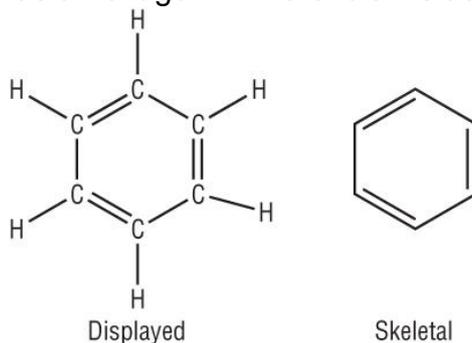# 1A – Benzene and Phenol
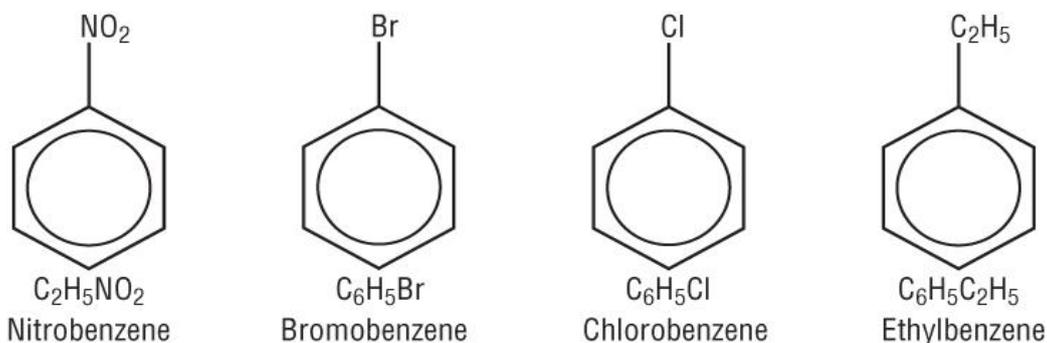
Introduction to aromatic chemistry
- This topic considers the chemistry of a group of hydrocarbons called **Arenes**.
- Benzene is usually shown as a hexagon with a circle inside:

Displayed   Skeletal

- Benzene is the simplest arene, C_6H_6.
- These compounds are often described as aromatic due to their 'aroma' or fragrant smell.

Naming compounds based on benzene:
- For a group to be attached to a benzene ring, a hydrogen must be replaced.
- Common groups are - Cl chloro, - Br Bromo, - NO_2 Nitro, and alkyl groups, - CH_3 Methyl:

NO_2	Br	Cl	C_2H_5
$C_2H_5NO_2$	C_6H_5Br	C_6H_5Cl	$C_6H_5C_2H_5$
Nitrobenzene	Bromobenzene	Chlorobenzene	Ethylbenzene

- If there is more than 1 group attached then we number to give the lowest value around the ring.
- We start numbering at the alkyl group / major functional group:

2-bromomethylbenzene   3-bromomethylbenzene   4-bromomethylbenzene
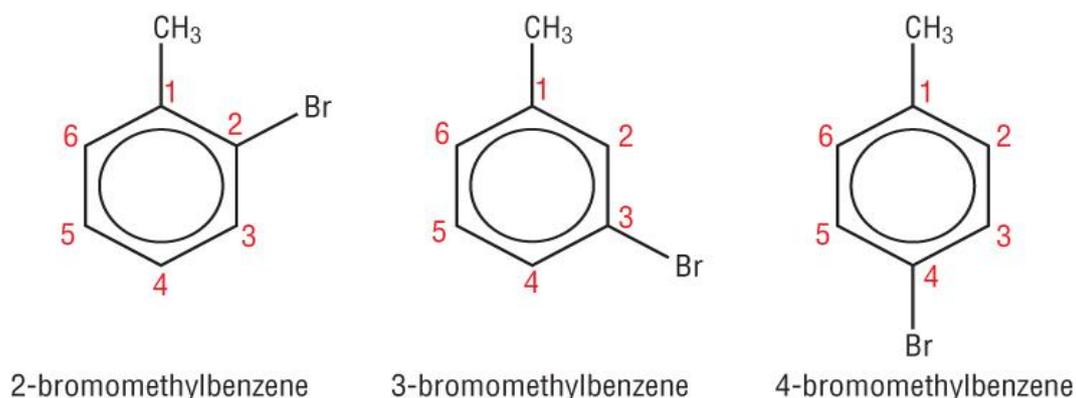
Benzene:

- Benzene is the feedstock for many other compounds including phenol, styrene, dyestuff.
- The major problem with benzene is that it is a carcinogen (cancer causing) molecule.
- Its main source is from crude but occurs naturally from volcanoes.

