

A competition to select the team to represent the

UNITED KINGDOM

at the

XXXVIIth INTERNATIONAL

CHEMISTRY OLYMPIAD

STUDENT QUESTION BOOKLET

Round I - 2005

* * * * *

- 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	<table border="1"> <tr> <td>symbol</td> </tr> <tr> <td>atomic number</td> </tr> <tr> <td>mean atomic mass</td> </tr> </table>										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
symbol																				
atomic number																				
mean atomic mass																				
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 carbon oxides

In addition to the two most common oxides – carbon monoxide and carbon dioxide – a few other compounds may be formed containing carbon and oxygen only. Each oxide may be prepared by the dehydration of the appropriate acid.



Carbon dioxide may be prepared by the reaction between an acid, such as hydrochloric acid, and a carbonate, such as calcium carbonate. Simply protonating the carbonate should yield carbonic acid, but this is unstable and readily loses water to form carbon dioxide.

- (a) i) Give the equation for the reaction between calcium carbonate and hydrochloric acid to form carbon dioxide.
- ii) Draw the structure of carbonic acid.

Carbon monoxide may be prepared by dehydrating methanoic acid with concentrated sulfuric acid at about 140 °C.

- (b) i) Write the equation for the reaction between methanoic acid and sulfuric acid.
- ii) Draw a 'dot and cross' structure for carbon monoxide.
- iii) Is the bond between the carbon and oxygen in carbon monoxide best described as a single, double or triple bond?

Poisonous carbon monoxide may be detected by its ability to reduce an aqueous solution of palladium(II) chloride to black metallic palladium (Pd).

- (c) Write the equation for the reaction between aqueous palladium(II) chloride and carbon monoxide.

'Carbon suboxide' is a foul-smelling gas obtained by fully dehydrating propan-1,3-dioic acid.

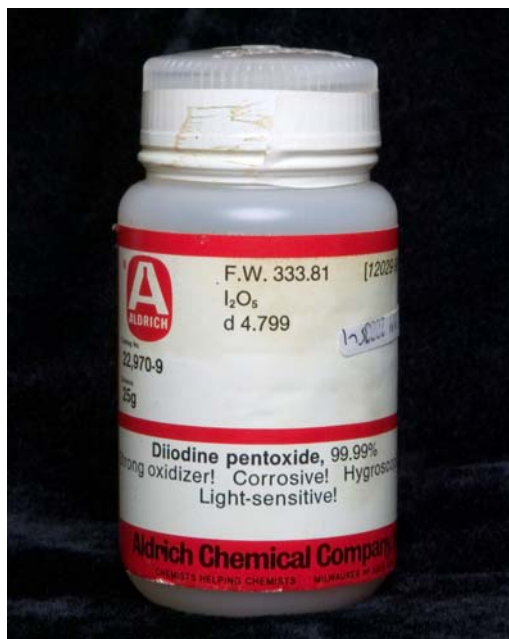
- (d) i) Draw the structure of propan-1,3-dioic acid and write a balanced equation for this acid forming carbon suboxide and water.
- ii) Draw a structure for carbon suboxide.

A fourth oxide of carbon has the formula $C_{12}O_9$ and may be obtained by fully dehydrating mellitic acid [benzene hexacarboxylic acid – $C_6(COOH)_6$].

- (e) Draw a structure for benzene hexacarboxylic acid and for $C_{12}O_9$.

2. This question is about diiodine pentoxide

Diiodine pentoxide, I_2O_5 , is a white crystalline powder that has the useful property of reacting quantitatively with carbon monoxide to yield iodine and one other product.



- (a) Suggest an equation for the reaction between I_2O_5 and carbon monoxide.

A 150 cm^3 sample of gas (at room temperature and pressure, r.t.p.) that was known to contain carbon monoxide was repeatedly passed over excess I_2O_5 at $170 \text{ }^\circ\text{C}$. The I_2O_5 became coloured with iodine. The iodine generated required exactly 8.00 cm^3 of $0.100 \text{ mol dm}^{-3}$ sodium thiosulfate solution to react with it. This reaction is:



- (b) Calculate the percentage by volume of carbon monoxide present in the sample of gas. [Assume 1 mol of any gas occupies 24.0 dm^3 at r.t.p.]

