Week 47

A-Level Chemistry

Homework bundle for this week

本周作业合集

exercises.lol

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31.1 Halogen compounds (halogenoarenes)

Name: _____ Class: _____ Date: _____ **Total: 27 marks**

KEY WORDS halogenoarene 卤代芳烃 • halogenoalkane 卤代烷 • catalyst 催化剂 • lone pair 孤对电子 • arene 芳烃

Objective

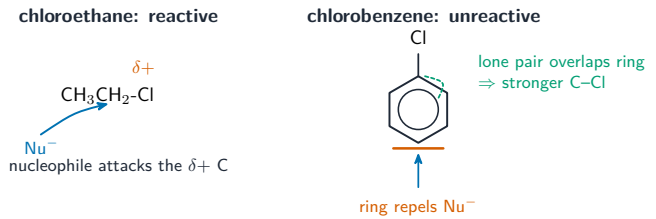
Build the skills to answer exam questions on **halogenoarenes** 卤代芳烃 — how they are made, and why they are far less reactive than **halogenoalkanes** 卤代烷 towards nucleophilic substitution.

You must be able to:

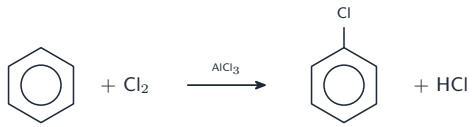
- give the reagents and conditions to make a halogenoarene from an arene
- explain why a halogenoarene resists nucleophilic substitution
- contrast its reactivity with a halogenoalkane

1 Worked examples

Reactivity compared



Chloroethane reacts (a nucleophile attacks the δ+ carbon); chlorobenzene does not — the Cl lone pair strengthens the C–Cl bond and the ring repels nucleophiles



Making a halogenoarene by substitution

- **make it:** arene + Cl_2/Br_2 with $AlCl_3$/$AlBr_3$ catalyst → halogenoarene (electrophilic substitution).
- **chlorobenzene is unreactive** because: (1) a Cl lone pair overlaps the ring, giving the C–Cl bond partial double-bond character → shorter, stronger, harder to break; (2) the electron-rich ring repels nucleophiles.

■ Why a halogenoarene barely reacts

In a **halogenoalkane** the C–X bond is polar and the halogen leaves readily, so nucleophilic substitution is easy. In a **halogenoarene** 卤代芳烃, where the halogen is attached **directly to a benzene ring**, substitution is extremely slow. Two reasons, and the exam wants both:

1. **The C–Cl bond has partial double-bond character.** A lone pair on the chlorine **overlaps with the delocalised π system** of the ring, so electron density is shared into the bond. It is therefore **shorter and stronger** than a normal C–Cl bond and much harder to break.
2. **The ring repels the nucleophile.** The delocalised π electrons above and below the ring create a region of high electron density, which repels an approaching lone pair.

The comparison the question always makes: chlorobutane is hydrolysed by warm aqueous NaOH, giving a precipitate with silver nitrate within minutes; chlorobenzene under the same conditions gives **no precipitate**, because no chloride ion is released. That contrast is the standard experimental evidence.

△ **Being attached to the ring changes the direction too.** A halogen on the ring is a **2,4-directing** group in further substitution, even though it deactivates the ring overall — a combination worth remembering because it looks contradictory.

Making them: chlorobenzene comes from benzene with Cl_2 and an $AlCl_3$ catalyst, anhydrous, at room temperature — electrophilic substitution, not addition, because addition would destroy the delocalisation.

Worked example. Explain why chlorobenzene gives no precipitate with aqueous silver nitrate after warming with NaOH, while 1-chlorobutane does within minutes.

1. In 1-chlorobutane the C–Cl bond is a normal polar single bond; the hydroxide attacks the $\delta+$ carbon and chloride ions are released, which give a white precipitate of AgCl.

2. In chlorobenzene a chlorine lone pair overlaps the ring's π system, giving the C–Cl bond partial double-bond character: it is shorter and stronger.
3. The ring's π electron density also repels the incoming hydroxide.
4. So no chloride is released, and no precipitate forms.

