

Benzene structure and electrophilic substitution

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

Name: _____ Date: _____ Class: _____

These 20 problems cover the structure of benzene, the evidence for delocalisation, and the mechanisms of nitration, halogenation and Friedel-Crafts reactions. Some require calculations of enthalpy, yield and atom economy, and others ask you to explain and describe.

The level is A Level chemistry, IB Chemistry and CBSE Class 11-12. Use A_r values from your data sheet and give each final answer in bold with a unit where needed.

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

Problem 1 Describing benzene (easy)

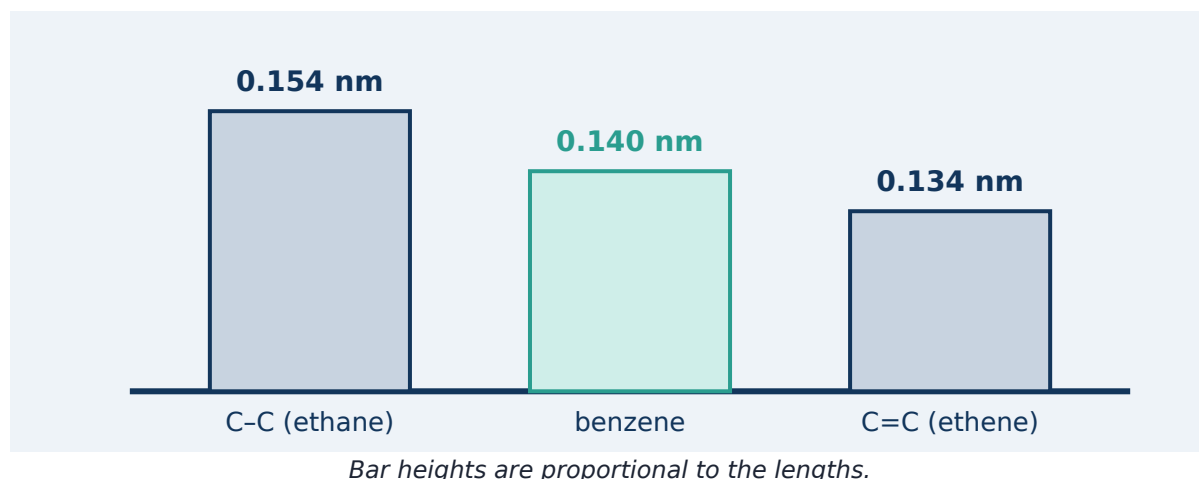
Answer the questions about benzene.

1. State its molecular formula.
2. State the bond angle between the carbon atoms in the ring.
3. State the number of delocalised electrons in the ring.
4. State the shape of the molecule.

Problem 2 Bond lengths (easy)

The figure shows typical bond lengths.

1. State which bond length benzene's C-C bonds are closest to.
2. Explain what the figure tells you about the structure of benzene.
3. Explain why this result is not what the Kekulé model predicts.



Problem 3 Naming arenes (easy)

Name each compound.

1. $\text{C}_6\text{H}_5\text{NO}_2$
2. $\text{C}_6\text{H}_5\text{Br}$
3. $\text{C}_6\text{H}_5\text{CH}_3$
4. $\text{C}_6\text{H}_5\text{NH}_2$

Problem 4 Reagents for substitution (easy)

State the reagents and any catalyst for each reaction of benzene.

1. Nitration
2. Bromination
3. Reaction with CH_3COCl

Problem 5 Why electrophiles? (easy)

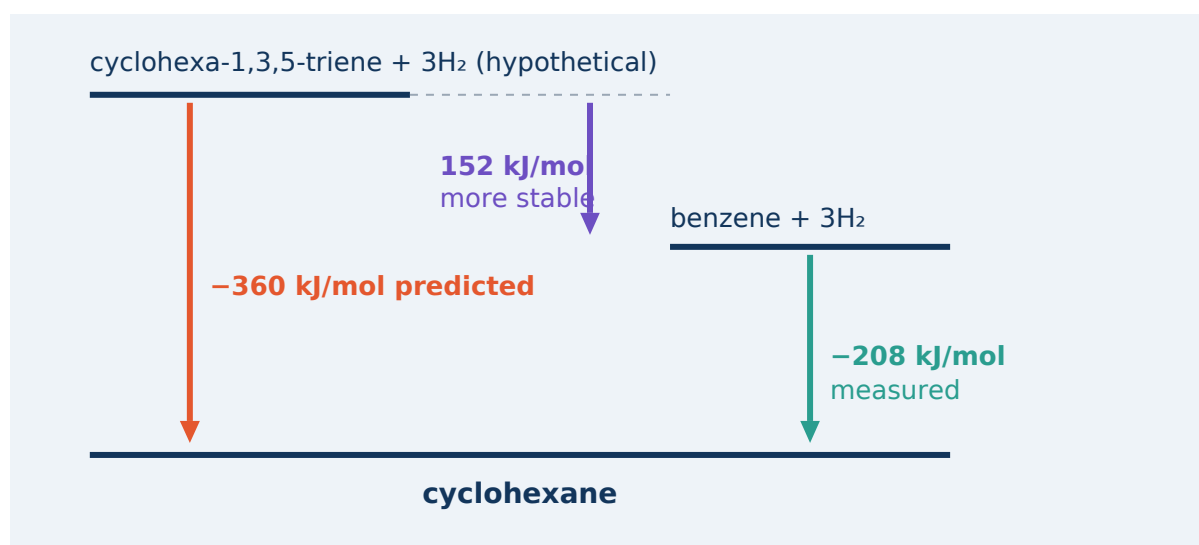
Benzene reacts with electrophiles, not nucleophiles.

