

George Facer

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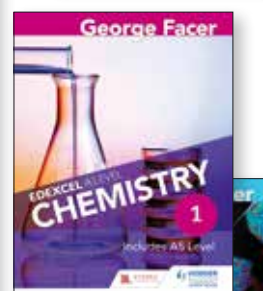
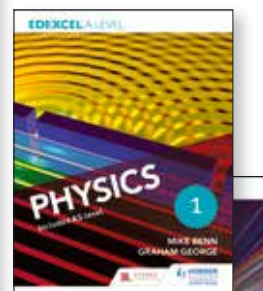
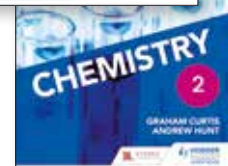
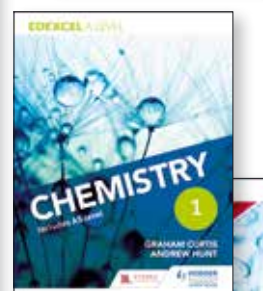
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Halogenoalkanes

Key term

A **halogenoalkane** is a compound in which one or more hydrogen atoms in an alkane has been replaced by halogen atoms and which has only single bonds in the molecule.

Halogenoalkanes have the general formula $C_nH_{(2n+1)}X$, where X is a halogen atom. They are named from the parent alkanes, with a number representing the carbon atom in the chain to which the halogen is joined.

The skeletal formulae, names and structural formulae of some halogenoalkanes are shown in Figure 11.1.

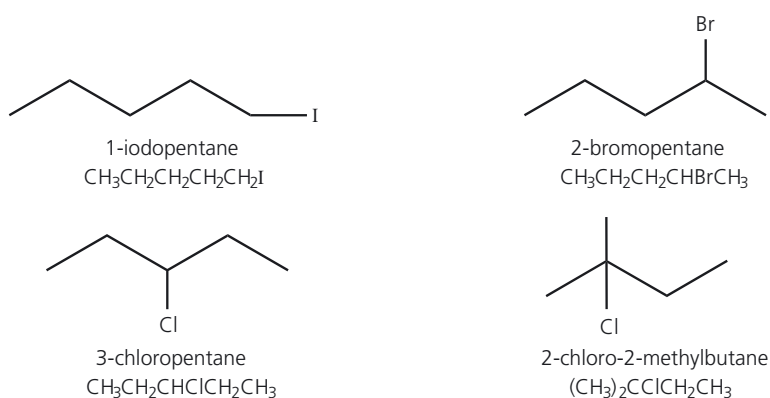


Figure 11.1 Some examples of halogenoalkanes.

Primary halogenoalkanes have no more than one carbon atom directly attached to the carbon in the C–halogen group. Some examples are shown in Figure 11.2.

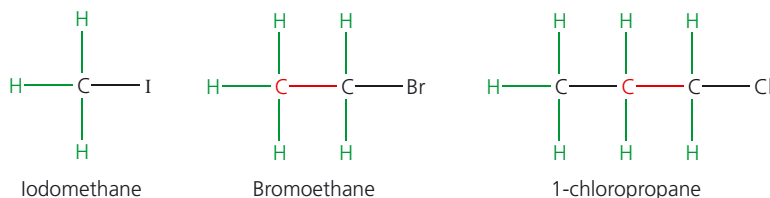


Figure 11.2 Primary halogenoalkanes.

Secondary halogenoalkanes have two carbon atoms (and hence only one hydrogen atom) directly attached to the carbon in the C–halogen group, for example, 2-chloropropane (Figure 11.3).

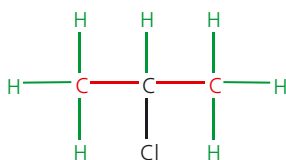


Figure 11.3 The structural formula of 2-chloropropane.

Tertiary halogenoalkanes have three carbon atoms (and hence no hydrogen atoms) directly attached to the carbon in the C–halogen group, for example, 2-chloro-2-methylpropane (Figure 11.4).

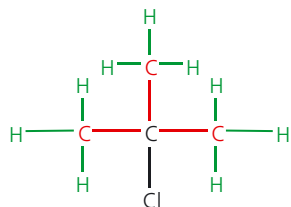


Figure 11.4 The structural formula of 2-chloro-2-methylpropane.

Halogens are electronegative elements. The carbon–halogen bond in halogenoalkanes is polarised, making the carbon atom δ^+ and the halogen atom δ^- as shown in Figure 11.5.

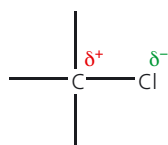


Figure 11.5 The polar nature of halogenoalkanes.

TEST YOURSELF

- 1 Draw the skeletal formulae of the isomers of C_4H_9Br stating whether they are primary, secondary or tertiary.

Physical properties

Chloromethane, bromomethane and chloroethane are gases at room temperature. Iodomethane and higher members of the homologous series are liquids. The boiling temperatures of halogenoalkanes are higher than those of alkanes, primarily because halogenoalkanes contain more electrons and so have stronger instantaneous induced dipole–induced dipole (London) forces between the molecules. In addition, because the molecules are polar, there are permanent dipole–dipole forces between the molecules which strengthen the intermolecular forces and so increase the boiling temperature.

Even though they are polar molecules, halogenoalkanes are insoluble in water. This is because the molecules contain neither δ^+ hydrogen atoms nor small δ^- atoms with a lone pair of electrons, so they cannot hydrogen-bond with water. They are, however, soluble in a variety of organic solvents, such as ethanol and ethoxyethane (ether), $C_2H_5OC_2H_5$.

TEST YOURSELF

- 2 Explain why iodoethane has a higher boiling point than iodomethane.

Key terms

A **substitution reaction** is a reaction in which an atom or group is replaced by another atom or group. There are always two reactants and two products in a substitution reaction.

A **nucleophile** is a species with a lone pair of electrons that is used to form a covalent bond with a δ^+ atom in another molecule.

Tip

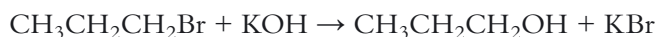
This reaction is sometimes carried out with the halogenoalkane dissolved in alcohol and the alkali dissolved in water. This is because the organic compound is not water soluble, and so little contact would occur between it and the hydroxide ions. If a solution of the alkali in *ethanol* is used, a different reaction occurs, particularly with secondary and tertiary halogenoalkanes (pages XXX-XXX).

Nucleophilic substitution reactions

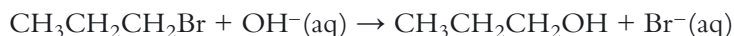
The halogen atom in a halogenoalkane molecule can be replaced by an $-\text{OH}$, $-\text{CN}$ or $-\text{NH}_2$ group. These reactions are examples of **nucleophilic substitution** because the attacking group is a **nucleophile**. In these reactions, the reagent forms a bond to the carbon using its lone pair of electrons and the halide ion is released.

Reaction with aqueous alkali

When a halogenoalkane is heated under reflux with an *aqueous* solution of an alkali, such as potassium hydroxide or sodium hydroxide, the halogen is replaced by an $-\text{OH}$ group and an alcohol is produced. For example with 1-bromopropane:



The ionic equation for this reaction is:



Reagent: potassium (or sodium) hydroxide

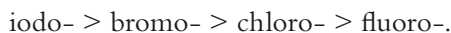
Conditions: warmed under reflux in *aqueous* solution

Product: propan-1-ol

Reaction type: nucleophilic substitution (also called hydrolysis)

A lone pair of electrons on the oxygen atom in the OH^- ion attacks the δ^+ carbon in the carbon–bromine bond and forms a new carbon–oxygen σ -bond. The bromine gains the electrons from the carbon–bromine σ -bond which breaks, forming a Br^- ion. In this example, the OH^- ion is the nucleophile.

The rate of this reaction varies considerably according to the halogen in the halogenoalkane. The rate of reaction is in the order:



The reason for this is the difference in bond enthalpies of the C–halogen bonds as given in Table 11.1.

Table 11.1 Bond enthalpies.

Bond	Average bond enthalpy/ kJ mol^{-1}
C–F	+484
C–Cl	+338
C–Br	+276
C–I	+238

A weaker carbon–halogen bond means that there is a smaller activation energy (page XXX) for a reaction which involves breaking that bond. The C–I bond is the weakest and so reactions involving iodoalkanes will have the lowest activation energy and thus the fastest rate.

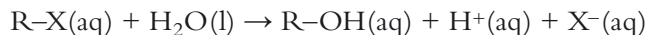
The rate of reaction also varies considerably according to the type of halogenoalkane involved. The rate of reaction is in the order:



The explanation for this is complex. A $-\text{CH}_3$ group (and to a lesser extent a $-\text{CH}_2$ group) has a tendency to push electrons in the σ -bond away from itself. This facilitates the release of the negative halide ion because there is a general shift of electrons away from the $-\text{CH}_3$ group towards the halogen atom.

Reaction with water containing silver nitrate solution

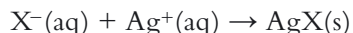
The halogenoalkane reacts with the water to form an alcohol and a solution that contains the halide as an anion:



(where X represents a halogen)

The reaction involves nucleophilic attack on the carbon atom joined to the halogen by the lone pair of electrons on the oxygen in water. Since water is not as good a nucleophile as hydroxide ions, the reaction is much slower than that with aqueous potassium hydroxide.