The structure of benzene:

- Faraday determined that the empirical formula was CH.
- It was later found that the Mr = 78. This suggested that the molecular formula was C_6H_6.
- The structure of benzene provided chemists with a major problem.
- The first structure suggested was:
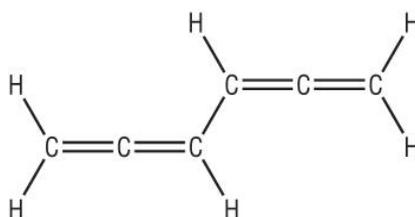
- The C=C suggests that benzene should be very reactive but in fact is very **un**reactive.
- Kekule suggested a ring structure after dreaming of snakes eating their tales:
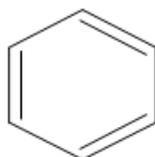
Questions 1-5 P5

The structure of benzene

Problems with Kekule structure:

- Although Kekule's structure explained the ring structure and the formula C_6H_6, there were still some chemical and physical properties that could not be explained by this structure.

Benzene's low reactivity:

- Kekule's structure failed to explain the low reactivity of benzene.
- According to the Kekule structure, 3 double bonds would be as (if not more) reactive as the alkenes.
- It is in fact quite unreactive compared to alkenes.

Kekule's equilibrium model of benzene

- Kekule suggested that this was due to an equilibria which involved the double bonds switching positions.
- He explained that the C=C changed position before any reactions could occur:
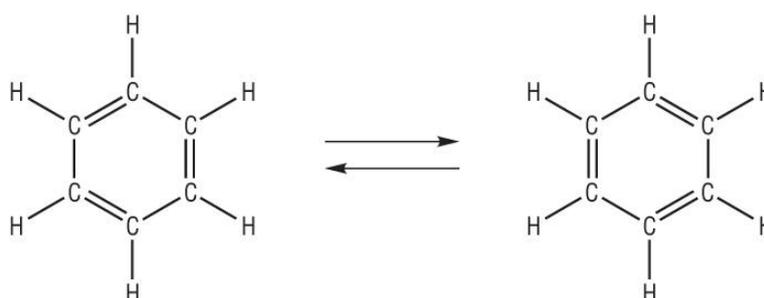
The carbon - carbon bond length in benzene:
- X - Ray diffraction threw some light on the structure.
- It was found that all the C-C bond lengths were equal in length.
- Kekule's structure would not be:

Or
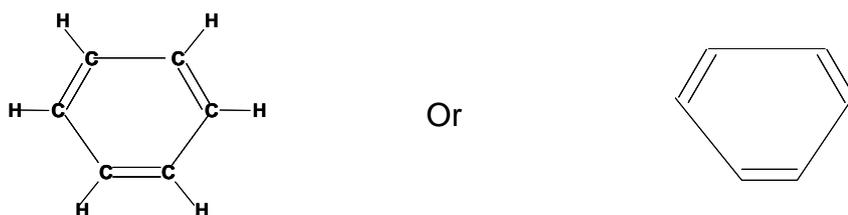
C – C 0.153nm cyclohexane
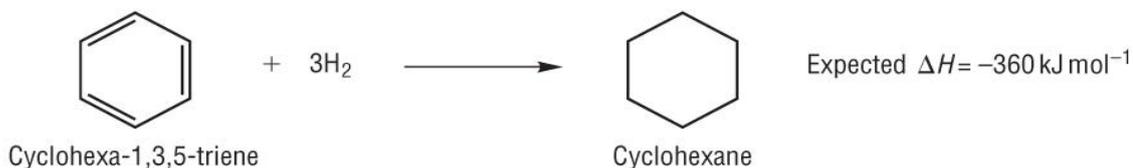
C = C 0.134nm cyclohexene

C – C 0.139nm benzene

This suggests that the C - C bond is somewhere between a single and double bond
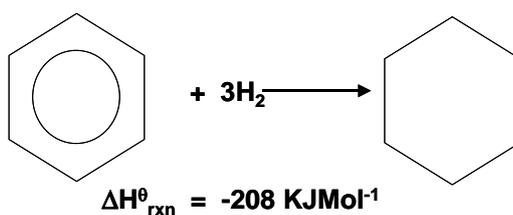**Hydrogenation of benzene**

