# **Organic chemistry**

## Topic 1 Introduction to organic chemistry

#### Nomenclature

A **functional group** is a group of atoms that are responsible for the characteristic reactions of a molecule.

A **molecular formula** shows the actual number of atoms of each element in a compound.

An **empirical formula** is the simplest whole number ratio of each element in a compound.

A **general formula** is an algebraic formula that can describe any member of a homologous series, e.g. alkenes:  $C_nH_{2n}$ .

A **displayed formula** shows how all the atoms are arranged and *all* the bonds between them.

A **structural formula** shows the arrangement of atoms in a molecule, carbon by carbon, with the attached hydrogens and functional groups *without* showing the bonds.

A **skeletal formula** shows the carbon skeleton with hydrogen atoms removed and functional groups present. Each carbon–carbon bond is shown as a line.

A **homologous series** is a family of organic compounds that possess the same general formula.

You must be able to use IUPAC rules to name organic compounds — either rings or chains with up to six carbon atoms.

1 Name the following organic compounds. (AO2)

18 marks

Compound	Name	Compound	Name
a H H H H H I I I I I	olena a chendic	CI H CI	ion platin si yeW od sector sector
H—C—C—C—C—C—H 		H—C—C—C—H 	
	A & Insure s	<b>d</b> H CH <sub>3</sub> H	and tacquist.
H H H 		H—C—C—C—H	
н сі н		н н н	
e H Cl CH <sub>3</sub> H H	with the water	f H CH <sub>3</sub> CI H H	
H—C—C—C—C—C—H H CH <sub>3</sub> CH <sub>3</sub> H H	Elises Londs	H—C—C—C—C—H	4
н сн³ сн³ н н		н сн <sub>3</sub> ст с₂н₅ н	

Compound	Name	Compound	Name
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	—н	h H OH H       H—C—C—C—H	polomod arb mana
		Н Н Н ж ж ж	poleman arb. it
i H—C—C—C— H—H—H		j H H O H H H C C C C C C H H H H H H	polomoit sitt is
k H H H H H C C C C C C C C O O O O	н	H H H H H H H	molecule q2
m H <sub>3</sub> C C=C H		п Н Н Н Н 	Skelarelom
• H H H H H H H H H H H H H H H H H H H	nig rolflwood exiftee stra east (Accid on Alsgry, that is live direction and a peacal grow and a	P	Maliarons amel/ (Paris and Paris and
$\begin{array}{c} \mathbf{q} \\ \text{CH}_3 \\ \text{H}_3 \text{C} - \begin{array}{c} \text{C} + \\ \text{C} + \\ \text{CH}_3 \end{array} \end{array}$	The proof of the first of the f	r HC=C-C=C H H	ucedolorism ucedolorism artisti sentim front rosta in use munifo s

Questions 2-4 refer to the compounds shown in the table above.

2 Write skeletal formula for these compounds. (AO2)

5 marks

- a compound a
- b compound b
- c compound k
- d compound l
- e compound m

W	rite the general formula of: (AO2)
a	the homologous series to which h belongs
Ь	the homologous series to which a belongs
c	the homologous series to which r belongs
W	hat is the molecular and empirical formula of: (AO2)
mo	olecule q?
mo	olecule k?
Na	ame the following compounds and the homologous series to which they belong. (AO2) 12 mark
	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>
	Name
	Homologous series
Ь	CH <sub>2</sub> =CHCH <sub>2</sub> CH <sub>3</sub>
	Name And a selection of the component of the selection of
	Homologous series
c	СН³СН³СН³СООН
	Name
	Homologous series
d	HOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>
	Name