The halide ion formed then reacts with silver ions from the silver nitrate to form a precipitate of silver halide:



The rates of the reaction of the halogenoalkanes can be compared by noting the time taken for the precipitates to appear. Equal volumes of each halogenoalkane are placed in test tubes, which are then put in a water bath at 60°C . Some silver nitrate solution is then added and the time taken for a precipitate of the silver halide to appear is noted.

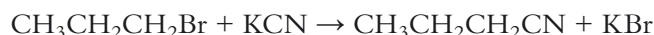
- Primary halogenoalkanes hardly react with water. The $\text{C}-\text{Cl}$ bond is too strong for any noticeable precipitate to be observed. 1-bromoalkanes give a precipitate very slowly; 1-iodoalkanes give a precipitate slightly more quickly.
- Secondary halogenoalkanes react slowly to form a secondary alcohol and a precipitate is soon observed. Precipitate formation is quicker with secondary iodoalkanes than with secondary bromoalkanes, which in turn form precipitates more quickly than secondary chloroalkanes.
- Tertiary halogenoalkanes react rapidly to produce a tertiary alcohol. A precipitate is seen as soon as the silver nitrate is added.

TEST YOURSELF

- 3 Explain why 2-iodopropane reacts with aqueous silver nitrate at a faster rate than 2-chloropropane.

Reaction with potassium cyanide

When a halogenoalkane dissolved in ethanol is warmed with aqueous potassium cyanide, a substitution reaction takes place and a nitrile which contains a $\text{C}\equiv\text{N}$ is formed. With 1-bromopropane the reaction is:



Reagent: potassium cyanide, KCN

Conditions: warmed under reflux in aqueous ethanol solution

Tip

This is similar to the stabilisation of a secondary carbocation in the addition of HBr to an asymmetrical alkene (see page XXX).

Tip

The halogenoalkanes are sometimes mixed with equal volumes of ethanol in order to improve solubility in the aqueous silver nitrate.

Tip

The carbon-halogen bond has been broken by water, so the reaction is called hydrolysis.

Tip

The product here has four carbon atoms in a single bonded chain and so the stem name is butan-.

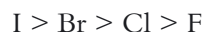
Product: 1-butanenitrile

Reaction type: nucleophilic substitution

This reaction is an example of an increase in the carbon chain length. The lone pair of electrons on the carbon atom of the CN^- ion attacks the δ^+ carbon atom of the halogenoalkane, forming a new carbon-carbon σ bond.

The rate of this reaction depends on the halogen and on whether the halogenoalkane is primary, secondary or tertiary (see page XXX).

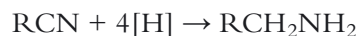
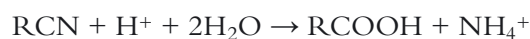
Rate:



and

tertiary > secondary > primary.

Nitriles are useful intermediate compounds in synthesis. They can be hydrolysed to an acid or reduced to a primary amine.



Key term

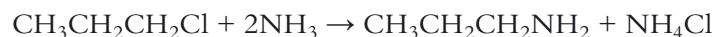
An **amine** is a molecule containing the $-\text{NH}_2$, $>\text{N}-\text{H}$ or $>\text{N}-$ group.

Reaction with ammonia

The reaction between a halogenoalkane and ammonia produces an **amine**.

Ammonia is a gas that is soluble in water. However, a solution cannot be heated under reflux because ammonia gas would be liberated. This would then escape because it would not be condensed by the reflux condenser. The halogenoalkane and the ammonia solution must therefore be heated in a sealed container. Alternatively, a concentrated ammonia solution can be used and the mixture left at room temperature for a long time.

A simplified equation for the reaction between 1-chloropropane and ammonia is:



Reagent: excess ammonia

Conditions: concentrated solution of ammonia at room temperature or heated in a sealed tube

Product: 1-aminopropane

Reaction type: nucleophilic substitution

The product, 1-aminopropane, can react with more 1-chloropropane to produce the secondary amine, $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NH}$, and some tertiary amine, $(\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{N}$.

Tip

Under these alkaline conditions, the salt NH_4Cl is produced rather than the acidic HCl . Stating that HCl is a product of this reaction is a common error.

Mechanism of nucleophilic substitution

Halogenoalkanes react with nucleophiles such as OH^- , H_2O , NH_3 and CN^- in substitution reactions. This is because the carbon atom joined to the halogen is slightly δ^+ and is, therefore, attacked by nucleophiles.

There are two distinct mechanisms by which halogenoalkanes react. Which mechanism is followed depends on whether they are primary, secondary or tertiary halogenoalkanes.

Primary halogenoalkanes

These react in an S_N2 reaction. The mechanism is a single step that goes through a transition state.

Mechanism of reaction with $\text{OH}^-(\text{aq})$

An example of an S_N2 mechanism involving a transition state is the reaction between hydroxide ions and bromoethane, as shown in Figure 11.6.

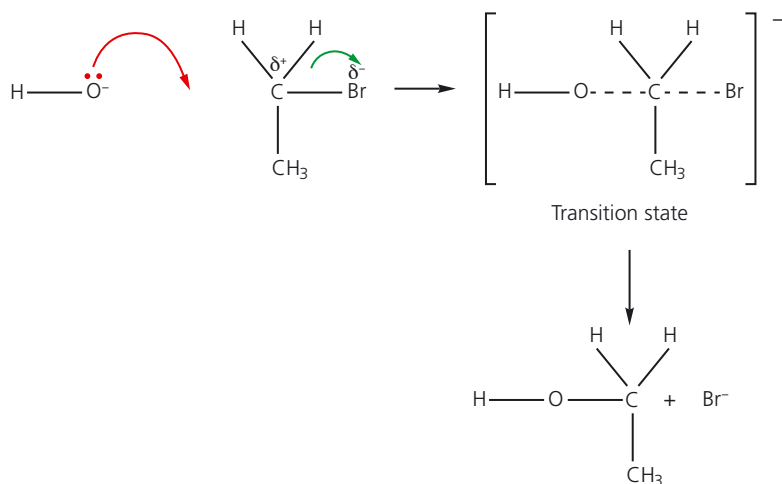


Figure 11.6 The reaction between hydroxide ions and bromoethane, showing the transition state.

The red curly arrow in Figure 11.6 shows the movement of a lone pair of electrons from the oxygen to the carbon as a covalent bond forms. The green arrow represents the electrons in the $\text{C}-\text{Br}$ σ -bond moving to the bromine atom as the bond breaks.

The transition state occurs when the new $\text{O}-\text{C}$ bond is half-formed and the $\text{C}-\text{Br}$ bond is half-broken.

The mechanism for the reaction with cyanide ions, ^-CN is similar, with the lone pair of electrons on the carbon atom forming a bond with the δ^+ carbon atom of the halogenoalkane.

The reaction profile diagram for this type of reaction is shown in Figure 11.7.

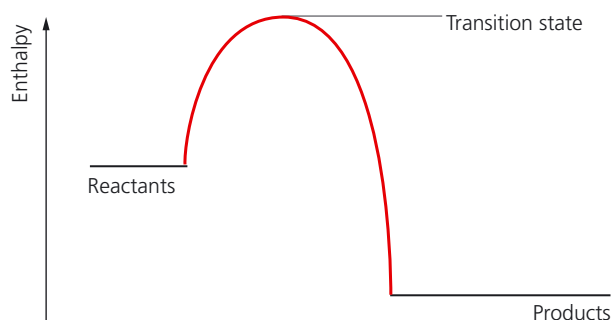


Figure 11.7 Reaction profile for an S_N2 reaction involving a transition state.

The energy released in the formation of the $\text{O}-\text{C}$ bond is enough to provide the energy to break the $\text{C}-\text{halogen}$ bond. The weaker the $\text{C}-\text{halogen}$ bond, the faster the rate of the reaction. Therefore, since the $\text{C}-\text{Cl}$ bond is the strongest and the $\text{C}-\text{I}$ bond is the weakest, the rate order is:



Key terms

An S_N2 reaction is so called because it is a substitution (S), is nucleophilic (N) and there are two species involved at the beginning of the mechanism.

A transition state is not a species that can be isolated. It changes immediately into the product. An analogy is that the transition state is like the top of a pass going from one valley to another.

Tip

Do not forget to include the negative charge on the transition state nor the δ^+ and δ^- charges on the halogenoalkane.

Tip

Make sure that the curly arrow starts from the carbon atom of the cyanide ion and not the nitrogen atom.

Key term

The mechanism is called S_N1 because it is a substitution (S), is nucleophilic (N) and there is only one species involved at the beginning of the mechanism.

Tip

The S_N1 mechanism has a lower activation energy with a tertiary halogenoalkane than with a primary one. This is because the carbocation intermediate is stabilised by the pushing effect of the three alkyl groups (see page XXX).

Tertiary halogenoalkanes

Tertiary halogenoalkanes react by S_N1 mechanisms.

This type of reaction takes place in two steps.

Step 1: the carbon–halogen bond breaks, a carbocation is formed and a halide ion is released. This is the slower rate-determining step.

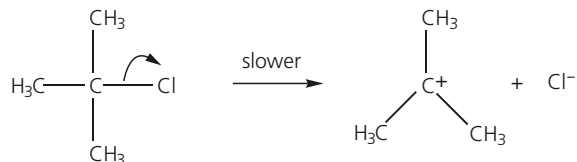


Figure 11.8

Step 2: the carbocation is attacked by the nucleophile in a faster reaction.