Hydrogenation of cyclohexene – one double bond

Cyclohexene   Cyclohexane $\Delta H = -120\,kJ\,mol^{-1}$

Hydrogenation of Kekulé's benzene: cyclohexa-1,3,5-triene – three double bonds

Cyclohexa-1,3,5-triene   Cyclohexane   Expected $\Delta H = -360\,kJ\,mol^{-1}$

- Compare the results with the known value for Benzene:-

ΔH^{θ}_{rxn} = -208 KJMol^{-1}

- This tells us that benzene is more stable than the Kekule model as less energy is given out:
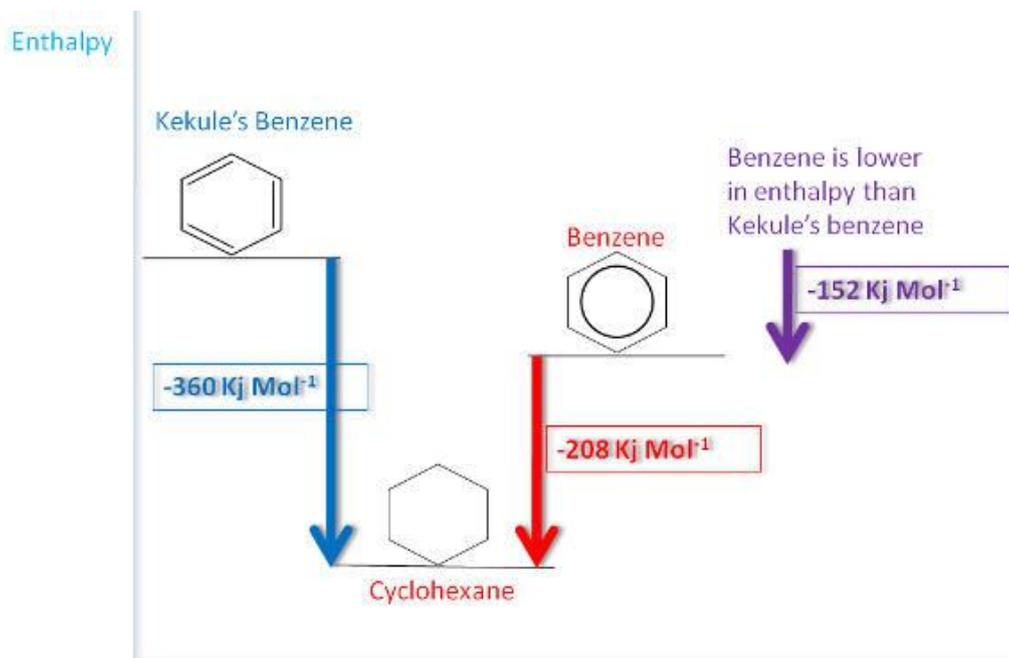
Qu 1 - 3 P 7

The delocalised model of benzene

- The weaknesses of the Kekule model lead to the delocalised model for benzene.
- Benzene has the following properties which need explaining:

    1) **6 carbon's and 6 hydrogen's.**

    2) **Arranged in a hexagonal ring.**

    3) **The shape around each carbon atom is trigonal planar with a bond angle of 120°.**

    4) **Carbon carbon bond lengths are all the same.**

- This can only be explained if we look at the bonding in benzene around the carbon atoms:

P orbital

σ bond with p orbitals overlapping to form a π bond in alkenes
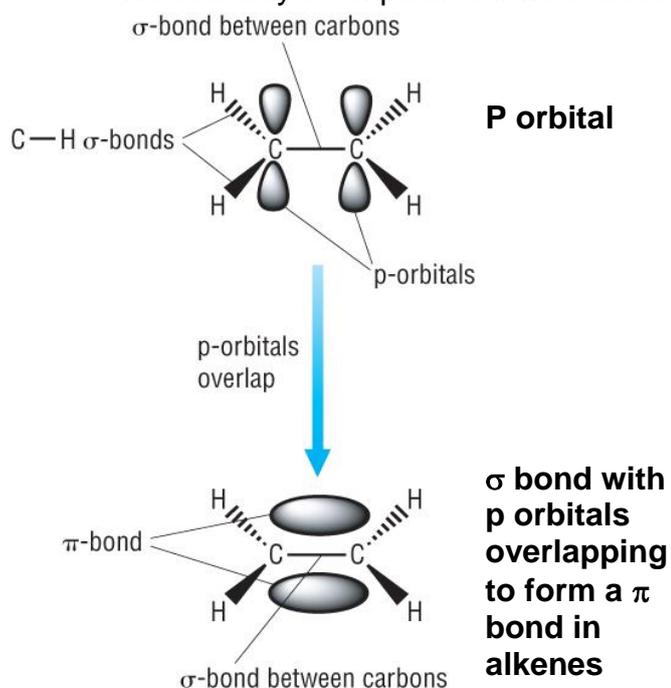
- Remember that sigma bonds, σ are covalent bonds with a maximum overlap.
- In alkenes, the second covalent bond is due to the overlap of 2 adjacent p orbitals to form a π bond.
- The alkenes have **4 electrons** between the carbon carbon double bond making it electron rich enough to polarise an electrophile.
- These electrons are localised - only in the C=C.

- Imagine 6 of these p orbitals on every carbon in benzene:
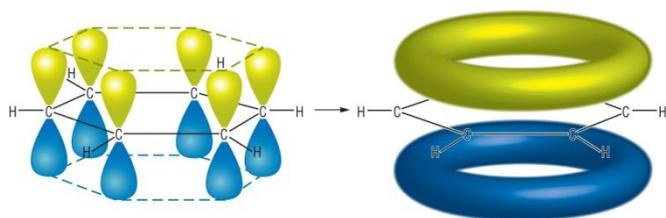
- if 2 x p orbitals can overlap forming a π bond then 6 x p orbitals can overlap forming a system of π orbitals spread over all 6 carbons.
- The 6 electrons can be anywhere in this system.
- This means that the electrons are not localised around 1 carbon but delocalised over all 6 carbons.

