

40th INTERNATIONAL CHEMISTRY OLYMPIAD 2008

UK Round One

STUDENT QUESTION BOOKLET

* * * * *

- The time allowed is 2 hours.
- Attempt all 6 questions.
- Write your answers in the special answer booklet.
- In your calculations, please write only the essential steps in the answer booklet.
- Always give the appropriate units and number of significant figures.
- You are provided with a copy of the Periodic Table.
- Do *NOT* write anything in the right hand margin of the answer booklet.

Some of the questions will contain material you will not be familiar with. However, by logically applying the skills you have learnt as a chemist, you should be able to work through the problems. There are different ways to approach the tasks – even if you cannot complete certain parts of a question, you may still find subsequent parts straightforward.

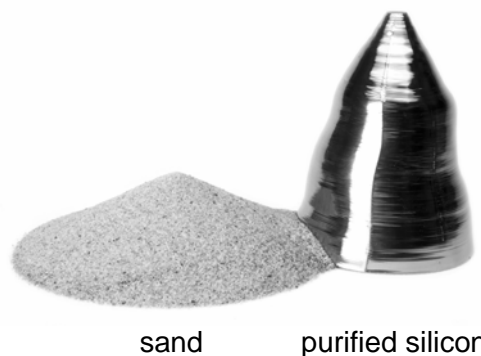
H 1 1.008																	He 2 4.003
Li 3 6.94	Be 4 9.01	<div>symbol atomic number mean atomic mass</div>										B 5 10.81	C 6 12.01	N 7 14.01	O 8 16.00	F 9 19.00	Ne 10 20.18
Na 11 22.99	Mg 12 24.31											Al 13 26.98	Si 14 28.09	P 15 30.97	S 16 32.06	Cl 17 35.45	Ar 18 39.95
K 19 39.102	Ca 20 40.08	Sc 21 44.96	Ti 22 47.90	V 23 50.94	Cr 24 52.00	Mn 25 54.94	Fe 26 55.85	Co 27 58.93	Ni 28 58.71	Cu 29 63.55	Zn 30 65.37	Ga 31 69.72	Ge 32 72.59	As 33 74.92	Se 34 78.96	Br 35 79.904	Kr 36 83.80
Rb 37 85.47	Sr 38 87.62	Y 39 88.91	Zr 40 91.22	Nb 41 92.91	Mo 42 95.94	Tc 43	Ru 44 101.07	Rh 45 102.91	Pd 46 106.4	Ag 47 107.87	Cd 48 112.40	In 49 114.82	Sn 50 118.69	Sb 51 121.75	Te 52 127.60	I 53 126.90	Xe 54 131.30
Cs 55 132.91	Ba 56 137.34	La* 57 138.91	Hf 72 178.49	Ta 73 180.95	W 74 183.85	Re 75 186.2	Os 76 190.2	Ir 77 192.2	Pt 78 195.09	Au 79 196.97	Hg 80 200.59	Tl 81 204.37	Pb 82 207.2	Bi 83 208.98	Po 84	At 85	Rn 86
Fr 87	Ra 88	Ac⁺ 89															

*Lanthanides	Ce 58 140.12	Pr 59 140.91	Nd 60 144.24	Pm 61	Sm 62 150.4	Eu 63 151.96	Gd 64 157.25	Tb 65 158.93	Dy 66 162.50	Ho 67 164.93	Er 68 167.26	Tm 69 168.93	Yb 70 173.04	Lu 71 174.97
+Actinides	Th 90 232.01	Pa 91	U 92 238.03	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103

1. This question is about the preparation of pure silicon for solar cells

Thousands of tonnes of silicon are produced each year to be used in solar cells. First, metallurgical grade silicon, MGS, is made by reducing quartz (SiO_2 , the major component of sand) with carbon in the form of coke and charcoal.

The MGS produced is typically between 98.5 and 99.5 % pure – nowhere near pure enough for the electronics industry. Typical impurities include metals such as iron and aluminium.



(a) Write an equation for the reaction between quartz and carbon to form silicon.

