RSC | Advancing the Chemical Sciences

I Ch O U K

39th INTERNATIONAL

CHEMISTRY OLYMPIAD

2007

UK Round One

STUDENT QUESTION BOOKLET

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- ■ **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.

Periodic Table

H 1 1.008																	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	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 launching the space shuttle

To launch the space shuttle, two propulsion systems are used. Most of the thrust for the first two minutes of flight comes from the two reusable solid rocket boosters. The so-called 'external tank' provides the remainder of the thrust needed to get the shuttle into orbit.

The external tank is filled with liquid hydrogen and liquid oxygen which react to form water. The solid rocket boosters use a mixture of aluminium powder and ammonium perchlorate, NH_4ClO_4, together with an iron oxide catalyst and an organic binder.
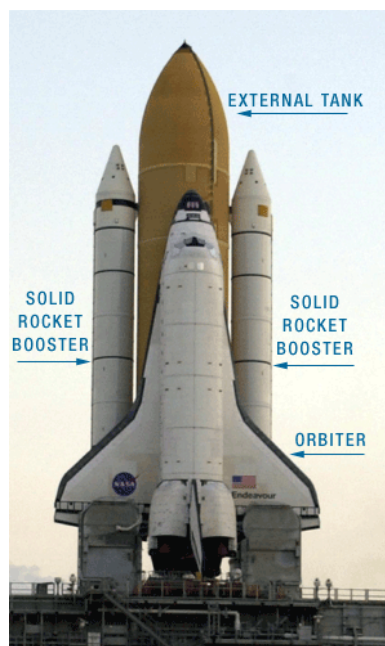
(a) Write the equation for the reaction between hydrogen and oxygen.

(b) The external tank has a mass of 27 tonnes (27,000 kg) when empty and 745 tonnes when full. Assuming these are present in the correct stoichiometric proportions, calculate the masses of hydrogen and oxygen in the external tank.

(c) In practice, the actual masses of hydrogen and oxygen used are 104 and 614 tonnes respectively. Given that the densities of liquid hydrogen and oxygen are 0.0708 and 1.141 g cm^{-3}, calculate the volumes of these liquids needed and hence the total capacity of the external tank in m^3.

The reaction that takes place during the combustion of the solid rocket booster fuel has been summarized as:

$$10Al(s) + 6NH_4ClO_4(s) \longrightarrow 4Al_2O_3(s) + 2AlCl_3(s) + 12H_2O(l) + 3N_2(g)$$
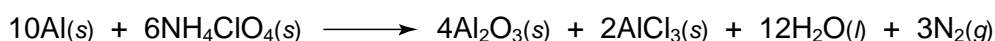
(d) Given the following standard enthalpies of formation, calculate the standard enthalpy change at 298 K for this reaction as given.

|	$NH_4ClO_4(s)$	$Al_2O_3(s)$	$AlCl_3(s)$	$H_2O(l)$
$\Delta_f H^{\ominus}$ / kJ mol^{-1}	−295.3	−1675.7	−704.2	−285.8

(e) Given that 450 tonnes of solid propellant are used in the solid rocket boosters in total, and that aluminium is the limiting reagent present at 16% in the mixture, calculate the energy released when this is reacted according to the above equation.

2. This question is about geometric shapes in chemistry

Phosphorus exists as a number of allotropes, the most reactive being white phosphorus. This was first prepared in the 17th century from the reduction of the phosphate present in urine.

Solid white phosphorus contains P_4 molecules, with each P atom at the vertex of a regular tetrahedron.

cuboctahedron
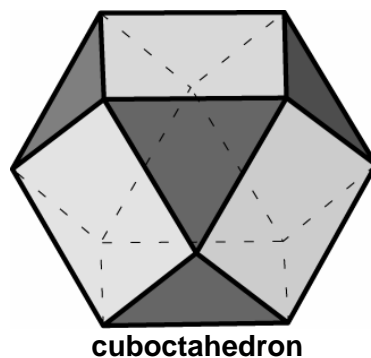
(a) Draw the structure of a molecule of P_4, showing all the chemical bonds.

(b) How many edges are there in total in a regular tetrahedron?

White phosphorus spontaneously ignites in air to form a mixture of phosphorus(III) oxide and phosphorus(V) oxide.

(c) Write an equation for the formation of **i)** phosphorus(III) oxide and **ii)** phosphorus(V) oxide from the elements.

The structure of each oxide is also based on a regular tetrahedron. The phosphorus atoms remain at the vertices but are no longer bonded to each other. Instead the P atoms are joined by bridging oxygens.

(d) Draw the structure of phosphorus(III) oxide.

Phosphorus(V) oxide has a further oxygen atom bonded to each phosphorus atom at the vertex of the tetrahedron.

(e) Draw the structure of phosphorus(V) oxide.

Each oxide reacts with water to form an acid – phosphorus(V) oxide forms phosphoric(V) acid, H_3PO_4.

(f) Draw the molecular structure of phosphoric(V) acid, showing all of the bonds.

(g) Write the equation for the reaction forming phosphoric(V) acid.