Diiodine pentoxide readily absorbs water and is sometimes supplied in a hydrated form, $H_xI_yO_z$. If this is heated to $200 \text{ }^\circ\text{C}$ it loses 1.766% of its mass to form pure I_2O_5 .

- (c) Calculate the empirical formula of the impure form, and write the equation for its dehydration.

I_2O_5 is an acid anhydride and reacts with excess water to produce the parent acid. This is analogous to the reaction between ethanoic anhydride and water to form ethanoic acid.

- (d) Suggest the formula for the simple parent acid of I_2O_5 , and write the equation for its formation from I_2O_5 . What is the oxidation state of the iodine in I_2O_5 ?
- (e) Suggest a structure for the parent acid and hence a structure for I_2O_5 .
- (f) The parent acid of I_2O_5 may be formed by reacting iodine, chlorine and water. Suggest an equation for this reaction.

3. This is a question about ants

The 'simplest' carboxylic acid is called methanoic acid and has formula HCOOH . It occurs naturally in ants and used to be prepared by distilling them! This gave rise to the earlier name for methanoic acid – *formic acid* – after the Latin word *formica* for ant.

When an ant bites, it injects a solution containing 50% by volume of methanoic acid. A typical ant may inject around $6.0 \times 10^{-3} \text{ cm}^3$ of this solution.



A *Formica rufa* worker ant, just after biting the photographer!

- (a) i) When you are bitten by an ant it does not inject you with all of its methanoic acid but keeps a little in reserve. Assuming a 'typical ant' injects 80% of its methanoic acid, what is the total volume of pure methanoic acid contained in a 'typical ant'?
- ii) How many 'typical ant' ants would have to be distilled to produce 1.0 dm^3 of pure methanoic acid?

Bicarbonate of soda (sodium hydrogencarbonate) is often used to treat ant stings.

- (b) i) Write the equation for the reaction between sodium hydrogencarbonate and methanoic acid.
- ii) Given that the density of methanoic acid is 1.2 g cm^{-3} , how many moles of methanoic acid does the 'typical ant' inject?
- iii) What mass of sodium hydrogen carbonate would be needed to neutralise completely the sting from this ant?
- (c) As soon as the methanoic acid is injected it dissolves in water in the body to produce a solution of methanoic acid. Assuming that it dissolves immediately in 1.0 cm^3 of water in the body calculate the concentration of the methanoic acid solution that is formed.
[You may ignore the volume of the methanoic acid itself in this calculation.]

The pH of a solution is related to the concentration of hydrogen ions as follows:

$$\text{pH} = -\log [\text{H}^+]$$

where $[\text{H}^+]$ stands for the concentration of hydrogen ions in mol dm^{-3} .

- (d) The pH of the methanoic acid solution produced above was 2.43. What is the concentration of hydrogen ions in this solution?

Methanoic acid is a weak acid and so is only partly ionised in solution



- (e) Calculate the percentage of methanoic acid molecules which are ionised in this solution.

The *acid dissociation constant*, K_a , is a measure of how ionised a weak acid is. For methanoic acid it is defined by the following expression where again square brackets written round a formula mean the concentration of that substance in mol dm^{-3}