2 Practice

2.1 Give the reagent and catalyst used to make chlorobenzene from benzene. [2]

2.2 State the type of reaction by which a halogenoalkane reacts with OH^-. [1]

2.3 Give the reagents and conditions for making chlorobenzene from benzene. [2]

2.4 Explain why the C–Cl bond in chlorobenzene is stronger than in chloroethane. [2]

2.5 State what is observed when chlorobenzene is warmed with aqueous sodium hydroxide and then acidified silver nitrate is added. [1]

3 Exam-style questions

3.1 Chlorobenzene is much less reactive than chloroethane towards OH^- because: [1]

- **A** the C–Cl bond in chlorobenzene is weaker
- **B** a chlorine lone pair overlaps the ring, strengthening the C–Cl bond
- **C** chlorobenzene has no C–Cl bond
- **D** the ring attracts nucleophiles

3.2 Which compound reacts fastest with warm aqueous NaOH? [1]

- **A** chlorobenzene
- **B** chloroethane
- **C** 2,4,6-trichlorophenol
- **D** they react at the same rate

3.3 Explain, in terms of bonding, why chlorobenzene does **not** undergo nucleophilic substitution under normal conditions. Give **two** reasons. [3]

3.4 Methylbenzene reacts with Cl_2 and $AlCl_3$. State the **two** organic products and explain why these positions are favoured. [2]

3.5 A student warms separate samples of 1-chlorobutane and chlorobenzene with aqueous sodium hydroxide, then acidifies each and adds aqueous silver nitrate.

(a) State what the student observes with each sample. [2]

(b) Explain, in terms of the C–Cl bond, why chlorobenzene behaves differently. [3]

(c) Give a second reason, in terms of the benzene ring, why nucleophilic attack on chlorobenzene is difficult. [2]

(d) Write the equation and name the mechanism for the hydrolysis of 1-chlorobutane. [3]

(e) Chlorine is described as deactivating but 2,4-directing. Explain what this means for a further substitution on chlorobenzene. [2]

Solutions

2.1 chlorine, Cl_2; with an $AlCl_3$ (aluminium chloride) catalyst.

2.2 nucleophilic substitution.

2.3 Chlorine with an aluminium chloride catalyst; anhydrous conditions at room temperature.

2.4 A lone pair on the chlorine overlaps with the delocalised π system of the ring, giving the bond partial double-bond character so it is shorter and stronger.

2.5 No precipitate is formed.

3.1 B. A Cl lone pair overlaps the delocalised ring, giving partial double-bond character and a stronger C–Cl bond.

3.2 B. Chloroethane (a halogenoalkane) reacts fastest; the aryl C–Cl bonds resist substitution.

3.3 a lone pair on chlorine overlaps the delocalised ring, giving the C–Cl bond partial double-bond character so it is shorter and stronger / harder to break; and the electron-rich ring repels the approaching nucleophile.

3.4 2-chloromethylbenzene and 4-chloromethylbenzene; the $–CH_3$ group directs the chlorine to positions 2 and 4.

3.5 (a) 1-chlorobutane gives a white precipitate of silver chloride; chlorobenzene gives no precipitate.
(b) In chlorobenzene a lone pair on the chlorine overlaps with the ring's delocalised π system; the C–Cl bond therefore has partial double-bond character and is shorter and stronger; it is not broken under these conditions, so no chloride ion is released.
(c) The delocalised π electrons lie above and below the ring, giving a region of high electron density which repels the approaching hydroxide ion.
(d) $CH_3CH_2CH_2CH_2Cl + OH^- \rightarrow CH_3CH_2CH_2CH_2OH + Cl^-$; nucleophilic substitution.
(e) Deactivating means the ring reacts more slowly than benzene, because chlorine withdraws electron density inductively; 2,4-directing means that when substitution does occur, the new group enters mainly at the positions next to and opposite the chlorine.

8 **(a)** In the electrophilic substitution of arenes, different substituents can direct to different ring positions.

(i) Describe the directing effect of the $–NO_2$ group. Explain your answer.

.....

..... [1]

(ii) The nitration of arenes uses a mixture of concentrated HNO_3 and concentrated H_2SO_4 to generate the NO_2^+ electrophile.

Write an equation for the formation of the NO_2^+ electrophile.

..... [1]

(b) Carbon-carbon bond formation is an important reaction in organic synthesis.

Fig. 8.1 shows the synthesis of compound **Q** from benzene in two reaction steps.