A quantitative method for determining phosphate levels in aqueous solution involves adding ammonium molybdate, $(NH_4)_2MoO_4$, to form a precipitate of ammonium molybdophosphate. The structure of this solid is based on a cuboctahedron (**shown above**). A molybdenum atom lies at each vertex of the cuboctahedron and these are joined by oxygen atoms with every edge of the cuboctahedron being bridged by an oxygen atom. A further oxygen atom is joined to every vertex. A single phosphate unit lies at the centre of the structure with each of its four oxygen atoms coordinating to three molybdenum atoms.

(h) Calculate the oxidation state of molybdenum in ammonium molybdate.

(i) How many **i)** vertices and **ii)** edges are there in a cuboctahedron?

(j) Calculate the number of **i)** molybdenum atoms and **ii)** oxygen atoms in the molybdophosphate ion.

(k) Given that no atom changes its oxidation state during the formation of ammonium molybdophosphate, calculate the overall charge of the molybdophosphate ion and hence the formula of ammonium molybdophosphate.

3. This question is about phosphate levels in our environment

Excess phosphate is undesirable in our water supply since it promotes the growth of algae. High phosphate levels in the blood (hyperphosphataemia), caused by an inability of the kidneys to filter out excess phosphate from food, cause a range of bone diseases. A safe level of phosphate in blood serum is <1.8 mmol dm^{-3}.

To determine the concentration of phosphate ions in solution, ammonium molybdophosphate (formed by the addition of ammonium molybdate, $(NH_4)_2MoO_4$, to phosphate ions) is titrated with NaOH using a phenolphthalein indicator. One mole of ammonium molybdophosphate contains one phosphate unit and requires 23 moles of NaOH in the titration before the end point is reached.

(a) Which **two** of the following statements explain why so many moles of hydroxide are needed per mole of ammonium molybdophosphate? Circle the correct options in the answer booklet.

      A   Sodium hydroxide is a weak alkali
      B   Ammonium molybdophosphate has a very high molecular mass
      C   The molybdenum-containing species is acidic
      D   Phosphate ions are acidic
      E   The molybdophosphate ion contains many molybdenums

(b) 10.0 cm^3 of treated blood serum was reacted with excess ammonium molybdate and the precipitated ammonium molybdophosphate required 17.25 cm^3 of 0.0100 mol dm^{-3} NaOH. Calculate the concentration of phosphate in the blood serum in mol dm^{-3}.

(c) The degree to which a phosphate ion is protonated in aqueous solution depends on the pH. Use the following data to calculate which form of phosphate is prevalent in blood serum at pH 7.4.

$$H_3PO_{4\,(aq)} \rightleftharpoons H^+_{\,(aq)} + H_2PO_4^-{}_{(aq)} \qquad K_{a1} = 7.9 \times 10^{-3} \text{ mol dm}^{-3}$$
$$H_2PO_4^-{}_{(aq)} \rightleftharpoons H^+_{\,(aq)} + HPO_4^{2-}{}_{(aq)} \qquad K_{a2} = 6.2 \times 10^{-8} \text{ mol dm}^{-3}$$
$$HPO_4^{2-}{}_{(aq)} \rightleftharpoons H^+_{\,(aq)} + PO_4^{3-}{}_{(aq)} \qquad K_{a3} = 4.4 \times 10^{-13} \text{ mol dm}^{-3}$$
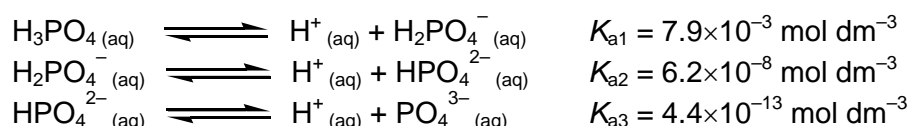
Lanthanum carbonate (marketed as *Fosrenol*^{TM}) is currently being used to treat hyperphosphataemia; aluminium sulfate has been used to control phosphate levels in ponds. Both $LaPO_4$ and $AlPO_4$ are essentially insoluble in water and are therefore removed as precipitates.

(d) Write the equation for the reaction between lanthanum carbonate and the hydrochloric acid present in the stomach.

The saturated concentrations of these phosphates can be worked out from their solubility products (K_{sp}):

$$K_{sp}(LaPO_4) = [La^{3+}{}_{(aq)}]_{sat}[PO_4^{3-}{}_{(aq)}]_{sat} = 7.08 \times 10^{-27} \text{ mol}^2 \text{ dm}^{-6}$$

$$K_{sp}(AlPO_4) = [Al^{3+}{}_{(aq)}]_{sat}[PO_4^{3-}{}_{(aq)}]_{sat} = 9.84 \times 10^{-21} \text{ mol}^2 \text{ dm}^{-6}$$

(e) Calculate the concentration of a saturated solution of lanthanum phosphate.

(f) If an equimolar solution of aluminium and lanthanum ions is added slowly to a solution containing phosphate ions, which phosphate would precipitate first?

4. This question is about the analysis of a flame-retardant

Retardol C, Pyroset TKC and Proban CC are three trade names given to a flame-retardant used to produce crease-resistant and flame-retardant finishes on textiles such as those used to make nightclothes for children.

The flame-retardant is a salt , $X^+ Y^-$, prepared by the reaction between phosphine, PH_3, and methanal in dilute aqueous acid. The anion Y^- simply depends on which acid was used in the preparation.

