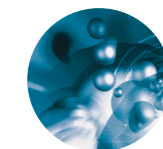


12.04 Alcohols from haloalkanes



OBJECTIVES

already from AS level, you

- know the definition of electronegativity
- understand that the electron distribution in a covalent bond may not be symmetrical

and after this spread you should understand

- that haloalkanes contain polar bonds
- that haloalkanes are susceptible to nucleophilic attack by OH⁻ ions
- the mechanism of nucleophilic substitution in primary haloalkanes

Primary haloalkanes

Haloalkanes such as bromoethane and 1-chlorobutane are **primary haloalkanes**. The carbon atom that their halogen atom is attached to is directly bonded to just one other carbon atom.

Haloalkanes contain a carbon–halogen bond. Apart from astatine at the bottom of group 7, all the halogens are more electronegative than carbon. This means that the carbon–halogen bond is a polar bond. The carbon atom has a partial positive charge δ^+ and the halogen atom has a partial negative charge δ^- . The carbon atom is **electron-deficient** because the halogen atom withdraws negative charge from it. The presence of the electron-deficient carbon atom makes haloalkanes liable to attack by nucleophiles.

Nucleophiles

In chemistry, **species** is a general term for an atom, ion, or molecule. A **nucleophile** is a species with a lone pair of electrons that is available to form a co-ordinate bond. Nucleophiles are attracted to regions of positive charge. Their name means **nucleus-loving**, since a nucleus is positively charged.

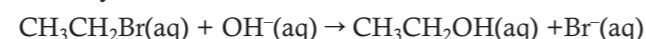
Nucleophiles can be

- negatively charged ions, such as OH⁻ and CN⁻
- molecules with a lone pair of electrons, such as H₂O and NH₃

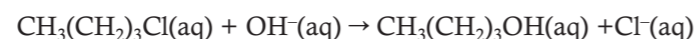
Nucleophiles like these can attack the electron-deficient carbon atom in a haloalkane molecule. They can bring about a reaction in which they replace the halogen atom. Reactions like these are called **nucleophilic substitution** reactions.

Nucleophilic substitution reactions

Bromoethane reacts with warm dilute sodium hydroxide solution or dilute potassium hydroxide solution to form ethanol:



This is a substitution reaction. The bromine atom has been replaced by OH. Similar reactions happen with other haloalkanes. For example, 1-chlorobutane reacts with warm dilute sodium hydroxide solution to form butan-1-ol:



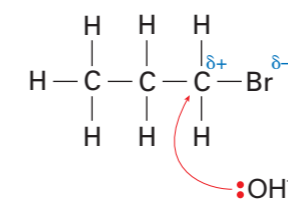
These reactions are nucleophilic substitution reactions because they involve a nucleophile, in this case the hydroxide ion OH⁻.

Reaction mechanism

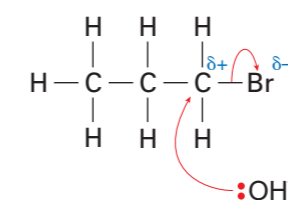
The reaction mechanism is shown with the help of curly arrows. A curly arrow indicates the movement of a pair of electrons from its tail to its head. A curly arrow can show the movement of

- a lone pair of electrons
- the pair of electrons in a covalent bond

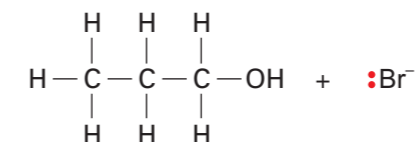
The reaction mechanism for nucleophilic substitution in 1-bromopropane by hydroxide ions is explained on the opposite page. It is shown broken down into steps for simplicity, but the events actually happen all at once.



1. In the first step, the nucleophile is attracted to the electron-deficient carbon atom. Notice that you should draw a lone pair of electrons in the nucleophile :OH⁻. The curly arrow is drawn from one side of the lone pair of electrons and points towards the electron-deficient carbon atom.