High purity silicon can be made from silane (SiH_4) and its derivatives. In one such scheme, silicon is first reacted with HCl at 300°C to form trichlorosilane and hydrogen. The trichlorosilane is then reduced in a hydrogen environment to form pure silicon.

(b) i) What is the bond angle in silane?

ii) Write the equation for the reduction of trichlorosilane with hydrogen.

This method is rather energy intensive – a more environmentally friendly method has recently been developed which requires a tenth of the energy. In this method ethanol reacts with silicon to form triethoxysilane and hydrogen. Upon heating, the triethoxysilane forms silane gas and tetraethoxysilane in a disproportionation reaction. The silane gas can be decomposed at high temperatures to give pure silicon.

(c) i) Write the equation for the disproportionation of triethoxysilane.

ii) Air must be excluded from the process to avoid the spontaneous ignition of the silane gas. Suggest an equation for this reaction.

An earlier method used to purify the silicon was *zone refining*. In this technique, a bar of impure silicon is melted at one end and then the melt zone is gradually moved along the bar, allowing the silicon to re-solidify behind this zone. Since the impurities are more soluble in the liquid silicon rather than the solid, as the silicon re-solidifies, the impurities become more concentrated in the moving melt zone and hence end up in the last region that re-solidifies.

During zone refining, the concentration, C_x , of a given impurity at position x in the re-solidified bar is given by:

$$C_x = kC_0(1-x)^{k-1}$$

where C_0 is the initial concentration of impurity (usually expressed in number of atoms of impurity per million atoms); x is distance along the bar from the start, expressed as a fraction between 0 and 1; k is a constant known as the *distribution coefficient* whose value depends on the particular impurity. For aluminium, $k = 2.00 \times 10^{-3}$; for iron, $k = 8.00 \times 10^{-6}$.

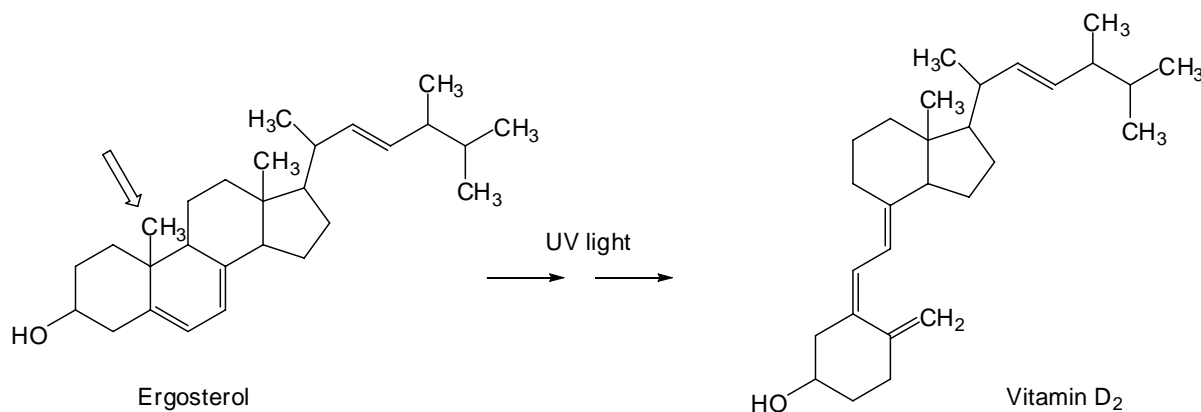
(d) i) If the initial concentration of aluminium impurity is 3300 ppm atoms, calculate the maximum local concentration of aluminium remaining (in ppm) after one melting, assuming the last 5% of the silicon bar is discarded.

ii) Assuming the only impurity present is iron at 1300 ppm atoms, calculate the minimum percentage of the silicon that would need to be discarded in order to reach the level desirable for photocells, <10 ppm.

2. This question is about the kinetics of Vitamin D production in mushrooms

Vitamin D is essential for healthy bone structure. Mushrooms are a rich source of ergosterol, a precursor of vitamin D₂. Cultivated mushrooms grown in the dark have little vitamin D₂, but when exposed to UV light, ergosterol is converted into vitamin D₂.

