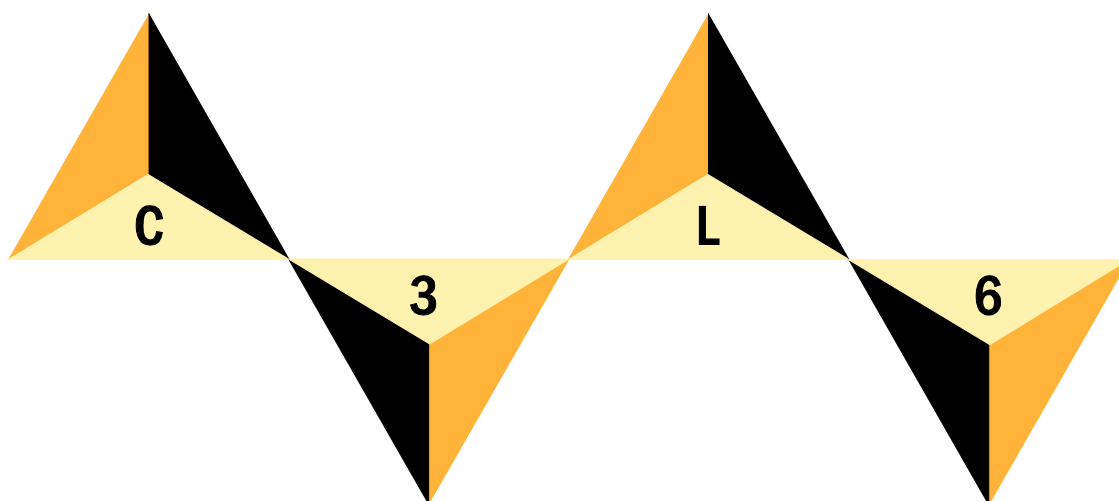




Cambridge Chemistry Challenge Lower 6th

June 2017

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.

H 1 1.008	2											13	14	15	16	17	He 2 4.003
Li 3 6.94	Be 4 9.01	symbol atomic number mean atomic mass										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	3	4	5	6	7	8	9	10	11	12	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 $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

1. This question is about pink tap-water.

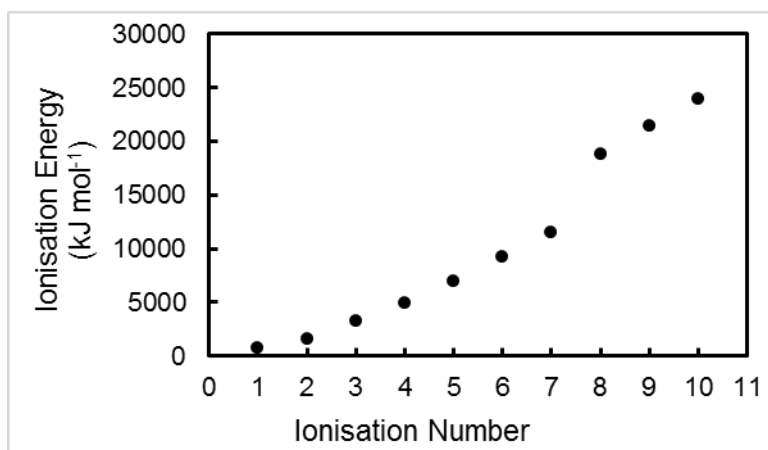
Potassium permanganate, KMnO_4 , which has a vivid purple colour in water, is used as an oxidising agent during the treatment of drinking water. The role of potassium permanganate is to remove iron, manganese and sulfur, a process that relies on the many possible oxidation states of manganese. In March 2017, residents of the Canadian town of Onoway found their water supplies had turned purple due to a leak of potassium permanganate solution into the water system. Fortunately, dilute potassium permanganate solutions have low toxicity; nonetheless residents were advised not to drink the water!



Section I – KMnO_4 and the MnO_4^- ion

- (a) Write down the electron configuration of manganese in terms of its subshells.