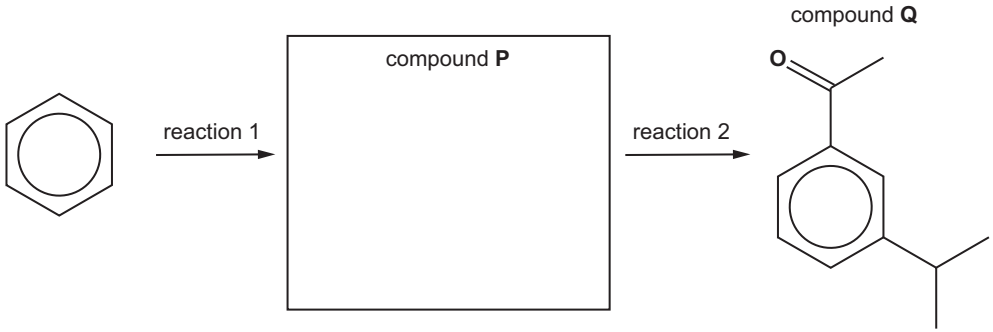


Fig. 8.1

(i) Draw the structure of compound **P** in the box in Fig. 8.1. [1]

(ii) Suggest reagents and conditions for reactions 1 and 2 in Fig. 8.1.

reaction 1 .....

reaction 2 .....
[2]

(c) Separate samples of C_6H_5Br and $C_6H_5CH_2Br$ are added to warm $AgNO_3(aq)$.

State the expected observations, if any. Explain your answer.

C_6H_5Br with $AgNO_3(aq)$ .....

$C_6H_5CH_2Br$ with $AgNO_3(aq)$ .....

explanation .....

.....

.....

.....

[3]

(d) Acyl bromides, RCOBr, react readily with H_2O.

The mechanism of this reaction is similar to that of the reaction of H_2O with acyl chlorides, RCOC*l*.

(i) Name the mechanism of this reaction.

..... [1]

(ii) Complete the mechanism in Fig. 8.2 for the reaction of RCOBr with H_2O.

Include all relevant lone pairs of electrons, curly arrows, charges and dipoles.

Draw the structure of the intermediate.

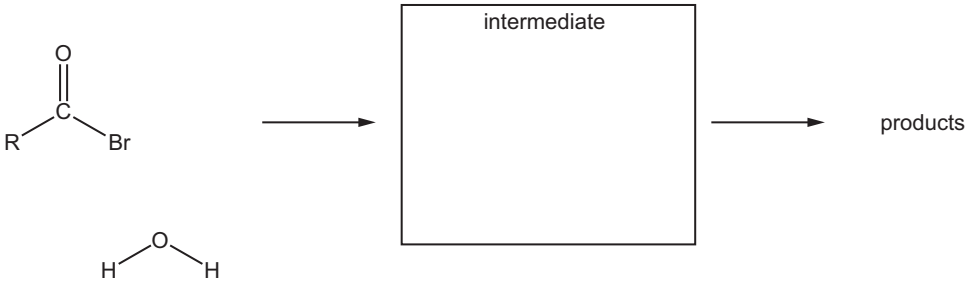


Fig. 8.2

[4]

[Total: 13]

8 **(a)** Describe the difference in reactivity between ethanoyl chloride and chlorobenzene with water.

Explain your answer.

.....

.....

.....

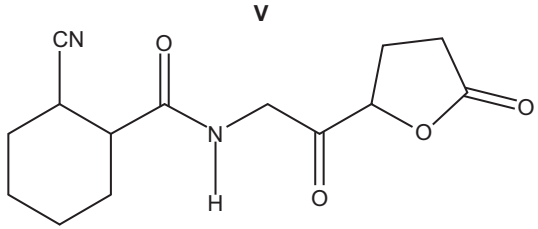
.....

.....

..... [2]

(b) The structure of compound **V** is shown.

V



(i) Name all the functional groups in **V**.

.....

.....

..... [2]

(ii) Deduce the number of possible optical isomers for **V**.

..... [1]

(iii) Suggest **one** reason, other than better biological activity and lower dosage required, why it is beneficial to synthesise a single optical isomer of **V** for use as a drug.

.....

.....

..... [1]

(c) A sample of **V** is hydrolysed with an excess of hot aqueous alkali.