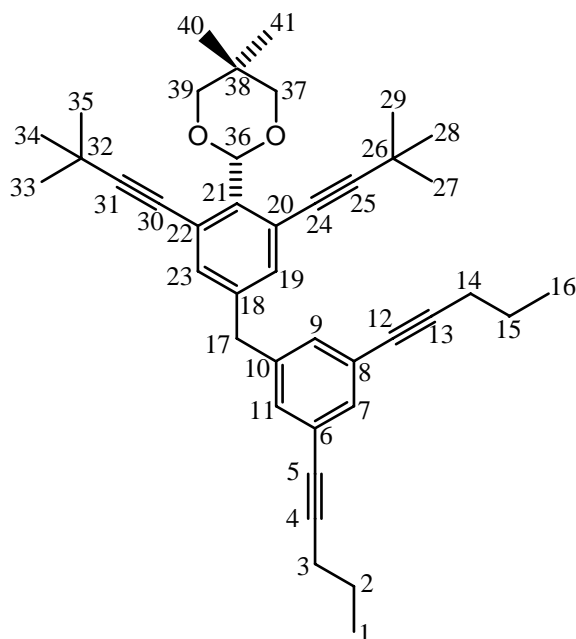
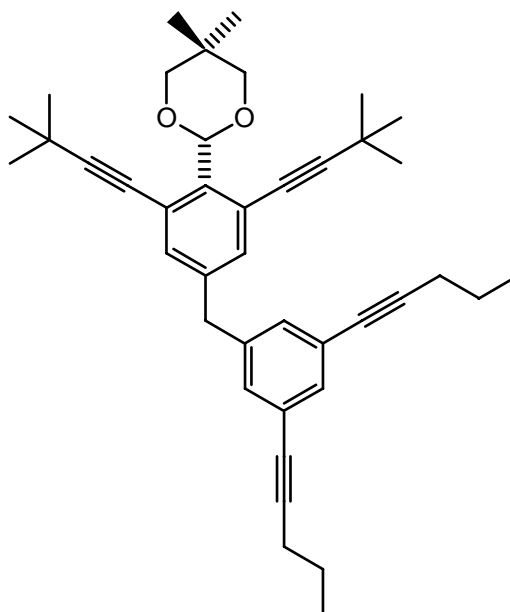
$$K_a = [\text{HCOO}^-][\text{H}^+] / [\text{HCOOH}].$$

- (f) Calculate the acid dissociation constant for methanoic acid.

4. This question is about the NMR spectra of NanoPutians

In June 2003, a research paper was published announcing the synthesis of the smallest representations of the human form: 2 nm tall anthropomorphic molecules, nicknamed 'NanoPutians' by their creators.

The molecules synthesised included 'NanoKid', 'NanoBaker' and 'NanoAthlete'. The compound shown to the right was called 'NanoBalletDancer' and has the formula $C_{41}H_{50}O_2$.



When assigning an NMR spectrum, the first step is to identify how many atoms there are in unique environments.

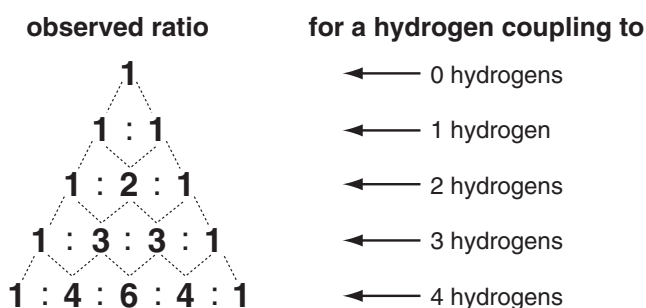
Both carbon atoms (^{13}C) and hydrogen atoms (1H) give NMR signals. Each atom *in a different environment* will give rise to one signal.

For example, in the structure of NanoBalletDancer, carbon atoms 37 and 39 are equivalent; we may write $37 \equiv 39$. Hence, although there are two carbon atoms (37 and 39) which have one oxygen atom attached, only *one* signal would be observed in a ^{13}C NMR spectrum due to these carbon atoms since they are equivalent.

- Which carbon atoms making up the benzene rings are equivalent? Write down $w \equiv x$, $y \equiv z$ etc for any equivalent atoms. How many signals *in total* would be observed due to benzene-ring carbons in a carbon NMR spectrum of NanoBalletDancer?
- List the groups of equivalent triple bond carbons in NanoBalletDancer. How many signals would be seen *in total* in the ^{13}C spectrum due to triple bond carbon atoms?
- How many different methyl groups ($-CH_3$ groups) are there in NanoBalletDancer? Again, list them in groups.
- How many different carbon environments are there in NanoBalletDancer – i.e. how many signals would be seen in total in the ^{13}C NMR spectrum?