The graph on the right shows the first ten successive ionisation energies of Mn(g) :



- (b) (i) Suggest the highest oxidation state that manganese can exhibit in its chemistry.
(ii) Briefly justify your answer.

Potassium permanganate contains the MnO_4^- oxyanion in which there are covalent bonds between manganese and oxygen.

- (c) (i) Draw a dot and cross diagram to illustrate the bonding in the MnO_4^- ion, showing only the electrons in the outer-shells of the atoms involved.
(ii) Suggest a value for the bond angle in MnO_4^- .

KMnO_4 , potassium manganate(VII), is produced industrially from the mineral pyrolusite, a naturally occurring source of manganese(IV) oxide. In the first step of KMnO_4 production pyrolusite is heated with potassium hydroxide in the presence of air, producing potassium manganate(VI) and one other product.

- (d) Write a balanced equation for this reaction [hint: consider the oxidation states].

The potassium manganate(VI) is then dissolved in a solution of potassium hydroxide and converted into potassium manganate(VII) by a process known as electrolytic oxidation. In this process, water is reduced to hydrogen gas.

- (e) (i) Remembering that reduction is the gain of electrons, write an *ionic* half equation for the reduction of water to hydrogen gas and hydroxide ions.
- (ii) Write an *ionic* half equation for the oxidation of manganate(VI) ions to manganate(VII) ions.
- (iii) Hence, or otherwise, write an equation for the conversion of aqueous potassium manganate(VI) to potassium manganate(VII).

Aqueous solutions of potassium manganate(VI) are only stable at high pH. At neutral pH the substance disproportionates; the reduction product is manganese(IV) oxide.

- (f) Write a balanced equation for this disproportionation reaction.

Section II – KMnO_4 in drinking water

It is thought that a faulty valve controlling the addition of potassium manganate(VII) was responsible for the purple water supply in Onoway. The exact concentration of the potassium manganate(VII) in the water supply has not been reported but solutions of concentration as low as 0.050 mg dm^{-3} are visibly coloured. The colour of solutions is quantified by measuring how much light is absorbed when light of a particular wavelength is passed through the solution. The absorbance, A , of a solution is given by the following equation:

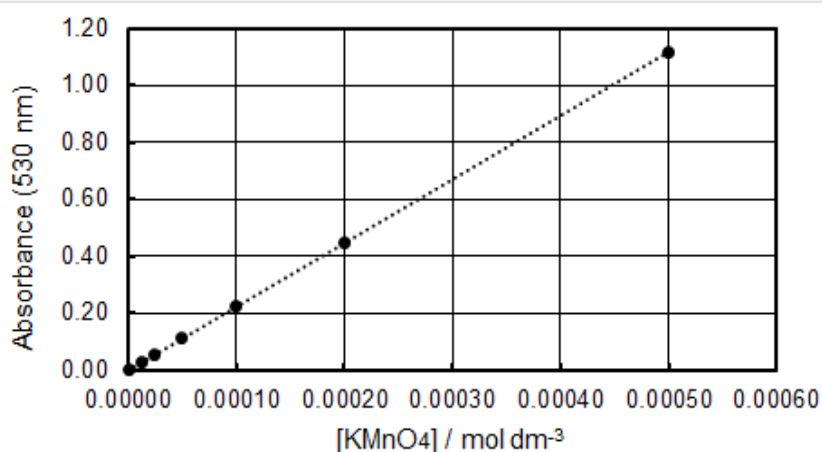
$$A = \epsilon c l$$

where c is the concentration of the solution in mol dm^{-3} , l is the depth of solution through which the light is passed (here 1.0 cm), and ϵ is the molar absorptivity for the particular compound being investigated at a particular wavelength of light used.

- (g) Given that the absorbance, A , has no units, and l is specified in cm, what are the units of the molar absorptivity, ϵ ?

The graph on the right shows the absorbance of various solutions of potassium manganate(VII) of different concentrations.

- (h) From this graph, calculate the value for the molar absorptivity of potassium manganate(VII) at 530 nm.