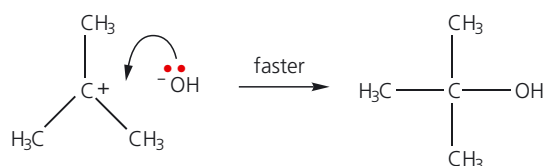


Figure 11.9

The rate of the first step is slower than that of the second step. Therefore, the activation energy for the first step is greater than that of step 2. This is shown in Figure 11.10.

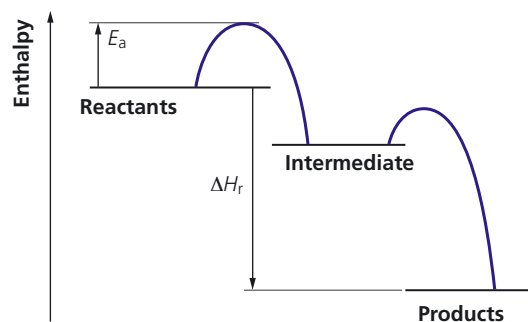


Figure 11.10 Reaction profile for an S_N1 reaction involving an intermediate.

Tip

When drawing diagrams like Figure 11.11, it does not matter whether you put the $-$ sign on the C or on the N, but the curly arrow must start from the carbon atom.

With cyanide ions as the nucleophile, the second step is the attack on the carbocation by the lone pair of electrons on the carbon atom of the cyanide ion, CN^- , thus forming a new carbon–carbon single bond.

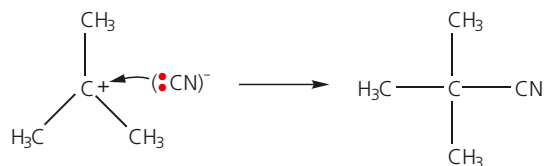


Figure 11.11

Secondary halogenoalkanes

The rate of reactions with S_N2 mechanisms decreases in the order

primary > secondary > tertiary halogenoalkane.

The rate of reactions with S_N1 mechanisms increases in the order

primary < secondary < tertiary halogenoalkane.

These relationships are shown graphically in Figure 11.12.

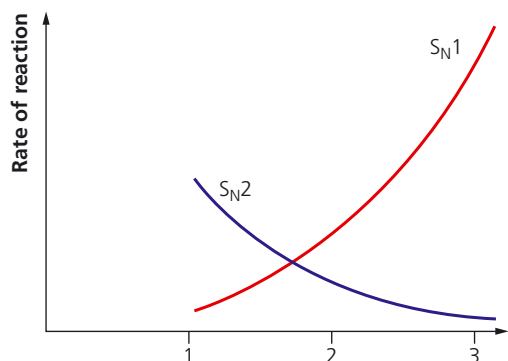


Figure 11.12 Different rates of S_N1 and S_N2 reactions.

Figure 11.12 shows that primary (1°) halogenoalkanes react almost entirely by an S_N2 mechanism and that tertiary (3°) halogenoalkanes react by an S_N1 mechanism. Secondary (2°) halogenoalkanes react by both mechanisms. However, S_N1 is faster and is, therefore, the dominant mechanism.

The overall rate is fastest with a tertiary halogenoalkane and slowest with a primary. For example, 2-chloro-2-methylpropane, $(CH_3)_3CCl$, produces an instant precipitate of silver chloride with aqueous silver nitrate, whereas 1-chloropropane gives a precipitate only after heating for a long period.

Mechanism of reaction with ammonia

With primary halogenoalkanes

The lone pair of electrons on the nitrogen atom attacks the δ^+ carbon atom. Ammonia is therefore the nucleophile. As this happens, the C-halogen bond breaks as in the S_N2 reaction on page 7. Note that the intermediate is neutral, because the attacking species is neutral.

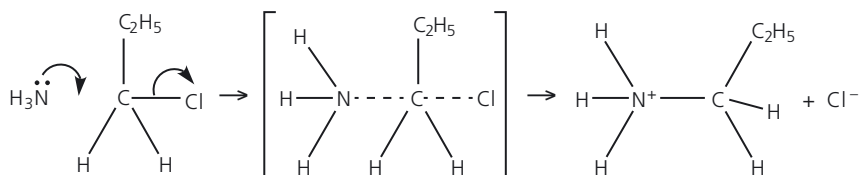


Figure 11.13

The final step is the loss of H^+ , which is removed by a second NH_3 molecule:

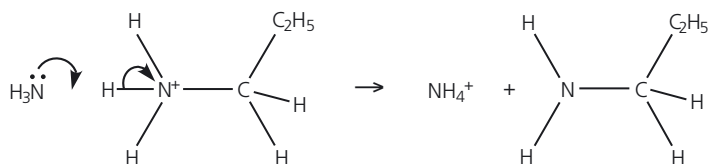


Figure 11.14

With tertiary halogenoalkanes

The first step is identical to the S_N1 reaction with aqueous OH^- ions.

The carbocation is then attacked by the lone pair of electrons in the NH_3 molecule.

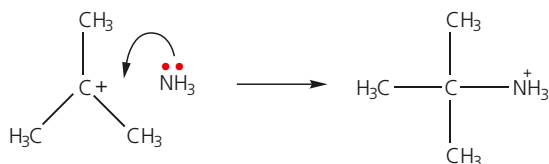


Figure 11.15

The last step is loss of H^+ as in the S_N2 mechanism shown in Figure 11.15.

Key term

An **elimination reaction** is a reaction in which two atoms, or one atom and one small group, are removed from adjacent carbon atoms, forming an unsaturated compound.

Elimination reaction

When a halogenoalkane is heated under reflux with a concentrated solution of potassium hydroxide in *ethanol*, the halogen atom is removed from the carbon atom to which it is attached and a hydrogen atom is removed from an adjacent carbon atom. The organic product is an alkene or a mixture of alkenes.

With either 1-chloropropane or 2-chloropropane, the only elimination product is propene as shown in Figure 11.16.

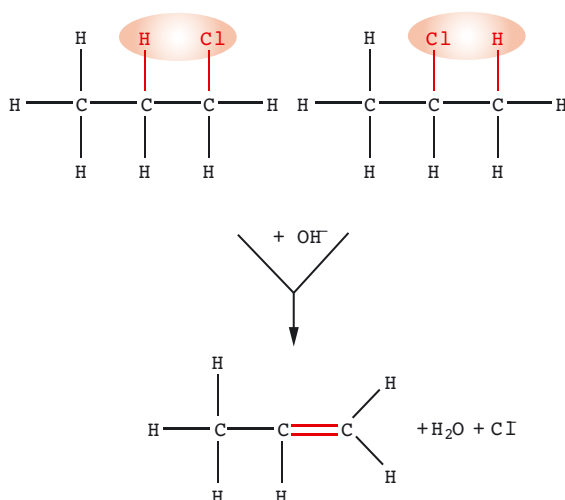


Figure 11.16 The elimination of HCl .

TIP

The conditions determine whether elimination or substitution takes place. For substitution, the alkali is aqueous and only gently heated; for elimination, it is dissolved in ethanol and heated under reflux.

Reagent: concentrated potassium hydroxide

Conditions: heat under reflux in solution in *ethanol*

Product: propene

Reaction type: elimination

1-chlorobutane produces but-1-ene:



However, 2-chlorobutane produces a mixture of but-1-ene and both geometric isomers of but-2-ene (Figure 11.18).



Figure 11.17 Heating under reflux.

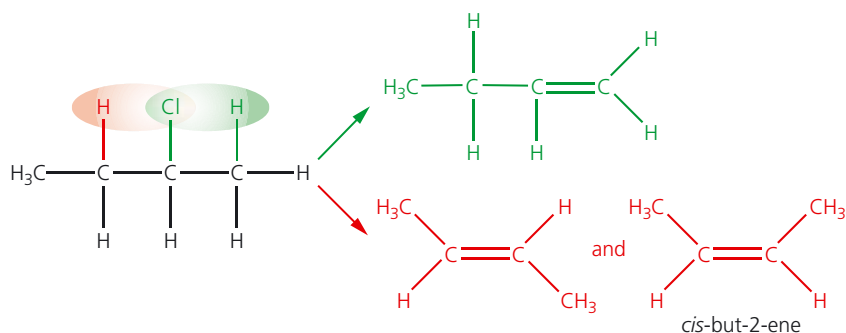


Figure 11.18

In practice, the situation is more complex because as well as elimination reactions, substitution reactions take place. Elimination is favoured by high temperatures in reactions with strong bases such as OH^- involving tertiary halogenoalkanes. Substitution is favoured by moderate temperatures in reactions with weak bases such as H_2O and NH_3 and involving primary halogenoalkanes. The reaction of bromoethane with hot ethanolic potassium hydroxide produces only about 1% ethene, whereas the reaction using 2-bromopropane gives about 80% propene. Tertiary halogenoalkanes give almost 100% alkenes as the product under these conditions.

TEST YOURSELF

4 Name and give the formula of the organic product of the reaction of 1-bromo-2-methylpropane with:

- an aqueous solution of potassium hydroxide
- a concentrated solution of sodium hydroxide in ethanol
- excess concentrated ammonia.

Summary of reactions of halogenoalkanes

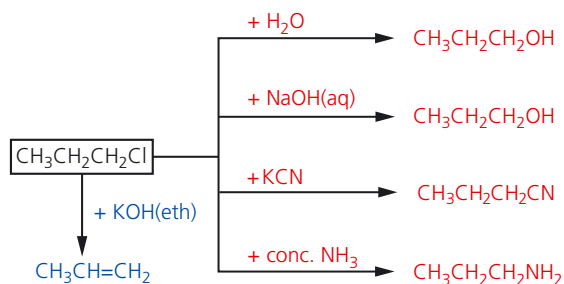


Figure 11.19

The reactions in red are nucleophilic substitution reactions.

