

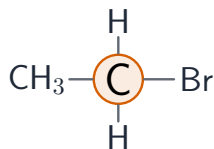
Exercise walk-through

15.1

Halogenoalkanes

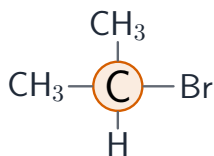
A-Level Chemistry

Three classes



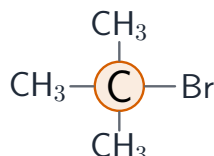
primary

1 C on the C-Br carbon



secondary

2 C



tertiary

3 C

A **halogenoalkane** has a C-X bond.

- **primary** – 1 carbon on the C-X carbon
- **secondary** – 2
- **tertiary** – 3

Two ways to make a halogenoalkane

A **halogenoalkane** is an alkane with one or more halogens in place of hydrogen – a C–X bond.

free-radical substitution

an alkane with Cl_2 or Br_2 in ultraviolet light

electrophilic addition

an alkene with a halogen X_2 , or with a hydrogen halide HX

The route decides the product: radicals give a mixture, an addition across a $\text{C}=\text{C}$ gives one place only.

Nucleophilic substitution

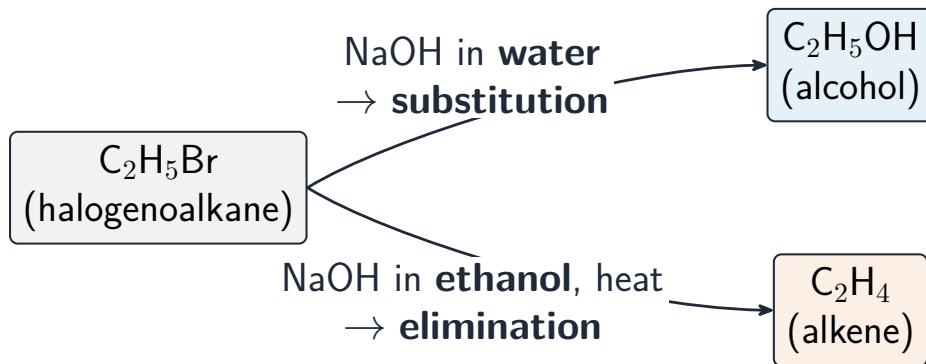


The polar carbon is attacked by a **nucleophile** :

- $\text{NaOH(aq)} \rightarrow$ an **alcohol**
- $\text{KCN} \rightarrow$ a **nitrile** (adds a carbon)
- $\text{NH}_3 \rightarrow$ an **amine**

Warm with **silver nitrate** to identify the halogen.

Substitution vs elimination



The conditions decide:

- NaOH in **water** → substitution (alcohol)
- NaOH in **ethanol**, heat → **elimination** (alkene)

The S_N1 and S_N2 mechanisms

Nucleophilic substitution can follow two routes:

- **S_N2**: one step. The nucleophile attacks at the same time as the halogen leaves, passing through a crowded **transition state** where both are half-bonded.
- **S_N1**: two steps. First the C–X bond breaks to give a **carbocation** ; then the nucleophile attacks it. The rate depends only on the halogenoalkane.
- **primary** halogenoalkanes mostly react by S_N2.
- **tertiary** halogenoalkanes mostly react by S_N1 (their carbocation is well stabilised).

Exercises 2.1·3.1

2.1 State the reagent and condition to convert a halogenoalkane into an alcohol. [2]

2.2 Name the organic product when a halogenoalkane reacts with KCN in ethanol. [1]

3.1 Which conditions favour **elimination** of a halogenoalkane to an alkene? [1]

☐

A NaOH in water, warm

B NaOH in ethanol, heat

C aqueous silver nitrate

D KCN in ethanol

Exercises 2.1·3.1

2.1 State the reagent and condition to convert a halogenoalkane into an alcohol. [2]

2.1

- aqueous sodium hydroxide, NaOH(aq); and heat
-

2.2 Name the organic product when a halogenoalkane reacts with KCN in ethanol. [1]

2.2

- a nitrile
-

3.1 Which conditions favour **elimination** of a halogenoalkane to an alkene? [1]

☐

A NaOH in water, warm

B NaOH in ethanol, heat

C aqueous silver nitrate

D KCN in ethanol

3.1 B

- NaOH in ethanol with heat favours elimination

Exercise 3.2

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

[1]

☐

A 1-chlorobutane

B 1-bromobutane

C 1-iodobutane

D they react at the same rate

Exercise 3.2

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

[1]

☐

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B 1-bromobutane

C 1-iodobutane

D they react at the same rate

3.2 C

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

Exercise 3.3

3.3 (a) Describe the S_N2 mechanism for the reaction of bromoethane with hydroxide ions. [3]

(b) Explain why tertiary halogenoalkanes tend to react by the S_N1 mechanism. [2]

Exercise 3.3

3.3 (a) Describe the S_N2 mechanism for the reaction of bromoethane with hydroxide ions. [3]

(b) Explain why tertiary halogenoalkanes tend to react by the S_N1 mechanism. [2]

Full solution 3.3

3.3

(a)

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

(b)

- the tertiary carbocation is stabilised by three electron-pushing alkyl groups, so the C-X bond breaks first to form it ($\text{S}_{\text{N}}1$)

Exercise 3.4

3.4 Explain why iodoalkanes are more reactive than chloroalkanes in substitution reactions. [2]

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3.4

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