

Arenes

A-Level Chemistry 9701 · Topic 30 revision notes

Everything from the 2 lessons of this topic on a few pages: the key idea of each lesson, the diagram to remember, the points to learn and the traps examiners set. Read it, cover it, test yourself.

1. Arenes

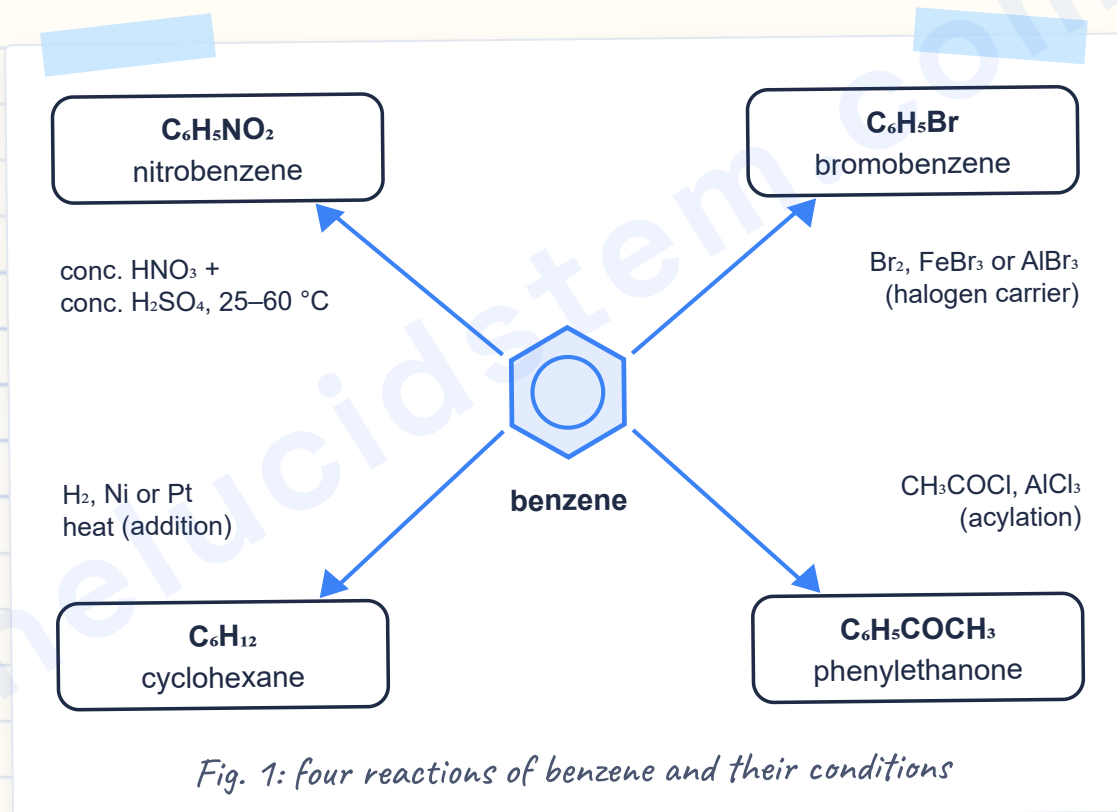
2. Electrophilic substitution

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1 Arenes

Syllabus 30.1

In **benzene**, C_6H_6 , each carbon is sp^2 hybridised: the ring is planar with 120° bond angles, and the six unhybridised p orbitals overlap sideways to form a **delocalised π system** above and below the ring. All six $C-C$ bonds are the same length (0.139 nm), between $C-C$ and $C=C$. Delocalisation makes benzene about 152 kJ mol^{-1} more stable than a ring of three separate double bonds, so it reacts by **electrophilic substitution**, keeping the ring intact. With a **halogen carrier** ($AlCl_3$, $AlBr_3$ or $FeBr_3$) it is halogenated; with **conc. HNO_3 + conc. H_2SO_4** at $25-60^\circ\text{C}$ it is nitrated; with RCI or $RCOCl$ and $AlCl_3$ it undergoes **Friedel-Crafts** alkylation or acylation. An alkyl **side chain** is oxidised to $-COOH$ by hot alkaline $KMnO_4$ then acid, and is chlorinated by free radicals in **UV light**; H_2 with a Ni or Pt catalyst and heat adds to give cyclohexane.