The reaction in blue is elimination.

Test for halogenoalkanes

- Add a few drops of the halogenoalkane to an aqueous solution of sodium hydroxide and warm for several minutes.
- Cool.
- Add dilute nitric acid until the solution is just acidic to litmus.
- Add silver nitrate solution.

Result

- Chloroalkanes give a white precipitate that is soluble in dilute ammonia solution.
- Bromoalkanes give a cream precipitate that is insoluble in dilute ammonia solution but soluble in concentrated ammonia.
- Iodoalkanes give a pale yellow precipitate that is insoluble in dilute and concentrated ammonia.

The sodium hydroxide solution hydrolyses the halogenoalkane and liberates the halide ion. The solution has to be made acidic to prevent the precipitation of silver oxide when the silver nitrate is added. The precipitates are silver chloride (soluble in dilute ammonia), silver bromide (soluble only in concentrated ammonia) and silver iodide (insoluble in concentrated ammonia).

Uses of halogenoalkanes

Solvents

Compounds with several halogen atoms are used as solvents to remove grease from metals before electroplating. An example is 1,1,2-trichloroethane.

Refrigerants

Fully substituted compounds, such as the CFCs freon 12, CF_2Cl_2 , and freon 113, $\text{CF}_2\text{ClCFCl}_2$, are used as coolants in refrigerators and in air conditioning. They were chemically inert, non-toxic and non-flammable. When released, however, their inert nature causes an environmental problem. They diffuse unchanged up into the stratosphere, where they are decomposed by ultraviolet radiation, producing chlorine radicals. The chlorine radicals break down ozone in a chain reaction. It has been estimated that a single chlorine atom will cause the decomposition of 100 000 ozone molecules. During the Antarctic winter, the chlorine radicals build up on ice crystals in the air, and when the ice is melted by the spring sun, massive depletion of the polar ozone occurs, causing a hole in the ozone layer in the southern hemisphere.

New refrigerant coolants, which contain hydrogen atoms as well as chlorine and fluorine, are being developed. An example is HCFC-22, which has the formula CHClF_2 . HCFCs have been more reactive and are broken down at lower altitudes, avoiding harm to the ozone layer. However, like CFCs, they are potent greenhouse gases.

Herbicides and pesticides

Herbicides kill plants. Two examples are 2,4-D and 2,4,5-T, which have structures as shown in Figure 11.20.

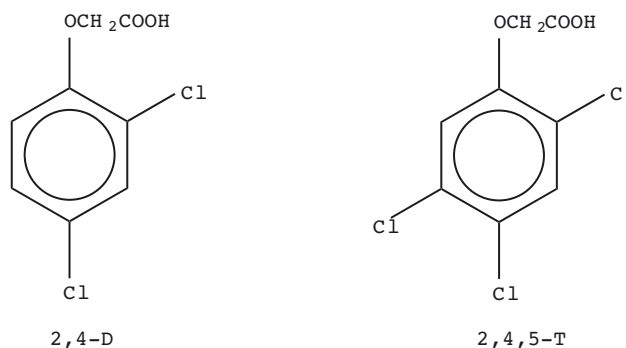


Figure 11.20 The structural formulae of two herbicides.

Pesticides kill insects. One of the most effective was DDT (dichlorodiphenyl-trichloroethane). Unfortunately, it was found that its concentration built up in the fat of animals high in the food chain, causing problems with reproduction. Therefore, its use has been banned in many countries. DDT eradicated malaria from some countries and helped to control it in others. Since its ban, deaths from malaria in some tropical countries have risen.

The problem associated with the use of halogen-containing herbicides and pesticides is that they are inert to chemical and biological attack. They remain in the environment for a very long period. In the 1970s, the US military sprayed the forests of Vietnam with the defoliant Agent Orange, a mixture of 2,4-D and 2,4,5-T, and its adverse effects are still being seen. These chemicals are inert mainly because of the strength of the carbon–chlorine bond, which is particularly strong if bonded to benzene rings, as in DDT.

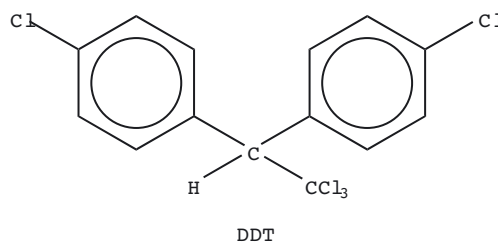


Figure 11.21 The structural formula for DDT.

Alcohols

In an **alcohol**, the other atoms attached to the carbon of the C–OH group must be either hydrogen or carbon.

Alcohols have the general formula $C_nH_{(2n+1)}OH$. They are named from the parent alkanes, with a number representing the carbon atom in the chain to which the –OH group is joined. The skeletal formulae, names and structural formulae of some alcohols are shown in Figure 11.22.

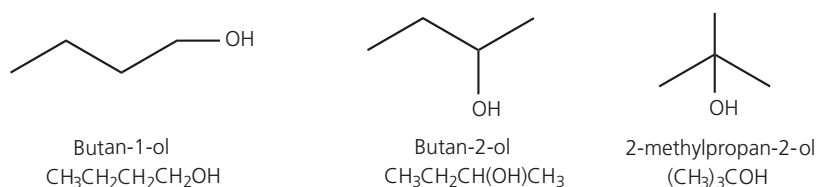


Figure 11.22 The structures of some common alcohols.

Primary alcohols have no more than one carbon atom attached directly to the carbon of the C–OH group. Methanol, CH_3OH , ethanol, CH_3CH_2OH , and propan-1-ol, $CH_3CH_2CH_2OH$, are all primary alcohols. All primary alcohols contain the – CH_2OH group.

Secondary alcohols have two carbon atoms (and hence only one hydrogen atom) directly attached to the carbon of the C–OH group. Propan-2-ol, $CH_3CH(OH)CH_3$, is a secondary alcohol. All secondary alcohols contain the $CH(OH)$ group.

Tertiary alcohols have three carbon atoms (and hence no hydrogen atoms) directly attached to the carbon of the C–OH group. 2-methylpropan-2-ol is a tertiary alcohol. Its structure is shown in Figure 11.23.

Key term

Alcohols are compounds that contain the hydroxyl, C–OH, group.

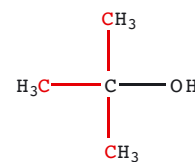


Figure 11.23 A tertiary alcohol, 2-methylpropan-2-ol.

TEST YOURSELF

5 Draw the skeletal formulae of:

- a primary alcohol of molecular formula $C_5H_{12}O$, which has a branched carbon chain
- a primary alcohol of molecular formula $C_5H_{12}O$, which has an unbranched carbon chain
- a secondary alcohol of molecular formula $C_5H_{12}O$
- a tertiary alcohol of molecular formula $C_5H_{12}O$.

Physical properties

Most alcohols are liquids at room temperature. This is because there is hydrogen bonding between alcohol molecules. The oxygen–hydrogen bond is very polar because of the difference in the electronegativity of the two elements. The δ^- oxygen in one alcohol molecule forms a hydrogen bond with the δ^+ hydrogen atom in another molecule (Figure 11.24). This intermolecular force is stronger than and in addition to the instantaneous induced dipole–induced dipole (London) forces such as those acting between alkane molecules and those between the polar halogenoalkane molecules. As the forces are stronger, more energy is required to separate the molecules, resulting in a higher boiling temperature.

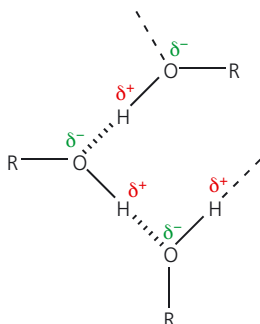


Figure 11.24 Hydrogen bonding between alcohol molecules.

The lower members of the homologous series of alcohols are all completely miscible with water. This means that they dissolve in water in all proportions. Higher members are less soluble because the large hydrocarbon part interferes with the hydrogen bonding between water molecules. The reason for the solubility is the hydrogen bonding between alcohol and water molecules (Figure 11.25). This is similar in strength to the hydrogen bonding in pure water and in pure alcohol.

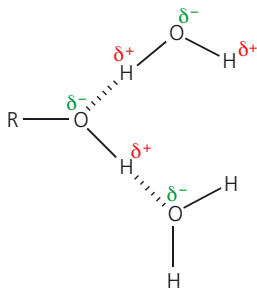


Figure 11.25 Hydrogen bonding between water and alcohol molecules.

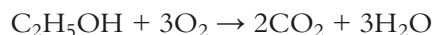
TEST YOURSELF

6 Explain why ethanol has a higher boiling point than methanol.

Reactions of alcohols

Combustion

Alcohols, like almost all organic chemicals, burn to form carbon dioxide and water. Ethanol burns with a clean flame:



Ethanol can be made by fermenting sugar or grain. Therefore, its use, when mixed with ordinary petrol, helps to reduce the carbon footprint of the fuel.

Halogenation (substitution by a halogen)

In a halogenation reaction, the $-\text{OH}$ group of an alcohol molecule is replaced by a halogen atom. The reactions below are the standard ways of preparing halogenoalkanes in the laboratory.

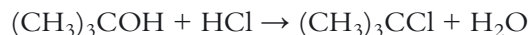
Chlorination

When solid phosphorus pentachloride is added to a dry alcohol, clouds of hydrogen chloride fumes are produced, mixed with the gaseous chloroalkane. Phosphorus oxychloride remains in the vessel.