- (i) What is the absorbance of a solution whose concentration is 0.050 mg dm^{-3} ?
- (j) (i) Assuming that the absorbance of the water in Onoway was 0.40, calculate the concentration (in mg dm^{-3}) of potassium manganate(VII) in the tap water.
- (ii) Assuming that the toxic dose for potassium manganate(VII) is 1.0 g per kg of body weight, what volume of contaminated tap water would a 75 kg Onoway resident have had to drink to consume a toxic dose?

Section III – Reactions of KMnO_4 .

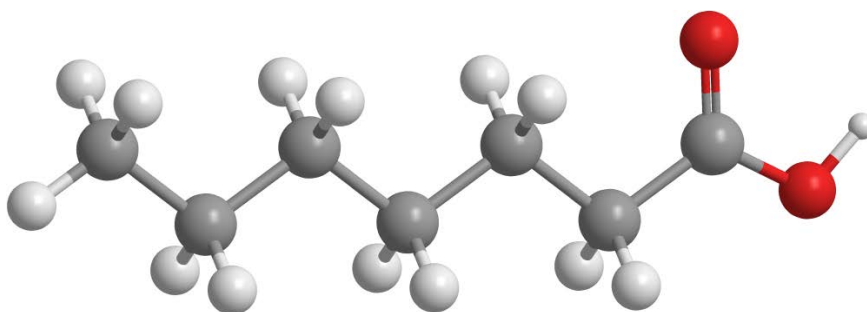
KMnO_4 reacts with concentrated H_2SO_4 under carefully controlled conditions to form a manganese-containing species, **Compound X**, with 49.5% Mn and 50.5% O by mass. Mass spectrometry shows the the empirical formula is also the molecular formula.

- (k) (i) Determine the molecular formula of **Compound X**.
 (ii) Hence write a balanced equation for the reaction of KMnO_4 with concentrated H_2SO_4 .
 (iii) Suggest a structure for a molecule of **Compound X**.

Compound X decomposes explosively to give MnO_2 and O_2 as the sole products. At 298 K the species involved in the reaction have the following standard enthalpy changes of formation:

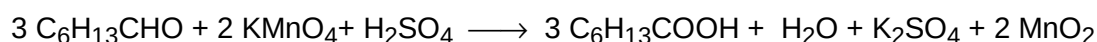
Compound	$\Delta_f H^\circ / \text{kJ mol}^{-1}$
Compound X (s)	– 742
MnO_2 (s)	– 520

- (l) Calculate the standard enthalpy change of reaction for the decomposition of one mole of **Compound X** at 298 K, assuming that solid MnO_2 forms in this reaction.



Potassium manganate(VII) is commonly used in the laboratory as an oxidising agent in organic chemistry. For example, it readily oxidises heptanal to heptanoic acid (shown above), an important precursor needed in the preparation of many organic compounds such as drugs, fragrances, and flavourings.

The equation for the oxidation of heptanal to heptanoic acid in aqueous conditions is:



- (m) The overall yield of this reaction is typically 77%. Assuming this is the case, and that a 10% excess of KMnO_4 is used in the synthesis, what mass of KMnO_4 is needed to make 300 g of heptanoic acid?

Whilst potassium permanganate is a common reagent, the sodium salt is harder to produce and is considerably more expensive. A supplier currently has 1 kg of solid KMnO_4 costing £54.20, whereas 500 ml of a 40% (by mass) aqueous solution of NaMnO_4 costs £67.80.

- (n) Calculate how many times more expensive it would be to carry out the oxidation of heptanal using NaMnO_4 rather than KMnO_4 .

2. This question is about drugs made from bromoalkanes

Bromoalkanes are useful starting materials for the synthesis of many drug molecules.

In some cases, the required bromoalkanes can themselves be made by the reaction of an alkane with bromine.



For parts (a)-(f) of this question you can assume that only one hydrogen atom in each alkane is replaced by a bromine atom when the alkanes react with bromine.

