

Benzene structure and electrophilic substitution

Chemistry grades 11-12 (A Level · IB · Class 11-12) · Worksheet answers

Each answer shows the reasoning step by step, with equations balanced and numbers in bold. For mechanism questions, mark schemes reward the curly arrow starting at the π electrons and the final loss of H^+ .

Level: Chemistry grades 11-12 (A Level · IB · Class 11-12) · **Curriculum:** A Level 3.3.10

Problem 1 Describing benzene

1. **C₆H₆**.
2. **120°**.
3. **Six** π electrons.
4. **Planar** (flat) hexagon.

Problem 2 Bond lengths

1. Benzene's C-C bonds are **0.140 nm**, halfway between the single and double bond lengths.
2. All six bonds are equal and intermediate in length, so the ring has delocalised electrons, not separate single and double bonds.
3. The Kekulé model has three short C=C bonds and three longer C-C bonds, so the lengths would alternate.

Problem 3 Naming arenes

1. **Nitrobenzene**.
2. **Bromobenzene**.
3. **Methylbenzene**.
4. **Phenylamine**.

Problem 4 Reagents for substitution

1. Concentrated HNO_3 and concentrated H_2SO_4 (catalyst), at about 50 °C.
2. Br_2 with $FeBr_3$ (or Fe) as a halogen carrier at room temperature.
3. CH_3COCl with **anhydrous $AlCl_3$** as catalyst (Friedel-Crafts acylation).

Problem 5 Why electrophiles?

1. An electrophile is an **electron-pair acceptor**.

2. The delocalised π electrons give a region of high electron density above and below the ring, which attracts positive or electron-deficient species.

Problem 6 Stabilisation energy

1. $3 \times (-120) = -360 \text{ kJ/mol}$.
2. $-208 - (-360) = 152 \text{ kJ/mol}$.
3. It shows that the delocalised ring is more stable than three separate C=C bonds.

Problem 7 Bromine water test

1. Electrophilic **addition** to the C=C bond.
2. Cyclohexene has a localised π bond with high electron density that polarises bromine. Benzene's electrons are spread over the ring and held more strongly, so it cannot polarise bromine enough to react.
3. Add a **halogen carrier such as FeBr₃**, or iron, with liquid bromine.

Problem 8 Making the nitronium ion

1. $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{H}_3\text{O}^+ + 2\text{HSO}_4^-$.
2. Sulfuric acid is a stronger acid and **protonates nitric acid**, which then loses water to form NO_2^+ ; it is regenerated at the end.
3. $\text{C}_6\text{H}_6 + \text{HNO}_3 \rightarrow \text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O}$.

Problem 9 Describing the mechanism

1. The positive charge is spread (delocalised) over the five carbon atoms that are not bonded to both H and Br.
2. A pair of π electrons from the ring forms a bond to the electrophile Br^+ , so the ring loses its full delocalisation.
3. The C-H bond electrons return to the ring while H^+ leaves, restoring the delocalised π system.
4. Bromine alone is not polarised enough; FeBr_3 accepts a Br^- to create a stronger electrophile, **Br^+ (or polarised Br_2)**.

Problem 10 Halogen carrier

1. $\text{Br}_2 + \text{FeBr}_3 \rightarrow \text{Br}^+ + \text{FeBr}_4^-$.
2. $\text{C}_6\text{H}_6 + \text{Br}_2 \rightarrow \text{C}_6\text{H}_5\text{Br} + \text{HBr}$.
3. FeBr_3 is regenerated when FeBr_4^- gives up Br^- to H^+ , forming HBr and FeBr_3 , so it is not used up.

Problem 11 Yield of nitrobenzene

1. $n = 15.6 \div 78.0 = 0.200 \text{ mol}$.

- $0.200 \times 123.0 = \mathbf{24.6\text{ g}}$.
- $18.5 \div 24.6 \times 100 = \mathbf{75.2\%}$.

Problem 12 Friedel-Crafts acylation

- $\text{C}_6\text{H}_6 + \text{CH}_3\text{COCl} \rightarrow \mathbf{\text{C}_6\text{H}_5\text{COCH}_3 + \text{HCl}}$.
- Anhydrous $\mathbf{\text{AlCl}_3}$; water would react with AlCl_3 and with CH_3COCl , destroying the catalyst and the reagent.
- The acylium ion, $\mathbf{\text{CH}_3\text{CO}^+}$.

Problem 13 Kekulé and isomers

- In the Kekulé structure the two carbons carrying Br would be joined by $\text{C}=\text{C}$ in one form and $\text{C}-\text{C}$ in the other, so two different isomers should exist. Only one has ever been found.
- In the delocalised model all $\text{C}-\text{C}$ bonds are the same, so there is just **one 1,2-dibromobenzene**.

Problem 14 Reading a table of reactivity

- Benzene does not react with bromine water or KMnO_4 , so it has **no localised $\text{C}=\text{C}$ bonds**.
- The reaction with Br_2 and FeBr_3 gives HBr , which means a hydrogen atom is replaced: **electrophilic substitution**.

Problem 15 Two-step synthesis

- Concentrated HNO_3 with concentrated H_2SO_4 at **not above $55\text{ }^\circ\text{C}$** (about $50\text{ }^\circ\text{C}$).
- $\text{C}_6\text{H}_5\text{NO}_2 + 6[\text{H}] \rightarrow \mathbf{\text{C}_6\text{H}_5\text{NH}_2 + 2\text{H}_2\text{O}}$.
- At higher temperature further substitution gives dinitrobenzene, lowering the yield of mononitrobenzene.

Problem 16 Atom economy

- Atom economy = $123.0 \div (78.0 + 63.0) \times 100 = 123.0 \div 141.0 \times 100 = \mathbf{87.2\%}$.
- Some benzene forms dinitrobenzene, some product is lost in washing and separation, and the reaction may not go to completion.

Problem 17 Dinitration

- $\text{C}_6\text{H}_5\text{NO}_2 + \text{HNO}_3 \rightarrow \mathbf{\text{C}_6\text{H}_4(\text{NO}_2)_2 + \text{H}_2\text{O}}$.
- $0.100 \times 168.0 = \mathbf{16.8\text{ g}}$.
- At higher temperature substitution happens more than once, so the product is not pure nitrobenzene.

Problem 18 Why substitution wins

1. Loss of H^+ regenerates the delocalised ring and gives a substituted benzene; addition would leave a non-aromatic product.
2. Addition would keep the energy cost of losing 152 kJ/mol of stabilisation, while substitution recovers it.
3. **Aromatic** compounds contain a planar ring with delocalised π electrons (6 in benzene).

Problem 19 Hydrogenation data

1. $2 \times (-120) = -240 \text{ kJ/mol}$.
2. The diene is only 8 kJ/mol more stable than predicted (-232 compared with -240), whereas benzene is **152 kJ/mol** more stable.
3. The unusual gain shows that benzene has exceptional delocalisation, which is the basis of its aromatic stability.

Problem 20 Is benzene unreactive?

Benzene is not truly unreactive, but it is less reactive than an alkene and prefers a different type of reaction. Its delocalised ring is 152 kJ/mol more stable than the Kekulé structure, so it does not decolourise bromine water and needs a strong electrophile such as NO_2^+ or Br^+ produced with a catalyst. The mechanism begins by sacrificing the delocalisation, which gives an activation barrier, but it ends by losing H^+ to restore the ring, giving substitution. Therefore: **benzene is resistant to addition but reacts readily by electrophilic substitution under suitable conditions.**