Tertiary alcohols are much more easily converted into halogenoalkanes in a substitution reaction.

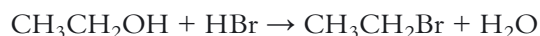
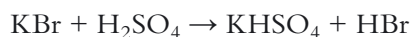
2-chloro-2-methylpropane can be prepared from 2-methylpropan-2-ol by heating it under reflux with concentrated hydrochloric acid.



The tertiary alcohol and an excess of concentrated hydrochloric acid are shaken together in a stoppered flask until a separate layer is formed on top of the acid. The mixture is transferred to a separating funnel and the lower aqueous layer discarded. The organic layer is washed with a solution of sodium hydrogen carbonate in order to remove any dissolved hydrochloric acid. The lower aqueous layer is discarded as before and the organic layer is dried with anhydrous sodium sulfate until the cloudy liquid goes clear. The product, a tertiary halogenoalkane, is poured into a distillation flask and distilled, collecting the liquid that boils off at the correct boiling point.

Bromination

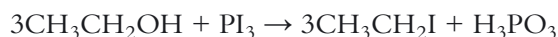
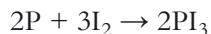
When an alcohol is heated under reflux with a mixture of potassium bromide and 50% sulfuric acid, hydrogen bromide is first produced, which then reacts with the alcohol to form a bromoalkane:



The acid used is only 50% concentrated to prevent the hydrogen bromide that is produced from being oxidised (by sulfuric acid) to bromine (page XXX).

Iodination

Warming a mixture of damp red phosphorus and iodine produces phosphorus triiodide, which then reacts with the alcohol to form the iodoalkane and phosphorus(III) acid.



The moisture is to bring the iodine and phosphorus, both of which are solids, into contact so that they can react.

Table 11.2 Halogenation of alcohols.

	Chlorination	Bromination	Iodination
Reagent	PCl_5 or conc. HCl	KBr and 50% H_2SO_4	I_2 and moist red phosphorus
Conditions	room temperature or heat under reflux	heat under reflux	warm
Product	A chloroethane	A bromoethane	An iodoethane
Reaction type	substitution	substitution	substitution

Oxidation

Primary and secondary alcohols are oxidised by a solution of potassium dichromate(VI) and dilute sulfuric acid. The **orange** potassium dichromate(VI) solution turns **green** because it is reduced to hydrated Cr^{3+} ions.

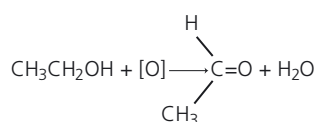
Tertiary alcohols are unaffected by this oxidising agent, which remains orange in colour.

TIP

[O] can always be used in the equations for oxidation reactions in organic chemistry.

Oxidation of a primary alcohol to an aldehyde

If a *primary* alcohol is heated with a mixture of potassium dichromate(VI) and sulfuric acid and the volatile product is allowed to escape, an aldehyde is produced. For example:



The aldehyde is not hydrogen bonded and so has a lower boiling temperature than the alcohol. Therefore it boils off from the hot reaction mixture. A suitable apparatus is shown in Figure 11.26.

Reagents: potassium dichromate(VI) and sulfuric acid

Conditions: add the oxidising agent to a mixture of excess hot ethanol and acid and distil off the aldehyde as it forms

Product: ethanal

Reaction type: oxidation

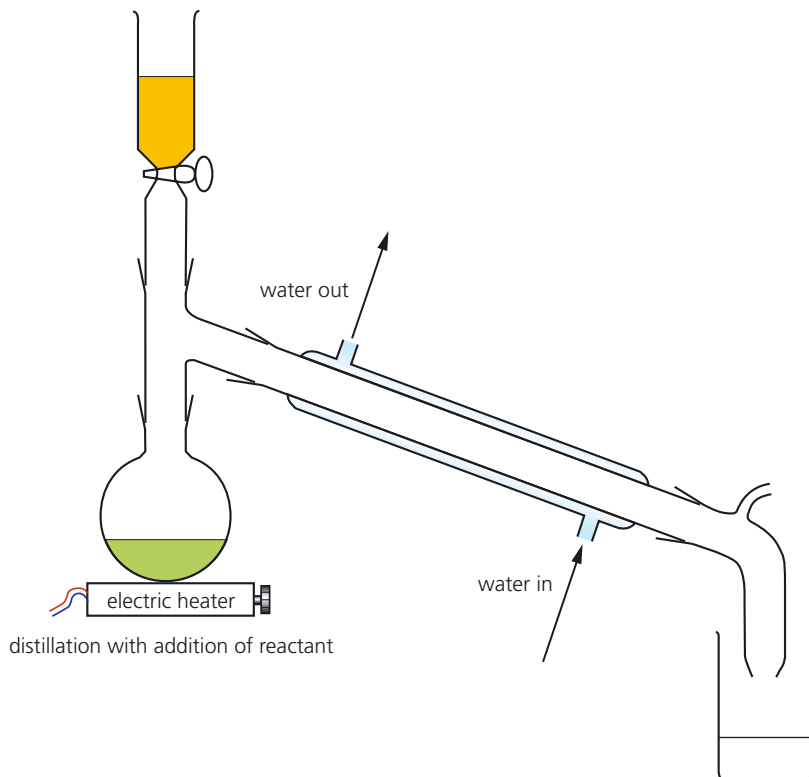
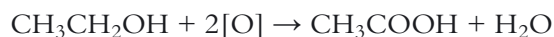


Figure 11.26 Apparatus for the oxidation of a primary alcohol to an aldehyde.

Oxidation of a primary alcohol to a carboxylic acid

If a primary alcohol is heated under reflux with the oxidising mixture, a carboxylic acid is formed. For example:



The acid can be distilled off after the reaction has gone to completion.

Reagents: excess potassium dichromate(vi) and sulfuric acid

Conditions: heat the mixture under reflux

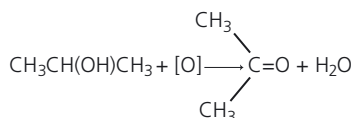
Product: ethanoic acid

Reaction type: oxidation

A suitable apparatus is shown in Figure 11.27. The orange potassium dichromate goes green as it is reduced to Cr^{3+} ions. After the reaction has finished the ethanoic acid is distilled off, using normal distillation apparatus.

Oxidation of a secondary alcohol to a ketone

If a secondary alcohol is heated under reflux with the oxidising mixture, a ketone is produced. For example:



Reagents: potassium dichromate(vi) and sulfuric acid

Conditions: heat the mixture under reflux

Product: propanone

Reaction type: oxidation

TIP

Make sure that you give the *full* name or formula when a reagent is asked for. Phrases such as 'acidified dichromate' will not score full marks.

A suitable apparatus is shown in Figure 11.27.

TIP

If you are asked to draw apparatus, make sure that:

- the apparatus is made up of specific pieces, such as the flask and the condenser, rather than one continuous piece of glassware
- the apparatus is open and not sealed (for heating under reflux, the apparatus is open at the top; for distillation, it is open at the receiving flask)
- you take care when drawing condensers; show the water going in at the bottom and out at the top.

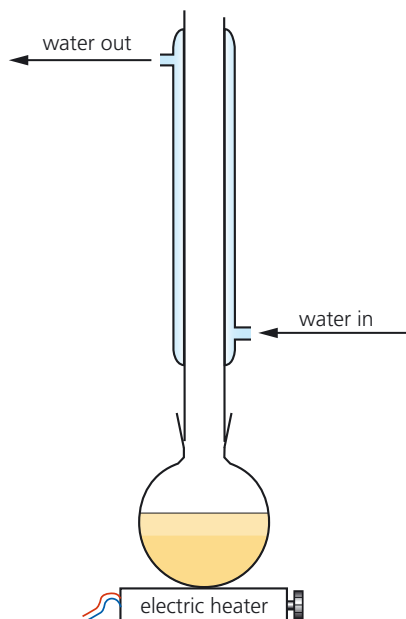


Figure 11.27 Reflux apparatus for the production of carboxylic acids and ketones.

Heating under reflux prevents volatile reactants from escaping the reaction mixture, so that a good conversion to product is achieved. After the reaction has finished, the reflux condenser is removed and the apparatus reassembled for ordinary distillation. Pure product is then obtained.

TEST YOURSELF

7 Identify the organic substance remaining when each of the following is heated under reflux with a solution of potassium dichromate(vi) in sulfuric acid.

- $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$
- $\text{C}_2\text{H}_5\text{C}(\text{OH})(\text{CH}_3)_2$
- $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$

Elimination

If a water molecule is eliminated from an alcohol, an alkene is formed. For example propan-2-ol forms propene:



There are two ways of carrying out this elimination:

- 1 pass the alcohol over heated aluminium oxide
- 2 mix the alcohol with phosphoric(v) acid and warm.

Cyclohexene can be prepared by mixing cyclohexanol with phosphoric(v) acid in a 2:1 ratio and heating gently. The cyclohexene distils off and can be collected after being condensed (see Figure 11.28).