(a) Draw the structures of phosphine and methanal, clearly indicating the geometry of each molecule.

The mass spectrum of X^+ (down to 50 m/z) is shown over the page, together with the proton and phosphorus-31 NMR spectra. The carbon-13 NMR spectrum of X^+ (not shown) shows there is just one environment of carbon atom in the cation.

(b) By inspection of the ^1H NMR spectrum, suggest the number of environments of hydrogen atoms in X^+. What is the ratio of the number of hydrogen atoms in the different environments?

When the sample is mixed with a little D_2O instead of H_2O, the signal at 6.25 ppm in the ^1H NMR spectrum disappears.

(c) What functional group does this suggest may be present in X^+?

The ^{31}P NMR spectrum shows one signal split into a multiplet due to coupling to hydrogens.

(d) How many hydrogen nuclei is the phosphorus coupling to?

The mass spectrum shows the molecular ion and a number of fragmentation peaks.

(e) i) The fragmentation process shows consecutive losses of a 30 mass unit. Suggest the formula for the fragment lost.

ii) Suggest a formula for the X^+ ion.

iii) A mass spectrum of the D_2O solution of X^+ no longer shows a peak at 155, but instead shows a peak at a higher m/z. At what value of m/z would you expect this new peak to come?

(f) i) Suggest a structure for the cation X^+, clearly indicating its geometry.

ii) Suggest a structure for the ion at $m/z = 65$.

Positive ion mass spectrum of X+

100
80
60
40
20
0

65

95

125

155

50   60   70   80   90   100   110   120   130   140   150   160   170   180   m/z

^{1}H NMR spectrum in H_2O + co-solvent

2.0 Hz

10× expansion

(H$_2$O)

4.45   4.40

11.0   10.0   9.0   8.0   7.0   6.0   5.0   4.0   3.0   2.0   1.0   ppm

2.0 Hz

^{31}P NMR spectrum in H_2O

27.00   26.95   26.90   26.85   ppm
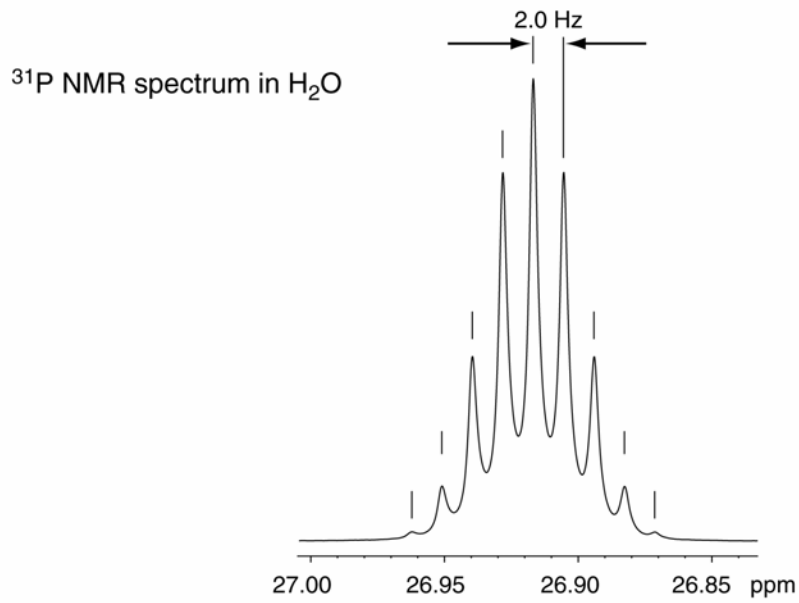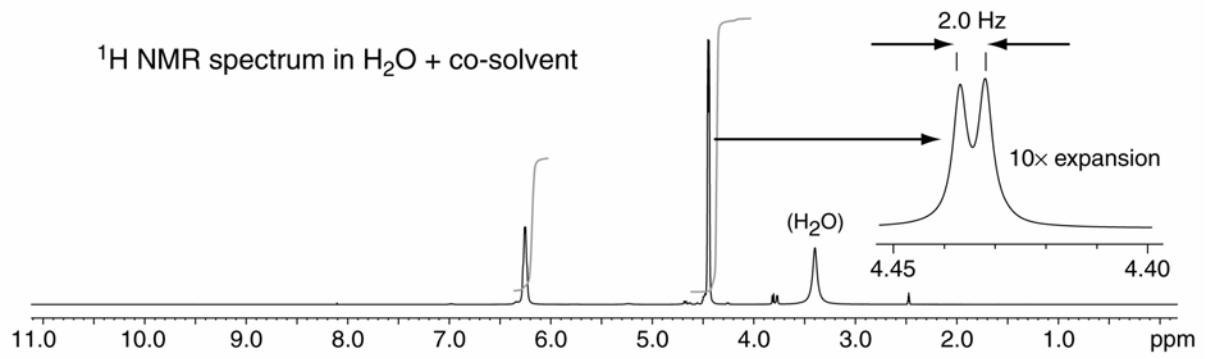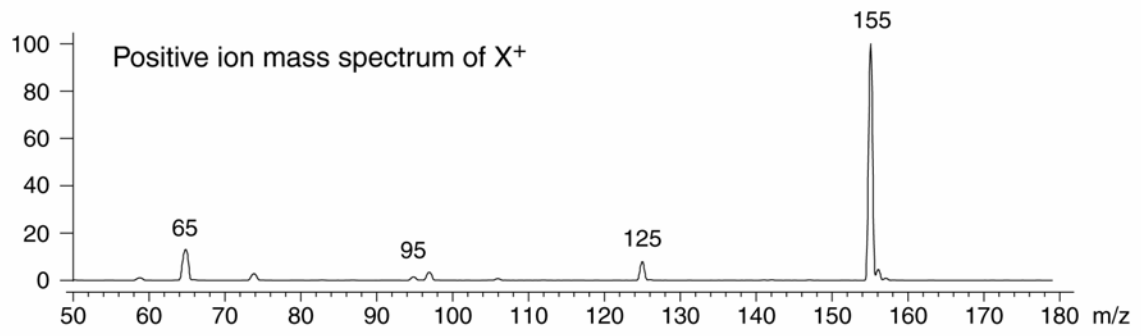
5. This question is about the synthesis of Tamiflu ™