Similarly, in ^1H NMR, the total number of signals depends on the number of different environments of hydrogen atoms in a structure. There are 13 different environments of hydrogens in NanoBalletDancer; their signals are labelled **A–M** in the spectrum below. The numbers of hydrogen atoms in each unique environment is given under the label. Hydrogen atoms in similar environments all have similar chemical shifts. For example, all the hydrogens on the benzene rings occur in the same region of the spectrum, i.e. they have a similar *chemical shift*.

However, ^1H NMR is complicated by *coupling*. If a hydrogen is within three bonds of another hydrogen *which is in a different environment*, instead of appearing as a single peak, its signal is split into a number of peaks. In general, if the hydrogen under consideration is within three bonds of n hydrogens in a different environment from the one under consideration, it will be split into $(n + 1)$ peaks. The ratio of the area under the peaks is given by Pascal's triangle as outlined below.

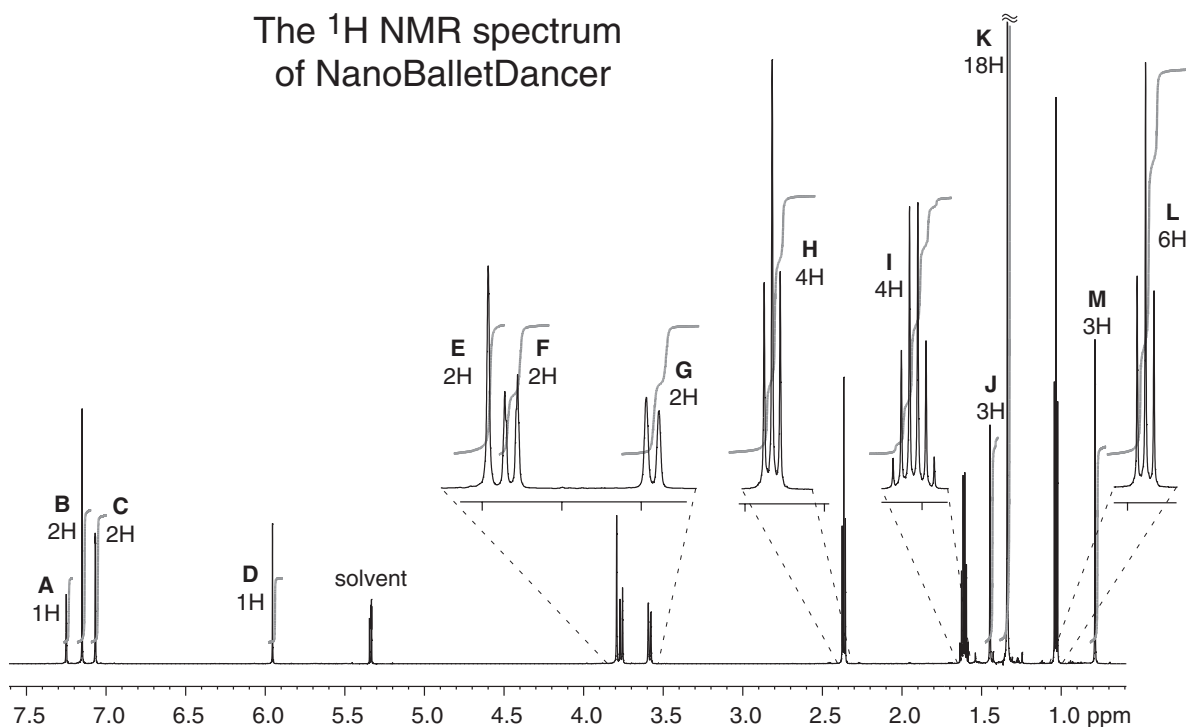


The signal for a given hydrogen is not split by any hydrogens *which are in the same environment* as it is in.