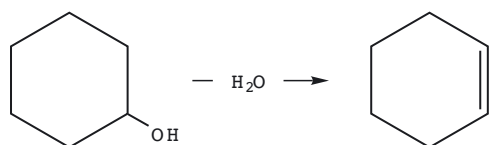
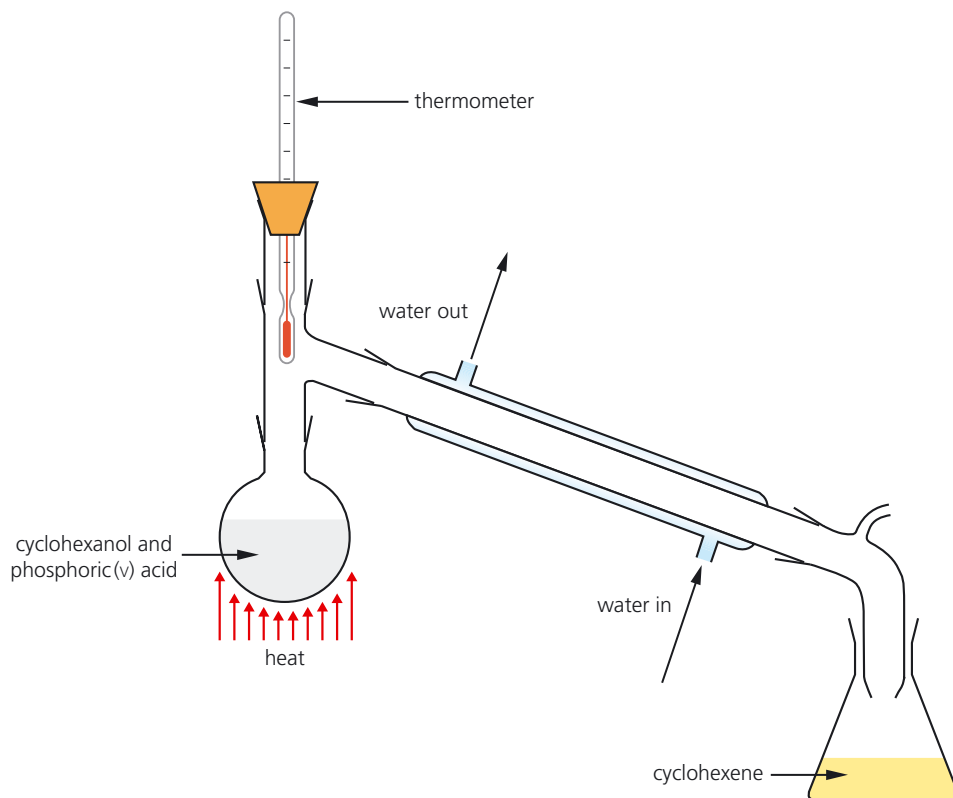


Figure 11.28 The laboratory preparation of cyclohexene.



The reaction mixture is gently heated and the vapour that comes off between 82 and 85 °C is condensed and collected. The cyclohexene has a lower boiling point than cyclohexanol as it is not hydrogen bonded. Thus it boils off leaving the less volatile alcohol behind.

Summary of reactions of alcohols

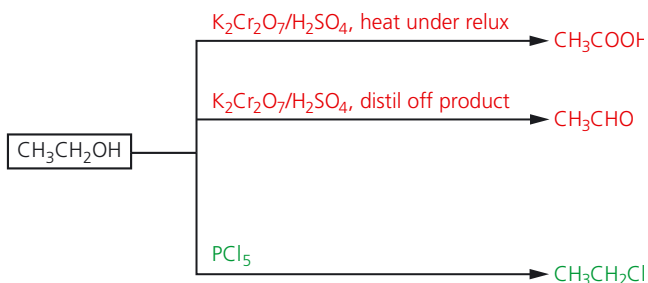


Figure 11.29 Summary of alcohol reactions.

The reactions in red are oxidation reactions.

The reaction in green is substitution (halogenation).

TIP

Do not say that *white fumes* or *white smoke* are produced. The steamy fumes of hydrogen chloride produce a white smoke (of ammonium chloride) when a glass rod dipped in concentrated ammonia is held in the fumes. A common error is to state that a positive result with this test means that the unknown is an alcohol. The correct answer for a positive PCl_5 test is that the unknown substance contains an $-\text{OH}$ group.

TIP

Both Fehling's and Benedict's are alkaline solutions containing blue complex copper(II) ions, the red precipitate is copper(I) oxide.

TIP

Do not forget to give the colour *before* as well as *after*.

Test for alcohols

Add phosphorus pentachloride to the *dry* substance under test. All alcohols will produce steamy fumes of hydrogen chloride. This is a test for an $-\text{OH}$ group, so the same result is obtained with carboxylic acids.

To distinguish between an acid and an alcohol, test the pH of the substance. Alcohols are neutral, whereas the pH of acids is less than 7.

Test to distinguish a primary alcohol from a secondary alcohol

- Warm with acidified potassium dichromate(VI).
- A primary alcohol will be oxidised to an aldehyde which then gives a red precipitate when warmed with blue Fehling's or Benedict's solution.
- Secondary alcohols give a ketone that does not react with Fehling's or Benedict's solution which will stay blue.

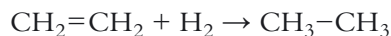
Test to distinguish a tertiary alcohol from primary and secondary alcohols

- Warm with acidified potassium dichromate(VI).
- Tertiary alcohols are not oxidised by a heated solution of potassium dichromate(VI) and sulfuric acid and so the solution stays orange.
- Primary and secondary alcohols reduce the dichromate(VI) ions and so turn the solution from orange to green.

Summary of types of reaction

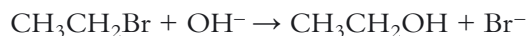
Addition

In an addition reaction two reactants form a single product. An example is the addition of hydrogen to an alkene:



Substitution

In a substitution reaction, one atom or group of atoms replaces another atom or group of atoms in a molecule. An example is the reaction between hydroxide ions and bromoethane:



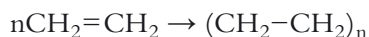
Elimination

In an elimination reaction, two atoms are removed from adjacent carbon atoms in a molecule of an organic substance. An example is the removal of a hydrogen and a chlorine atom from 2-chloropropane to form propene:



Polymerisation

Polymerisation occurs when thousands of monomer molecules join together to form a long polymeric chain. An example is the polymerisation of ethene to poly(ethene):



Oxidation

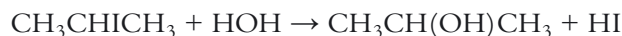
In organic chemistry, oxidation is best defined as the addition of oxygen or the removal of hydrogen.

Secondary alcohols are oxidised to ketones. Two hydrogen atoms are removed from the alcohol. Therefore, it is oxidised:



Hydrolysis

Hydrolysis occurs when water, often with a catalyst of acid or alkali, splits an organic molecule into two parts. The $-\text{OH}$ group joins one part and the hydrogen atom joins the other part. An example is the hydrolysis of 2-iodopropane:



Summary of type of reagent

Free radical

A **free radical** is formed when a bond breaks homolytically, with one electron going to each atom in the bond. When chlorine is exposed to ultraviolet light, the $\text{Cl}-\text{Cl}$ bond breaks homolytically and two chlorine radicals are produced. A fishhook arrow in Figure 11.30 shows the movement of each electron.

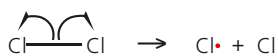


Figure 11.30

Nucleophile

Nucleophiles can be:

- negative ions – for example, OH^- , I^- and CN^-
- neutral molecules containing oxygen or nitrogen atoms, for example, water and ammonia.

Nucleophiles attack δ^+ centres in molecules.

Electrophile

The **electrophile** forms a covalent bond with a pair of electrons from the electron-rich site. Electrophiles can be:

- positive ions, for example, H^+
- δ^+ atoms in molecules, for example, the δ^+ hydrogen atom in HBr
- neutral molecules that can be polarised, for example, $\text{Br}-\text{Br}$.

TIP

A bond in a molecule breaks heterolytically when it is attacked by a nucleophile. Heterolytic fission of a bond results in both bonding electrons going to the same atom. For example, when the OH^- nucleophile attacks chloroethane, both electrons in the $\text{C}-\text{Cl}$ bond go to the chlorine, forming a Cl^- ion.

TIP

The oxidation agent is usually written as $[\text{O}]$ in oxidation equations.

Key terms

A **free radical** is an atom or group of atoms with an unpaired electron that it uses to form a covalent bond.

A **nucleophile** is a species with a lone pair of electrons that it uses to form a covalent bond.

An **electrophile** is a species that attacks places of high electron density, for example, the $\text{C}=\text{C}$ group in alkenes.

Understanding organic reactions

Organic reactions can be learnt or they can be understood. The first thing to do is to look at the molecule and ask yourself some questions:

- Is it polar with a δ^+ site? If so, it is likely to be attacked by nucleophiles. A halogenoalkane has a δ^+ carbon joined to the halogen and so undergoes substitution reactions with nucleophiles, resulting in the loss of a halide anion. As ions are formed during this type of reaction, it is usually carried out under aqueous conditions.
- Does it have an electron-rich site such as a non-polar π -bond? If so, it is likely to be attacked by an electrophile and the π -electrons will form a new bond with the electrophile. Alkenes are attacked by electrophiles.
- Is the molecule non-polar, without a site of high electron density? If so, it will react with free radicals. Light or peroxides are usually needed to produce the free radicals, so a non-aqueous solvent (or gaseous-phase reaction) and ultraviolet light will probably be necessary. Alkanes react in this way.
- Which bond will break in an organic molecule? Rarely will a C–H or a C–C σ bond break. C=C, O–H or C–OH are more likely to be broken.

Quantitative organic chemistry

Key terms

The **empirical formula** of a substance is the simplest whole number ratio of the atoms of each element in the substance.