Tamiflu is the anti-influenza drug currently being used to treat so-called 'Bird-flu'. Its structure is shown on the right. The bold wedged bond is coming out of the plane of the paper, the hashed bonds are going into the plane.

Tamiflu[TM]

$C_{16}H_{28}N_2O_4$
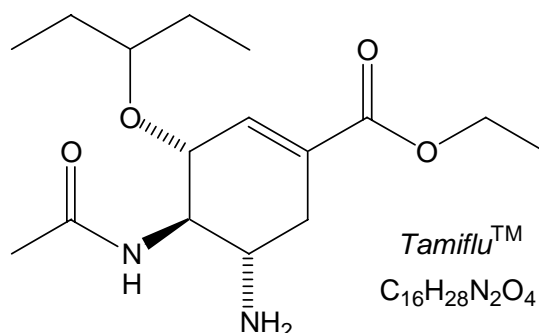
In order to increase its solubility, Tamiflu is actually sold as the phosphate salt.

(a) On the structure in your answer booklet, circle the atom which will be protonated in the salt.

One of the problems in the synthesis of the drug is ensuring the correct stereochemistry at each of the stereogenic (chiral) centres in the structure.

(b) i) On the structure in your answer booklet, mark with an asterix each chiral centre.

ii) What is the total number of stereoisomers possible for this structure?

Two syntheses of Tamiflu which have been tried start from the naturally occurring products *Quinic acid* and *Shikimic acid*.

Quinic acid

$C_7H_{12}O_6$

Shikimic acid

$C_7H_{10}O_5$
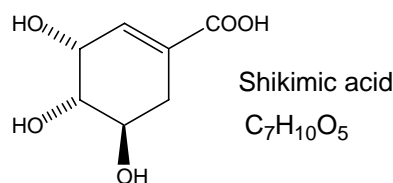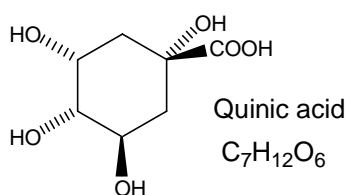
Shikimic acid has the advantage of already having the double bond in place but quinic acid has the advantage of being much cheaper.

One of the problems using either acid is trying to control which of the –OH groups reacts in a given step. The first step starting from quinic acid is therefore to protect the two –OH groups on the same side of the ring on adjacent carbon atoms by forming a so-called *acetal* group by the acid-catalysed reaction with propanone:

propanone
/ H⁺ cat

– H_2O

$C_7H_{12}O_6$

$C_{10}H_{16}O_6$
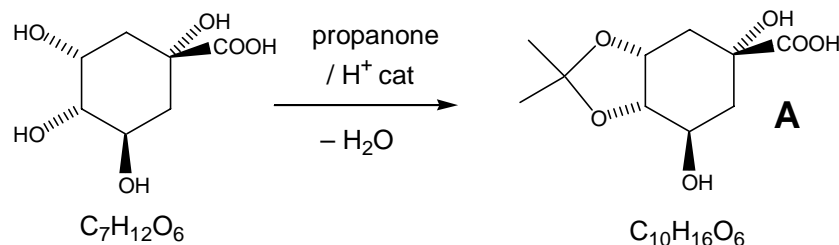
The next steps in the synthesis are outlined below. Inorganic by-products are not shown in the scheme.