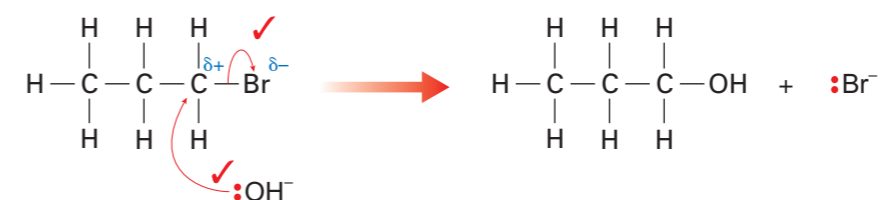


2. In the next step, the pair of electrons in the C–Br bond moves towards the bromine atom with its partial negative charge. Notice that the tail of the curly arrow starts from the bond and is not in mid-air above it.



3. In the final step, the hydroxide ion has donated one of its lone pairs of electrons to form a new bond with the carbon atom. The C–Br bond has broken to release a bromide ion.

The complete mechanism is drawn like this:



4. The complete reaction mechanism, with ticks to show the features an examiner is likely to look for in an examination.

The reaction mechanism for other haloalkanes will be just the same: you only need to change the halogen or carbon chain in your diagram.

Check your understanding

1. Define the term 'nucleophile' and give two examples of nucleophiles.
2. What does the curly arrow in a reaction mechanism show?
3. A substitution reaction happens when chloroethane reacts with warm sodium hydroxide solution.
 - a Name the organic compound formed in the reaction.
 - b Outline the mechanism for the reaction.

OBJECTIVES

already from AS level, you understand

- that haloalkanes are susceptible to nucleophilic attack by OH⁻ ions
- the mechanism of nucleophilic substitution in primary haloalkanes

and after this spread you should

- understand that the carbon-halogen bond enthalpy influences the rate of hydrolysis
- understand that haloalkanes are susceptible to nucleophilic attack by CN⁻ ions and ammonia
- appreciate the usefulness of these reactions in organic synthesis

Haloalkanes and reactivity

The rate of nucleophilic substitution depends upon the halogen in the haloalkane. It would be tempting to think that fluoroalkanes would be the most reactive, because fluorine is the most reactive halogen. But this is not the case. The reactivity of the haloalkanes depends upon the strength of the carbon-halogen bond. The lower its bond enthalpy, the weaker it is and the more easily it is broken.

bond	mean bond enthalpy (kJ mol ⁻¹)
C-F	484
C-Cl	338
C-Br	276
C-I	238

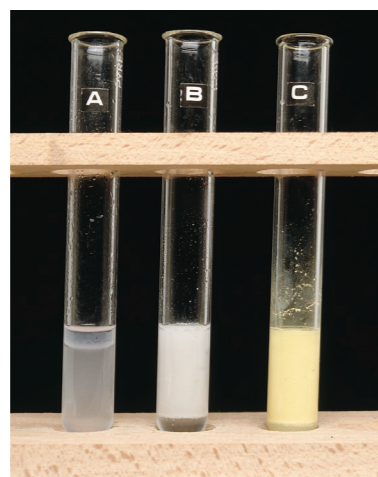
The carbon-fluorine bond is the strongest carbon-halogen bond.

The carbon-halogen bond is weakest in iodoalkanes, so these are the most reactive. The reactivity decreases going to bromoalkanes and then to chloroalkanes. The carbon-fluorine bond is so strong that the fluoroalkanes are not readily attacked by nucleophiles. This trend can be seen in the reaction of haloalkanes with water.

Hydrolysis of haloalkanes

The oxygen atom in the water molecule has two lone pairs of electrons. So water can act as a nucleophile. It is a weaker nucleophile than the hydroxide ion but it can still produce the same products in reactions with haloalkanes. The reaction is called a **hydrolysis** reaction because water is used to break down the haloalkane. The rate of hydrolysis can be followed using silver nitrate solution.