In a kinetics experiment, different mushroom varieties were irradiated with UV light for varying periods of time and then analysed for their concentrations of ergosterol and vitamin D₂.



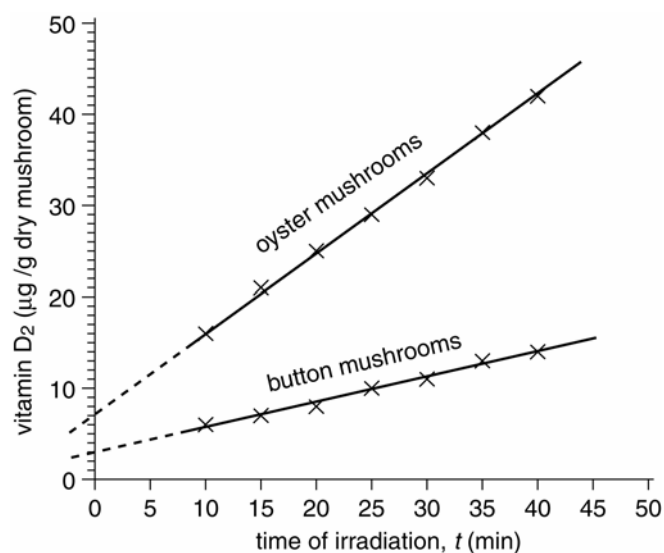
- (a) Circle all the chiral centres on the structure of ergosterol in your answer booklet.
- (b) During the reaction, one of the hydrogens from the methyl group marked with an arrow on the structure of ergosterol above is transferred to a different carbon in the product. On the structure of vitamin D₂ in your answer booklet, circle the carbon atom to which the hydrogen is transferred.

The kinetics of production of vitamin D₂ from ergosterol were expected to be of the form:

$$\text{rate of production of vitamin D}_2 = k \times [\text{ergosterol}]^a$$

where k is the rate constant for the particular mushroom;
[ergosterol] is the concentration of the reactant ergosterol;
 a is the order of reaction with respect to the concentration of ergosterol.

The concentrations of vitamin D₂ in oyster mushrooms and button mushrooms after irradiating the mushrooms for different periods of time are shown over the page. Both graphs are linear.



- (c) By examining the graphs, what is the value of a , the observed order of reaction with respect to [ergosterol]?

minus one zero one two three

(Circle the correct answer in your answer booklet.)

- (d) From the graph, determine the rate constant for the production of vitamin D_2 from oyster mushrooms. Include the correct units in your answer.
- (e) Estimate the amount of vitamin D_2 in 10 g of dried button mushrooms that have been irradiated for 1 hour.

The rate constant for the production of vitamin D_2 is found to vary with temperature according to the Arrhenius equation:

$$k_{(T)} = A \times e^{(-E_a/RT)}$$

where $k_{(T)}$ is the rate constant at temperature T ;

A is a constant;

E_a is the activation energy for the reaction;

T is the temperature in K;

R is the gas constant = $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$.

- (f) Given that the rate constant for the production of vitamin D_2 from shiitake mushrooms at 35°C is *twice* that at 25°C , calculate the activation energy for the reaction.

3. This question is about mercury fulminate

Mercury(II) fulminate, $\text{HgC}_2\text{N}_2\text{O}_2$, has been known as a super-sensitive explosive for 300 years, but – being so difficult to handle – its crystal structure was only determined in 2007. To avoid setting off an explosion, the compound had to be synthesised in the dark in a process that the researchers describe as “quite tricky”.

On detonation mercury(II) fulminate decomposes forming three products: two of these are gases, two are elements.



- (a) Write the equation for the detonation of mercury(II) fulminate.
- (b) Calculate, using an energy cycle or otherwise, the standard enthalpy change of reaction for this detonation using the following standard enthalpies of formation, $\Delta_f H^\ominus$.