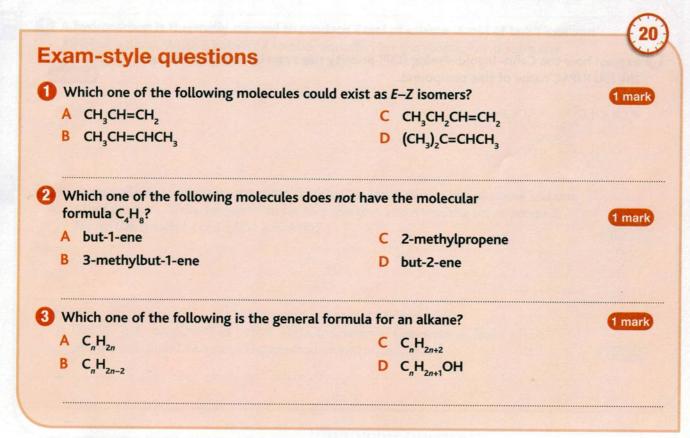
e	CH <sub>3</sub> COCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> Name	
	Name	
	Homologous series	
f	(CH <sub>3</sub> ) <sub>2</sub> CHOH Name	
	Name	
	Homologous series	ACHO EL TROM EL TROM EL TROM EL ACHO EL TROM E

#### Isomerism

Structural isomers are compounds with the same molecular formula but different structural formulae. There are three types. Chain isomers occur when there is more than one way of arranging the carbon chain of a molecule — they have similar chemical properties but slightly different physical properties. The more branched the isomer the weaker the van der Waals forces between the molecules and the lower the boiling point. Position isomers have the same carbon chain but the functional group is bonded to different carbons. Functional group isomers have the same molecular formula but different functional groups.

**Stereoisomers** have the same structural and molecular formulae but a different arrangement of atoms in three-dimensional (3D) space. There are two types of stereoisomers: *E–Z* isomers and optical isomers (studied in year 2).

There is an energy barrier to free rotation about a *planar* carbon–carbon double bond and it is this restricted rotation which leads to *E–Z* isomerism in some alkenes. For a compound to have *E–Z* isomers, it must contain a carbon–carbon double bond and each carbon in the double bond must be attached to two different atoms or groups.



Which one of the following is the correct IUPAC name for the structure shown below?



- A 2-methylpent-1-ene
- B 2-propylprop-1-ene

- C 2,4-dimethylbut-1-ene
- D 2-methylhexene
- 6 Cinnamyl alcohol has a smell similar to hyacinths. It has the following structure, which contains a number of functional groups.

a What are the two functional groups present in cinnamyl alcohol?

2 marks

b Draw the structures of the E and Z isomers.

2 marks

c Explain why cinnamyl alcohol has E–Z isomers.

1 mark

d What are structural isomers?

1 mark

6 Explain how the Cahn-Ingold-Prelog (CIP) priority rules can be used to deduce the full IUPAC name of this compound.

6 marks

# Topic 3 Halogenoalkanes

### Nucleophilic substitution and elimination

The carbon–halogen bond in halogenoalkanes is polar and the  $\delta$ + carbon can be attacked by nucleophiles, such as OH<sup>-</sup>, CN<sup>-</sup> and NH<sub>3</sub>. A **nucleophile** is a lone-pair donor. A general mechanism for nucleophilic substitution is shown below. X is the halogen and Nu is the nucleophile.

A **hydrolysis** reaction is a reaction in which C–X bonds are broken by water molecules. It is often catalysed by an acid or base. The ease of hydrolysis of halogenoalkanes increases down group 7, with the weakest bonds of lowest bond enthalpy hydrolysed most quickly — i.e. those in iodo compounds.

$$R \longrightarrow C \xrightarrow{\delta^{+}} \mathbf{X}^{\delta^{-}} \longrightarrow R \longrightarrow C \longrightarrow Nu + \mathbf{X}^{-}$$

$$Nu:= A \longrightarrow A$$

Reagent	Conditions and equation	Mechanism	Product
Sodium hydroxide	Halogenoalkane is dissolved in a little ethanol, heated under reflux with <i>aqueous</i> sodium hydroxide e.g. CH <sub>3</sub> CH <sub>2</sub> Br + NaOH → CH <sub>3</sub> CH <sub>2</sub> OH + NaBr	Nucleophilic substitution (primary halogenoalkanes favour substitution)	Alcohol
Potassium cyanide	Halogenoalkane dissolved in ethanol, heated under reflux with aqueous solution of KCN or NaCN e.g. CH <sub>3</sub> CH <sub>2</sub> Br + CN <sup>-</sup> → CH <sub>3</sub> CH <sub>2</sub> CN + Br	Nucleophilic substitution	Nitrile
Concentrated ammonia	Halogenoalkane dissolved in ethanol, heated with excess concentrated ammonia solution in a sealed tube e.g. CH <sub>3</sub> CH <sub>2</sub> Cl + 2NH <sub>3</sub> → CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub> + NH <sub>4</sub> Cl	Nucleophilic substitution	Amine
Sodium hydroxide	Halogenoalkane dissolved in ethanol, hot ethanolic potassium (or sodium) hydroxide solution e.g. $CH_3CH_2CH_2Br + KOH \rightarrow C_3H_6 + KBr + H_2O$	Elimination (tertiary halogenoalkanes favour elimination)	Alkene