1. Define the term electrophile.
2. Explain why the benzene ring attracts electrophiles.

Problem 6 Stabilisation energy (medium)

Use the enthalpy level diagram. ΔH (hydrogenation) of cyclohexene is -120 kJ/mol and of benzene is -208 kJ/mol .

1. Calculate the predicted value for a Kekulé benzene.
2. Calculate the stabilisation energy.
3. State what this energy shows.



Benzene is 152 kJ/mol more stable than the localised triene would be.

Problem 7 Bromine water test (medium)

Cyclohexene decolourises bromine water immediately, but benzene does not.

1. Name the type of reaction of cyclohexene.
2. Explain the difference in behaviour using electron density.
3. State what conditions would make benzene react with bromine.

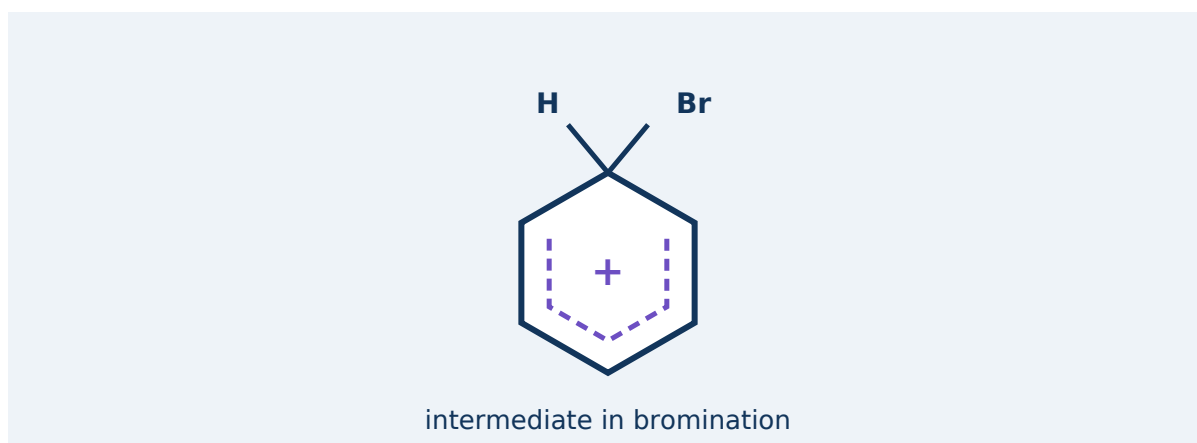
Problem 8 Making the nitronium ion (medium)

1. Write the equation for the formation of NO_2^+ from HNO_3 and H_2SO_4 .
2. State the role of sulfuric acid.
3. Write the equation for the nitration of benzene.

Problem 9 Describing the mechanism (medium)

The figure shows the intermediate formed when bromine attacks benzene.

1. State what the dashed arc represents.
2. Describe how the intermediate forms from benzene.
3. Describe how it forms bromobenzene.
4. Explain why the catalyst FeBr_3 is needed.



Dashed arc: the positive charge is spread over five carbon atoms.

Problem 10 Halogen carrier (medium)

1. Write the equation for the reaction of Br_2 with FeBr_3 that produces an electrophile.
2. Write the equation for the overall bromination of benzene.
3. Explain why FeBr_3 is called a catalyst.

Problem 11 Yield of nitrobenzene (medium)

Bilal nitrates 15.6 g of benzene ($M = 78.0 \text{ g/mol}$) and obtains 18.5 g of nitrobenzene ($M = 123.0 \text{ g/mol}$).

1. Calculate the moles of benzene.
2. Calculate the theoretical mass of nitrobenzene.

3. Calculate the percentage yield.

Problem 12 Friedel-Crafts acylation (medium)

Phenylethanone is made from benzene and ethanoyl chloride, CH_3COCl .