- (e) Into how many peaks will the signal from a hydrogen that couples with 5 other hydrogens be split? What will the ratio of the peaks be?

It is possible to assign the ^1H NMR spectrum of NanoBalletDancer by considering the numbers of hydrogens in different environments, their chemical shifts, and their coupling patterns. For example, the signal at 7.15 ppm (**B**) is due to the hydrogen atoms on carbons 19 and 23.

- (f) On the table in your answer sheet, assign (as far as possible) which signals are due to which hydrogen atoms. The assignment for signal **B** has already been filled in on the answer sheet. (For some signals, it might not be possible to decide between two alternative assignments – in which case just write ‘... or ...’ on the answer sheet.)



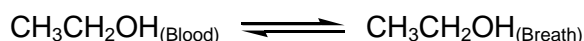
5. This question is about the Breathalyser

Some self-test breathalyser kits use the redox reaction between ethanol and acidified potassium dichromate to estimate blood alcohol.

The alcohol gets into the blood by absorption through the stomach wall; most is broken down in the liver to carbon dioxide and water – the rest leaves the body through sweat, in the breath and by excretion in urine.

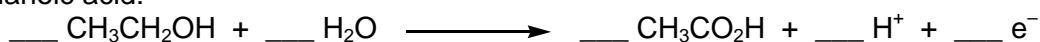


Alcohol concentration in the blood can be estimated by analysing the alcohol in the breath because an equilibrium is set up between the alcohol in the blood and the alcohol in the air in the lungs:



At body temperature, the concentration of alcohol in the blood is about 2300 times that in the breath.

- (a) i) On your answer sheet, complete the half equation for the oxidation of ethanol to ethanoic acid:



- ii) On the answer sheet, complete the half equation for the reduction of the dichromate ion in acid solution.



- iii) Combine these to give an overall equation for this reaction.

- iv) Assuming that the acid used is sulfuric acid and the dichromate salt is potassium dichromate, write a balanced equation for the reaction.

The breathalyser kit consists of a plastic bag that is inflated with 1000 cm^3 of breath and a glass tube containing the dichromate crystals. When the bag is connected to the tube and the breath is expelled through the tube the crystals change colour as they are reduced. The proportion of the crystals that change colour indicates the amount of alcohol present.

The current legal maximum blood alcohol concentration when driving in Britain is $80 \text{ mg per } 100 \text{ cm}^3$ of blood.

- (b) i) What is the corresponding breath alcohol concentration in $\mu\text{g per } 1000 \text{ cm}^3$ of breath?