Carrier for the ring, UV for the chain.

- ✓ **Halogenation:** $X_2 + AlCl_3/AlBr_3/FeBr_3$.
- ✓ **Nitration:** conc. HNO_3 + conc. H_2SO_4 , 25–60 °C.
- ✓ **Friedel-Crafts:** RCI or $RCOCl + AlCl_3$.
- ✓ **Side chain:** Cl_2/UV substitutes; hot alkaline $KMnO_4$ then acid gives $-COOH$.

Watch out!

Benzene does **not** decolourise bromine water; it needs pure Br_2 **and** a halogen carrier, and the reaction is substitution (HBr is the by-product), not addition. Nitration uses **concentrated** HNO_3 and **concentrated** H_2SO_4 , kept at or below about 60 °C to avoid further nitration. Chlorine plus **UV light** attacks the side chain; chlorine plus **$AlCl_3$** attacks the ring. Side-chain oxidation turns the whole alkyl group into **$-COOH$** , whatever its length, and it needs acid at the end.

2 Electrophilic substitution

Syllabus 30.1

In **electrophilic substitution** a strong electrophile is made first: for nitration, $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{H}_3\text{O}^+ + 2\text{HSO}_4^-$. A curly arrow from the **delocalised π system** to the electrophile forms a new C-E bond, giving a positive **intermediate** (an arenium ion) in which the delocalisation is **partly broken**: four electrons over five carbons. A curly arrow from the C-H bond back into the ring then removes **H^+** and **restores the aromatic ring**. Benzene substitutes rather than adds because addition would destroy the stable delocalised system. Substituents already on the ring direct the next group: **$-\text{OH}$, $-\text{NH}_2$, $-\text{CH}_3$ and $-\text{Cl}$** send it to the **2- and 4-positions**, while **$-\text{NO}_2$ and $-\text{COOH}$** send it to the **3-position**. Electron-donating groups **activate** the ring; electron-withdrawing groups (and halogens) **deactivate** it.

Nitration of benzene: electrophilic substitution

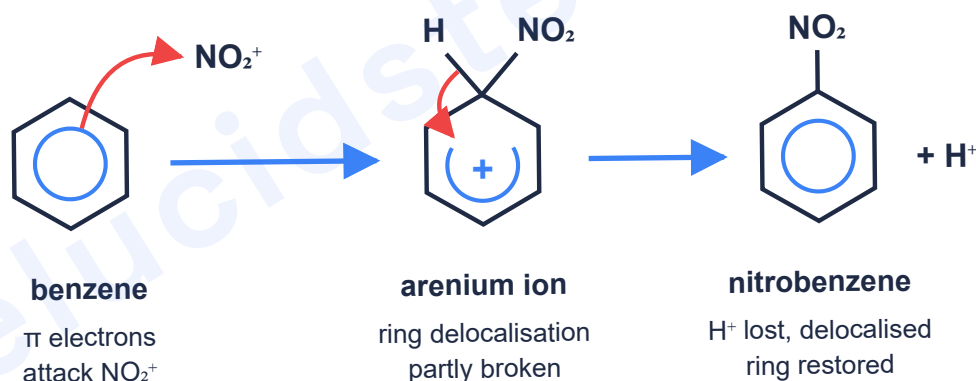


Fig. 1: the electrophilic substitution mechanism for the nitration of benzene

Electrophile, intermediate, lose H^+ .

- ✓ **Nitronium:** $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$.
- ✓ **Arrow 1:** ring to electrophile; **arrow 2:** C-H into ring.
- ✓ **2,4-directing:** $-OH$, $-NH_2$, $-CH_3$, $-Cl$.
- ✓ **3-directing:** $-NO_2$, $-COOH$; both deactivate.

Watch out!

The first curly arrow starts from the **delocalised ring** (the circle), not from a $C=C$ or a $C-H$ bond, and ends at the electrophile's atom. The intermediate's horseshoe must **not** include the sp^3 carbon, and the $+$ goes inside it. The second arrow starts from the **C-H bond**, and the product is H^+ , not H_2 or H^- . In the nitronium equation it is $2H_2SO_4$. Halogens direct to **2 and 4** even though they **deactivate** the ring; $-NO_2$ and $-COOH$ direct to **3**.