Cambridge Chemistry Challenge Lower 6th

June 2016

Some of the material in this booklet might be familiar to you, but other parts may be completely new. The questions are designed to be more challenging than those on typical AS papers, but you should still be able to attempt them. Use your scientific skills to work through the problems logically.

If you do become stuck on one part of a question, other parts might still be accessible, so do not give up. Good luck!

- The time allowed is 90 mins.
- Attempt all the questions.
- Write your answers in the answer booklet provided, giving only the essential steps in any calculations.
- Specify your answers to the appropriate number of significant figures and give the correct units.
- Please do not write in the right-hand margin.
- A periodic table and necessary constants are included on the next page.

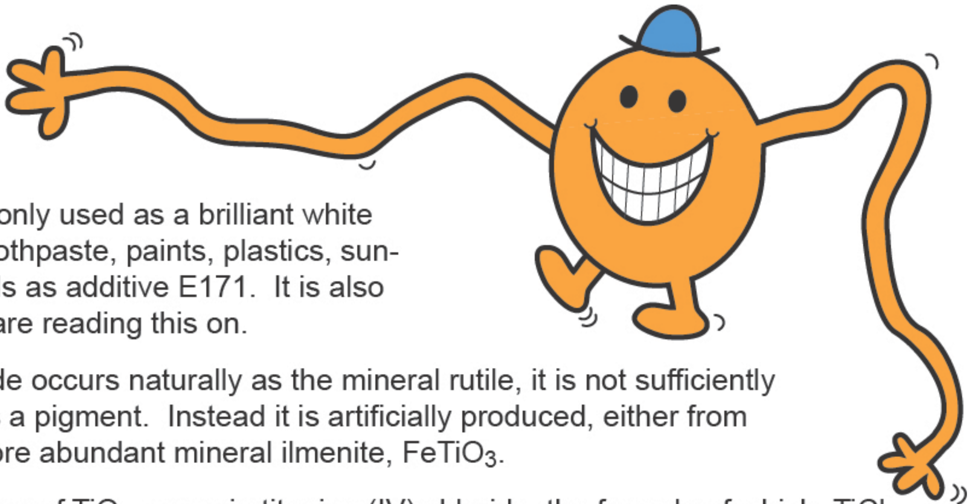
symbol
atomic number
mean atomic mass

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H 1 1.008																	**He** 2 4.003
Li 3 6.94	**Be** 4 9.01											**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

The Avogadro constant $N_A = 6.022 \times 10^{23}$ mol^{-1}

1. This question is about titanium dioxide, TiO_2, and titanium chlorides, $TiCl_x$.



Titanium dioxide is commonly used as a brilliant white pigment for instance in toothpaste, paints, plastics, sun-screens, and even in foods as additive E171. It is also coated on the paper you are reading this on.

Although titanium dioxide occurs naturally as the mineral rutile, it is not sufficiently pure in this form to use as a pigment. Instead it is artificially produced, either from crude rutile, or from its more abundant mineral ilmenite, $FeTiO_3$.

One industrial preparation of TiO_2 goes via titanium(IV) chloride, the formula of which, $TiCl_4$, has given rise to its industrial nickname, 'Tickle'.

(a) Knowing the two common oxidation states of iron, what are the possible oxidation states of the titanium in ilmenite, $FeTiO_3$?

In the so-called 'chloride process', titanium(IV) chloride is formed from the titanium ore and carbon.

(b) Assuming the products are metal chlorides and carbon monoxide, give equations for:

(i) the reaction between rutile (TiO_2), chlorine, and carbon

(ii) the reaction between ilmenite ($FeTiO_3$), chlorine and carbon, given that during this process the iron in the ilmenite is oxidised.

The $TiCl_4$ may easily be separated and purified because of its low boiling point, 136 °C.

