Unit 15 · Aromatic Hydrocarbons

ANSWER KEY · FOR TEACHERS

Full marks 33

Give the marks for the points in the marking scheme; an answer in other words that says the same is right.

1 True or false

i. ✗ **False**: Benzene gives neither test for unsaturation: its π electrons are delocalized, and adding anything would break that up. **U · 3**

ii. ✓ **True**

iii. ✗ **False**: It is not aromatic: its CH_2 carbon is sp^3 and breaks the ring of p orbitals.

iv. ✓ **True**

v. ✗ **False**: In sunlight they give benzene hexachloride by addition; chlorobenzene needs $FeCl_3$ in the dark.

vi. ✗ **False**: $-NO_2$ is a meta director.

Each carries 0.5 mark.

2 Label the diagram

1. π cloud above the ring 2. π cloud below the ring **K · 1**

Each carries 0.5 mark.

3 Multiple choice

i. **c.** furan **A · 1**

Furan is cyclic and flat, with a p orbital on every ring atom, and has 6 π electrons (two C=C and one lone pair of its oxygen): 4n + 2 with n = 1.

ii. **c.** 3 **U · 1**

Two groups on a benzene ring can be ortho (1,2-), meta (1,3-) or para (1,4-).

iii. **b.** acetophenone and ethanoic acid **K · 1**

Friedel–Crafts acylation: $C_6H_6 + (CH_3CO)_2O \rightarrow C_6H_5COCH_3 + CH_3COOH$.

iv. **a.** an ortho–para director and a ring activator **U · 1**

Its lone pair is pushed into the ring, leaving extra electrons on C-2, C-4 and C-6, so electrophiles attack there, faster than in benzene.

v. **c.** 1,3-dinitrobenzene **A · 1**

Above 60 °C a second NO_2 goes in, and since $-NO_2$ is a meta director it goes to C-3: m-dinitrobenzene.

4 Short answers

a. **MARKING SCHEME** **U · 2**

✓ Its six π electrons are delocalized round the ring, making it unusually stable (resonance energy).

✓ Addition would destroy the delocalized ring; substitution replaces an H and keeps the aromatic ring.

b. **MARKING SCHEME** **K · 2**

✓ Any one, e.g. benzene is stable to addition and does not decolorize bromine water.

✓ Any second, e.g. all six C–C bonds are equal, 139 pm; only one 1,2-disubstituted benzene is found, not two.

c. **MARKING SCHEME** **A · 2**

✓ $C_6H_6 + Cl_2 \xrightarrow[\text{dark}]{FeCl_3} C_6H_5Cl + HCl$: electrophilic substitution.

✓ $C_6H_6 + 3\,Cl_2 \xrightarrow{\text{sunlight}} C_6H_6Cl_6$: addition.

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d. MARKING SCHEME U · 3

- ✓ Cyclic, a p orbital on every ring atom, and flat.
- ✓ $(4n + 2)\ \pi$ electrons with n a whole number.
- ✓ Cyclobutadiene: 4 π electrons, n = 0.5: not aromatic (antiaromatic).

5 Long answer

ANSWER U · 4

Benzene is warmed with concentrated nitric acid and concentrated sulphuric acid at 50–60 °C:
$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$.
The electrophile forms when sulphuric acid protonates nitric acid, which loses water:
$HNO_3 + 2\,H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2\,HSO_4^-$.
Slow step: two of the ring's π electrons bond to the N of NO_2^+; the attacked carbon becomes sp^3, holding both H and NO_2, and the ring carries a positive charge, shared by resonance: the arenium ion (σ complex).
Fast step: HSO_4^- takes the H^+ from the sp^3 carbon; the C–H electrons go back into the ring and the aromatic ring is whole again, as nitrobenzene.

MARKING SCHEME

- ✓ Conditions: conc. HNO_3 + conc. H_2SO_4 at 50–60 °C, and the overall equation.
- ✓ Formation of NO_2^+.
- ✓ Slow step: attack giving the arenium ion.
- ✓ Fast step: loss of H^+ restores the ring.

6 Numerical problems

a. ANSWER A · 4

i. $C_6H_5COONa + NaOH \xrightarrow[\text{heat}]{CaO} C_6H_6 + Na_2CO_3$

ii. Sodium benzoate, M = 144: 7.2 ÷ 144 = 0.050 mol, giving 0.050 mol of benzene (M = 78): 0.050 × 78 = **3.9 g**; volume = 3.9 ÷ 0.877 = **4.4 cm³**.

iii. 0.050 mol of Na_2CO_3 (M = 106): **5.3 g**.

MARKING SCHEME

- ✓ The balanced equation.
- ✓ 0.050 mol.
- ✓ 3.9 g and 4.4 cm^3 of benzene.
- ✓ 5.3 g of Na_2CO_3.

b. ANSWER A · 4

i. $3\,C_2H_2 \rightarrow C_6H_6$; $C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$

ii. Ethyne = 13.44 ÷ 22.4 = 0.600 mol, giving 0.600 ÷ 3 = 0.200 mol of benzene = 0.200 × 78 = **15.6 g**.

iii. Nitrobenzene (M = 123) at 75%: 0.200 × 0.75 = 0.150 mol × 123 = **18.5 g**.

MARKING SCHEME

- ✓ Both equations.
- ✓ 0.600 mol of ethyne, 0.200 mol of benzene.
- ✓ 15.6 g of benzene.
- ✓ 18.5 g of nitrobenzene.

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7 Think

ANSWER HA · 3

Chlorine is very electronegative, so it pulls electrons out of the ring through its σ bond; this makes the whole ring poorer in electrons, and chlorobenzene reacts more slowly than benzene (a deactivator). But chlorine also has lone pairs, which it can push into the ring by resonance, and these put extra electron density on the ortho and para carbons, so an electrophile that does attack goes there. The pull through the bond wins on speed; the push by resonance decides the position.

MARKING SCHEME

- ✓ Electron withdrawal through the bond (electronegativity) deactivates the ring.
- ✓ Lone pairs pushed into the ring by resonance enrich the ortho and para carbons.
- ✓ The first sets the rate, the second the position.

8 Activity: Two flames (at home, with an adult)

(not marked)

WHAT STUDENTS SHOULD FIND

The candle's yellow flame leaves black soot on the spoon; the blue gas flame leaves it almost clean. Benzene burns with a yellow, sooty flame like the candle's: it has one hydrogen for every carbon, so with so much carbon not all of it finds oxygen, and the rest leaves as soot.

Marks by level	Knowledge	Understanding	Application	Higher ability	Total
Marks	4	14	12	3	**33**

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