Reflux (repeated boiling and condensing a liquid) is used to prepare an organic liquid. The liquid is distilled off and purified by shaking with solvent in a separating funnel followed by a second distillation.

An **elimination reaction** is one in which a small molecule such as a hydrogen halide is removed from a larger molecule. The mechanism is:

$$R \longrightarrow C \longrightarrow Br \longrightarrow H \longrightarrow H \longrightarrow H \longrightarrow H$$

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# Ozone depletion

Ozone  $(O_3)$  is formed naturally in the upper atmosphere:  $O_2 \rightarrow 2O^{\bullet}$  and  $O_2 + O^{\bullet} \rightarrow O_3$ . It is beneficial because it absorbs ultraviolet (UV) radiation, which can cause sunburn, skin cancer and ageing of the skin.

Chlorofluorocarbons (CFCs) cause 'holes' in the ozone layer because their carbon-chlorine bonds are broken down by UV light to produce chlorine radicals:

$$CCl_3F \rightarrow CCl_2F^{\bullet} + Cl^{\bullet}$$

These chlorine radicals react with ozone molecules:

$$Cl^{\bullet} + O_3 \rightarrow O_2 + ClO^{\bullet}$$
 and  $ClO^{\bullet} + O_3 \rightarrow 2O_2 + Cl^{\bullet}$ 

The chlorine radical is not destroyed, so it acts as a catalyst in the decomposition of ozone.

CFCs were used as solvents and refrigerants as they were unreactive, non-flammable and non-toxic. Alternative chlorine-free compounds, such as trifluoromethane, cannot produce chlorine radicals and are now used instead of CFCs and cause less harm to the ozone layer.

- 1717	hich one of the following is removed from bromoethane when it is reacted with nanolic sodium hydroxide? (AO2)	1 ma
A	Br <sub>2</sub> multipos sucesups rithin anstrudomendal fig neitheas and not not not upon a sithin	
В	H <sub>2</sub> O (FOA) Jauborg and and amale abinorby	
C	HBr	
D	NaBr	
W	hich one of the following cannot act as a nucleophile? (AO2)	1 ma
A	CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	
В	CH <sub>4</sub>	
C	CN-	
D	H <sub>2</sub> O	
	Which one of the halogenoakalkanes 1-chlorobutane, 1-bromobutane and 1-iodobutane reacts most readily with aqueous sodium hydroxide? Explain your answer. (AO2)	mar
	Romobutane is made from butan 1-si as follows:	
Shrui	tassium bromide is dissolved in warm water and the mixture cooled. Concentrated sail	
D	Write the equation for the reaction of 1-bromobutane with ethanolic sodium	

	a	Name and outline the mechanism for the reaction of 1-bromobutane with ethanolic sodium hydroxide. (AO1 AO2)	4 m
		Name:	O-bris.
en Yan Olymia			
ille d			
8,075			
ne e			
	Ь	Explain why 1-bromo-2-methylbutane is an isomer of 1-bromobutane. (AO1)	067 S 1 m
	C	2-bromo-2-methylpentane is heated with potassium hydroxide dissolved in ethanol. Name the two isomers that could be formed. (AO2)	2 m:
	d	Write an equation for the reaction of 1-bromobutane with aqueous sodium hydroxide. Name the organic product. (AO1)	2 ma
	е	Name and outline the mechanism of the reaction of 1-bromobutane with aqueous sodium hydroxide. (AO1/AO2)  Name:	4 ma
		Name.	
SIAN.			
Sales Sa			
	f	Explain why the carbon-halogen bond in halogenoalkanes is polar. (AO2)	2 ma
6	1-1	Bromobutane is made from butan-1-ol as follows:	
		tassium bromide is dissolved in warm water and the mixture cooled. Concentrate	
		d is added slowly with constant stirring. Butan-1-ol is added and the mixture hea flux for 2 hours. The mixture is then distilled until no more oil drops of bromobut	