The **displayed formula** of an atom shows every atom and every bond.

Formulae

For example, the molecular formula of ethanoic acid is $C_2H_4O_2$ and that of glucose is $C_6H_{12}O_6$.

The molecular formula of a compound shows the number of atoms of each element in one molecule of the substance.

For example, the **empirical formula** for both ethanoic acid and glucose is CH_2O .

For example, the structural formula of glucose is shown in Figure 11.31.

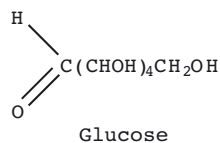


Figure 11.31

The structural formula is an unambiguous structure that shows how the atoms in the molecule are arranged.

For example, the **displayed formula** of glucose is shown in Figure 11.32.

The *displayed* or *full* structural formula of a compound shows every atom and every bond.

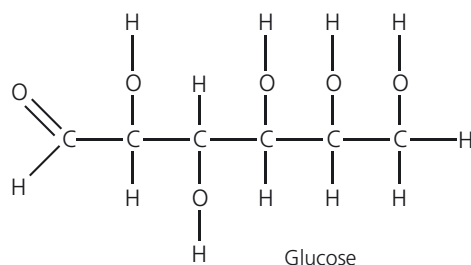


Figure 11.32

Glucose also exists as a six-membered ring compound, as shown in Figure 11.33.

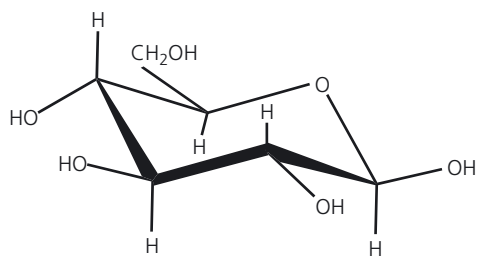


Figure 11.33

Empirical formula

This can be worked out from the percentage by mass of each element in the compound. The calculation is done in three stages.

Step 1: divide each percentage by the relative atomic mass of the element to give the number of moles of each element in 100 g of the compound.

Step 2: these values, which are the relative number of moles of each element, are then divided by the smallest value. Give the results to one decimal place.

Step 3: if the numbers are not whole numbers, multiply by 2 to see if that converts them into integers. If not, try multiplying by 3 and so on, until all the values are whole numbers.

The integers obtained in the final step are the simplest ratio of the numbers of each element present in the compound. The empirical formulae can now be written.

TIP

The calculation is best done in the form of a table.

EXAMPLE 1

A compound contains 62.1% carbon, 10.3% hydrogen and 27.6% oxygen by mass. Calculate its empirical formula.

Answer

Element	%	Divide by RAM	Divide by the smallest	Ratio
carbon	62.1	$62.1/12 = 5.175$	$5.175/1.725 = 3$	3
hydrogen	10.3	$10.3/1 = 10.3$	$10.3/1.725 = 5.97 \rightarrow 6$	6
oxygen	27.6	$27.6/16 = 1.725$	$1.725/1.725 = 1$	1

The empirical formula is C_3H_6O .

A second method for calculating empirical formulae involves the use of combustion analysis.

EXAMPLE 2

When 1.00 g of a compound containing carbon, hydrogen and oxygen only was burnt in excess air, 1.74 g of carbon dioxide and 0.947 g of water were formed. Calculate its empirical formula.

Answer

Moles of $\text{CO}_2 = 1.74/44 = 0.0395 = \text{moles of C}$

Mass of carbon = $0.0395 \times 12 = 0.475 \text{ g}$

Moles of $\text{H}_2\text{O} = 0.947/18 = 0.526$

Moles of H = $2 \times 0.526 = 0.105 = \text{mass of hydrogen}$

Mass of oxygen = $1.00 - (0.475 + 0.105) = 0.42 \text{ g}$

Moles of O = $0.42/16 = 0.02625$

To get ratio by moles divide by the smallest moles (oxygen)

Carbon = $0.0395/0.02625 = 1.5$ Hydrogen = $0.105/0.02625 = 4$ Oxygen = 1

Simplest whole number ratio is 3 C to 8 H to 2 O, so empirical formula is $\text{C}_3\text{H}_8\text{O}_2$.

Molecular formula

If the molar mass is known, the molecular formula can be calculated from the empirical formula. This is done in three stages.

Step 1: calculate the empirical mass.

Step 2: divide the molar mass by the empirical mass. The answer is a whole number.

Step 3: multiply the number of atoms of each element by the integer obtained in Step 2 to give the actual numbers of atoms of each element in the molecule.

TIP

Make sure that you show your working when calculating the molecular formula from the empirical formula.

EXAMPLE 3

A substance X has the empirical formula, CH. The molar mass of X is 78 g mol^{-1} . Calculate the molecular formula.

Answer

Step 1: empirical mass = $12 + 1 = 13$

Step 2: $\frac{\text{molar mass}}{\text{empirical mass}} = \frac{78}{13} = 6$

Step 3: molecular formula = C_6H_6

Reaction yield

Theoretical yield

The **theoretical yield** is calculated in three steps:

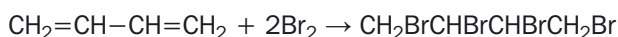
Step 1: calculate the amount of reactant in moles.

Step 2: use the reaction stoichiometry to calculate the amount of product in moles.

Step 3: Convert moles of product to mass of product.

EXAMPLE 4

Calculate the theoretical yield when 1.23 g of buta-1,3-diene reacts with excess bromine according to the equation:



Answer

Step 1: molar mass of buta-1,3-diene = 54 g mol^{-1}

$$\text{amount of buta-1,3-diene} = \frac{1.23 \text{ g}}{54 \text{ g mol}^{-1}} = 0.0228 \text{ mol}$$

Step 2: ratio of product to reactant = 1:1

The bromine is in excess, so the ratio of product to buta-1,3-diene is 1:1

amount of product = 0.0228 mol

$$\begin{aligned} \text{Step 3: molar mass of product} &= 54 + (4 \times 80) \\ &= 374 \text{ g mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{theoretical yield} &= \text{amount of product (moles)} \times \text{molar mass} \\ &= 0.0228 \text{ mol} \times 374 \text{ g mol}^{-1} \\ &= 8.53 \text{ g} \end{aligned}$$

Key term

The **theoretical yield** is the mass of product that would be formed if the reaction went to 100% completion, with no side reactions.

Percentage yield

The actual yield is the measured mass of the product obtained in the experiment and is usually given in the question. The theoretical yield has to be calculated from the equation and the mass of reactant.

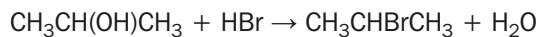
Key term

The **percentage yield** is defined as:

$$\% \text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

EXAMPLE 5

When 3.21 g of propan-2-ol was heated under reflux with 50% sulfuric acid and potassium bromide, 4.92 g of 2-bromopropane was produced. Calculate the percentage yield.



Answer

$$\begin{aligned}\text{amount of propan-2-ol} &= \frac{3.21 \text{ g}}{60 \text{ g mol}^{-1}} \\ &= 0.0535 \text{ mol}\end{aligned}$$

$$\text{ratio of product to reactant} = 1:1$$

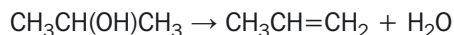
$$\text{amount of 2-bromopropane} = 0.0535 \text{ mol}$$

$$\begin{aligned}\text{theoretical yield} &= 0.0535 \times 123 \text{ g mol}^{-1} \\ &= 6.58 \text{ g}\end{aligned}$$

$$\begin{aligned}\% \text{ yield} &= \frac{4.92 \text{ g} \times 100}{6.58 \text{ g}} \\ &= 74.8\%\end{aligned}$$

EXAMPLE 6

The dehydration of a secondary alcohol, such as propan-2-ol, should result in a 75% yield. Calculate the volume of propene gas, $\text{CH}_3\text{CH}=\text{CH}_2$, that should be obtained when 2.46 g of propan-2-ol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$, is dehydrated.



(Under the conditions of the experiment, the molar volume of a gas = $24 \text{ dm}^3 \text{ mol}^{-1}$.)

Answer

$$\text{amount of propan-2-ol} = \frac{2.46 \text{ g}}{60 \text{ g mol}^{-1}} = 0.0410 \text{ mol}$$

$$\text{ratio of propene to propan-2-ol} = 1:1$$

$$\text{theoretical yield of propene} = 0.0410 \text{ mol}$$

$$= 0.041 \text{ mol} \times 24 \text{ dm}^3 \text{ mol}^{-1} = 0.984 \text{ dm}^3$$

$$\text{actual yield} = 75\% \text{ of theoretical yield}$$

$$= 0.984 \text{ dm}^3 \times \frac{75}{100}$$

$$= 0.74 \text{ dm}^3 = 740 \text{ cm}^3$$

If a reaction takes place in two steps, each with a 60% yield, the percentage yield for the overall reaction is:

$$60\% \text{ of } 60\% = \frac{60}{100} \times \frac{60}{100} = 36\%$$

Summary tasks

Can you

- draw skeletal formulae for alcohols and halogenoalkanes
- give examples of alcohols and halogenoalkanes that are primary, secondary or tertiary
- explain why ethanol is soluble in water whereas chloroethane is not?

Check that you can write equations for the reactions of alcohols such as propan-1-ol with

- oxygen (combustion)
- oxidising agents such as acidified potassium dichromate(VI)
- phosphorus(V) chloride
- phosphorus(III) iodide
- concentrated sulfuric acid.