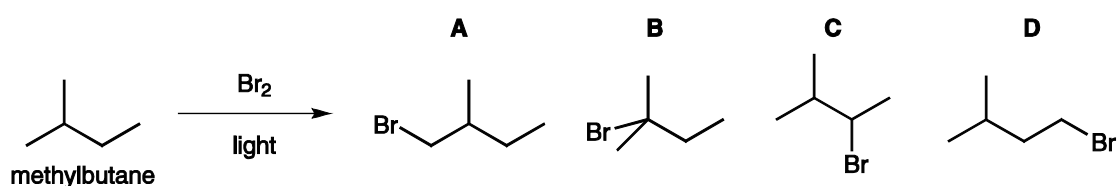
- (a) (i) One mole of ethane (C_2H_6) reacts with one mole of bromine to give bromoethane (C_2H_5Br). Write a balanced equation for this reaction. State symbols are not required.
- (ii) How would you classify this reaction? (circle only one in the answer booklet)

Addition Elimination Substitution Hydrolysis Cracking Polymerisation

- (iii) The reaction between ethane and bromine requires light and does not proceed in the dark. The light is needed to break a bond to start the reaction. Which bond is broken by the light?

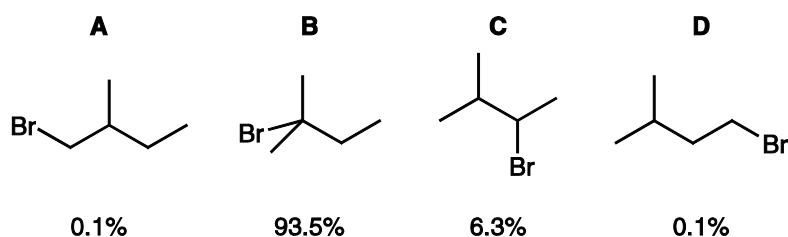
When ethane reacts with bromine, any one of the six hydrogen atoms can be replaced. The symmetry in the molecule of ethane means that all six of these hydrogen atoms are equivalent and so there is only one possible product no matter which hydrogen is replaced.

With larger alkanes, there is often the possibility of forming different structural isomers of the bromoalkane product, depending upon which hydrogen atom is replaced by a bromine atom. In the bromination of methylbutane, four different bromoalkanes can be formed (labelled A-D).



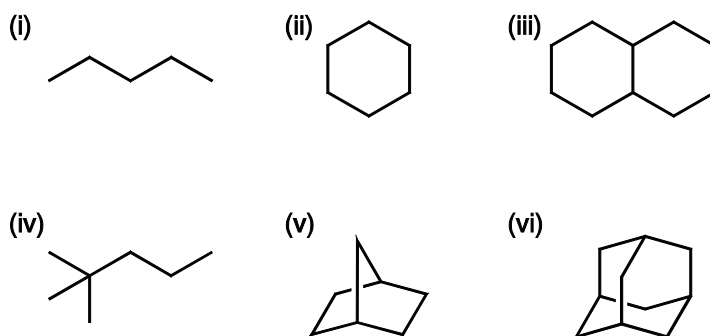
- (b) Assuming all the hydrogen atoms present in methylbutane are equally likely to be replaced during this reaction, which of the bromoalkanes A-D would you expect to be formed in the *smallest* proportion? Give the letter (A-D) and the systematic name of this bromoalkane.
- (c) Using the same assumption as in part (b) above, calculate the percentage of the four products A-D that you would expect to find in the mixture.

When this reaction was performed in the laboratory, the actual ratio of the products obtained (to the nearest 0.1%) was as follows:

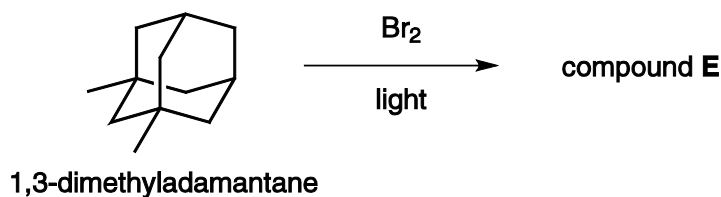


To determine which position is most reactive under these conditions (i.e. the preference of any particular hydrogen to be replaced by a bromine) we have to compare the ratio of the percentage of each product actually produced with that predicted in part (c). This gives a measure of the inherent reactivity of each position.