A	ethanol + catalyst	**B**	Cl–S(=O)(=O)–CH₃	**C**	SO₂Cl₂ + base	**D** + **E** + **F**

A
$C_{10}H_{16}O_6$

C
$C_{13}H_{22}O_8S$

D major product

E unwanted isomer

F $C_{13}H_{21}ClO_7S$ left over intermediate
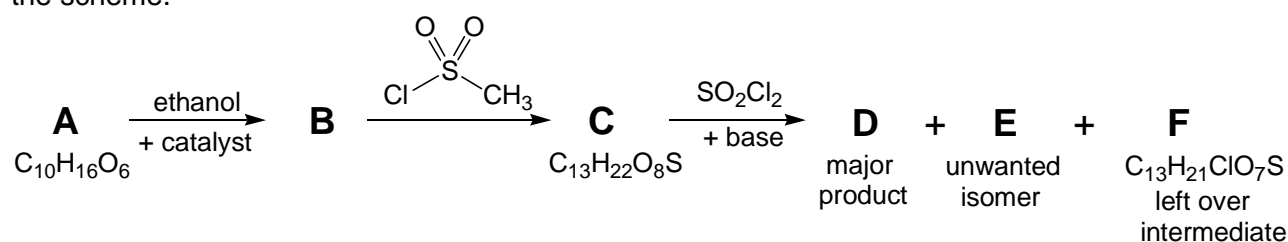
**D** reacts with an excess of pentan-3-one to give **G** as shown below.
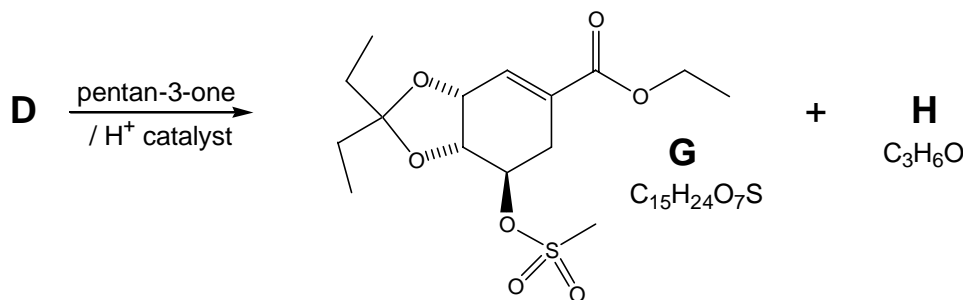
(c) Draw the structures of compounds **B**, **C**, **D**, **E** and **F** and for the by-product **H**, showing the correct stereochemistry by the use of bold and hashed bonds as appropriate.

G may easily be prepared from the more expensive Shikimic acid as outlined below. Inorganic by-products are not shown.
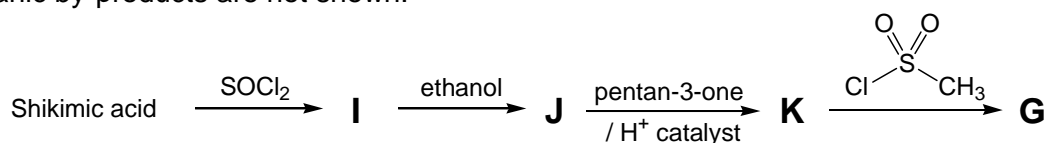
(d) Draw the structures of compounds **I**, **J**, and **K** showing the correct stereochemistry as appropriate.

The acetal in **G** may be opened up under reducing conditions to give mainly **L** (shown below). On treatment with base **L** cyclises to give **M** which contains a 3-membered ring. The new ring is opened up with sodium azide yielding a mix of isomers, **N** and **O** either of which yields the same cylic compound **P** on treatment with trimethylphosphine. Further treatment with sodium azide opens the new ring to give mainly **Q** which upon acylation and hydrogenation finally yields neutral Tamiflu as outlined below.
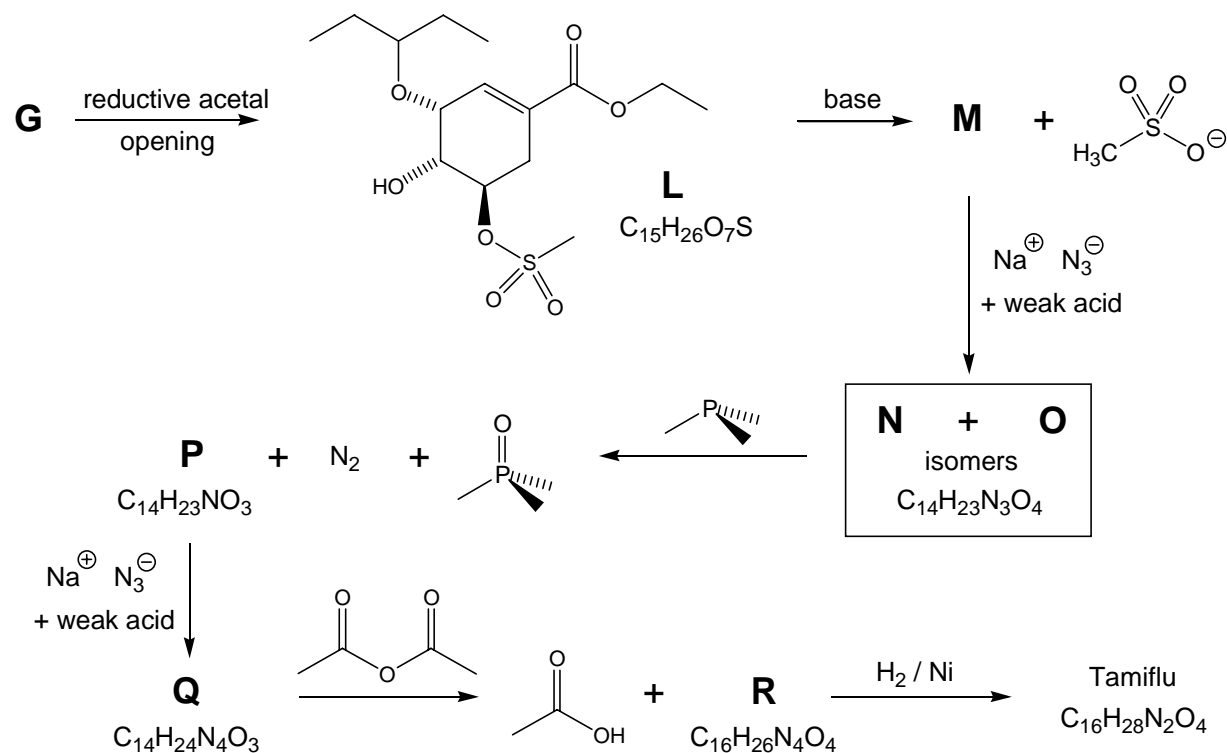
(e) On the structure in your answer booklet, circle the most acidic proton in **L** which is removed by the base.