The products are isolated from the reaction mixture at pH 12.

Draw the structures of the **two** organic products of the **complete** alkaline hydrolysis of **V** in Fig. 8.1.

Fig. 8.1

[3]

(d) A polypeptide formed from four amino acids, **A**, **B**, **C** and **D**, is completely hydrolysed and then analysed by gas–liquid chromatography.

The chromatogram produced is shown in Fig. 8.2.

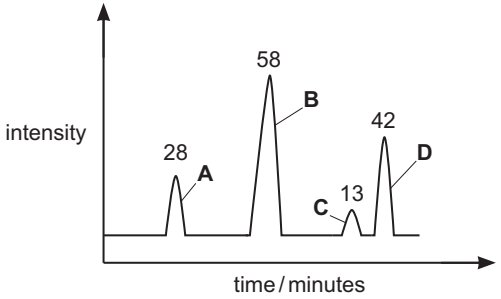


Fig. 8.2

The number above each peak represents the area under the peak.

The area under each peak is proportional to the mass of the respective amino acid in the mixture.

(i) Calculate the percentage by mass of amino acid **A** in the original mixture.

percentage by mass of amino acid **A** = ... [1]

(ii) The retention time for amino acid **D** is the longest.

Explain why **D** has a longer retention time than the **other** amino acids **A**, **B** and **C**.

.....

.....

.....

..... [1]

[Total: 11]

Important values, constants and standards

molar gas constant	$R = 8.31\,\text{J K}^{-1}\,\text{mol}^{-1}$
Faraday constant	$F = 9.65 \times 10^{4}\,\text{C mol}^{-1}$
Avogadro constant	$L = 6.02 \times 10^{23}\,\text{mol}^{-1}$
electronic charge	$e = -1.60 \times 10^{-19}\,\text{C}$
molar volume of gas	$V_m = 22.4\,\text{dm}^3\,\text{mol}^{-1}$ at s.t.p. (101 kPa and 273 K) $V_m = 24.0\,\text{dm}^3\,\text{mol}^{-1}$ at room conditions
ionic product of water	$K_w = 1.00 \times 10^{-14}\,\text{mol}^2\,\text{dm}^{-6}$ (at 298 K (25 °C))
specific heat capacity of water	$c = 4.18\,\text{kJ kg}^{-1}\,\text{K}^{-1}$ ($4.18\,\text{J g}^{-1}\,\text{K}^{-1}$)

The Periodic Table of Elements

Group 1	2												13	14	15	16	17	18
							1 H hydrogen 1.0											2 He helium 4.0
3 Li lithium 6.9	4 Be beryllium 9.0												5 B boron 10.8	6 C carbon 12.0	7 N nitrogen 14.0	8 O oxygen 16.0	9 F fluorine 19.0	10 Ne neon 20.2
11 Na sodium 23.0	12 Mg magnesium 24.3												13 Al aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 Cl chlorine 35.5	18 Ar argon 39.9
19 K potassium 39.1	20 Ca calcium 40.1	21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	29 Cu copper 63.5	30 Zn zinc 65.4	31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9	36 Kr krypton 83.8
37 Rb rubidium 85.5	38 Sr strontium 87.6	39 Y yttrium 88.9	40 Zr zirconium 91.2	41 Nb niobium 92.9	42 Mo molybdenum 95.9	43 Tc technetium –	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57–71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium –	85 At astatine –	86 Rn radon –
87 Fr francium –	88 Ra radium –	89–103 actinoids	104 Rf rutherfordium –	105 Db dubnium –	106 Sg seaborgium –	107 Bh bohrium –	108 Hs hassium –	109 Mt meitnerium –	110 Ds darmstadtium –	111 Rg roentgenium –	112 Cn copernicium –	113 Nh nihonium –	114 Fl flerovium –	115 Mc moscovium –	116 Lv livermorium –	117 Ts tennessine –	118 Og oganesson –

Key

atomic number
atomic symbol
name
relative atomic mass

lanthanoids	57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium –	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0
actinoids	89 Ac actinium –	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium –	94 Pu plutonium –	95 Am americium –	96 Cm curium –	97 Bk berkelium –	98 Cf californium –	99 Es einsteinium –	100 Fm fermium –	101 Md mendelevium –	102 No nobelium –	103 Lr lawrencium –