(c) What type of structure and bonding is found in solid $TiCl_4$? Circle the correct answer in the answer booklet.

ionic　　giant covalent　　simple molecular (simple covalent)

In the final stage of the production, the $TiCl_4$ reacts with oxygen gas to form the TiO_2, regenerating chlorine gas according to the equation:

$$TiCl_4(g) + O_2(g) \longrightarrow TiO_2(s) + 2Cl_2(g) \qquad \Delta H° = -175 \text{ kJ mol}^{-1}$$

	substance	value / kJ mol^{-1}
standard enthalpy change of formation, $\Delta_f H°$	TiO_2(s)	-939
standard enthalpy change of atomization, $\Delta_{at} H°$	Ti(s)	473
bond strength	Cl_2(g)	242

(d) Using the above thermodynamic data, by finding the standard enthalpy change of formation of $TiCl_4$(g), or otherwise, calculate the average bond strength in $TiCl_4$.

New paving blocks, such as those used in the High Street in Kendal shown on the left, use the photo-catalytic properties of titanium dioxide to remove pollutants from the air. Known as Noxer blocks, they are particularly good at removing nitrogen oxides, commonly represented as NO_x.

The nitrogen oxides desired to be removed from the air are nitrogen dioxide, NO_2, and nitrogen monoxide, NO. Both are produced by traffic pollution, and both species are radicals, i.e. they contain an unpaired electron.

(e) **(i)** Draw a dot-and-cross diagram to show the bonding in nitrogen dioxide.

(ii) The bond angle in NO_2 is within 1° of one of the following. Circle the correct angle in your answer booklet.

90° 105° 109° 115° 120° 135° 180°

The Noxer blocks essentially work by first using UV light to split water on the surface of the TiO_2 to give the hydroxyl radical, an electron, and a proton:

$$H_2O \xrightarrow{\text{UV light}} HO^{\bullet} + e^- + H^+$$

The hydroxyl radical can then react with nitrogen dioxide to form a single product. The electron can react with oxygen molecules from the air to form the superoxide ion, O_2^-, which can then react with nitrogen monoxide, NO, to form a single, charged species. The four reactions may be combined to give one equation showing the production of a solution that is washed away when it rains.

(f) **(i)** Give the equation for the reaction between NO_2 and the hydroxyl radical, and give the name the product formed.

(ii) Give the equation for the reaction between the superoxide ion and nitrogen monoxide.

(iii) Give an equation for the net reaction which takes place on the TiO_2 to remove the oxides of nitrogen and <u>underline</u> the species being reduced in the equation.

(g) When heated under an atmosphere of hydrogen gas, titanium(IV) chloride forms titanium(III) choride and another substance. Give a balanced equation for this process.

When titanium(III) chloride is heated, it undergoes the following reaction:

$$2TiCl_3(s) \rightleftharpoons TiCl_2(s) + TiCl_4(g)$$

(h) (i) Which of the following best describes what happens to the titanium during this reaction? (Circle the best answer in your answer booklet.)

oxidation reduction disproportionation nothing

(ii) The standard entropy change for a reaction, ΔS°, gives a measure of the change in the amount of disorder that takes place during the reaction (i.e. [amount of disorder in the products] – [the amount of disorder in the reactants]). Would you expect ΔS° for this reaction to be positive or negative? Briefly justify your answer.

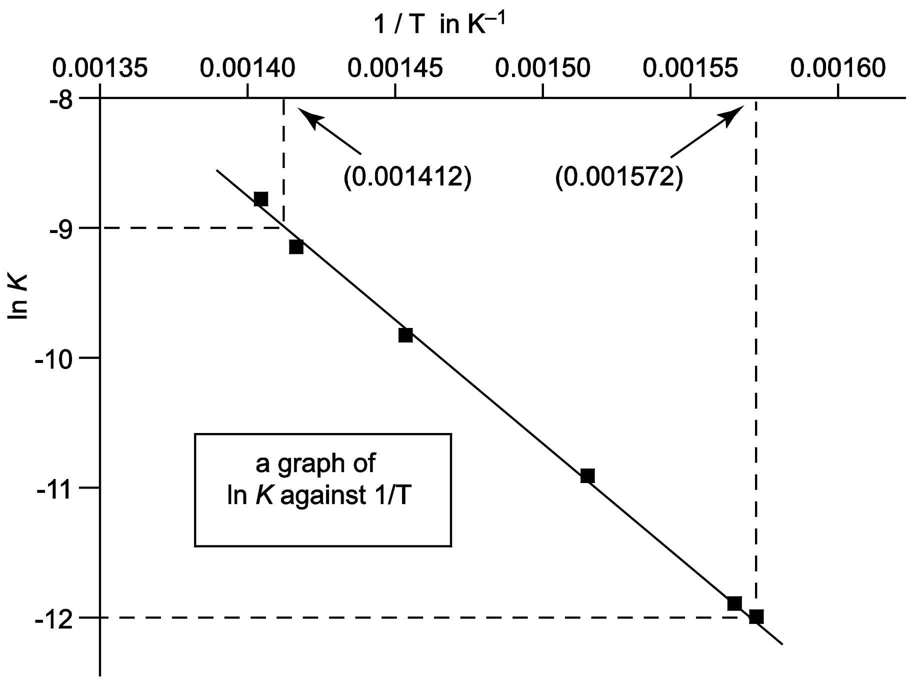
(iii) How would you expect the position of equilibrium to vary with temperature if the standard enthalpy change for the reaction were negative? Briefly justify your answer.