As the water and haloalkane react, halide ions are formed. These react with the silver ions to form precipitates. When the hydrolysis of chloroethane, bromoethane, and iodoethane is followed using silver nitrate solution, silver iodide forms faster than silver bromide. Silver chloride is the slowest to form.

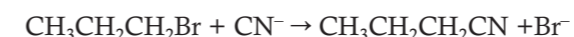


A contains a faint white precipitate of AgCl.
B contains a significant cream precipitate of AgBr.
C contains a distinct yellow precipitate of AgI.

Reaction with cyanide ions

The cyanide ion, CN⁻, acts as a nucleophile. It reacts with haloalkanes to produce nitriles. The cyanide ion is provided by sodium cyanide, NaCN, or potassium cyanide, KCN. These need to be dissolved in ethanol and heated with the haloalkane for the reaction to work.

1-Bromopropane reacts with hot ethanolic sodium hydroxide solution to form butanenitrile:

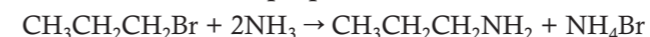


This is a nucleophilic substitution reaction. The reaction mechanism is the same as the one where OH⁻ is the nucleophile.

The nitrile formed in the reaction has one more carbon atom than the original haloalkane. This is very useful when making new substances.

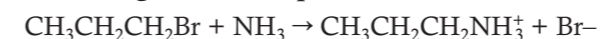
Reaction with excess ammonia

Ammonia, NH₃, acts as a nucleophile as its nitrogen atom has a lone pair of electrons. Ammonia reacts with haloalkanes to produce amines. These have an amine group NH₂. For example 1-bromopropane reacts with ammonia to form 1-aminopropane:

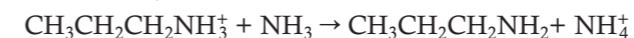


Two ammonia molecules are needed to react with one haloalkane molecule. One acts as a nucleophile and the other acts as a base.

Step 1 Ammonia acting as a nucleophile:



Step 2 Ammonia acting as a base:



Here the ammonia molecule accepts a hydrogen ion from the positively charged intermediate.

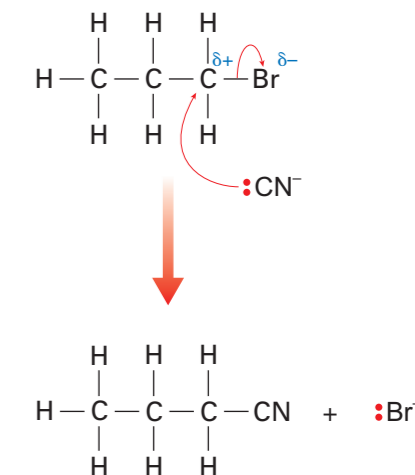
The ammonium ion from step 2 and the bromide ion from step 1 form ammonium bromide.

Why excess ammonia?

One example of a primary amine is 1-Aminopropane. Its nitrogen atom has a lone pair of electrons. Once it has formed in the reaction mixture, the primary amine can act as a nucleophile, just like ammonia. It can react with a haloalkane to form a secondary amine. This can react further to form a tertiary amine, and eventually a quaternary ammonium salt can be formed. The use of excess ammonia reduces these reactions and ensures that the main product is a primary amine.

Check your understanding

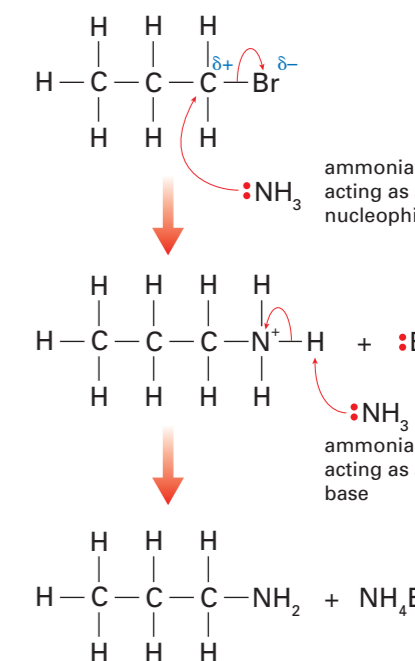
- Explain why iodoalkanes are more reactive than chloroalkanes.
- A substitution reaction happens when chloroethane reacts with hot ethanolic potassium cyanide solution.
 - Name the organic compound formed in the reaction.
 - Outline the mechanism for the reaction.
- Outline the mechanism for the substitution reaction between chloroethane and excess ammonia.



