Arenes

The structure and stability of benzene, its reactions, electrophilic substitution mechanisms for halogenation, nitration and Friedel-Crafts, and phenol.

The structure of benzene

Benzene is C_6H_6, a planar ring of six carbon atoms with all C–C bond lengths equal and all bond angles 120°.

The delocalised model

Each carbon uses three of its four outer electrons to form σ bonds (to two carbons and one hydrogen). The fourth is in a p **orbital** perpendicular to the ring. The six p orbitals **overlap sideways** to make a ring of **delocalised π electron density** above and below the plane of the ring.

The ring may be drawn as a hexagon with a circle inside it, or as the Kekulé structure with alternating double bonds, as appropriate in equations and mechanisms.

Evidence for the structure and stability

Evidence	Finding	Conclusion
Thermochemical	The hydrogenation of cyclohexene is -120 kJ mol^{-1}. For a Kekulé benzene with 3 double bonds, the expected value is -360 kJ mol^{-1}. The measured value is about -208 kJ mol^{-1}, **152 kJ less exothermic**	Benzene is more **stable** than Kekulé's structure, by about 152 kJ mol^{-1} (the **delocalisation energy**)
X-ray diffraction	All C–C bond lengths are **0.140 nm**, between C–C (0.154 nm) and C=C (0.134 nm)	No alternate single and double bonds
Infrared	No absorption typical of an isolated $C=C$ bond	No localised double bonds
Chemical	Does not decolourise bromine water; reacts by substitution, not addition	Electrons not localised

Why benzene is resistant to addition

In an alkene the π bond is **localised** between two carbons, so the electron density there is high and it polarises bromine easily. In benzene the π electrons are **delocalised** over six carbons, so the electron density at any one position is lower and a bromine molecule is **not polarised enough** to react. Benzene

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needs a **catalyst** and a stronger electrophile. If it did undergo addition, it would lose the stable delocalised ring, so **substitution** (which keeps the ring) is preferred.

Reactions of benzene

Reaction	Reagents and conditions	Product
Combustion	Oxygen	CO_2 and H_2O, with a **smoky flame** (high carbon to hydrogen ratio)
Bromination	Br_2 with $FeBr_3$ (or iron) halogen carrier, room temperature	Bromobenzene
Nitration	**Concentrated HNO_3 and concentrated H_2SO_4**, below 55 °C	Nitrobenzene
Sulfonation	Fuming sulfuric acid	Benzenesulfonic acid
Friedel–Crafts alkylation	A halogenoalkane with $AlCl_3$	Alkylbenzene
Friedel–Crafts acylation	An acyl chloride with $AlCl_3$	Phenyl ketone

Keep the temperature **below 55 °C** during nitration, to avoid dinitration.

Mechanism: electrophilic substitution

General steps:

1. An **electrophile**, E^+, is generated.
2. The delocalised π electrons attack E^+ (curly arrow from the ring to E^+). This forms a **carbocation intermediate** in which the delocalisation is partly lost.
3. A base removes H^+ from the carbon bearing E (curly arrow from the C–H bond back to the ring), restoring the delocalised ring. The **catalyst is regenerated**.

Generating the electrophile

- **Bromination**: $Br_2 + FeBr_3 \rightarrow Br^+ + FeBr_4^-$ (the halogen carrier accepts a bromide, polarising the bromine). The electrophile is Br^+.
- **Nitration**: $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$. The electrophile is the **nitronium ion**, NO_2^+. Sulfuric acid acts as an acid, and nitric acid as a base.
- **Friedel–Crafts alkylation**: $CH_3Cl + AlCl_3 \rightarrow CH_3^+ + AlCl_4^-$. For acylation, $CH_3COCl + AlCl_3 \rightarrow CH_3CO^+ + AlCl_4^-$.

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In each case the H^+ lost from the ring reacts with the $AlCl_4^-$ or $FeBr_4^-$ to regenerate the catalyst ($H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$).

> **In the mechanism show the intermediate as a partial ring (a horseshoe) with a + charge inside, and with the H and E on the carbon at the top. The curly arrow goes from the ring (not from an atom) to the electrophile.**

Phenol

Phenol, C_6H_5OH, has an $-OH$ group on a benzene ring. It reacts with **bromine water** at room temperature, with no catalyst, to give a **white precipitate of 2,4,6-tribromophenol**, and the bromine water is decolourised.

$$C_6H_5OH + 3Br_2 \rightarrow C_6H_2Br_3OH + 3HBr$$

> **NOTE**
>
> Phenol is more reactive than benzene because a lone pair on the oxygen is **delocalised into the ring**, which **increases the electron density** of the ring. This polarises bromine, so the ring attacks the electrophile without a catalyst.

> **TRY IT**
>
> Methylbenzene is nitrated. How many products might form, and why is a lower temperature used?

The methyl group directs substitution to the 2 and 4 positions, so 2-nitromethylbenzene and 4-nitromethylbenzene form. The temperature is kept low so that only one nitro group is added. (In an exam the question will state the groups.)

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