The position of equilibrium is given by the value of the equilibrium constant, *K* (the larger *K*, the more products). The precise way that *K* varies with temperature, *T*, is given by the equation:

$$\ln K = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R}$$

where *R* is the gas constant, 8.314 J K^{-1} mol^{-1} and ΔH° and ΔS° are standard enthalpy and entropy changes for the reaction.

(j) A graph showing how *K* varies with temperature for this reaction is plotted below. Use this to calculate the standard enthalpy change, and the standard entropy change for this equilibrium.

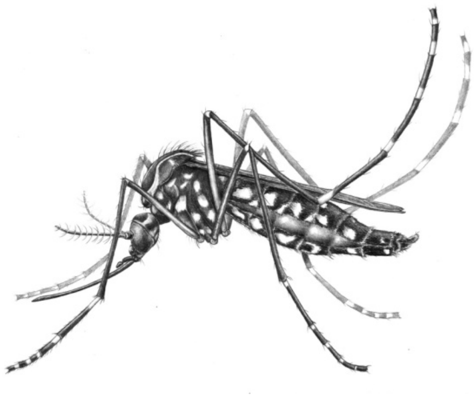


(k) The melting and boiling points of titanium(II) chloride are 1035 and 1500 °C, and metallic titanium may be obtained by electrolysing molten $TiCl_2$ in molten $CaCl_2$. What type of structure and bonding is found in solid $TiCl_2$? Circle the correct answer in the answer booklet.

ionic giant covalent simple molecular (simple covalent)

2. This is a question about Pyrethroid insecticides

The recent discovery that Zika virus infection during pregnancy is likely to be linked to the birth defect microcephaly led the World Health Organization to declare Zika virus a Public Health Emergency of International Concern on 1st February 2016.



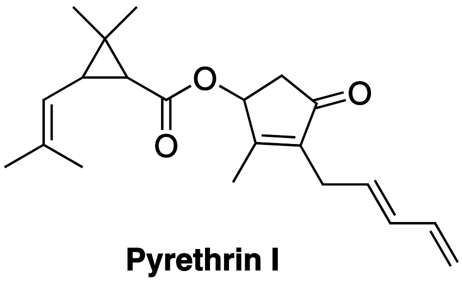
Zika virus is transmitted to humans when they are bitten by infected *Aedes* mosquitos. There is no current vaccine or therapeutic agent against Zika, thus reducing both the mosquito population and the probability of being bitten are vital to reducing the infection rate.

The use of insecticide treated mosquito nets can be an effective way to reduce infection with mosquito-borne diseases. The pyrethroid family of insecticides is commonly used to treat mosquito nets due to their lower environmental impact than organophosphate insecticides and their low toxicity in humans.

Section I - Pyrethrins

Pyrethroids are synthetic compounds based on the naturally occurring pyrethrins. Pyrethrins are produced in chrysanthemum flowers (historically known as pyrethrum) and have been in use as an insecticide since the early 1900s.

The structure of the one of the six pyrethrins produced in the flowers is shown below:



Pyrethrin I
Mr: 328.4

(a) Give the molecular formula of **Pyrethrin I**.

