Unit 9 · Haloarenes

WORKSHEET

Full marks 33

Name _____ Class _____ Roll no. _____ Date _____ Marks _____ / 33

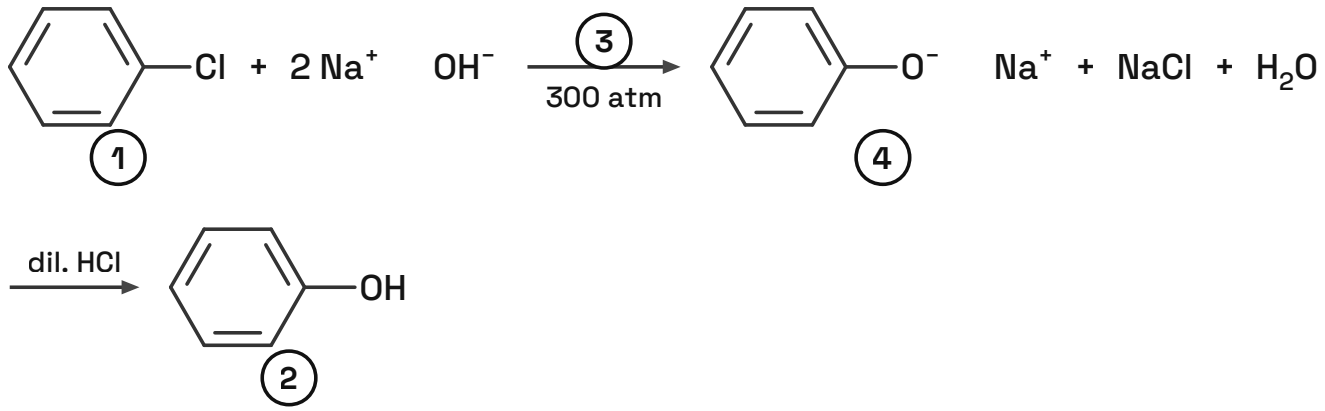
1 Key words [4]

Match each term in column A with its meaning in column B. Two meanings in column B are not needed. Each match carries 0.5 mark.

Column A		Column B
1. haloarene	☐	**a.** joining an aryl halide and an alkyl halide with sodium in dry ether
2. ortho isomer	☐	**b.** replacing the diazonium group by a halogen with a copper(I) halide
3. para isomer	☐	**c.** putting an acyl group on a ring with $AlCl_3$
4. diazotization	☐	**d.** the isomer with the two groups on neighboring ring carbons, 1,2
5. Sandmeyer reaction	☐	**e.** the isomer with the two groups opposite each other, 1,4
6. Fittig reaction	☐	**f.** turning aniline into benzenediazonium chloride with $NaNO_2$ and HCl at 0–5 °C
7. Wurtz–Fittig reaction	☐	**g.** a compound with a halogen on a carbon of an aromatic ring
8. Dow's process	☐	**h.** a halogen on a carbon outside the ring
		i. making phenol from chlorobenzene with NaOH at high temperature and pressure
		j. joining two aryl halides with sodium in dry ether

2 Label the diagram [2]

The diagram shows Dow's process. Write what belongs in place of 1 to 4. Each carries 0.5 mark.



1. _____ **2.** _____

3. _____ **4.** _____

3 Multiple choice [5]

Choose the correct option for each of the following questions.

i. How many structural isomers does dichlorobenzene, $C_6H_4Cl_2$, have? [1]

a. 2 **b.** 3

c. 4 **d.** 6

ii. Benzenediazonium chloride is turned into bromobenzene by warming it with: [1]

a. KBr **b.** CuBr and HBr

c. Br_2 and $FeBr_3$ **d.** NaBr and H_2SO_4

iii. Bromobenzene and bromoethane are treated together with sodium in dry ether. The product wanted from this reaction is: [1]

a. biphenyl **b.** toluene

c. ethylbenzene **d.** butane

iv. Which of these is a haloarene? [1]

a. $C_6H_5CH_2Cl$ (benzyl chloride) **b.** $C_6H_{11}Cl$ (chlorocyclohexane)

c. $ClC_6H_4CH_3$ (4-chlorotoluene) **d.** $CH_2{=}CHCl$ (chloroethene)

v. Chlorobenzene is heated with copper(I) cyanide in pyridine at about 200 °C. The organic product is: [1]

a. chlorobenzonitrile **b.** benzonitrile, C_6H_5CN

c. phenyl isocyanide, C_6H_5NC **d.** benzoic acid

4 Short answers [7]

Write short answers to the following questions.