[Note that not all of the data are required.]

compound	$\text{HgC}_2\text{N}_2\text{O}_2$	HgO	CO	CO_2	NO	NO_2
$\Delta_f H^\ominus / \text{kJ mol}^{-1}$	+386	–91	–111	–394	+90	+33

Mercury(II) fulminate can be described as *organometallic*, meaning that it has a metal-carbon bond. The fulminate ion is a triatomic ion with a charge of minus one. The infrared spectra of fulminates include a bond stretch in the triple-bond region.

- (c) Suggest a structure for mercury(II) fulminate, showing the number and type of bonds between the atoms.

Mercury(II) cyanate is an isomer of mercury(II) fulminate. In fact cyanates and fulminates were the first known examples of isomers in chemistry. Mercury(II) cyanate is not organometallic but its infrared spectrum does contain a bond stretch in the triple-bond region.

- (d) Suggest the structure of mercury(II) cyanate, showing the number and type of bonds between the atoms.

Protonation of cyanates yields cyanic acid, which isomerises to form isocyanic acid, HNCO . This then spontaneously trimerises to form cyanuric acid, $(\text{HNCO})_3$. There are two different structures for cyanuric acid which both exist in equilibrium. In both structures the three atoms for any given element occupy symmetrically equivalent positions; one structure appears to be aromatic.

- (e) Showing all bonds, draw the two possible structures for cyanuric acid.

4. This question is about aluminium chemistry and rat poison

Aluminium metal reacts with various non-metals to form simple, binary compounds. The reaction with phosphorus forms aluminium phosphide, AIP. This compound has been used as a rodenticide.

The type of bonding in aluminium compounds depends on which element it is bonded to. For example, aluminium oxide is predominantly ionic, whereas aluminium chloride (empirical formula AlCl_3) shows characteristics of covalent bonding.



- (a) How many electrons are around each Al atom in a covalently bonded AlCl_3 molecule?

In the vapour phase at 150-200 °C, aluminium chloride exists as a molecule, **A**, which has an M_r of 266.66.

- (b) i) What is the molecular formula of **A**?
- ii) Suggest a structure for **A**.
- iii) How many electrons are around each Al atom in your structure of **A**?

Aluminium phosphide is hydrolysed by water to generate the highly toxic gas phosphine, PH_3 . Phosphine is similar in structure to ammonia, and like NH_3 , PH_3 can act as a ligand using its lone pair.

- (c) Write an equation for the hydrolysis of AIP.

There has been interest in various compounds containing Al-P covalent bonds as precursors for AIP. When equal moles of $t\text{Bu}_2\text{AlH}$ and Ph_3SiPH_2 are dissolved in solvent at 25°C, hydrogen gas is evolved and a white crystalline solid **B** is produced ($t\text{Bu} = (\text{CH}_3)_2\text{CHCH}_2^-$; $\text{Ph} = \text{C}_6\text{H}_5^-$).

- (d) How many electrons are around Al in the covalently bonded $t\text{Bu}_2\text{AlH}$?

The mass spectrum of **B** gives a peak with highest m/z value at 864.

- (e) i) Using your answer to (b) as a guide, suggest a structure for compound **B**.
- ii) Compound **B** shows isomerism. Draw structures to indicate the three-dimensional shape of two geometric isomers of **B**.

When warmed, **B** is converted to **C** with the evolution of methylpropane. The ^{31}P -NMR spectrum of **C** showed it to have a single environment for phosphorus, and ^{13}C -NMR showed equal numbers of $t\text{Bu}$ - and Ph_3Si - groups. Further analysis showed the compound to have four Al and four P atoms in the molecule.

- (f) Suggest a structure for compound **C**.

When **C** is heated to temperatures above 150°C, it starts to decompose, yielding Ph_3SiH and a gas **D**. By 500°C, all that remains is aluminium phosphide.

- (g) Identify the gas **D**.