(b) (i) Assuming that only C=C bonds react, how many moles of Br_2 will react with a 500 mg sample of **Pyrethrin I**.

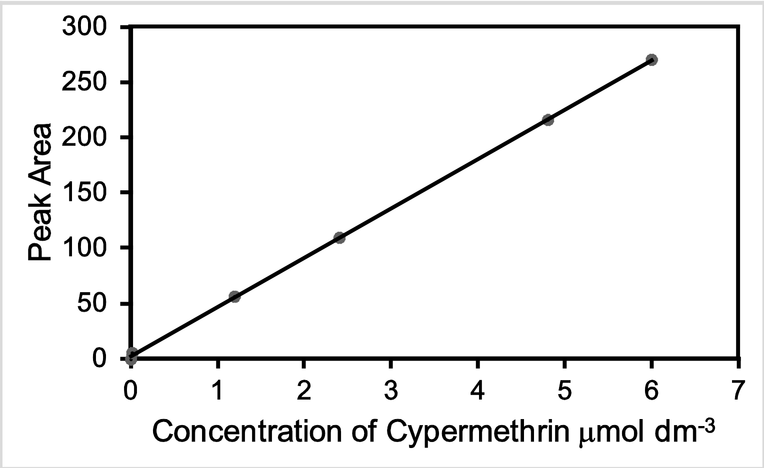
(ii) Hence determine the volume of 0.0500 mol dm^{-3} bromine water that would react with a 500 mg sample of **Pyrethrin I**. Please give your answer in cm^3.

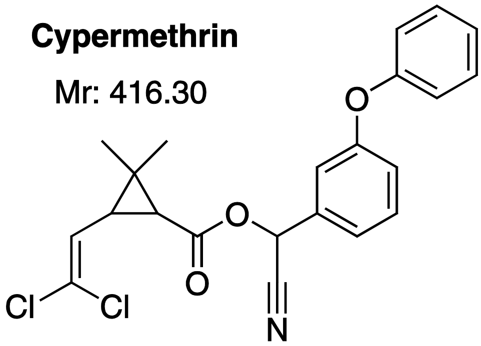
Section II – Pyrethroids

Pyrethrins break down rapidly under UV light and so were replaced by synthetic pyrethroids in the mid-20th century. Although pyrethroids show low toxicity towards mammals, their increased use and better stability than pyrethrins means that there is a risk that they will become concentrated in the food chain. One technique used to accurately determine the concentration of pyrethroids in food is liquid chromatography followed by mass spectrometry (LC-MS). Here the chromatography is used to separate different compounds and mass spectrometry to identify and quantify them.

The calibration line showing the peak size of the molecular ion peaks for five different concentrations of **Cypermethrin** in pureed blueberries is shown below. The equation for the line of best fit for the data is:

$$\text{Peak area} = 44.547 \times (\text{Concentration of Cypermethrin} / \mu\text{mol dm}^{-3}) + 2.403.$$





The amount of **Cypermethrin** that can be consumed without risk, the MRL (minimum risk level), is 0.020 mg kg $^{-1}$ day^{-1}. 4 blueberries were ground into a sample that had a volume of 15 cm^3 and the peak area observed to be 4.8.

(c) **(i)** What is the concentration of **Cypermethrin** in the sample?

(ii) Calculate the mass of **Cypermethrin** in the sample.