1. Write the equation.
2. Name the catalyst and explain why the reaction must be dry.
3. Name the electrophile.

Problem 13 Kekulé and isomers (medium)

Kekulé suggested two forms of 1,2-dibromobenzene, one with a $\text{C}=\text{C}$ bond between the Br-carbons and one with a $\text{C}-\text{C}$ bond.

1. Explain why this was a problem for the model.
2. State how the delocalised model solves it.

Problem 14 Reading a table of reactivity (medium)

Compare the observations in the table.

Reagent: bromine water | acidified KMnO_4 | Br_2 with FeBr_3

Cyclohexene: decolourises | decolourises | decolourises

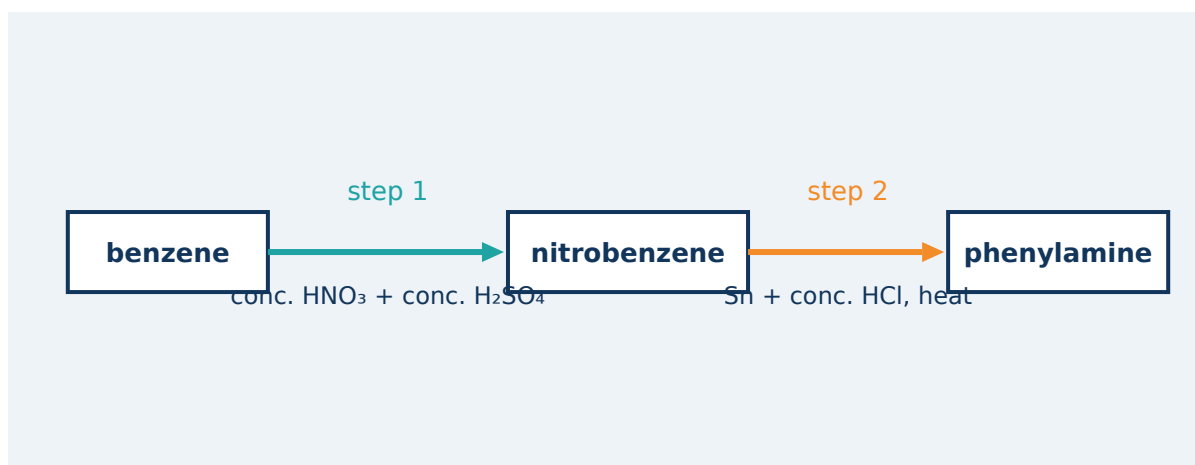
Benzene: no change | no change | decolourises, HBr fumes

1. State what the first two columns show about benzene.
2. State what the third column shows about the type of reaction benzene undergoes.

Problem 15 Two-step synthesis (hard)

The figure shows benzene converted to phenylamine.

1. Name the conditions for step 1 and give the temperature limit.
2. Write an equation for step 2 using $[\text{H}]$ for the reducing agent.
3. Explain why the temperature limit is needed in step 1.



Two-step route to an aromatic amine.

Problem 16 Atom economy (hard)

Nitration: $\text{C}_6\text{H}_6 + \text{HNO}_3 \rightarrow \text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O}$.

1. Calculate the atom economy to 3 significant figures (M: C_6H_6 78.0, HNO_3 63.0, $\text{C}_6\text{H}_5\text{NO}_2$ 123.0).
2. Suggest one reason the actual yield is less than 100 %.

Problem 17 Dinitration (hard)

If the temperature rises above 55 °C, a second nitro group enters the ring.

1. Write the equation for the formation of 1,3-dinitrobenzene ($\text{C}_6\text{H}_4\text{N}_2\text{O}_4$) from nitrobenzene.
2. Calculate the mass of 1,3-dinitrobenzene (M = 168.0 g/mol) from 0.100 mol of nitrobenzene with 100 % yield.
3. Explain why the temperature is kept low.

Problem 18 Why substitution wins (hard)

After an electrophile attacks benzene, the ring can either add a nucleophile or lose H^+ .

1. Explain which path gives a more stable product.
2. Use the stabilisation energy of 152 kJ/mol in your explanation.
3. State what the term aromatic means.

Problem 19 Hydrogenation data (hard)

Enthalpy changes of hydrogenation: cyclohexene –120 kJ/mol; cyclohexa-1,3-diene –232 kJ/mol; benzene –208 kJ/mol.

1. Calculate the value predicted for cyclohexa-1,3-diene with two isolated double bonds.
2. Compare the extra stability of the diene with that of benzene.
3. Explain what the data suggest about benzene.

Problem 20 Is benzene unreactive? (hard)

Write a short paragraph evaluating the statement: benzene is unreactive. Use evidence from its stability, its mechanism and the need for strong reagents.