

Cambridge Chemistry Challenge Lower 6th

June 2015

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.

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

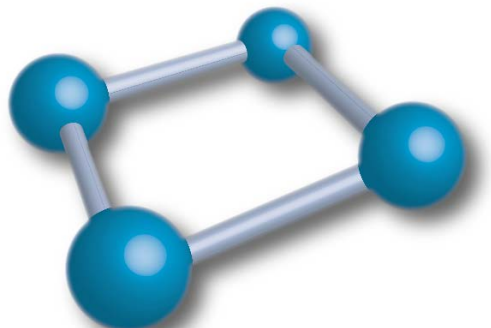
symbol
atomic number
mean atomic mass

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

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

1. This question is about O₄ sports drinks

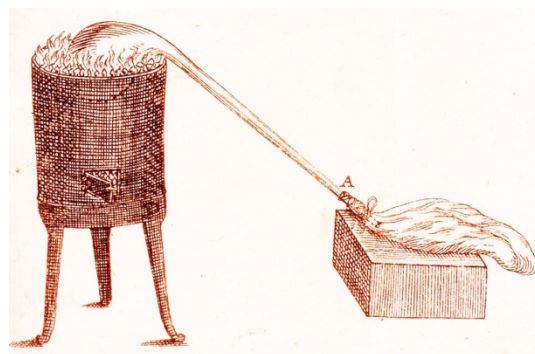
Tetraoxygen, O₄ (puckered ring)



A number of so-called 'sports drinks' have appeared on American markets claiming to contain dissolved oxygen in the form of O₄ molecules.

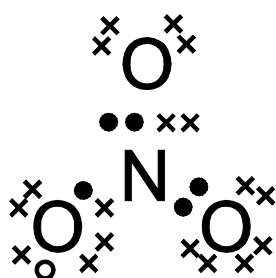
Information from the website of one company claims: *The oxygen is stabilized using our patented process, which mixes together water, oxygen and minerals, altering the unstable O₂ molecule to create a stable O₄ molecule.*

Despite the fanciful claims of the manufacturers, the most stable form of oxygen is O₂. This was first prepared around 1770 by the Swedish chemist Carl Wilhelm Scheele by heating various substances, including mercury(II) oxide, silver(I) carbonate, potassium nitrate(V), or a mixture of concentrated sulfuric acid and manganese(IV) oxide, and collecting the gas in a bladder.



- (a) Give the chemical equations for Scheele's preparation of oxygen by heating the substances or mixtures below. In each equation, underline the element which has been **reduced** during the process.
- (i) mercury(II) oxide
 - (ii) silver(I) carbonate
 - (iii) potassium nitrate(V) [the product contains the nitrate(III) ion]
 - (iv) concentrated sulfuric acid and manganese(IV) oxide

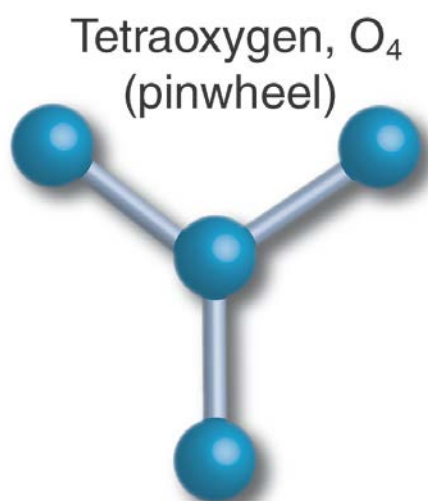
A dot-and-cross diagram for the nitrate(V) ion, NO₃⁻, is shown below. There are a number of other species which may be described as being *isoelectronic* with the nitrate(V) ion. Such species have the same geometry as the NO₃⁻ ion, the same *total* number of electrons as the NO₃⁻ ion with the electrons arranged in a similar manner, but one or more of the nuclei have been replaced with those from different elements.



- electron from central atom (N)
- × electron from surrounding oxygen
- additional electron

- (b) Using the same coding as above and taking care with any extra electrons and hence overall charges, give the formula, and draw the dot-and-cross diagram, for the species isoelectronic with the nitrate ion, NO_3^- , where the central nitrogen has been replaced by:
- (i) carbon
 - (ii) boron
 - (iii) oxygen
- (c) Give the formula for, and name of, the neutral species isoelectronic with the nitrate(III) ion.