a 	Why is the concentrated sulfuric acid added slowly with stirring? (AO3)	1 mark
ь ь	During preparation brown fumes are seen. Suggest what they are and how they are formed. (AO3)	2 marks
c	What is meant by the phrase heated under reflux? (AO1)	1 mark
d	What is the purpose of washing the bromobutane with aqueous sodium hydrogencarbonate? (AO3)	1 mark
e	Describe in detail how you would practically wash the bromobutane with the aqueous sodium hydrogencarbonate. (AO1)	3 marks
126 19	Strate entra day stad?  Bew Shimond day stad?  Bew Shimond day stad?  Bew Shimond day stade.	,183 C POH(0)
f	Why was the anhydrous magnesium sulfate added? (AO3)	1 mark

### Topic 4 Alkenes

### Structure, bonding and reactivity

Alkenes are **unsaturated hydrocarbons** with the general formula  $C_nH_{2n}$ . They contain a double C=C covalent bond, which is a centre of high electron

density, making it open to attack by **electrophiles** (electron-pair acceptors).

#### Addition reactions of alkenes

They undergo **addition reactions** in which the double covalent bond is broken and two species add across the double bond to produce one product.

Reaction	Example	Conditions
Addition of HBr	alkene + hydrogen bromide $\rightarrow$ bromoalkane $CH_2=CH_2+HBr \rightarrow CH_3CH_2Br$	Bubble in HBr gas at room temperature.
Addition of H <sub>2</sub> SO <sub>4</sub>	alkene + $H_2SO_4 \rightarrow$ alkyl hydrogensulfate $CH_2=CH_2 + H_2SO_4 \rightarrow CH_3CH_2OSO_3H$	Concentrated sulfuric acid at room temperature
Addition of Br <sub>2</sub>	alkene + bromine $\rightarrow$ dibromoalkane $CH_2=CH_2+Br_2\rightarrow CH_2BrCH_2Br$ This is a test for unsaturation — orange bromine water turns colourless.	Shake with bromine water at room temperature.

The mechanism for all addition reactions is electrophilic addition. The intermediate formed is called a **carbocation** (a positive ion where the positive charge is on a carbon atom).

An unsymmetrical alkene is one in which the groups or atoms attached to either end of the C=C are different, e.g.

propene and but-1-ene. When unsymmetrical alkenes undergo addition reactions, the major product is formed via the most stable carbocation intermediate. The order of stability of carbocations is tertiary > secondary > primary. To work out the major product, remember that the hydrogen becomes attached to the carbon that has the most hydrogen atoms attached.

$$H_3C$$
 $CH_3$ 
 $CH_3$ 

### Addition polymers

An **addition polymer** is a long-chain molecule formed by the repeated addition reaction of many alkene monomers. Polymers no longer have a double bond and as a result they are unreactive. A **monomer** is a small molecule that combines with other monomers to make a polymer. The polymers are named based on the alkene from which they are formed — for example, ethene forms poly(ethene).

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The letter n on both sides of the equation represents a large number of ethene molecules that have to add to each other.

poly(ethene) polymer

H

H

ethene (monomer)

H

Poly(chloroethene) is commonly called PVC. Plasticisers are chemical substances used to make polymers like PVC softer and more flexible.

	repeating unit	Compound	Unplasticised PVC (uPVC)	Plasticised PVC
H	H	Property	Hard, rigid, inflexible	Softer and flexible
 <u> </u>	- C	Use	Window and door frames	Electrical wire insulation, clothing, Wellington boots