6 x p orbitals π **delocalised orbital**

- 6 electrons are delocalised in this system.
- This means that each C - C has 3 electrons. 2 in the σ bond and 1 from the delocalised π system.
- This makes it slightly less electron rich than alkenes which means that they are not as good at polarising electrophiles.
- The bonding in benzene **cannot** therefore be described as **3 C = C and 3 C – C** bonds.
- One way of thinking about it is that the bonds between the carbons is somewhere in between (6 x 1 $^1/_2$ bonds!!)
- The bonding but must be considered as a delocalised electron charge cloud spread out over the whole ring.
- This gives rise to certain difficulties when drawing the structure of benzene as:-

    – Represents 2e's in a bond

    = Represents 4e's in a double bond

- As neither of these is appropriate to show the distribution of electrons in benzene, the following structure is often used:-
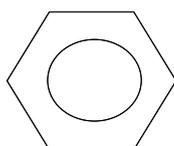
The delocalised model of benzene and chemical reactivity:

- Benzene is more stable than expected, less so than alkenes.
- This is because the electron density between the carbon atoms is less than in alkenes.
- This makes them attract electrophiles less well than alkenes:

Reaction with	Alkenes	Benzene
Decolorise bromine water	✓	✗
Strong acids, HCl	✓	✗
Halogens, Cl_2	✓	✗

- If it was an addition reaction like the alkenes then the delocalised ring structure would be disrupted as the electrons would be needed to form bonds with the electrophile.
- This would make the product less stable than benzene meaning the reaction would be energetically unfavourable.
- For these reasons, benzene undergoes **substitution** instead of **addition** in order to maintain the delocalised electron system and its stability.   **Qu 1 - 4 P 9**

Benzene and its reactions
Reactivity
- Benzene in toxic and carcinogenic so Methylbenzoate (or methoxy benzene), a derivative of benzene is used:-
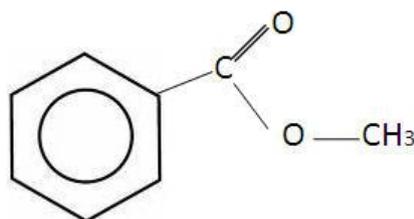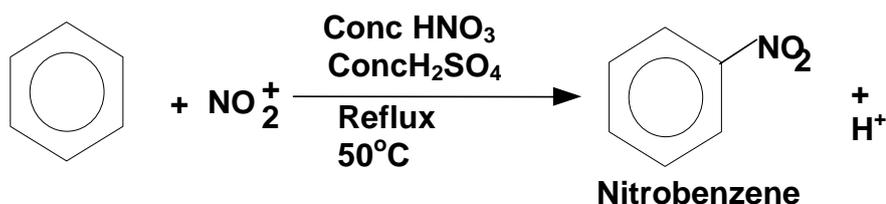

Electrophilic substitution

- Methoxybenzene is slightly more reactive than benzene. The conditions involving benzene will be more severe.

1) Nitration of benzene
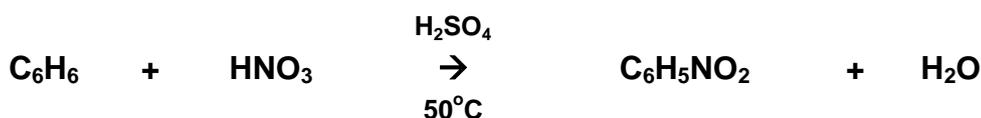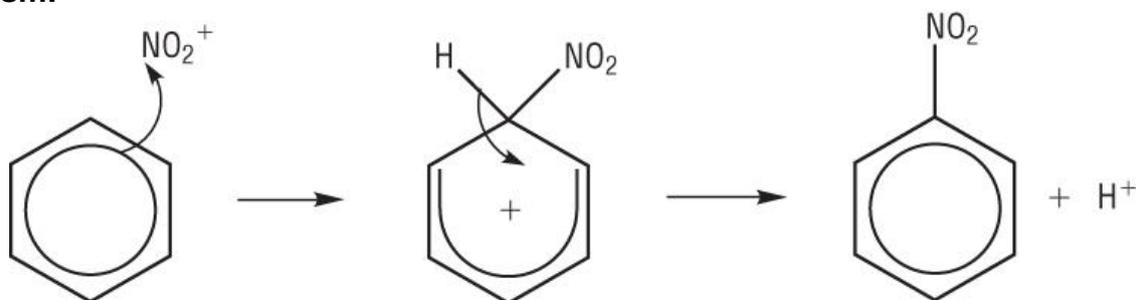- Nitration of benzene requires the production of a more reactive nitryl ion:

$$HNO_3 \quad + \quad H_2SO_4 \quad \rightarrow \quad NO_2^+ \quad + \quad HSO_4^- \quad + \quad H_2O$$

Nitryl ion is electrophile

Nitrobenzene

- The H^+ generated will react with HSO_4^- forming sulphuric acid, H_2SO_4. This means sulphuric acid is a catalyst

$$H^+ \quad + \quad HSO_4^- \quad \rightarrow \quad H_2SO_4$$

- The reaction fro the nitration of benzene is:

$$C_6H_6 \quad + \quad HNO_3 \quad \xrightarrow[50^oC]{H_2SO_4} \quad C_6H_5NO_2 \quad + \quad H_2O$$

Mechanism:

- The benzene ring is rich with electrons which mean the ring will attract an electrophile.
- A pair of electrons move from the ring to the nitryl ion forming a covalent bond.
- This disrupts the delocalisation of the benzene ring to 4 electrons over the remaining 5 carbon atoms leaving a positive charge.
- The loss of the hydrogen (proton) puts 2 electrons back into the benzene. This restores the full delocalised π electron system.