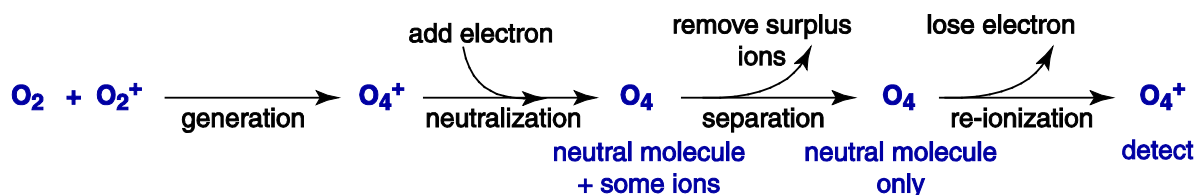
Whilst the company suggest their O_4 exists as a puckered ring (shown earlier), other geometries have been suggested, including a so-called 'pinwheel' structure shown on the right. This planar structure has been calculated to be 89.3 kJ mol^{-1} higher in energy than the puckered ring. In each structure, the bond lengths are the same.



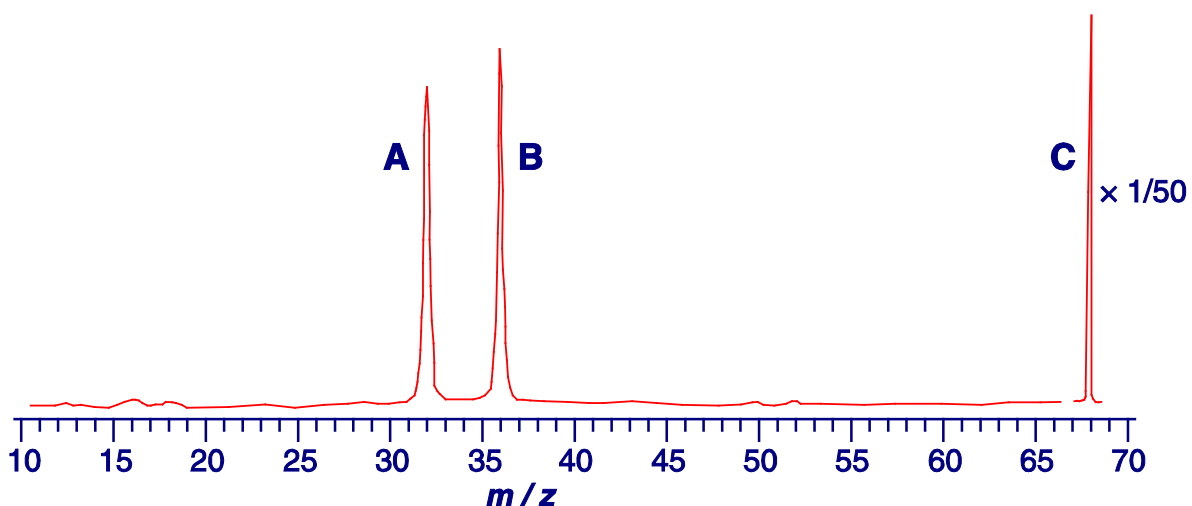
The standard enthalpy of formation of pinwheel O_4 is calculated to be $480.0 \text{ kJ mol}^{-1}$.

- (d) Given the activation energy for the dissociation of puckered ring O_4 into $2\text{O}_2(\text{g})$ has been calculated to be 48.7 kJ mol^{-1} , with the aid of a diagram or otherwise, calculate the activation energy for the formation of puckered ring O_4 from $\text{O}_2(\text{g})$.

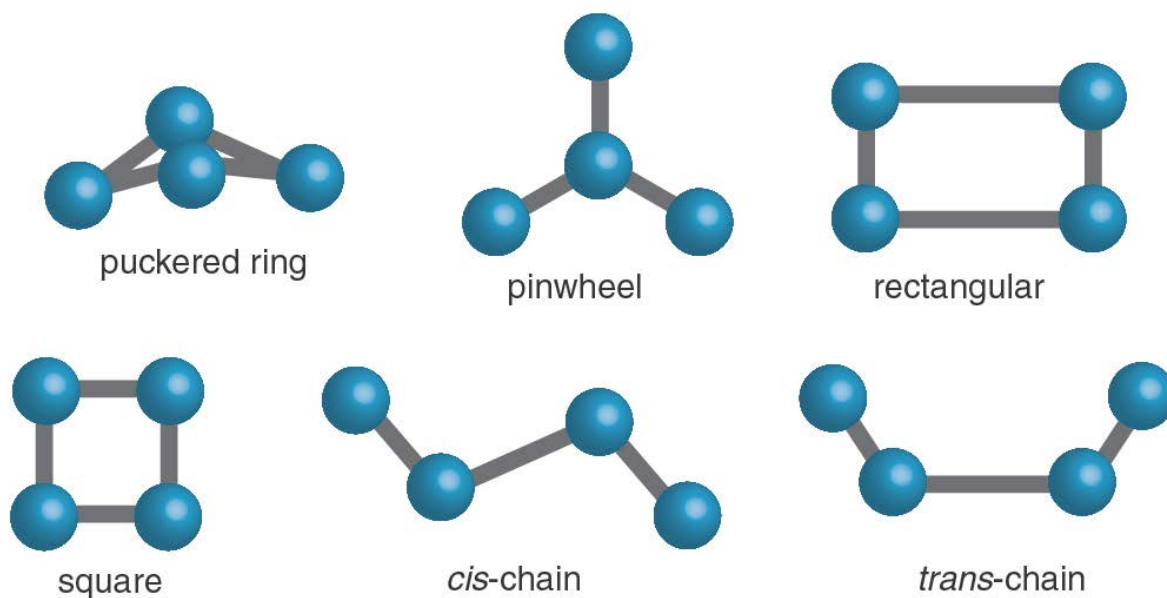
The closest any researchers have come to detecting an O_4 molecule is using a type of mass spectrometry called neutralization-reionization MS (NR-MS). In this technique, the slightly more stable O_4^+ ion was made by the collision between an O_2 molecule and O_2^+ ion. Some of the resulting O_4^+ ions were then neutralized by the addition of an electron. Any charged species were removed from the mixture by deflection to leave a stream of neutral O_4 molecules. These were then re-ionized by removing an electron and any resulting O_4^+ ions and their decay products were detected. This process is summarized below:



In one experiment, the O_4^+ ion was prepared from a mixture of isotopically pure $^{16}\text{O}_2$ and $^{18}\text{O}_2$. The resulting ion had the formula $^{16}\text{O}_2^{18}\text{O}_2^+$. The final mass spectrum is shown over the page.



- (e) Give the formulae (specifying the particular isotopes) for the ions **A**, **B**, and **C**.
- (f) Which of the following shapes of O_4 are most consistent with the data from the NR-MS experiment? Tick one or more in your answer booklet.



The researchers concluded that the O_4 molecule is not stable, but is *metastable*, i.e. it has a fairly short existence, but can exist as a molecule. The minimum lifetime was calculated from the time-of-flight of the neutral molecule – i.e. the time it took after formation to travel the distance in the instrument before being re-ionized.

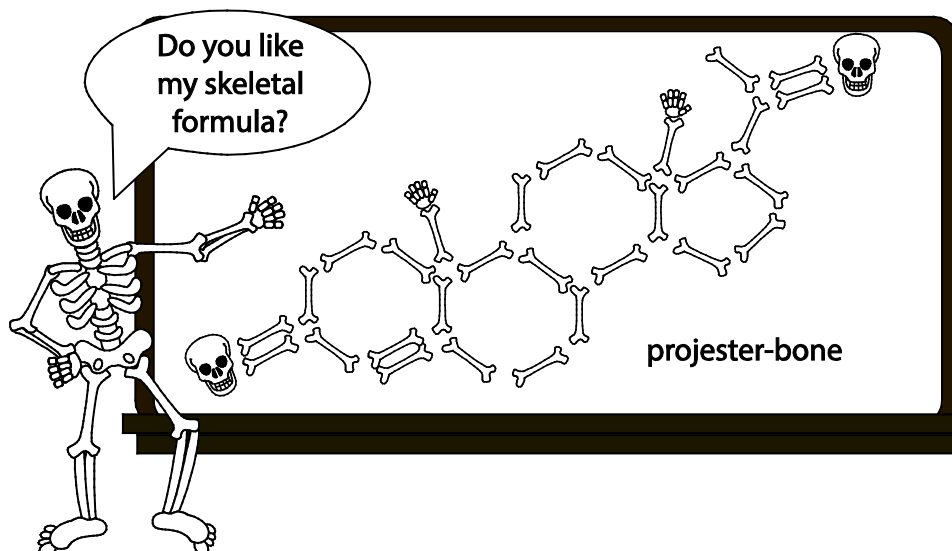
- (g) Calculate the approximate time (in seconds) an $^{18}O_4$ molecule would take to travel the 10.0 cm path inside the instrument if initially accelerated to 4.00 keV.

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

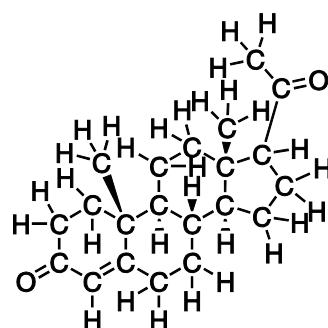
$$\text{Avogadro constant} = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$\text{The kinetic energy of a particle of mass } m \text{ moving and velocity } v \text{ is given by } \text{k.e.} = \frac{1}{2} m v^2$$

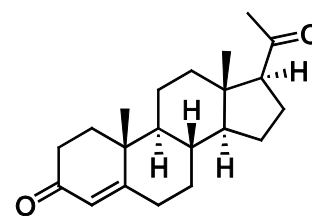
2. This question is about skeletal formulae



At school, most organic molecules are drawn as structural formulae. Whilst this is a good way of drawing small molecules, it becomes confusing for larger molecules. With complicated molecules, such as Progesterone shown on the right, it is better to draw them as skeletal formulae.