Do you know

- the test for alcohols and for halogenoalkanes
- the laboratory preparation of halogenoalkanes?

Make sure that you can write equations for the reactions of halogenoalkanes such as 2-bromopropane with

- dilute aqueous OH^- ions
- water in the presence of Ag^+ ions
- concentrated OH^- ions dissolved in ethanol
- excess ammonia.

Can you draw, using curly arrows, $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ mechanisms and know which is correct for a given halogenoalkane?

Copy the diagram below and make sure that you know the correct reagents and any necessary conditions.

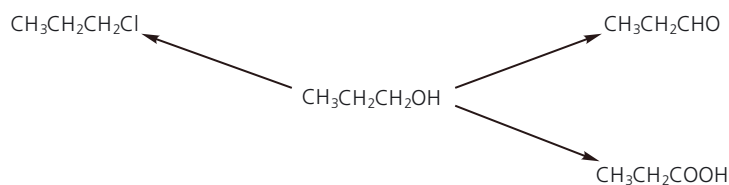


Figure 11.34

Copy the diagram below and make sure that you know the correct reagents and any necessary conditions.

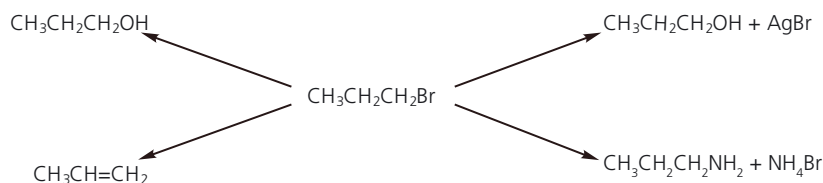
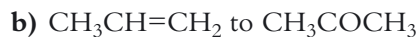
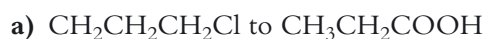


Figure 11.35

Questions

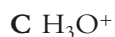
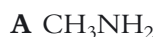
- Which of the following is the most polar molecule and which is the least polar?
 - chloromethane, bromomethane or iodomethane
 - fluoromethane or methanol
- Explain why fluoromethane is insoluble in water, whereas methanol is totally soluble.
- Give an example of a halogenated polymer. State one use of this polymer and one environmental problem related to its disposal.
- You are given three unlabelled samples of organic liquids. You know that one is hexene, one is hexanol and the other is hexanoic acid. Describe how you would identify each substance.
- Describe the mechanism of the reaction between 2-bromobutane and aqueous hydroxide ions.
- Suggest the mechanism for the reaction between 2-chloropropane and cyanide ions ($\text{C}\equiv\text{N}^-$) in aqueous solution.
- Explain why it is necessary to have some ethanol present for the reaction between dilute aqueous sodium hydroxide and 2-iodopentane.
- A chloroalkane contains 37.2% carbon and 55.0% chlorine by mass. Calculate its empirical formula.
- A carboxylic acid contains 50% carbon, 5.6% hydrogen and 44.4% oxygen by mass. It turns brown bromine water colourless.
 - Calculate the empirical formula of the acid.
 - Suggest the simplest structural formula for this acid.
- A compound X contains 53.3% carbon, 11.1% hydrogen and 35.6% oxygen by mass.
 - Calculate the empirical formula of X.
 - The molar mass of X is 90 g mol^{-1} . Deduce the molecular formula of X.
 - When excess phosphorus pentachloride was added, 9.0 g of dry X gave off 4.8 dm^3 of hydrogen chloride gas. Suggest one structural formula for X, giving your reasons. (Under the conditions of the experiment, 1 mol of gas occupies 24 dm^3 .)
- 5.67 g of ethanol was added to a hot solution of potassium dichromate(VI) and sulfuric acid. The ethanal produced was distilled off and 4.88 g of pure ethanal was obtained. Calculate the percentage yield.
- 2-iodopropane can be made from 1-chloropropane by the two stage synthesis:
$$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} \rightarrow \text{CH}_3\text{CH}=\text{CH}_2 \rightarrow \text{CH}_3\text{CHICH}_3$$
If stage 1 has a 30% yield and stage 2 has a 90% yield, calculate the mass of 2-iodopropane made from 78.5 g of 1-chloropropane.

13 Outline a synthetic route in not more than three steps to convert the following. For each step give the reagent and the conditions.



Exam practice questions

1 a) Which is **not** a nucleophile?



b) i) Which describes the reaction between 2-chloropropane and aqueous sodium hydroxide?

A free radical substitution

B nucleophilic substitution

C electrophilic addition

D oxidation

ii) Identify the product in (b)(i).

c) Which describes the reaction between bromine and methane?

A free radical substitution

B nucleophilic substitution

C electrophilic addition

D oxidation

d) Which describes the reaction between ethanol and excess acidified potassium dichromate(vi)?

A free radical substitution

B nucleophilic substitution

C electrophilic addition

D oxidation

e) i) Which describes the reaction between hydrogen bromide and propene?

A free-radical substitution

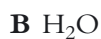
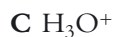
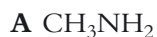
B nucleophilic substitution

C electrophilic addition

D oxidation

ii) Identify the major product in (e)(i).

2 a) Which is **not** a nucleophile?



b) i) Which describes the reaction between 2-chloropropane and aqueous sodium hydroxide?

A free radical substitution

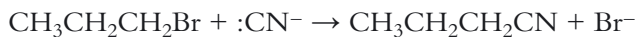
B nucleophilic substitution

C electrophilic addition

D oxidation (1)

ii) Identify the product in (b)(i). (1)

c) Cyanide ions react with 1-bromopropane in a nucleophilic substitution reaction.



i) Draw a mechanism for this reaction. (3)

ii) Explain why the reaction between cyanide ions and 1-iodopropane is faster. (2)

iii) Explain why the reaction of a nucleophile such as cyanide ions with 2-methyl-2-bromopropane goes via a different mechanism. (2)

3 a) You are given three unlabelled bottles containing halogenoalkanes with different halogens. Describe a test that you would do to find which was a bromoalkane. (2)

b) Name the organic product of the reaction of 2-bromopropane with

i) excess ammonia (1)

ii) a concentrated solution of potassium hydroxide in ethanol. (1)

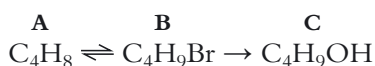
c) 2-bromo-2-methylpropane can be prepared from 2-methylpropan-2-ol.

i) Name the reagents and the conditions. (2)

ii) In the preparation the halogenoalkane boils off leaving behind any unreacted alcohol. Explain why this is so. (2)

d) Write skeletal formulae of the three branched chain primary alcohols of formula $\text{C}_5\text{H}_{11}\text{OH}$. (3)

4 Consider the following series of reactions and then answer the questions that follow:



a) i) Compound A is an alkene that has two geometric isomers. Draw their structural formulae. (2)

ii) State the two features of the molecule that makes this isomerism possible. (2)

iii) Stating what you would see, give a simple chemical test for the functional group present in compound A. (2)

iv) What type of reaction is the conversion of compound A to compound B?

A free radical substitution

B nucleophilic substitution

C electrophilic addition

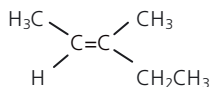
D oxidation (1)

v) Draw the mechanism for the reaction of compound A with hydrogen bromide. In your mechanism, the alkene (A) can be

represented simply as:



- vi)** What type of reaction is the conversion of compound B to compound A? (1)
- b) i)** The reaction of compound B to give compound C is a nucleophilic substitution. What is meant by the term nucleophile? (1)
- ii)** Give the full structural formula of compound C. (1)
- iii)** Give a simple chemical test for the functional group in compound C. Describe what you would see as a result of this test. (2)
- iv)** Give the full structural formula for the compound obtained by heating compound C with acidified potassium dichromate solution. (2)
- c)** The alkene 3-methylpent-2-ene has two geometric isomers. Giving your reasons, state whether the isomer shown below is the *E*-isomer or the *Z*-isomer. (2)



- 5 a)** Draw the mechanism for the substitution reaction of 2-methyl-2-bromopropane with ammonia. You should include all relevant lone pairs of electrons. (4)
- b)** Suggest the skeletal formula of the product of reacting iodoethane with the primary amine $C_2H_5NH_2$. (2)
- c)** Explain why water at room temperature and not hot aqueous sodium hydroxide is used for the hydrolysis of a tertiary halogenoalkane. (2)
- d)** Explain why the major product of the reaction of gaseous hydrogen bromide with propene is 2-bromopropane and not 1-bromopropane. (3)
- 6 a)** Methanol is manufactured by the reversible reaction between hydrogen and carbon monoxide over a suitable catalyst at a moderate temperature.



Explain why

- i)** a high temperature is not used
- ii)** a high pressure is used
- iii)** a catalyst is used. (6)
- b)** Explain why methanol is very soluble in water. (2)
- c)** Write structural formulae, showing any double bonds, of the organic products of the reactions of methanol with
- i)** excess acidified potassium dichromate(vi) when heated under reflux

- ii)** damp red phosphorus and iodine. (2)
- d)** Which describes the reaction between ethanol and excess acidified potassium dichromate(vi)?
- A** free radical substitution
 - B** nucleophilic substitution
 - C** electrophilic addition
 - D** oxidation (1)
- e)** Which of the following alcohols does not produce a green solution when warmed with acidified potassium dichromate(vi)?
- A** ethanol
 - B** butan-2-ol
 - C** 2-methylbutan-2-ol
 - D** hexan-3-ol (1)

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