(f) Draw the structures of compounds **M**, **N**, **O**, **P**, **Q** and **R** again showing the correct stereochemistry as appropriate.

6. This question is about chlorine dioxide

Chlorine dioxide, ClO_2, was the first oxide of chlorine to be discovered. Although unstable as a liquid or gas, it is now produced on a very large scale for the bleaching of wood pulp and for water treatment. More recently, it has been used to remove mould from houses flooded following Hurricane Katrina in New Orleans.

A mobile chlorine dioxide generator used for decontamination

(a) Draw a 'dot & cross' diagram of a ClO_2 molecule showing the outershell electrons. Give an estimate of the O-Cl-O bond angle.

Chlorine dioxide was first obtained by Humphry Davy by the very hazardous disproportionation of chloric acid, $HClO_3$, formed by adding concentrated sulfuric acid to a solid chlorate such as $KClO_3$. The other products of this disproportionation reaction are water and perchloric acid, $HClO_4$.

(b) **i)** Give the oxidation states of chlorine in ClO_2, $HClO_3$ and $HClO_4$.

   ii) Using these oxidation states, or otherwise, write a balanced equation for the formation of ClO_2 from $HClO_3$.

   iii) Give the structure of a molecule of perchloric acid. What is the bond angle in the perchlorate ion?

For safety reasons, chlorine dioxide is usually generated where it is to be used. For pulp bleaching, ClO_2 is made by the partial reduction of $NaClO_3$ under acidic conditions using a variety of reducing agents, for example, sulfur dioxide.

(c) Write a balanced equation for the formation of ClO_2 by this reaction, using sulfuric acid for acidification (there is only one other product).

In the laboratory, ClO_2 is produced by the reaction between $NaClO_3$ and oxalic acid, $(COOH)_2$, again in the presence of sulfuric acid. This also generates CO_2, which dilutes the ClO_2.

(d) Write a balanced equation for the formation of ClO_2 by this reaction.

The company *Sabre* produce their ClO_2 by oxidising sodium chlorate(III) with chlorine gas.

(e) **i)** Suggest the formula for sodium chlorate(III).

   ii) Write a balanced equation for the formation of ClO_2 from chlorine and sodium chlorate(III).

Acknowledgements

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UK Round One - 2007

MARKSCHEME

Notes

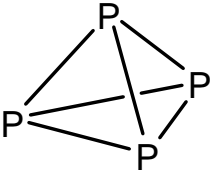**Chemical equations may be given as sensible multiples of those given here.**
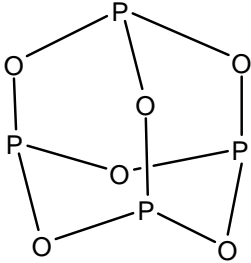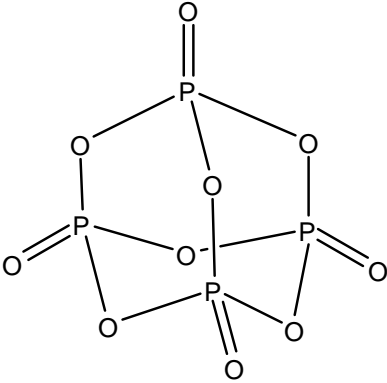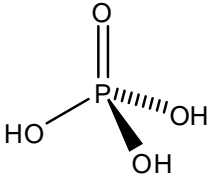
State symbols do not need to be included in the chemical equations to obtain the mark(s).