Nitration of methylbenzene
- Methyl benzene used to be called toluene.
- The nitration of toluene forms nitro toluene.
- This can be nitrated in the 2,4,6 position:
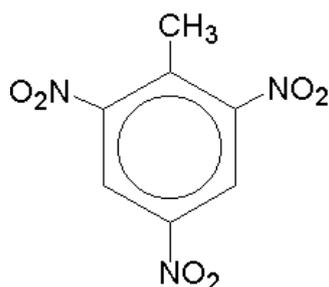
2) Halogenation of benzene

- Benzene will not react with bromine on its own. It requires the help of a type of catalyst called a halogen carrier.
- These halogen carriers include:

    $FeCl_3$, $FeBr_3$, $AlCl_3$, $AlBr_3$ (depending on which halogen you are adding)

    Fe can be used on its own as it will react with any halogen forming $FeHal_3$
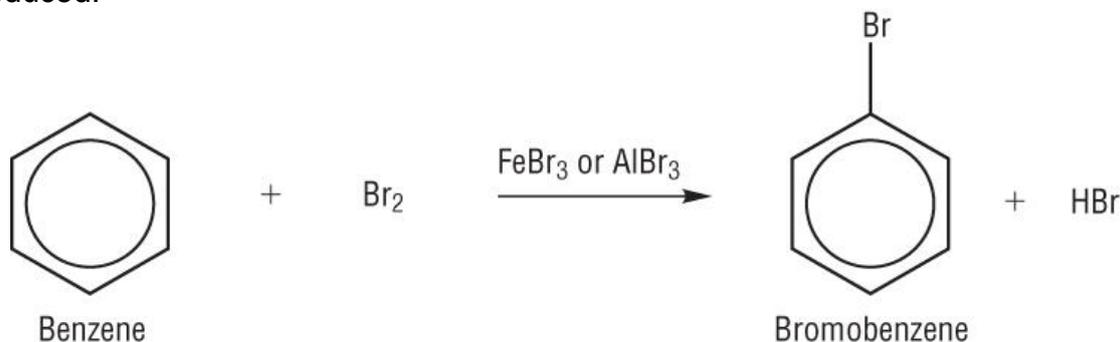
- These reactions involve electrophilic substitution (as with nitration) where a hydrogen is substituted with a halogen.

The reaction with chlorine and bromine:
- When a benzene ring reacts with chlorine, chlorobenzene and hydrogen chloride is produced.
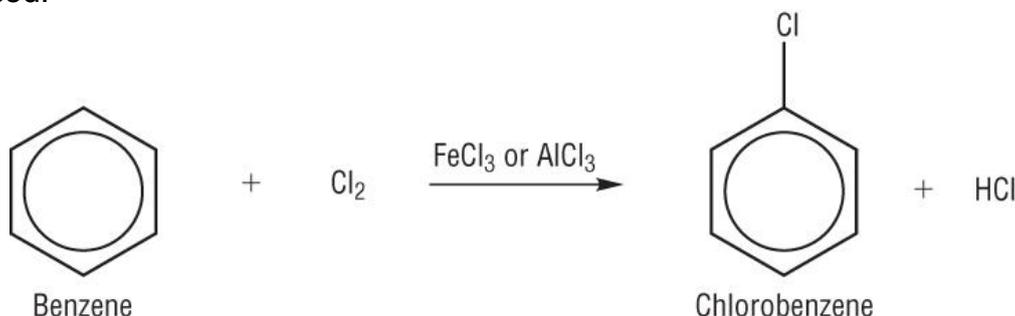
- When a benzene ring reacts with bromine, bromobenzene and hydrogen bromide is produced.

- Bromobenzene is used in production of pharmaceuticals.
- Similarly the reaction with chlorine (and $FeCl_3$) gives chlorobenzene and hydrogen chloride.
- Chlorobenzene is used in the production of pesticides.