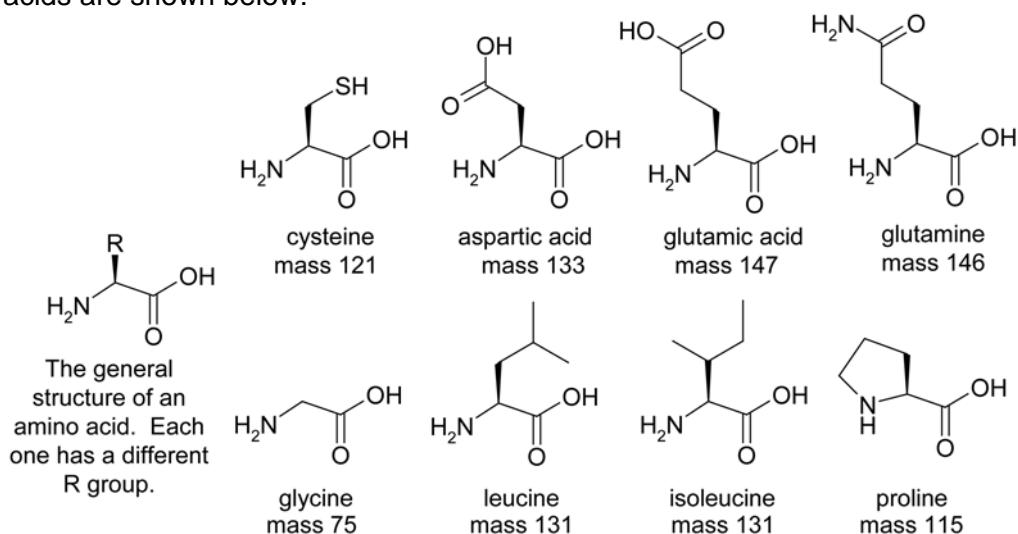
5. This question is about toxins from cone snails

Cone snails are predators that use venom to capture prey. The toxic species in the venom are polypeptides. Cone snail toxins are of pharmaceutical interest as starting points for the development of new anaesthetics. A number of research groups are working towards identifying the amino acid sequences of new cone snail toxins.

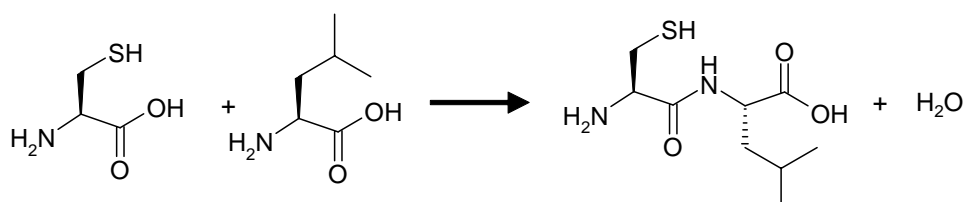


The cone snail *Conus textile*

Polypeptides are polymers of amino acids; the structures and relative masses of some amino acids are shown below:

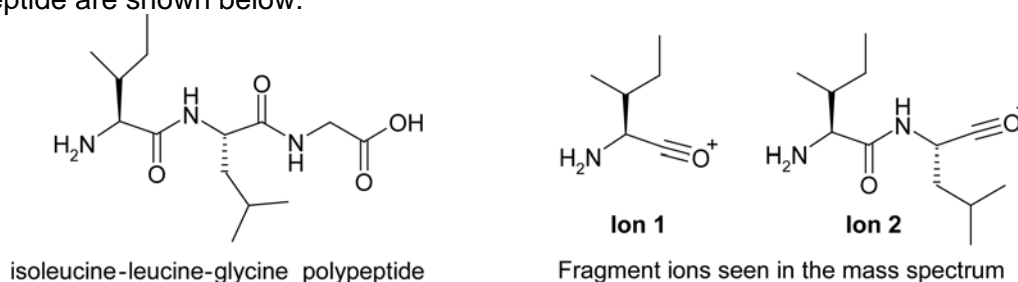


When amino acids form a polypeptide, an amide bond is made and water is lost:



In biological systems the function of a polypeptide depends on the order of the amino acids in the sequence. By convention, a polypeptide is drawn starting with the amine group on the left, hence the sequence of the polypeptide shown above is cysteine-leucine NOT leucine-cysteine.