Answers should be given to an appropriate number of significant figures although the marker should penalise this only once.
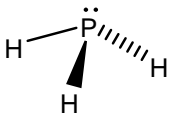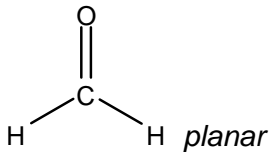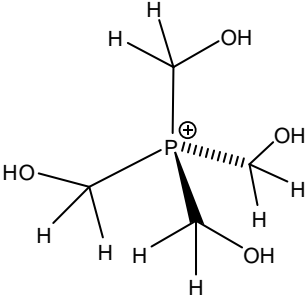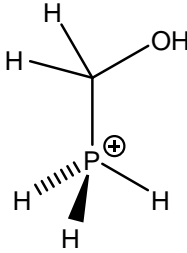
As a general rule, markers should aim to reward correct chemistry. Errors cannot be ignored but markers should ensure that candidates are not penalised for _trivial_ errors.
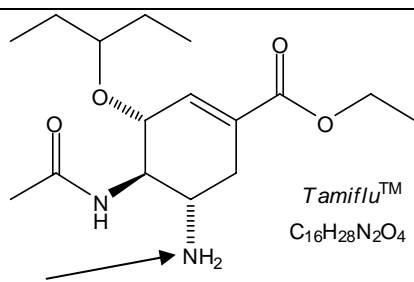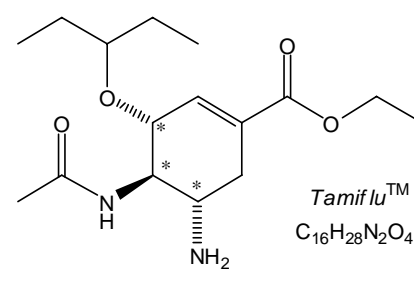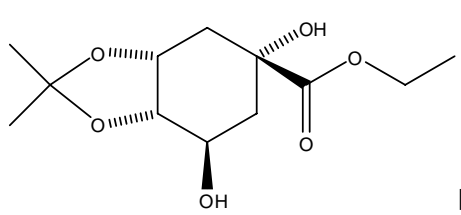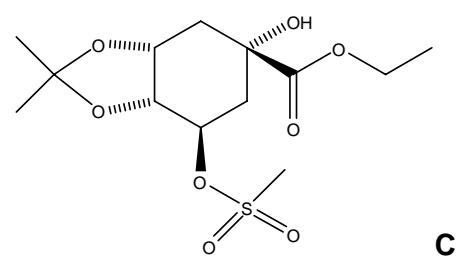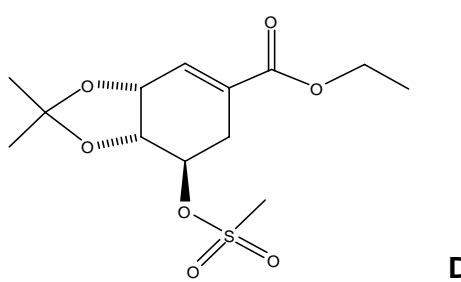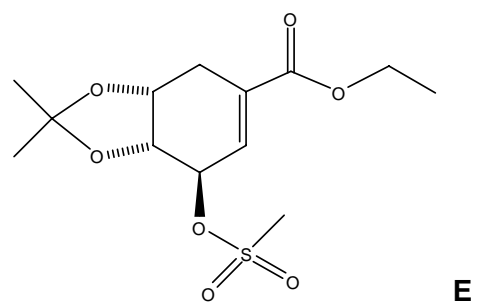
Total mark: 73
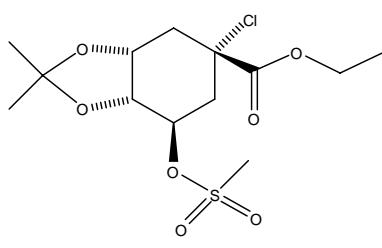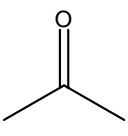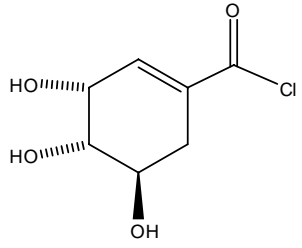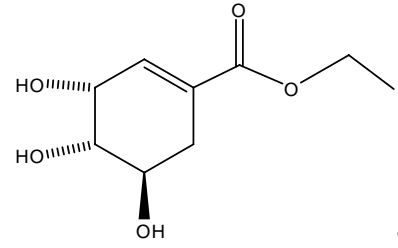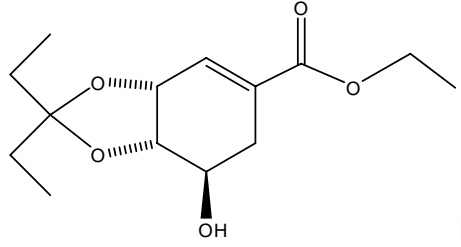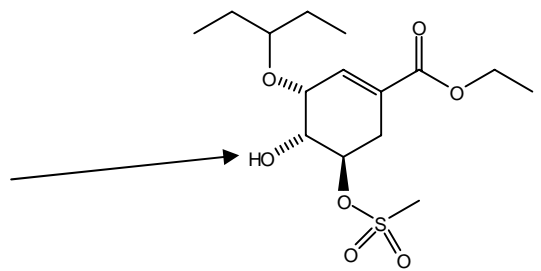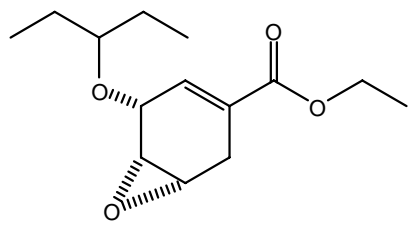
Question 1			**Mark**
(a)		$H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$	1
(b)		Mass of hydrogen = 80 t	1
		Mass of oxygen = 638 t	1
(c)		Volume of hydrogen = 1470 m^3 Volume of oxygen = 538 m^3 Total tank capacity = 2010 m^3 _2 marks if total tank capacity correct. If incorrect, allow 1 mark for volume of H_2 **or** O_2 correct._	2
(d)		- 9769 kJ mol^{-1}	1
(e)		2.6 MJ (2.6 x 10^9 kJ) _Don't penalise if – sign present; allow 1 for correct working even if final answer incorrect._	2
			Marks = 8