The reaction mechanism for nucleophilic substitution by cyanide ions.

Naming nitriles

The nitrile group can be shown as $\text{—C}\equiv\text{N}$ or just —CN . Nitriles are named using the suffix nitrile. The carbon atom in the nitrile group is included when counting the carbon atoms in the main chain. So, CH_3CN is ethanenitrile, not methanenitrile.



The reaction mechanism for nucleophilic substitution by excess ammonia.

12.06 Alkenes from haloalkanes

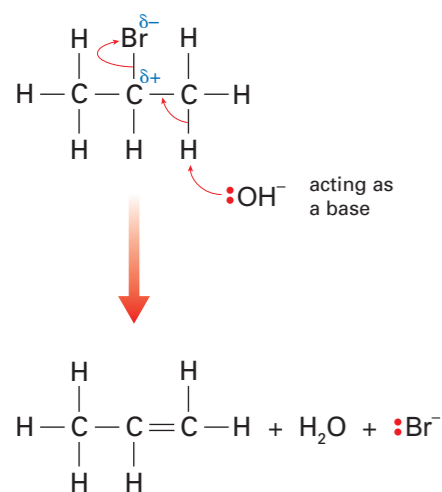
OBJECTIVES

already from AS level, you understand

- the mechanism for nucleophilic substitution in haloalkanes

and after this spread you should

- understand the role of the hydroxide ion as a nucleophile and as a base
- understand concurrent substitution and elimination in haloalkane reactions
- appreciate the usefulness of this reaction in organic synthesis



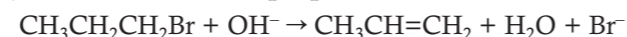
The reaction mechanism for elimination in 2-bromopropane to form propene.

A summary of the conditions needed to favour substitution or elimination reacts in haloalkanes.

When a haloalkane reacts with excess ammonia, the ammonia can act as a nucleophile and as a base. The hydroxide ion can also act as a nucleophile and as a base. A substitution reaction happens when the hydroxide ion acts as a nucleophile, producing an alcohol. But when the hydroxide ion acts as a base, an elimination reaction happens. It produces an alkene instead of an alcohol.

Elimination from haloalkanes

If 2-bromopropane is heated strongly with concentrated sodium or potassium hydroxide in ethanol, propene is formed:



The mechanism needs three curly arrows to describe it. They show that

- the hydroxide ion forms a co-ordinate bond with a hydrogen atom
- the bonding pair of electrons from the carbon-hydrogen bond forms a second covalent bond between two carbon atoms
- the carbon-bromine bond breaks, releasing a bromide ion

Note that all three pairs of electrons move simultaneously and there is no **intermediate** species. The hydrogen atom that is attacked is joined to a carbon atom next to the carbon atom with the carbon-halogen bond. The hydrogen atom is removed as a hydrogen ion, H^+ , which is accepted by the hydroxide ion to form water. This is how the hydroxide ion acts as a base here.

Concurrent substitution and elimination

When haloalkanes react with hydroxide ions, both types of reaction can happen together. This is called *concurrent substitution and elimination*. The reaction conditions can be adjusted to favour one type of reaction over the other.

- Substitution is favoured by using warm, dilute aqueous sodium hydroxide or potassium hydroxide.
- Elimination is favoured by using hot, concentrated ethanolic sodium hydroxide or potassium hydroxide.