Polypeptides are often sequenced using mass spectrometry. In a mass spectrometer the polypeptide breaks into fragments with the amide bonds being the most likely to be broken. By comparing the masses of the different ions formed it is possible to work out the amino acid sequence. The major ions seen in the fragmentation of an isoleucine-leucine-glycine polypeptide are shown below:



In all parts of this question you should use the mass of the most common isotopes of each of the elements: 12 for C, 14 for N, 16 for O and 1 for H.

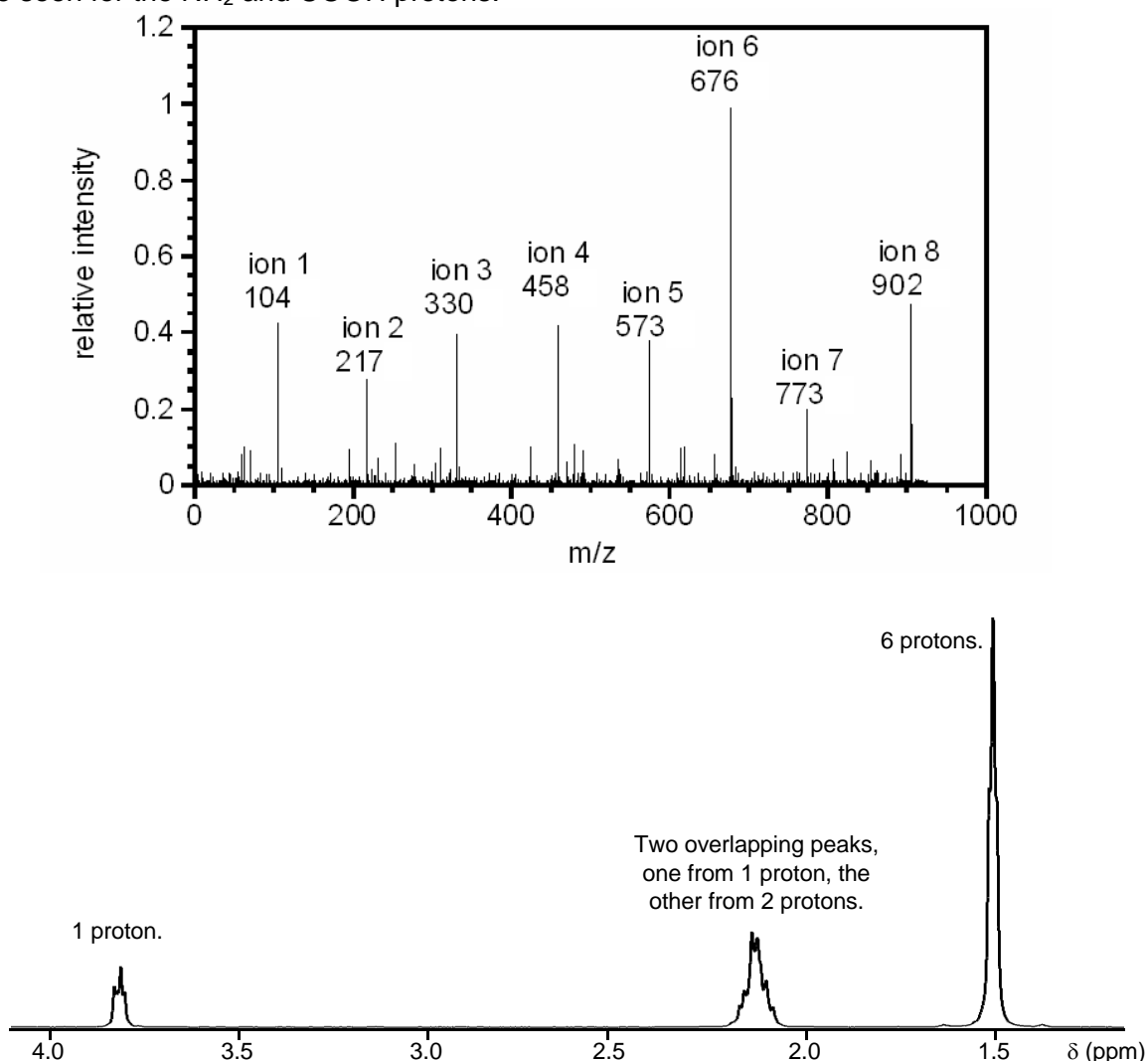
- (a) i) What is the mass of the isoleucine-leucine-glycine polypeptide?
 ii) What is the mass of **ion 1**?
 iii) What is the mass of **ion 2**?

