Unit 9 · Haloarenes

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 Key words

1. haloarene → **g.** a compound with a halogen on a carbon of an aromatic ring
2. ortho isomer → **d.** the isomer with the two groups on neighboring ring carbons, 1,2
3. para isomer → **e.** the isomer with the two groups opposite each other, 1,4
4. diazotization → **f.** turning aniline into benzenediazonium chloride with $NaNO_2$ and HCl at 0–5 °C
5. Sandmeyer reaction → **b.** replacing the diazonium group by a halogen with a copper(I) halide
6. Fittig reaction → **j.** joining two aryl halides with sodium in dry ether
7. Wurtz–Fittig reaction → **a.** joining an aryl halide and an alkyl halide with sodium in dry ether
8. Dow's process → **i.** making phenol from chlorobenzene with NaOH at high temperature and pressure

K · 4

Each carries 0.5 mark.

2 Label the diagram

1. chlorobenzene
2. phenol
3. 623 K
4. sodium phenoxide

K · 2

Each carries 0.5 mark.

3 Multiple choice

i. **b.** 3 — K · 1

The two chlorines can be **ortho** (1,2), **meta** (1,3) or **para** (1,4): **3** isomers.

ii. **b.** CuBr and HBr — K · 1

This is the **Sandmeyer reaction**: $C_6H_5N_2{+}Cl^- \xrightarrow{CuBr,\ HBr} C_6H_5Br + N_2$. Only the iodide needs no copper: KI alone gives iodobenzene.

iii. **c.** ethylbenzene — A · 1

The **Wurtz–Fittig** reaction joins the aryl and the alkyl group:
$C_6H_5Br + C_2H_5Br + 2\,Na \rightarrow C_6H_5C_2H_5 + 2\,NaBr$, ethylbenzene. (Biphenyl and butane also form a little, from two of the same kind.)

iv. **c.** $ClC_6H_4CH_3$ (4-chlorotoluene) — U · 1

Only in **4-chlorotoluene** is the chlorine on a carbon of the benzene ring. In benzyl chloride it is on the CH_2 outside the ring; chlorocyclohexane has no aromatic ring; chloroethene has none at all.

v. **b.** benzonitrile, C_6H_5CN — U · 1

The chlorine is replaced by –CN only under these harsh conditions: $C_6H_5Cl + CuCN \rightarrow C_6H_5CN + CuCl$, **benzonitrile**.

4 Short answers

a. MARKING SCHEME — U · 2

✓ The balanced equation.
✓ o- and p-dichlorobenzene, the para isomer major.

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b. MARKING SCHEME U · 2

✓ Fittig: biphenyl (equation).
✓ Reduction: benzene (equation).

c. MARKING SCHEME A · 3

✓ Diazotization equation.
✓ The condition 0–5 °C (with $NaNO_2$ and HCl).
✓ Warming with KI gives iodobenzene (equation).

5 Long answer

ANSWER U · 4

Reason (any one): by resonance a lone pair of chlorine spreads into the ring, so the C–Cl bond is partly double (169 pm, against 177 pm in CH_3Cl) and harder to break; or the carbon is sp^2, holding the bond more tightly; or the ring's electrons repel the nucleophile.

–OH (Dow's process): $C_6H_5Cl + 2\,NaOH \xrightarrow{623\ K,\ 300\ atm} C_6H_5ONa + NaCl + H_2O$, then

$C_6H_5ONa + HCl \rightarrow C_6H_5OH + NaCl$.

–NH_2: with ammonia and copper(I) oxide at about 200 °C and 60 atm:

$C_6H_5Cl + 2\,NH_3 \xrightarrow{Cu_2O} C_6H_5NH_2 + NH_4Cl$.

A **nitro group** ortho or para to the chlorine pulls electrons out of the ring, so the carbon holding Cl attracts the nucleophile, and the substitution goes far more easily, at a much lower temperature; each extra nitro group helps more.

MARKING SCHEME

✓ One reason (partial double bond by resonance, sp^2 carbon, or repulsion by the ring).
✓ Dow's process: the conditions and equations, to phenol.
✓ With NH_3 and Cu_2O, hot and under pressure, to aniline (equation).
✓ An o- or p- nitro group withdraws electrons and makes the substitution much easier.

6 Numerical problems

a. ANSWER A · 4

i. $M(C_6H_6) = 78$ g/mol: 15.6/78 = **0.200 mol**.
ii. $M(C_6H_5Cl) = 72 + 5 + 35.5 = 112.5$ g/mol: $0.200 \times 112.5 =$ **22.5 g**.
iii. $22.5 \times 0.75 =$ **16.9 g**.
iv. Cl_2: $0.200 \times 22.4 =$ **4.48 L**; HCl: $0.200 \times 36.5 =$ **7.30 g**.

MARKING SCHEME

✓ 0.200 mol of benzene.
✓ 22.5 g of chlorobenzene.
✓ 16.9 g at 75%.
✓ 4.48 L of Cl_2 and 7.30 g of HCl.

b. ANSWER A · 4

i. $M = 14 \times 12 + 9 + 5 \times 35.5 =$ **354.5 g/mol**; % Cl = 177.5/354.5 × 100 = **50.1%**.
ii. 22.5/112.5 = 0.200 mol C_6H_5Cl gives 0.100 mol DDT: $0.100 \times 354.5 =$ **35.5 g**.
iii. 0.100 mol chloral; $M = 24 + 1 + 16 + 3 \times 35.5 = 147.5$: **14.8 g**.
iv. $35.5 \times 0.80 =$ **28.4 g**.

MARKING SCHEME

✓ 354.5 g/mol and 50.1% chlorine.
✓ 35.5 g of DDT (two chlorobenzene for one DDT).
✓ 14.8 g of chloral.
✓ 28.4 g at 80%.

7 Think

ANSWER

Nitrate first. Chlorine is an ortho and para director, so nitration with conc. HNO_3 and conc. H_2SO_4 gives mostly 1-chloro-4-nitrobenzene (separated from the ortho isomer).

Then **hydrolyze** with aqueous NaOH, and acidify. The nitro group para to the chlorine pulls electrons

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from the ring, so the chlorine is replaced far more easily, at a much lower temperature than the 623 K and 300 atm that chlorobenzene itself needs (Dow's process). Hydrolyzing first would need those harsh conditions.

MARKING SCHEME

- ✓ Nitrate first: Cl directs to para, giving 1-chloro-4-nitrobenzene.
- ✓ Then hydrolysis with NaOH (and acid) gives 4-nitrophenol.
- ✓ The para nitro group makes the hydrolysis much easier, avoiding Dow's harsh conditions.

8 Activity: Three dichlorobenzenes

(not marked)

WHAT STUDENTS SHOULD FIND

Only the **para** isomer looks the same after a half turn, and only in it do the two C–Cl bond pulls point exactly opposite and cancel: its dipole moment is 0 (o- 2.50 D, m- 1.72 D). Being symmetrical, its molecules pack closely in a crystal, so it melts much higher (53 °C) and is a solid at room temperature; the other two are liquids.

Marks by level	Knowledge	Understanding	Application	Higher ability	Total
Marks	8	10	12	3	**33**

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