Function of the halogen carrier (catalyst):
- Benzene is more stable than alkenes which means that Br_2 is not a strong enough electrophile.
- Although benzene has delocalised electrons, it is not sufficiently electron rich to polarise a bromine molecule like an alkene (count the electrons!)
- The halogen carrier generates a Br^+ which is a more powerful electrophile than a bromine molecule (because it is more positive)
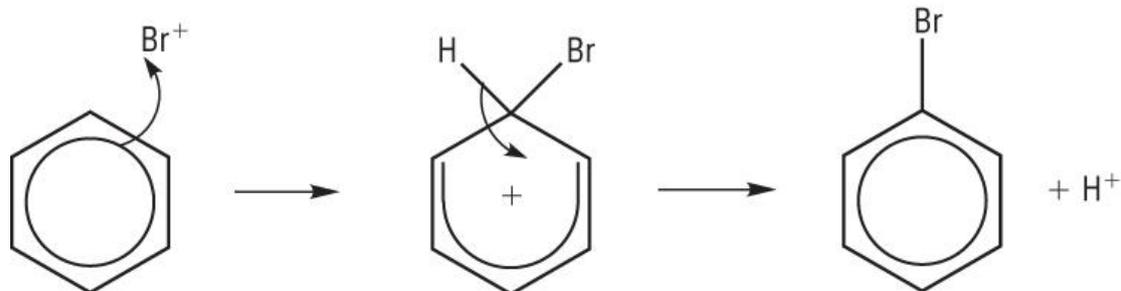
$$FeBr_3 \ + \ Br_2 \ \rightarrow \ FeBr_4^- \ + \ Br^+$$

Mechanism:

- The benzene ring is rich with electrons which mean the ring will attract an electrophile.
- A pair of electrons move from the ring to the bromonium ion forming a covalent bond.
- This disrupts the delocalisation of the benzene ring to 4 electrons over the remaining 5 carbon atoms leaving a positive charge.
- The loss of the hydrogen (proton) puts 2 electrons back into the benzene. This restores the full delocalised π electron system.

Regeneration of the halogen carrier (catalyst):
- The hydrogen ion generated reacts with $FeBr_4^-$ regenerating the halogen carrier catalyst and hydrogen bromide
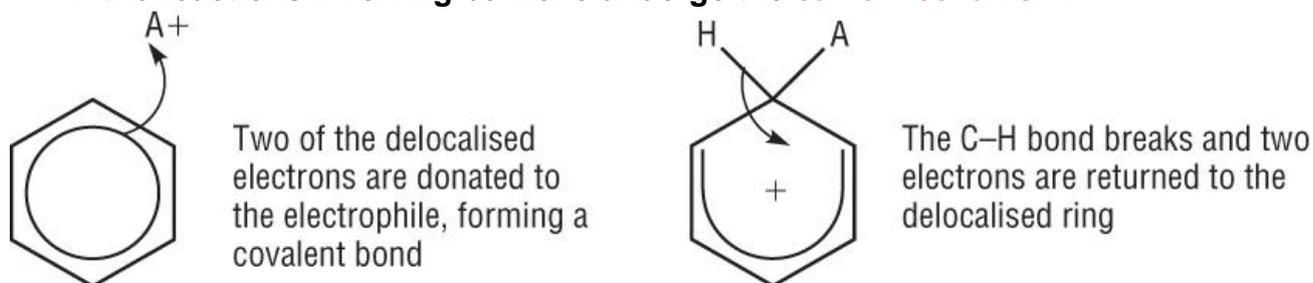
$$FeBr_4^- \ + \ H^+ \ \rightarrow \ FeBr_3 \ + \ HBr$$

Other halogens
- The reactions and mechanisms are the same for all halogenation reactions, Cl_2 with $FeCl_3$ etc.

Mechanisms for benzene:

All the reactions involving benzene undergo the **same mechanism**:

Two of the delocalised electrons are donated to the electrophile, forming a covalent bond

The C–H bond breaks and two electrons are returned to the delocalised ring

- The benzene ring is electron rich which means the ring will attract an electrophile.
- A pair of electrons move from the ring to the electrophile forming a covalent bond.
- This disrupts the delocalisation of the benzene ring to 4 electrons over the remaining 5 carbon atoms leaving a positive charge.
- The intermediate is unstable meaning the second step is rapid
- The loss of the hydrogen (proton) puts 2 electrons back into the benzene. This restores the full delocalised π electron system.
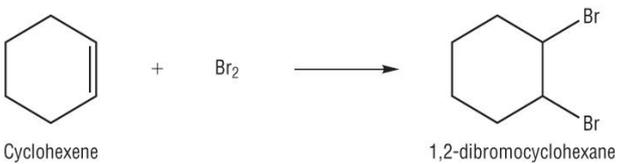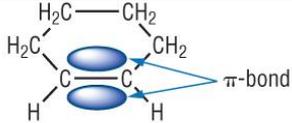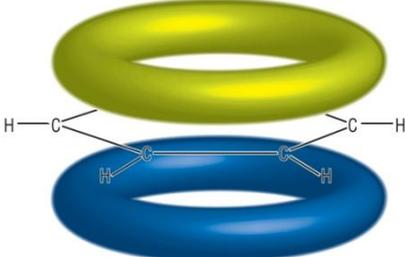
Full mechanism:

Unstable intermediate
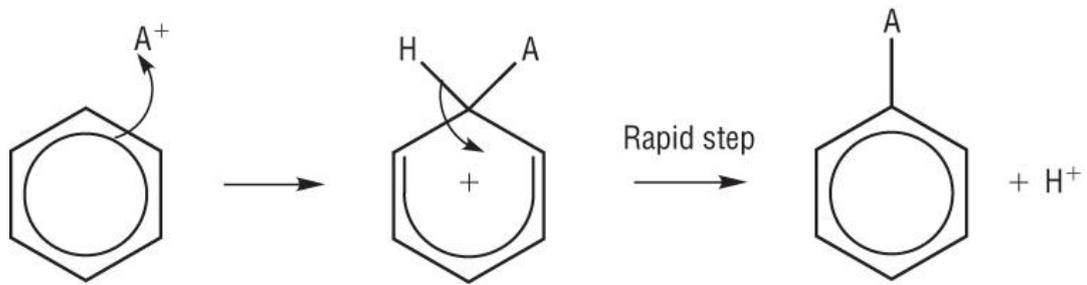
Qu 1 - 4 P11 / 1 - 3 P13

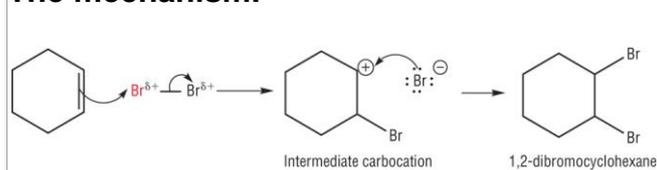# The reactivity of alkenes and benzene

Cyclohexene vs Benzene

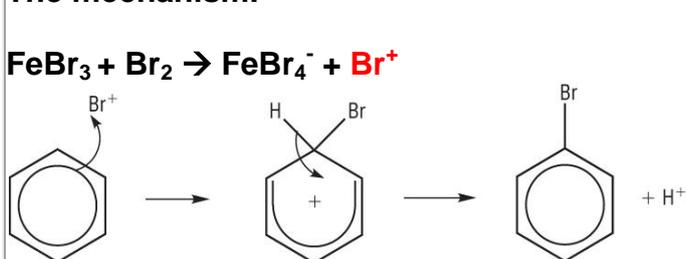| Cyclohexene	Benzene
• We already know that an alkene such as cyclohexene will decolourise bromine water:	• When benzene reacts with bromine, a halogen carrier is required:
The difference between an alkene and benzene is the electron density	
• An alkene has **2e** from a σ bond and **2e** from the localised π bond = **4e** • This has a high electron density = electron rich. • This will polarise an incoming electrophile like bromine sufficiently that it will react with the alkene readily. • Alkenes do not need Br$^+$ so do not need a halogen carrier.	• Benzene has **6** delocalised π electrons distributed over **6 bonds**. This averages **1e** per C-C bond. • Benzene's **C-C bonds** have **2e** from a σ bond and **1e** from the delocalised π system = **3e** • This does not have the electron density of an alkene = less electron rich. • This will not polarise an electrophile sufficiently enough to react. • Benzene requires Br$^+$ (more positive) so needs a halogen carrier:
The mechanism: 	The mechanism: **FeBr$_3$ + Br$_2$ → FeBr$_4^-$ + Br$^+$** **FeBr$_4^-$ + H$^+$ → FeBr$_3$ + HBr**
• Alkenes add electrophiles (chlorine) to themselves.	• Benzene substitutes electrophiles (bromine) with hydrogen.
Electrophilic addition	**Electrophilic substitution**

Qu 1-2 P15

Phenols

- In alcohols the OH group is attached to an alkyl group.
- In phenol, the OH group is attached directly to the benzene ring.
- Phenols are used in **antiseptics**.
- It is described as an aromatic alcohol:
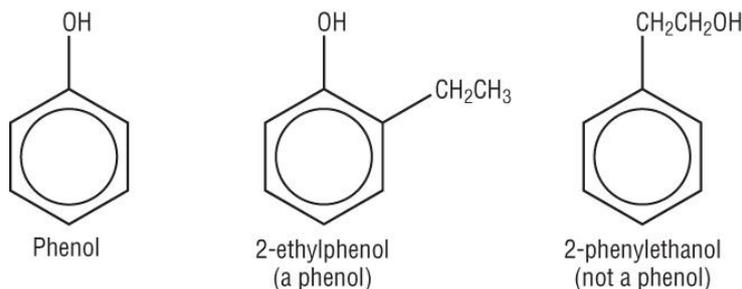

Reactions of phenol

- Phenol is toxic and corrosive therefore a safer alternative is used which will show the chemistry of phenol. Methyl 4-hydroxybenzoate is used as a safe alternative:

1. Solubility in water

- Phenol is sparingly soluble in water.
- The OH in phenol will form hydrogen bonds just like ethanol.
- The large benzene ring limits its solubility only being able to form weak van der Waals.