VV	hich one of the following hydrocarbons contains a double bond? (AO2)	1 mark
A	C <sub>2</sub> H <sub>6</sub>	
В	C <sub>5</sub> H <sub>12</sub> of the state of the s	
C	C <sub>6</sub> H <sub>12</sub>	
D	$C_7H_{16}$	
	hich one of the following is the name of the mechanism for the reaction between lorine and ethene? (AO1)	1 mark
A	electrophilic addition	
В	electrophilic substitution	
C	nucleophilic addition	
D	nucleophilic substitution	
Bu	t-1-ene and butane are hydrocarbons, each belonging to a different homologous se	eries.
Bu	t-1-ene and butane are hydrocarbons, each belonging to a different homologous so Draw the displayed and the skeletal formula of but-1-ene and butane. (AO2)	THE BUILDING
		eries. 4 marks

	WE Established to a constant of the second s	
	ii Name and draw a mechanism for this reaction. (AO2)	4 mar
	Name:	
e	In the reaction of but-1-ene with hydrogen bromide a major and minor product can be produced. Identify the major and minor product. (AO2)	2 mar
	(SOA) Starod adupt a saleshed such Milenius (Marine Marine)	
f	But-2-ene can be polymerised. Name the polymer and draw the repeating unit in the polymer produced. (AO2/1)	2 mari
	Name:	

#### **Exam-style questions**



- 1 A hydrocarbon contains 84.7% carbon by mass and has an M<sub>r</sub> greater than 50 but less than 60. Which one of the following statements is correct?
  - A The empirical formula is C<sub>2</sub>H<sub>4</sub>.
  - B The empirical formula is C<sub>2</sub>H<sub>5</sub>.
  - C The molecular formula is C<sub>4</sub>H<sub>8</sub>.
  - D The molecular formula is C<sub>4</sub>H<sub>10</sub>.
- 2 Which statement is true about the reaction between hydrogen bromide and ethene?



- A The product is unsaturated.
- B The transition state is neutral.
- C The product can exist as two different structural isomers.
- D The hydrogen bromide splits into two ions.

0			
•	To determine the ease of hydrolysis of chloroalkanes, bromoalkanes and iodoalkanes the following experiment was carried out.		
	Equal amounts of each halogenoalkane were placed in separate test tubes in a water bath at 50°C.		
	A test tube containing a mixture of ethanol and aqueous silver nitrate was heated in the same water bath.		
	When all test tubes reached the same temperature equal volumes of the ethanol and aqueous silver nitrate mixture were added to each halogenoalkane and the clock started.  The time taken for a precipitate to form in each test tube was recorded.		
	a State the meaning of the term hydrolysis.		
	b What steps were taken to ensure that this practical was a fair test? 2 mar		
	c In this experiment three different precipitates form. Name each precipitate and state its colour.  3 mart		
	d Explain why precipitates form in this experiment. Include an ionic equation in your answer.  5 mark		
	e State and explain which of the chloroalkane, bromoalkane or iodoalkane formed a precipitate first.  2 mark		
	f Why is ethanol added in this experiment?		
4	CF <sub>2</sub> Cl <sub>2</sub> is a CFC. A carbon-chlorine bond in CF <sub>2</sub> Cl <sub>2</sub> breaks in the upper atmosphere and forms a reactive species.		
	a Give the IUPAC name for CF <sub>2</sub> Cl <sub>2</sub> .		
	b What condition causes the carbon-chlorine bond to break?		

c Write an equation for the formation of the reactive species. 1 mark d One of the reactive species acts as a catalyst in the decomposition of ozone. Write two equations to show how this species acts as a catalyst. 2 marks 5 Propenenitrile (CH,=CHCN) can be prepared in the laboratory from chloroethene and sodium cyanide. 1 mark a Write an equation for the reaction. b Write the molecular and empirical formula of propenenitrile. 2 marks c Propenenitrile (CH<sub>2</sub>=CHCN) can be polymerised to make Orlon, a fibre used for making clothes. 1 mark i Draw the structure of Orlon showing two repeating units. 1 mark ii Why is propenenitrile able to polymerise?

+ -× =

### **Topic 5 Alcohols**

### Alcohol production

Alcohols contain the hydroxyl functional group –OH. The general formula of alcohols is  $C_nH_{2n+1}OH$ .