- (d) What is the relative reactivity of replacing a hydrogen to form compound **B** compared with replacing a hydrogen to form compound **C**?
- (e) By considering the symmetry of the following alkanes or otherwise, determine how many different bromoalkane structural isomers could be formed by replacement of one hydrogen atom with a bromine.

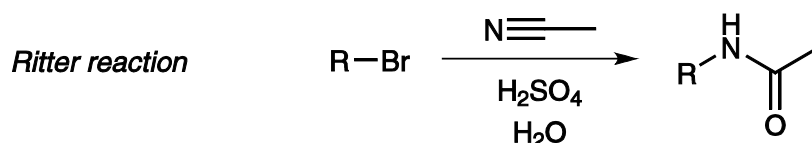


Memantine is one of the only drugs available to help lessen the symptoms of diseases such as Alzheimer's. The synthesis of memantine begins with the bromination of 1,3-dimethyladamantane to form compound **E**, which replaces a single hydrogen atom with a bromine.

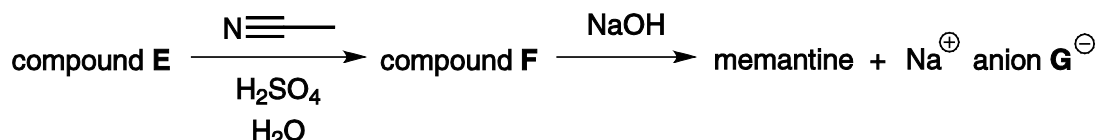


- (f) (i) How many different structural isomers of the bromoalkane **E** could possibly be formed by replacing one hydrogen in 1,3-dimethyladamantane with bromine?
- (ii) In the synthesis of memantine in the laboratory, only one structural isomer of **E** was formed. By considering the information earlier in this question, draw the structure of this isomer (add the bromine to the framework in your answer booklet).

The conversion of **E** into memantine requires only two more steps. The first of these steps is achieved in a reaction called a *Ritter reaction*. In scheme for this reaction, shown below, the letter *R* represents an alkyl group.



The conversion of **E** into memantine is shown below.



- (g) By modifying the structures shown in your answerbooklet, draw the structures of compound **F**, memantine, and anion **G⁻** (which has an RMM of 59.0).

The drug *carpipramine* is used for the treatment of schizophrenia and anxiety. The synthesis of carpipramine uses 1,3-dibromopropane as one of the starting materials.

- (h) Draw the other structural isomers of dibromopropane (C₃H₆Br₂).

If two moles of bromine are added to one mole of propane and then the mixture subjected to light, a mixture of these dibromopropanes can be produced.

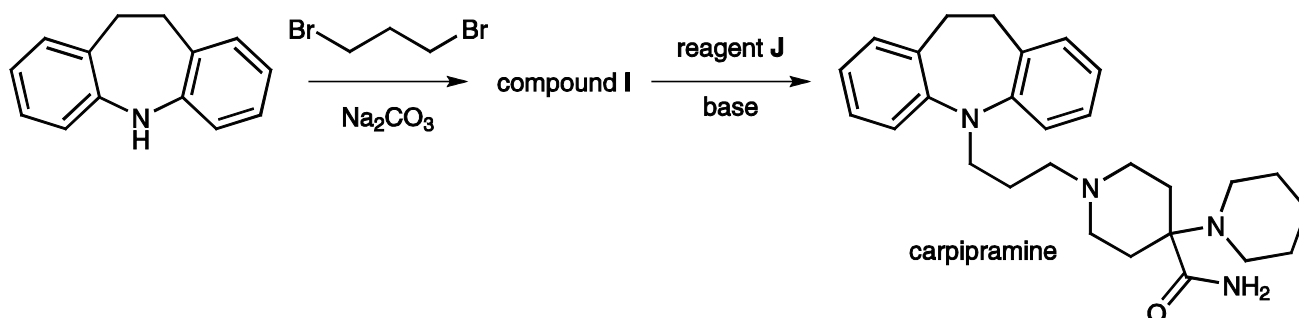
- (i) Calculate the percentage of 1,3-dibromopropane that would be produced in this mixture if all the hydrogen atoms were equally likely to be replaced in this reaction.