Question 2				Mark
(a)				1
(b)		Number of edges: 6		1
(c)	i)	$P_4 + 3O_2 \longrightarrow P_4O_6$	(*allow mark for any correctly balanced equation giving P_2O_3 or P_4O_6*)	1
	ii)	$P_4 + 5O_2 \longrightarrow P_4O_{10}$	(*allow mark for any correctly balanced equation giving P_2O_5 or P_4O_{10}*)	1
(d)		Structure of phosphorus(III) oxide:	**(e)** Structure of phosphorus(V) oxide:	1 + 1
(f)		(*stereochemistry not required*)		1
(g)		$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$	(*allow balanced equation from P_2O_5*)	1
(h)		Oxidation state of molybdenum: $+ 6$	(*sign not essential for mark*)	1
(i)	**(i)**	Number of vertices: 12	**(ii)** Number of edges: 24	1 + 1
(j)	**(i)**	Number of Mo atoms: 12	**(ii)** Number of O atoms: 40 (*allow 1 mark for 36 O atoms*)	1 + 2
(k)		Overall charge of the molybdophosphate ion: $- 3$		1
		Formula of ammonium molybdophosphate: $(NH_4)_3Mo_{12}O_{40}P$ (*allow variants e.g. $N_3H_{12}Mo_{12}O_{40}P$*)		1
				Marks = 16

Question 3			Mark
(a)		**C & E**	1
(b)		Concentration of phosphate: 7.5×10^{-4} mol dm^{-3} *(2 marks for fully correct answer, allow 1 mark for correct working if final answer incorrect)*	2
(c)		Form of phosphate: HPO_4^{2-}	1
(d)		$6HCl + La_2(CO_3)_3 \longrightarrow 2LaCl_3 + 3CO_2 + 3H_2O$ *(2 marks if completely correct; 1 mark if incorrect equation but formula for $La_2(CO_3)_3$ is correct)*	2
(e)		8.41×10^{-14} mol dm^{-3}	1
(f)		$LaPO_4$	1
			Marks = 8

Question 4			Mark
(a)		*pyramidal not planar* *planar*	1 + 1
(b)		Number of environments of hydrogen: 2 Ratio: 1:2	1 + 1
(c)		Functional group: -OH *(or alcohol, hydroxyl)*	1
(d)		Number of hydrogen nuclei: 8	1
(e)	(i)	Formula for fragment: CH_2O	1
	(ii)	Formula for the X$^+$ ion: $C_4H_{12}O_4P^{\oplus}$ *(allow correct variants)*	1
	(iii)	*m/z* value: 159	1
(f)	(i)	Structure for X$^+$: (ii) Structure for ion at *m/z* = 65:	1 + 1
			Marks = 11

Question 5			Mark
(a)		*TamifIu*^{TM} is written in image; Atom/group indicated should be circled	1
(b)	**(i)**		1
	(ii)	Total number of stereoisomers: $2^3 = 8$	1
		For parts (c), (d) and (f): for each of the structures, award 1 mark if completely correct as shown below. Deduct ½ mark (for each structure) if stereochemistry incorrect.	
(c)		**B** **C**	1 1
		D **E**	1 1

(c)		**F** **H**	1 1
(d)		**I** **J**	1
			1
		K	1
(e)			1
(f)	**M**		1

Question 5 continued			Mark
(f)	N (or O)		1
	O (or N)		1
	P		1
	Q		1
	R		1
			Mark = 19

Question 6				Mark
(a)		Bond angle: 110 – 120° *(actual angle: 117.4)*		1 1
(b)	(i)	Oxidation state of chlorine in ClO_2: + 4 Oxidation state of chlorine in $HClO_3$: + 5 Oxidation state of chlorine in $HClO_4$: + 7 *Award 2 marks for all 3 correct, 1 mark for 2 correct*		2
	(ii)	$3HClO_3 \longrightarrow 2ClO_2 + HClO_4 + H_2O$		1
	(iii)	Structure: 	Bond angle: 109.5° (109° 28') *(allow 109°)*	1 1
(c)		$2NaClO_3 + SO_2 \xrightarrow{(H_2SO_4)} 2ClO_2 + Na_2SO_4$ *Allow as ionic*		1
(d)		$2NaClO_3 + (COOH)_2 + H_2SO_4 \longrightarrow 2ClO_2 + 2CO_2 + 2H_2O + Na_2SO_4$ *Allow as ionic: $2ClO_3^- + (COOH)_2 + 2H^+ \longrightarrow 2ClO_2 + 2CO_2 + 2H_2O$*		1
(e)	(i)	$NaClO_2$		1
	(ii)	$2NaClO_2 + Cl_2 \longrightarrow 2ClO_2 + 2NaCl$		1
				Marks = 11