2. Acidic properties

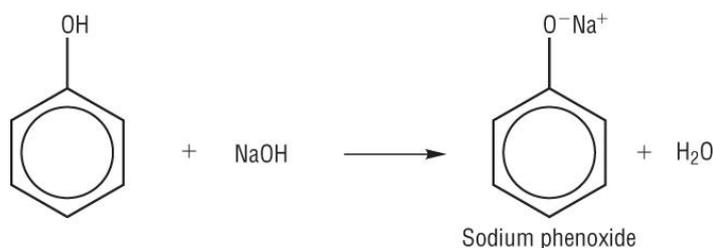- Phenol is a weak acid because it partially dissociates in water:
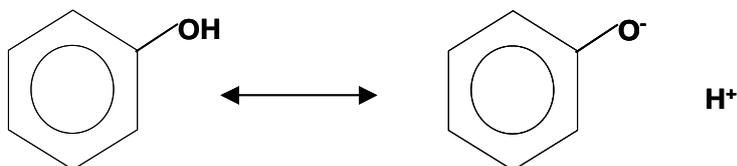
Phenol Phenoxide
a) Reaction with sodium hydroxide:

- Remember:

   Acid   +   metal hydroxide   →   salt   +   water

- Phenol (a weak acid) will react with sodium hydroxide forming sodium phenoxide (a salt) and water:

Sodium phenoxide

   C_6H_5OH + $NaOH$ → $C_6H_5O^-Na^+$ + H_2O

b) Reaction with sodium:

- Remember:

Acid + metal → salt + hydrogen

- Phenol (a weak acid) will react with sodium forming sodium phenoxide (a salt) and hydrogen:

Sodium phenoxide

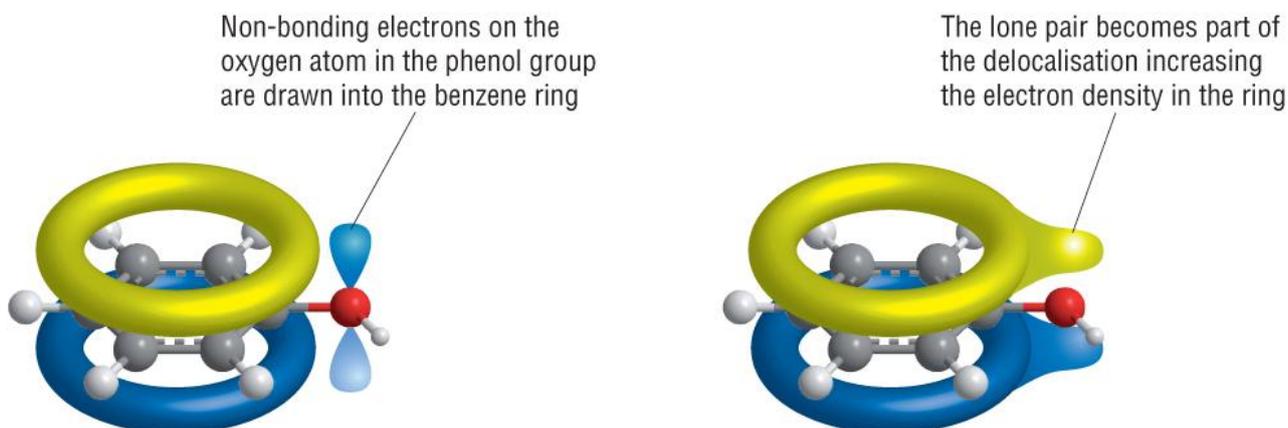$$2C_6H_5OH + 2Na → 2C_6H_5O^-Na^+ + H_2$$

3. Reaction with bromine

- The bromination of phenol does not require a halogen carrier like benzene.
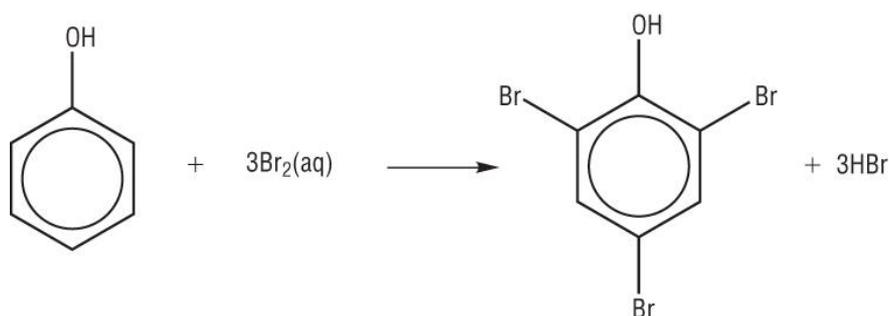
2,4,6 – tribromophenol

- This means that something in its structure must make in more reactive than benzene.
- The electron density in the benzene ring must be greater than that of benzene.
- The difference between benzene and phenol is the OH group.
- The oxygen atom in the OH group has a lone pair of **p orbital electrons**.
- These are able to delocalise with the π **electrons** in the benzene ring:

Non-bonding electrons on the oxygen atom in the phenol group are drawn into the benzene ring

The lone pair becomes part of the delocalisation increasing the electron density in the ring

- This gives the benzene ring in phenol a high electron density = electron rich, the ring is said to be **activated**.

- This will polarise and attract an incoming electrophile like bromine sufficiently that it will react readily.
- So phenols do not require a halogen carrier.

Uses of phenols:

- **Antiseptics**
- Synthesis of dyes and aspirin
- Explosives
- Resins (plastic like materials, and / or glues).

Qu 1 - 3 P17 / 1 - 3 P19
Qu 1- 4 P41
Qu 1 - 3 P43