a. Write the equation for the chlorination of chlorobenzene with chlorine and anhydrous $FeCl_3$. Name the products, and say which is the major one. [2]

b. Write balanced equations for: a. the Fittig reaction of chlorobenzene; b. the reduction of chlorobenzene with Ni–Al alloy and NaOH. Name the organic product of each. [2]

c. How is iodobenzene prepared from aniline? Write the equations, with the conditions. **[3]**

5 Long answer **[4]**

Write a long answer to the following question.

Haloarenes are much less reactive than haloalkanes in nucleophilic substitution. Give one reason. How can the chlorine of chlorobenzene be replaced by –OH and by $–NH_2$? Write the equations, with the conditions. How does a nitro group at the ortho or para position change the reaction?

6 Numerical problems **[8]**

Solve the following problems. Show your working. Take H = 1, C = 12, O = 16, Cl = 35.5; one mole of a gas at STP fills 22.4 L.

a. 15.6 g of benzene is chlorinated with chlorine in the presence of anhydrous $FeCl_3$ in the dark, to give chlorobenzene: $C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$ **[4]**

i. How many moles of benzene are used?
ii. Find the mass of chlorobenzene formed if the reaction were complete.
iii. The yield is 75%. What mass of chlorobenzene is obtained?
iv. Find the volume of chlorine at STP needed for the complete reaction, and the mass of hydrogen chloride given off.

Answer:

b. DDT is made by heating chlorobenzene with chloral and concentrated sulphuric acid: **[4]**

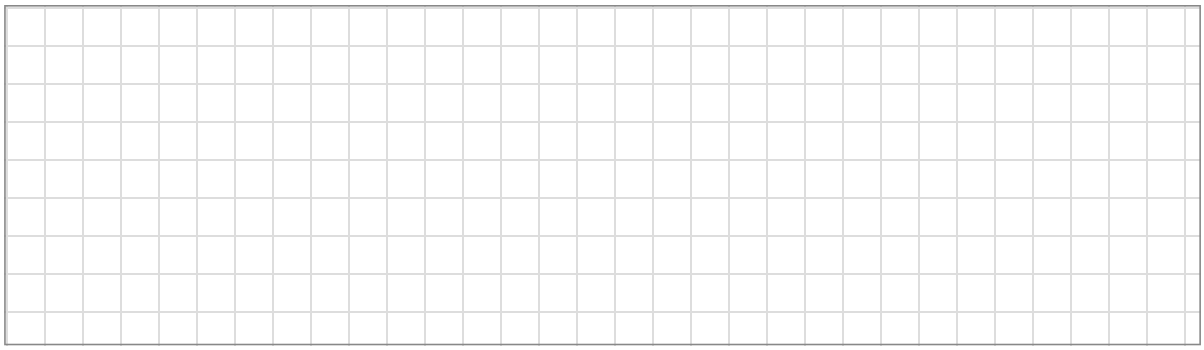
$2\,C_6H_5Cl + CCl_3CHO \rightarrow (ClC_6H_4)_2CH{-}CCl_3 + H_2O$

i. Find the molar mass of DDT, $C_{14}H_9Cl_5$, and its percentage of chlorine.

ii. What mass of DDT can be made from 22.5 g of chlorobenzene?

iii. What mass of chloral, CCl_3CHO, is needed for it?

iv. If the yield is 80%, what mass of DDT is obtained?



Answer: _____

7 Think **[3]**

Plan a two-step synthesis of 4-nitrophenol from chlorobenzene. Should the chlorobenzene be nitrated first or hydrolyzed first? Explain your choice, and write the two steps.

8 Activity: Three dichlorobenzenes (not marked)

Make models of o-, m- and p-dichlorobenzene with a model kit (or with paper hexagons and two colored pins). For each, decide whether the molecule looks the same after a half turn, and whether the pulls of its two C–Cl bonds cancel.

Isomer	Same after a half turn?	Bond pulls cancel (no dipole)?	Predicted: highest melting point?
o- (1,2-)			
m- (1,3-)			
p- (1,4-)			

Compare your predictions with the measured melting points: o- −17 °C, m- −25 °C, p- 53 °C. Why is only the para isomer a solid at room temperature?