Unfortunately, no 1,3-dibromopropane is produced at all when this reaction is attempted in the laboratory as the reaction favours other isomers. However, another hydrocarbon (**H**) does react with bromine to give 1,3-dibromopropane. This hydrocarbon contains 85.63% carbon by mass, and when it reacts with bromine, gives no other products other than 1,3-dibromopropane.

- (j) (i) Draw the structure of **H**.
(ii) How would you classify the reaction of this hydrocarbon **H** with bromine to form 1,3-dibromopropane? (circle only one in your answer booklet)

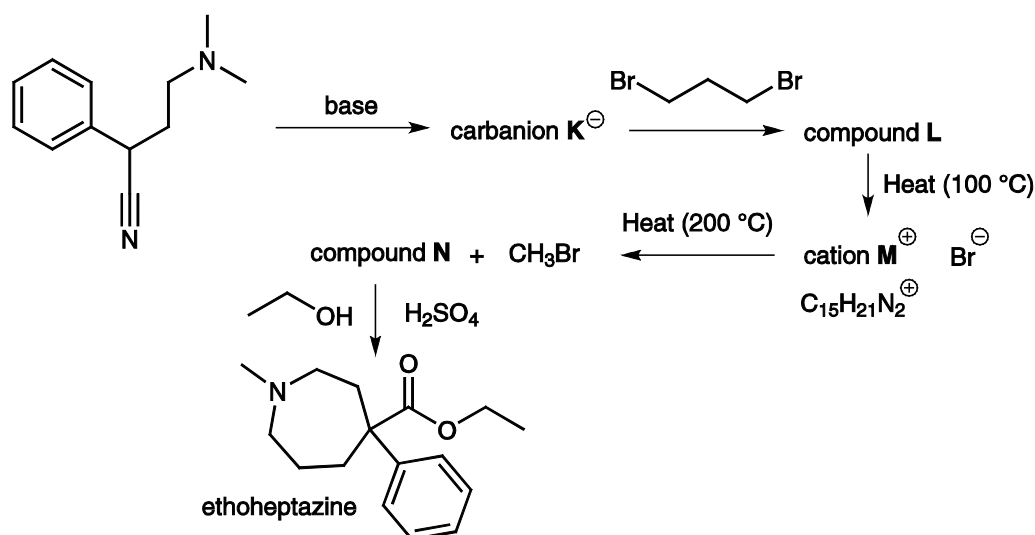
Addition Elimination Substitution Hydrolysis Cracking Polymerisation

The synthesis of caripramine is shown below:



(k) Draw the structures of compound I and reagent J.

1,3-Dibromopropane is also used in the synthesis of the drug *ethoheptazine*, used to treat pain and anxiety. The synthesis is shown below:



The carbon atoms in ethoheptazine which are not already present in the starting material either come from 1,3-dibromopropane or from ethanol. No C–C bonds are broken during the synthesis.

- (l) (i) In the answer book, circle the three carbon atoms in ethoheptazine which come from 1,3-dibromopropane.
- (ii) In the answer booklet, circle the two carbon atoms in ethoheptazine which come from ethanol.

The synthesis of ethoheptazine takes five steps. In the first step, the starting material is deprotonated to give K^- which is a carbanion (*i.e.* an ion in which a carbon atom has a negative charge).

(m) Draw the structures of carbanion K^- , compound L, cation M^+ and compound N.

Acknowledgements

We would like to thank those who support C3L6:

University of Cambridge Department of Chemistry

St Catharine's College, Cambridge

Corpus Christi College, Cambridge

The Worshipful Company of Goldsmiths