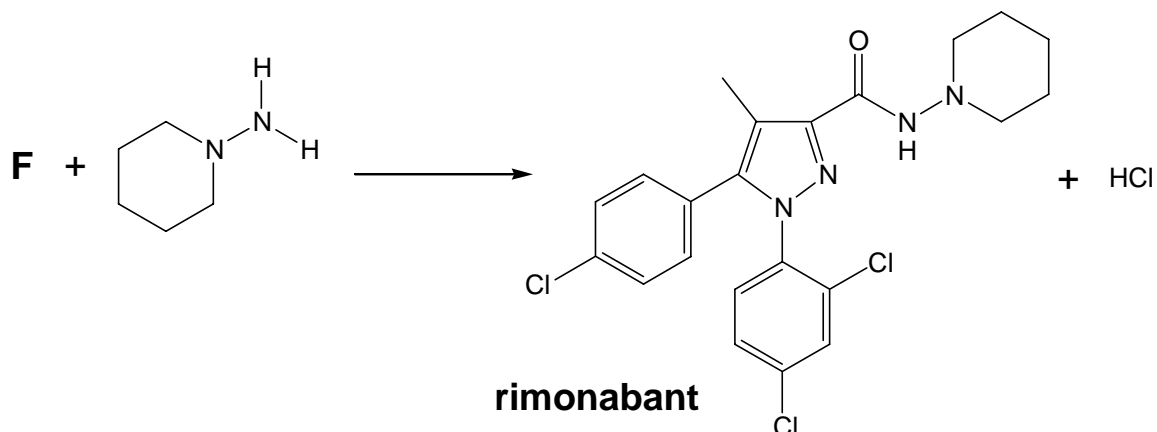
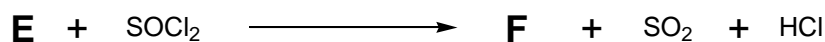
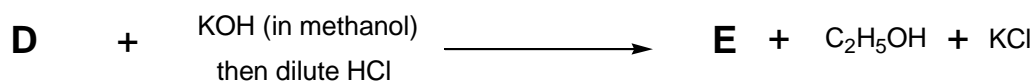
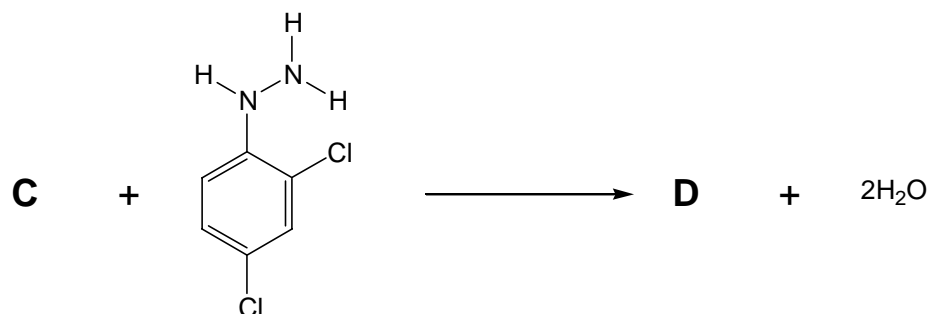
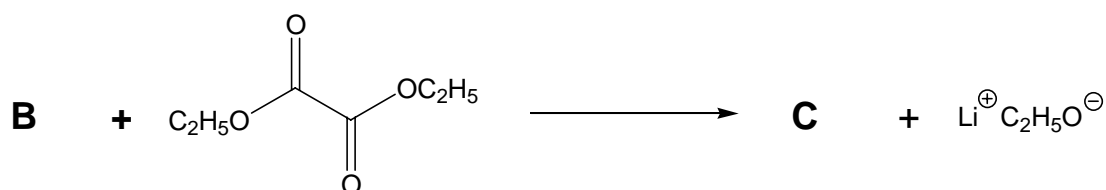
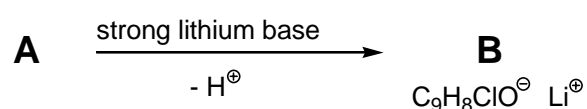
- ii) Assuming that the tube must be able to test breath at least three times over the legal limit, what mass of potassium dichromate should the tube contain?

- iii) What colour change would you expect for a positive result?

6. This question is about the synthesis the new wonder-drug 'Rimonabant'

In September 2004 the drug company *Sanofi-Synthelabo* announced a new compound to help fight both obesity and smoking. The structure of the drug *rimonabant* (to be marketed under the trade name *Acomplia*) is given below together with an outline of its synthesis.

Draw the structures for the starting materials chlorobenzene and propanoyl chloride, and compounds **A** – **F**.



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

The experts from JAWS anthill for the factual information on ants and for the photograph of the *Formica Rufa* worker ant. www.anthill.org.uk

Professor James M. Tour and his research group for the kind loan of a sample of NanoBalletDancer.

Chanteau and Tour, *Synthesis of Anthropomorphic Molecules: The NanoPutians*
Journal of Organic Chemistry, 2003, Vol 68(23), p8750-8766

The NMR department of the University of Cambridge, Department of Chemistry for running the 700 MHz ¹H NMR spectrum of NanoBalletDancer.

The synthesis of Rimonabant is taken from

A. Makriyannis *et al*, *Structure-Activity Relationships of Pyrazole Derivatives as Cannabinoid Receptor Antagonists*
Journal of Medicinal Chemistry, 1999, Vol. 42(4), p769-776