A polypeptide, **X**, of mass 976 was isolated from a cone snail. It was found by chemical analysis to have the following amino acid composition:

2 x cysteine, 1 x aspartic acid, 1 x glutamic acid, 1 x glutamine, 1 x glycine, 1 x isoleucine, 1 x leucine and 1 x proline.

- (b) How many unique polypeptide sequences can be formed using all these amino acids?

The fragmentation mass spectrum of **X** and the ^1H NMR spectrum of the third amino acid in the sequence are shown below. Under the conditions used for the NMR spectrum no peaks are seen for the NH_2 and COOH protons.



- (c) The last two amino acids in the sequence are glutamic acid-glycine. What is the sequence of the first 7 amino acids? [The structures and masses of the amino acids are shown at the top of the previous page.]

6. This question is about the synthesis of Fexofenadine.

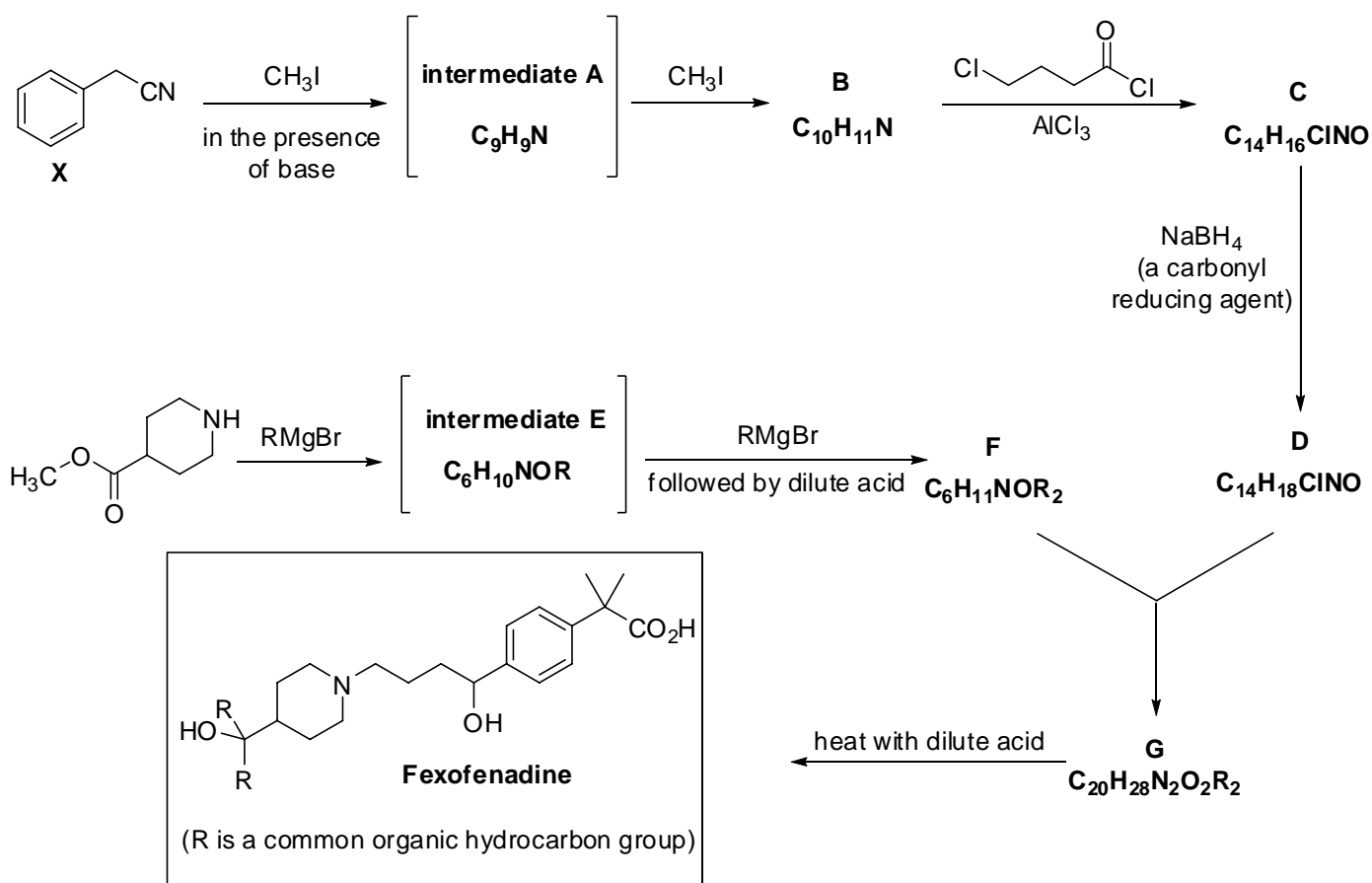
Antihistamines are taken to reduce the effects of allergic reactions in the body. The drug fexofenadine is used to treat sneezing, runny nose and itchy eyes experienced by hay fever sufferers, without causing drowsiness.