To some extent the two reactions are always in competition with each other because hydroxide ions can act both as a nucleophile and as a base.

type of reaction	reaction conditions			hydroxide ion acts as a:
	temperature	hydroxide	solvent	
substitution	low	dilute	water	nucleophile
elimination	high	concentrated	ethanol	base

The favoured type of reaction is also influenced by whether the haloalkane is a primary, secondary, or tertiary haloalkane. This is often shortened to 1°, 2°, and 3°. Look at the carbon atom to which the halogen atom is attached. This is directly attached to

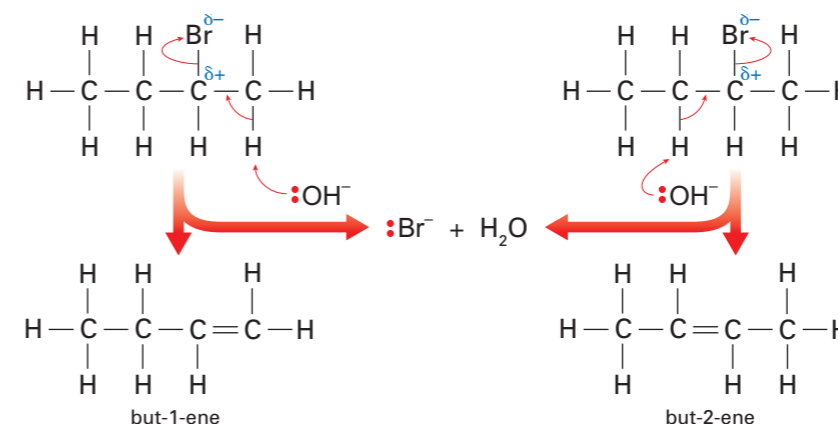
- one other carbon atom in a primary haloalkane
- two other carbon atoms in a secondary haloalkane
- three other carbon atoms in a tertiary haloalkane

haloalkane	example	substitution	elimination
primary	$\begin{array}{c} \text{H} \\ \\ \text{CH}_3-\text{C}-\text{Br} \\ \\ \text{H} \end{array}$ bromoethane	most likely	least likely
secondary	$\begin{array}{c} \text{H} \\ \\ \text{CH}_3-\text{C}-\text{Br} \\ \\ \text{CH}_3 \end{array}$ 2-bromopropane		
tertiary	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{Br} \\ \\ \text{CH}_3 \end{array}$ 2-bromo-2-methylpropane	least likely	most likely

Substitution is most likely in primary haloalkanes and elimination is most likely in tertiary haloalkanes.

Two elimination products

Only one product of elimination is possible from 2-bromopropane. But two products of elimination are possible from longer, unsymmetrical secondary haloalkanes. For example, the bromine atom in 2-bromobutane is joined to the second carbon atom of four. As a result, elimination produces but-1-ene and but-2-ene. The diagram shows how this works.



Elimination in 2-bromobutane produces but-1-ene and but-2-ene.

Check your understanding

- 2-Bromopentane reacts with hot ethanolic potassium hydroxide to produce pent-2-ene:

$$\text{CH}_3(\text{CH}_2)_2\text{CHBrCH}_3 + \text{KOH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_3 + \text{H}_2\text{O} + \text{KBr}$$
 - What type of reaction is this?
 - Explain why the potassium ion, K^+ , is a spectator ion in this reaction.
 - Outline a mechanism for this reaction.
 - Give the structural formula and name of another alkene that could be formed by the reaction mixture.
 - Suggest the conditions needed to favour the production of pentan-2-ol in the reaction instead of pentene.

Refluxing

Organic reactions are often slow, so the reaction mixture may need to be heated for several hours. During this time, the volatile substances may well boil away. A method called refluxing is used to stop this happening. A condenser is fitted into the neck of the reaction vessel. As vapours rise from the boiling reaction mixture, they are cooled and condensed, so they fall back into the reaction vessel.



Refluxing is often used for haloalkane substitution reactions with cyanide ions, and haloalkane elimination reactions with hydroxide ions.