Exercise walk-through

Halogenoalkanes ▪ 15.1

eXercise

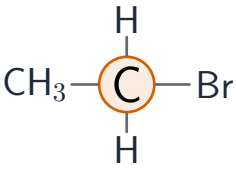
You must be able to

- classify halogenoalkanes and describe their nucleophilic substitution reactions
- describe the elimination reaction and the S_N1 and S_N2 mechanisms
- explain the different reactivities in terms of C–X bond strength

Method — Classes and nucleophilic substitution

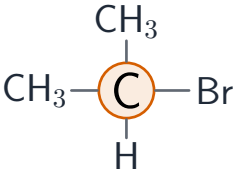
The polar C–X carbon is attacked by **nucleophiles**: NaOH(aq) → alcohol; KCN/ethanol → nitrile (+1 C); NH /ethanol/pressure → amine. **Test the halogen** with AgNO in ethanol (white AgCl, cream AgBr, yellow AgI).

Method — Classes and nucleophilic substitution



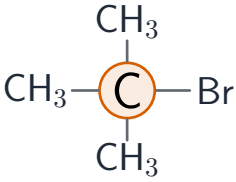
primary

1 C on the C–Br carbon



secondary

2 C

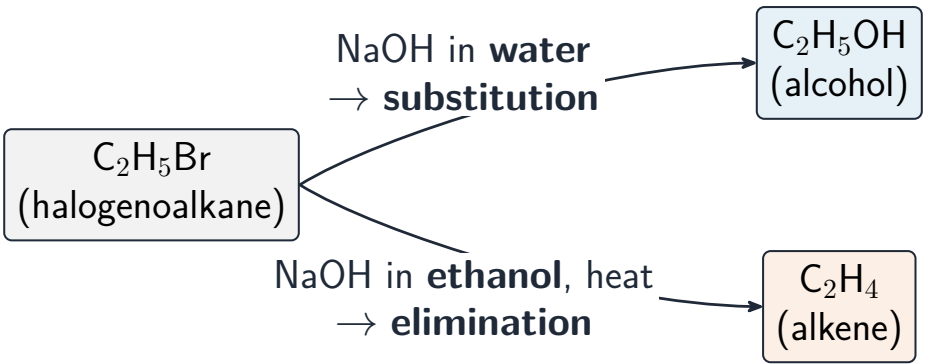


tertiary

3 C

Primary, secondary, tertiary halogenoalkanes set by carbons on the C–X carbon

Method — Substitution vs elimination



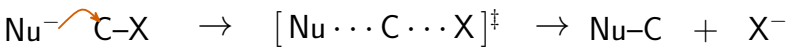
NaOH in water substitutes to an alcohol; NaOH in ethanol eliminates to an alkene

Method — S$_\text{N}$1 and S$_\text{N}$2

S_N2: one step (rate depends on both). S_N1: via a carbocation (rate depends only on the halogenoalkane)
Primary $\rightarrow$ mostly S_N2; tertiary $\rightarrow$ mostly S_N1 (stable carbocation).

Method — S$_\text{N}$1 and S$_\text{N}$2

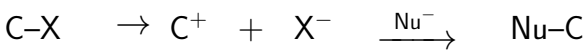
S_N2: one step



rate depends on both reactants

transition state

S_N1: two steps

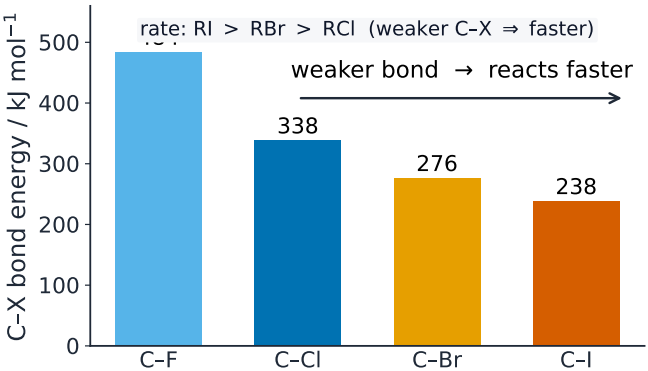


rate depends on R–X only

carbocation

S N 2 one step via a transition state; S N 1 two steps via a carbocation

Method — Reactivity



C–X bond energy falling from C–F to C–I; weaker bond reacts faster

Practice 2.1 ▪ 2 marks

State the reagent and condition to convert a halogenoalkane into an alcohol.

Solution 2.1

Method: Classes and nucleophilic substitution

Worked steps

aqueous sodium hydroxide, NaOH(aq) B1; and heat B1.

Practice 2.2 ▪ 1 mark

Name the organic product when a halogenoalkane reacts with KCN in ethanol.

Solution 2.2

Method: Classes and nucleophilic substitution

Worked steps

a nitrile B1.

Exam-style 3.1 ▪ 1 mark

Which conditions favour **elimination** of a halogenoalkane to an alkene?

A NaOH in water, warm

B NaOH in ethanol, heat

C aqueous silver nitrate

D KCN in ethanol

Solution 3.1

Method: Substitution vs elimination

A NaOH in water, warm

B NaOH in ethanol, heat ✓

C aqueous silver nitrate

D KCN in ethanol

Worked steps

B. NaOH in ethanol with heat favours elimination.

Exam-style 3.2 ▪ 1 mark

Which halogenoalkane reacts **fastest** with aqueous silver nitrate?

A 1-chlorobutane

B 1-bromobutane

C 1-iodobutane

D they react at the same rate

Solution 3.2

Method: Reactivity

A 1-chlorobutane

B 1-bromobutane

C 1-iodobutane ✓

D they react at the same rate

Worked steps

C. The C–I bond is weakest, so the iodoalkane reacts fastest.

Exam-style 3.3 ▪ 3 marks

(a) Describe the S_N2 mechanism for the reaction of bromoethane with hydroxide ions.
(b) Explain why tertiary halogenoalkanes tend to react by the S_N1 mechanism.

Solution 3.3

Worked steps

(a) the OH nucleophile attacks the $\delta+$ carbon (curly arrow from the lone pair) **M1**; at the same time the C–Br bond breaks, with both electrons going to Br **M1**; passing through a transition state with both half-bonded, giving ethanol and Br **A1**.

(b) the tertiary carbocation is stabilised by three electron-pushing alkyl groups **M1**, so the C–X bond breaks first to form it (S_N1) **A1**.

Exam-style 3.4 ▪ 2 marks

Explain why iodoalkanes are more reactive than chloroalkanes in substitution reactions.

Solution 3.4

Method: Reactivity

Worked steps

the C–I bond is weaker (lower bond energy) than C–Cl M1, so it breaks more easily, making the substitution faster A1.