Fexofenadine, structure shown below, is sold as the hydrochloride salt with each tablet containing 112 mg of fexofenadine as 120 mg of the salt with HCl.

- (a) **i)** On the structure in your answer booklet, circle the atom which will be protonated in the salt.
- ii)** Given that 112.00 mg of fexofenadine is actually contained in 120.14 mg of the salt, calculate the relative molecular mass of fexofenadine.
- iii)** Given your answer to part (ii), suggest what common organic group R is in the structure of fexofenadine below.

A synthesis of Fexofenadine is shown below.



- (b) Draw out the structure of starting material **X** and indicate which hydrogen atoms are removed by the base in the first step of the synthesis.
- (c) Draw the structures of compounds / intermediates **A** to **G**.

Acknowledgements & References

References for questions

- Q1. "Purification of metallurgical grade silicon by a solar process" G. Flamant *et al.*
Solar Energy Materials & Solar Cells, 2006, p2099-2106
and
"Historical overview of silicon crystal pulling development" Werner Zulehner
Materials Science and Engineering, B73, 2000, p7-15
- Q2. "Kinetics of the conversion of ergosterol in edible mushrooms" Viraj J. Jasinghe *et al.*
Journal of Food Engineering, 2007, Vol 79 p864-869.
- Q3. "The Crystal and Molecular Structure of Mercury Fulminate" W. Beck *et al.*
Zeitschrift für anorganische und allgemeine Chemie, 2007, Vol 633 p1417-1422.
- Q4. "New Aluminum Phosphide Precursor" Alan H. Cowley *et al.*
Angewandte Chemie International Edition, 1990, Vol 29 p1409-1410.
- Q5. "A vasopressin/oxytocin-related conopeptide with g-carboxyglutamate at position 8"
Carolina Möller and Frank Marí
Biochemical Journal, 2007, Vol 404 p413-419.
- Q6. "A new synthesis of carboxyterfenadine (fexofenadine) and its bioisosteric tetrazole
analogs", B. Di Giacomo *et al.*
Il Farmaco, 1999, Vol 54 p600-610.

The Chemistry Olympiad Committee would like to thank the following people / organisations for their help and advice in the preparation of this paper.

David Paul and Bruce Livett at the University of Melbourne for the picture of the cone snail.

Anthony Lim, a second year Natural Sciences student at the University of Cambridge, for the cartoon used in question 4.

The photography department of the University of Cambridge, Department of Chemistry for the photographs used in questions 1, 2, and 6.

The UK Chemistry Olympiad is supported by **INEOS**

INEOS is a leading global manufacturer of petrochemicals, specialty chemicals and oil products. It comprises 19 businesses each with a major chemical company heritage. The production network spans 73 manufacturing facilities in 19 countries throughout the world. The chemicals INEOS produce enhance almost every aspect of modern life.