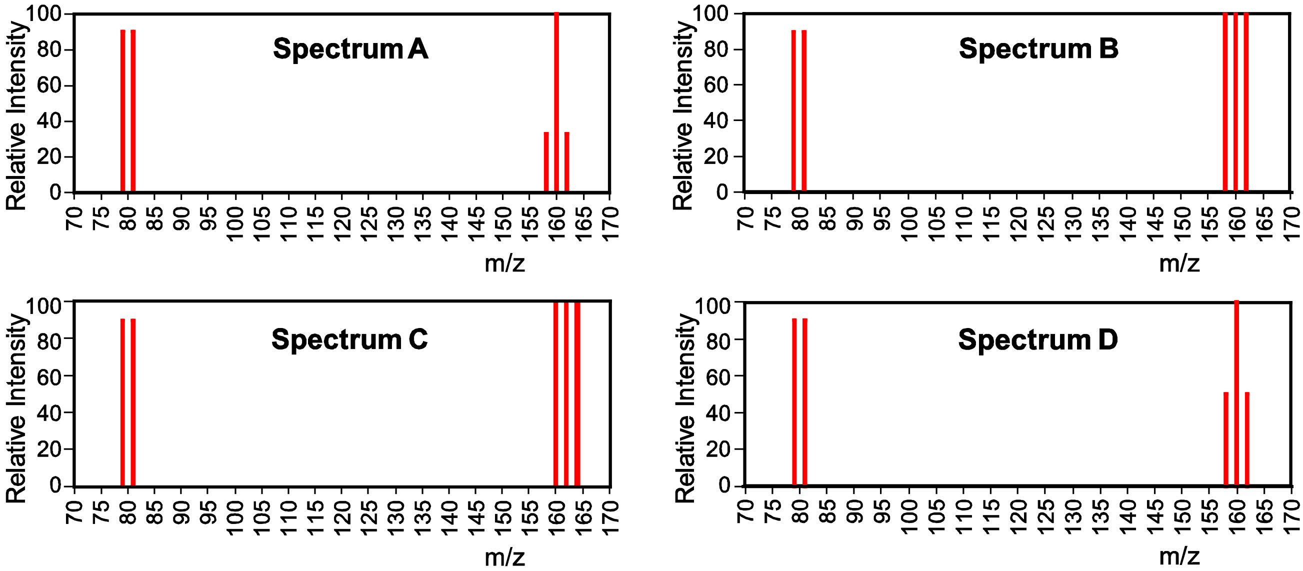
(iii) How many blueberries can a 15 kg toddler consume per day without exceeding the MRL?

Many of the pyrethroids, including **Cypermethrin**, contain the halogens chlorine and bromine which complicates the interpretation of the mass spectrum. Bromine naturally occurs as two stable isotopes, ^{79}Br and ^{81}Br, with approximately equal abundance. Chlorine also has two main stable isotopes: ^{35}Cl and ^{37}Cl at 75% and 25% abundance respectively.

(d) Write down all of the possible ways of forming a Br_2 molecule from ^{79}Br and ^{81}Br.

(e) Which of the four mass spectra shown overleaf would you expect to match that of Br_2?

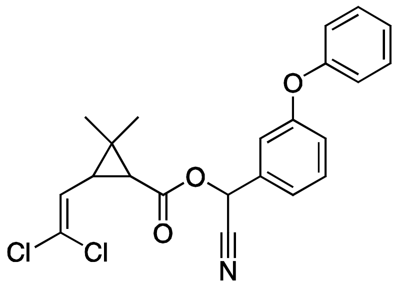
(Circle the correct option in your answer booklet.)



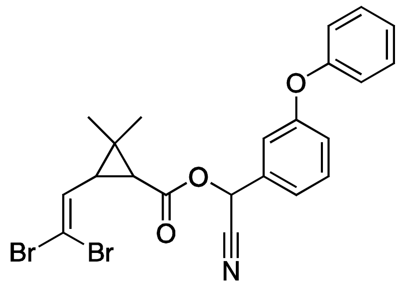
(f) **(i)** What m/z values will the peaks corresponding to Cl_2 in a mass spectrum have?

(ii) What will the relative intensities of peaks corresponding to Cl_2 in a mass spectrum be?

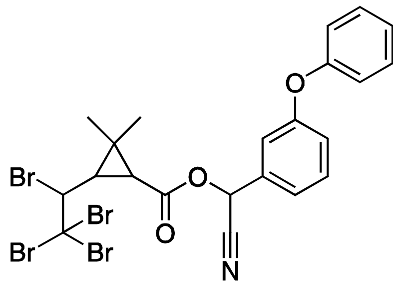
(g) For each of the compounds below give the m/z values for all of the molecular ions and their corresponding relative intensities:



