhydrous A*l*C*l*$_3$
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 ———> $C_6H_5COCH_3$ + HC*l***

mechanism

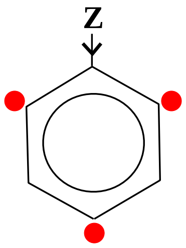


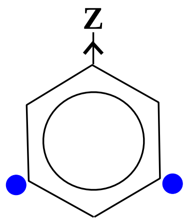
FURTHER SUBSTITUTION OF BENZENE

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**



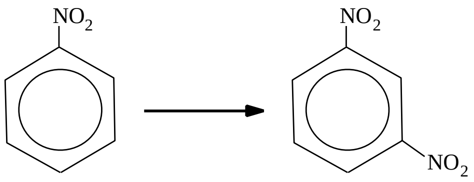


Group	**ELECTRON RELEASING**	**ELECTRON WITHDRAWING**
Example(s)	OH, CH_3	NO_2
Electron density of ring	Increases	Decreases
Ease of substitution	Easier	Harder
Position of substitution	2,4,and 6	3 and 5

Examples

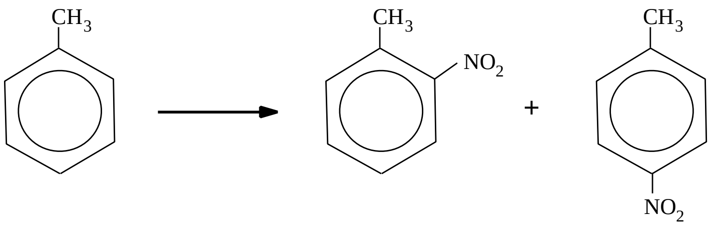
Substitution of nitrobenzene is...

- more difficult than with benzene - NO_2 is electron withdrawing
- produces a 1,3 disubstituted product - NO_2 directs to the 3 *(meta)* position

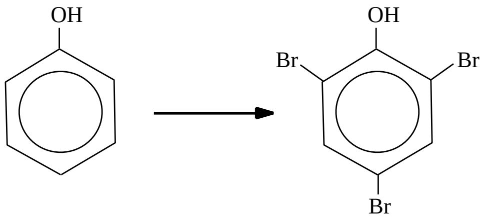


Substitution of methylbenzene is...

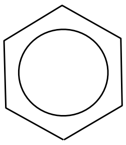
- easier than with benzene - CH_3 is electron releasing
- produces a mixture of isomers - CH_3 directs to 2 *(ortho)* and 4 *(para)* positions



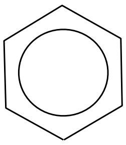
Some groups make substitution so much easier that multiple substitution takes place



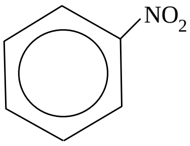
Q.4 *Draw structures for the* ***monosubstituted*** *organic product(s) of the following reactions.*



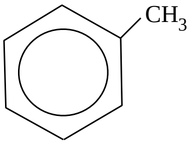
$\xrightarrow{\text{c. } HNO_3 \text{ / c. } H_2SO_4}$



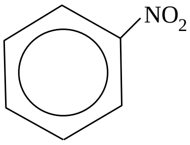
$\xrightarrow{C_2H_5Cl \text{ / } AlCl_3}$



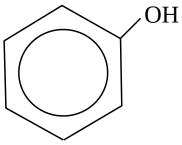
$\xrightarrow{C_2H_5Cl \text{ / } AlCl_3}$



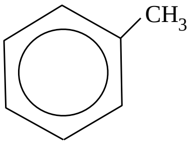
$\xrightarrow{CH_3Cl \text{ / } AlCl_3}$



$\xrightarrow{Br_2 \text{ / } FeBr_3}$

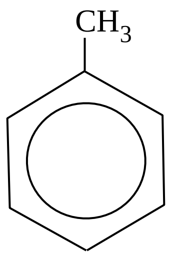


$\xrightarrow{\text{c. } HNO_3 \text{ / c. } H_2SO_4}$



$\xrightarrow{Cl_2 \text{ / } FeCl_3}$

METHYLBENZENE

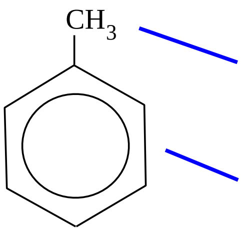


Introduction
- methylbenzene used to be called toluene
- it has a methyl group attached directly to the benzene ring
- it has the formula $C_6H_5CH_3$

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	$\mathbf{C_6H_6 + CH_3Cl \longrightarrow C_6H_5CH_3 + HCl}$

Reactions
- there are two parts to the methylbenzene molecule

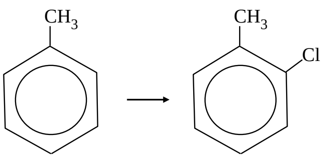


the **alkyl side chain** undergoes **free radical substitution**

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)*

a)



b)