In industry ethanol is produced by fermentation, in which yeast converts sugars such as glucose into ethanol and carbon dioxide at a temperature of 35°C and in the absence of air:

 $C_6H_{12}O_6(aq) \rightarrow 2CH_3CH_2OH(aq) + 2CO_2(g)$ 

The ethanol is separated by fractional distillation and can then be used as biofuel. A **biofuel** is a fuel that is made from renewable plant material.

A **carbon-neutral** activity is one that has no net annual emissions of carbon dioxide to the atmosphere. Theoretically, as shown in the table below, bioethanol can be considered a carbon-neutral fuel.

Carbon dioxide removed from the atmosphere	Carbon dioxide released to the atmosphere
In photosynthesis $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$	In fermentation 2 molecules of $CO_2$ released $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$
e transportate à sellente de la com- leure le recepte de <b>debudratione. Al</b> overtament des europes d <b>estricte</b> de	In combustion 4 molecules of $CO_2$ released $2C_2H_5OH + 6O_2 \rightarrow 4CO_2 + 6H_2O$ (2 molecules of ethanol burnt to use all the ethanol produced in fermentation)
Total: 6 molecules of CO <sub>2</sub> removed	Total: 6 molecules of CO <sub>2</sub> released

Bioethanol is not totally carbon-neutral because the machinery planting, harvesting and transporting the sugar crop and the production of fertilisers for the crop are powered by burning fossil fuels, which releases carbon dioxide.

A major advantage of bioethanol is that the crops are a *renewable* resource. Disadvantages include that our food supply may be depleted, as increasingly land is being used to grow crops for fuel and the production of crops is subject to the weather and climate.

Very pure alcohol is produced in industry by hydration of alkenes using steam, a catalyst of concentrated

phosphoric acid on a silica surface at 60 atm and 600 K. **Hydration** is the addition of water to a molecule:

$$CH_2 = CH_2 + H_2O(g) \Leftrightarrow C_2H_5OH.$$

Excess ethene is used to give a high yield and unreacted ethene and steam are recycled back over the catalyst.

The mechanism for the formation of ethanol by the reaction of steam in the presence of a phosphoric acid  $(H_3PO_4)$  catalyst is electrophilic addition.

- 1 Alcoholic drinks contain ethanol formed by fermentation.
  - a Write an equation for the reaction which occurs during fermentation. (AO1)

1 mark



#### Oxidation of alcohols

A **primary alcohol** has one alkyl group bonded to the carbon atom that is bonded to the OH group. (The exception to this is methanol, which is classed as primary.) They are oxidised to aldehydes:

$$C_2H_5OH + [O] \rightarrow CH_3CHO + H_2O$$

and then to carboxylic acids:

$$C_2H_5OH + 2[O] \rightarrow CH_3COOH + H_2O$$

To obtain the aldehyde, heat with oxidising agent in distillation apparatus — this removes the aldehyde from

the oxidising mixture immediately. To obtain the acid, use excess oxidising agent and heat under reflux.

A **secondary alcohol** has two alkyl groups bonded to the carbon that is bonded to the OH group and oxidises to form a ketone when heated with the oxidising agent (acidified potassium dichromate(vi)) under reflux.

$$CH_3CH(OH)CH_3 + [O] \rightarrow CH_3COCH_3 + H_2O$$

A **tertiary alcohol** has three alkyl groups bonded to the carbon that is bonded to the OH group and cannot be oxidised.

#### Elimination

Alkenes can be produced from alcohols by acidcatalysed elimination reactions at 170°C and using a concentrated sulfuric acid catalyst. A molecule of water is removed (**dehydration**). Alkenes produced by this method can be used to produce addition polymers without using monomers derived from

$$C_3H_7OH \rightarrow C_3H_6 + H_2O$$

The mechanism is:

- 2 Butan-2-ol, propan-1-ol and 2-methylbutan-2-ol are alcohols.
  - a Classify each of these alcohols as primary, secondary or tertiary.

3 marks

butan-2-ol

propan-1-ol

2-methylbutan-2-ol

b State the colour change, if any, and the name of the product when each of these alcohols is warmed with acidified potassium dichromate(vi) solution.

butan-2-ol

propan-1-ol

2-methylbutan-2-ol

3 marks

# =

Write a balanced symbol equation for the dehydration of butan-2-ol.

1 mark