Cypermethrin
$C_{22}H_{19}Cl_2NO_3$



Deltamethrin
$C_{22}H_{19}Br_2NO_3$



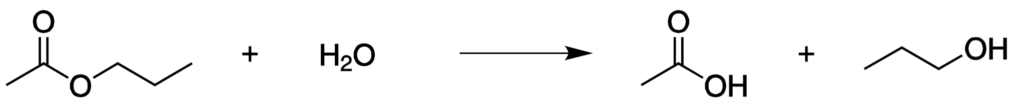
Tralomethrin
$C_{22}H_{19}Br_4NO_3$

Deltamethrin is one of the most commonly used insecticides for the treatment of mosquito nets worldwide. The recommended concentration of **Deltamethrin** on a mosquito net is 55 mg m^{-2}.

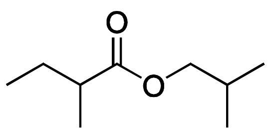
(h) Assuming that all of the **Deltamethrin** is absorbed by the net, what volume of 10% (10 g / 100 cm^3) **Deltamethrin** solution would be needed to treat a net of surface area 12.5 m^2 ?

Section III – Pyrethroid Metabolism in Mammals

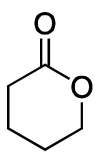
The pyrethroids have low toxicity in mammals due to rapid hydrolysis of the ester bond to give to non-toxic products. In ester hydrolysis water attacks the carbonyl group forming a transient tetrahedral species which then breaks down to give a carboxylic acid and an alcohol.



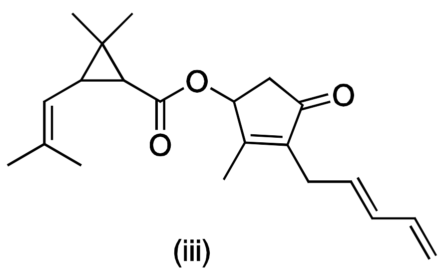
(j) Draw the products obtained from the hydrolysis of the compounds shown below:



(i)



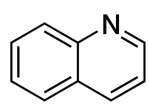
(ii)



(iii)

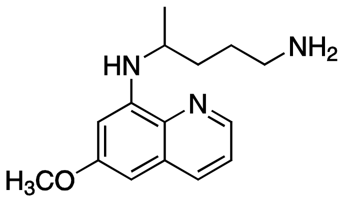
Section IV – Primaquine

Although the Zika virus was only recently discovered, chemical compounds have been used to combat mosquito-borne diseases for hundreds of years. Most chemical compounds used to treat the disease malaria are based around the compound quinolone, shown on the right. One of these drugs, Primaquine, is the only known drug to cure both relapsing and acute malaria infections.

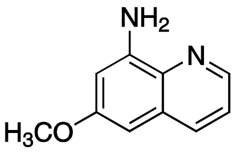


Quinoline

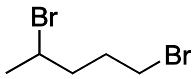
In the synthesis of Primaquine, all of the carbon atoms in the desired product originate from **Reagent U** and **Reagent V**.



Primaquine



Reagent U



Reagent V

The NH_2 group in reagent **U** is a good nucleophile and reagent **V** is a good electrophile. However, attempting to synthesise Primaquine by the nucleophilic substitution reaction between these two reagents is problematic as there are a number of different products that can form. Starting from one molecule of **Reagent V**, and reacting with **U** using only the nitrogen in the NH_2 group as the nucleophilic atom, it is possible to form *four* molecules: two are structural isomers, and two others have different molecular formulae.

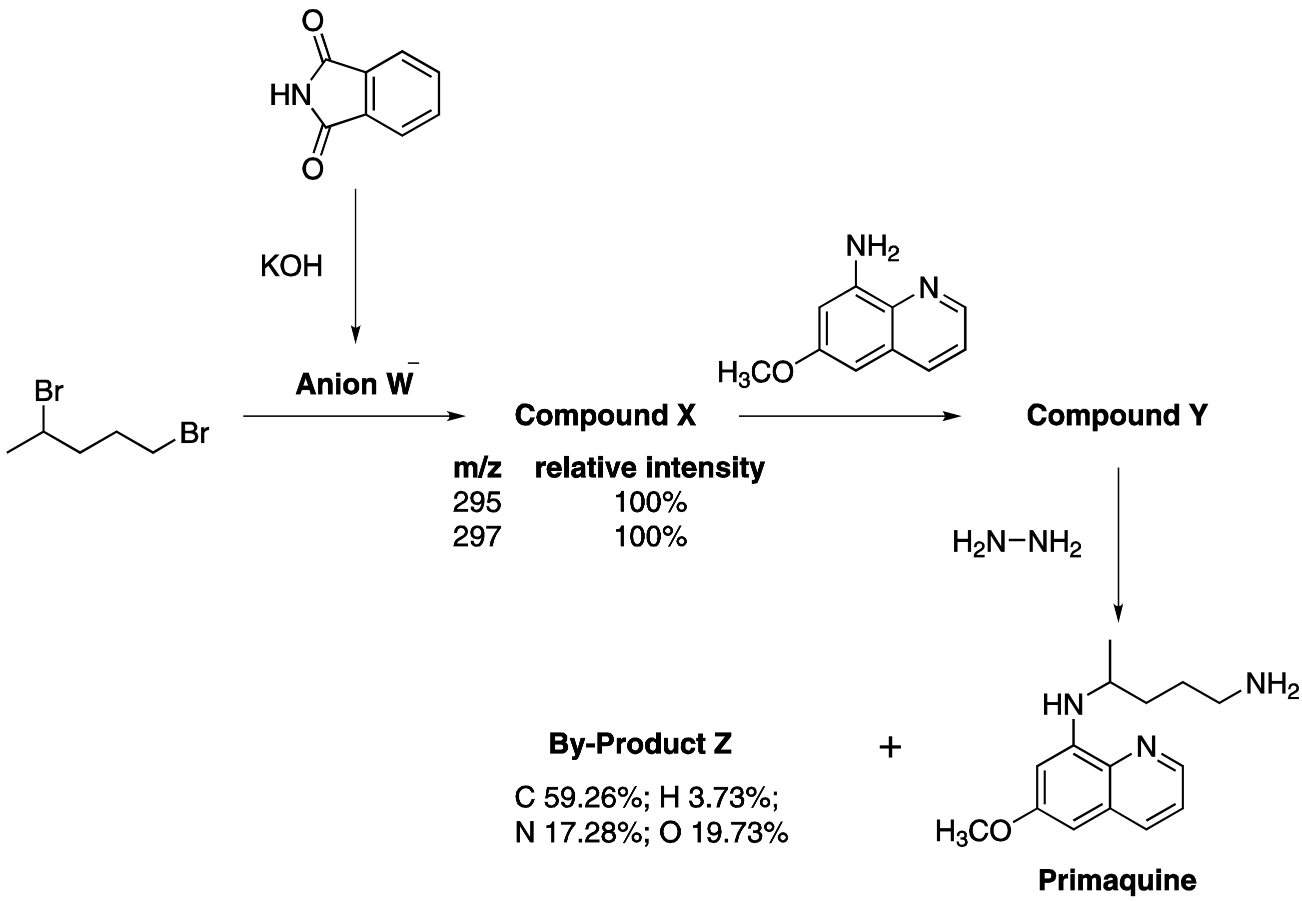
(k) Draw the structures of the four possible products.

Only one of the four products is a useful compound for the synthesis of Primaquine.

(l) (i) Circle the structure from your four products that is the useful one.

(ii) Suggest the reagent you would treat this product with to give Primaquine.

The useful product is actually only formed in minor amounts in the reaction between **U** and **V** and so the synthesis of Primaquine is carried out over several steps as shown below.



(m) Draw the structures of **Anion W⁻**, **Compound X**, **Compound Y** and **By-Product Z**.

Acknowledgements

We would like to thank those who support C3L6:

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St Catharine's College, Cambridge

References for Question 1
Photograph of the Noxer Blocks in Kendall supplied by Marshalls plc.

Journal of Physical Chemistry, **60**, 1956, 316-319
"*Thermodynamics of the titanium chlorides.*"
Benjamin Sanderson and George MacWood.

References for Question 2
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Hydrolytic metabolism of pyrethroids by human and other mammalian carboxyesterases. Ross M.K. *et al*.

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