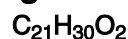


Structural Formula



Skeletal Formula

Progesterone



Various different representations of organic molecules are shown in **Table 1**.

Table 1				
1	2	3	4	5
6	7	8	9	

- (a) In your answer booklet indicate which (if any) of the molecules shown in Table 1 are the same as those given below. If there are none, write zero.

(i) ethene

(ii) butane

(iii)

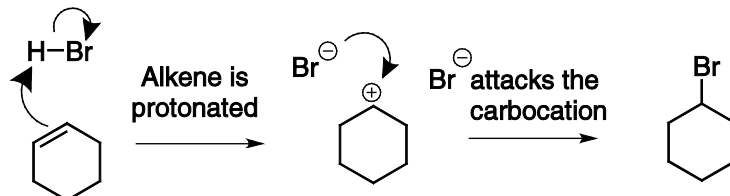
(iv) *trans*-but-2-ene

Alkenes react with HBr to produce bromoalkanes.

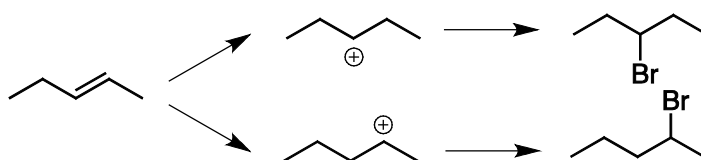
- (b) In your answer booklet, circle all the terms that can be used to describe the reaction of alkenes with HBr:

Free radical Electrophilic Nucleophilic Addition Substitution

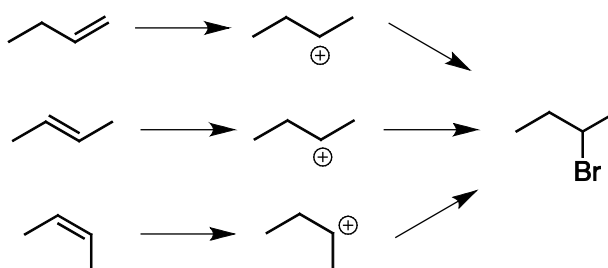
The reaction of HBr with alkenes occurs *via* a carbocation intermediate as shown below:



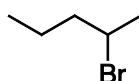
The reaction of HBr with certain alkenes gives more than one product as two different cations can be formed (n.b. often there are major and minor products of these reactions but we are not considering this here).



Equally the same bromoalkane may be formed from several different alkenes:

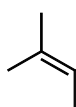


- (c) Draw the three possible alkenes which could have reacted with HBr to form the molecule shown below:

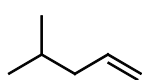


- (d) For each of the following alkenes, choose which bromoalkanes from **Table 2** could be formed in a reaction with HBr (ignoring minor and major products).

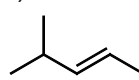
i)



ii)



iii)



iv)

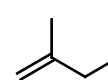
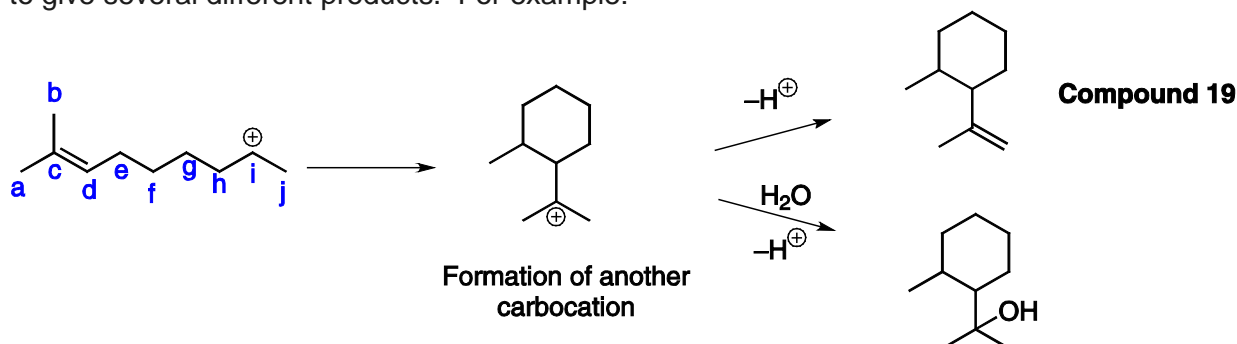


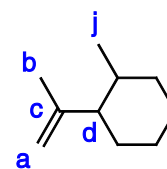
Table 2				
10	11	12	13	14
15	16	17	18	

In the absence of strong nucleophiles in the solution, such as Br^- , the carbocation can be attacked by the electrons in a $\text{C}=\text{C}$ double bond somewhere else in the molecule, which act as a nucleophile. This leads to the cyclization of the molecule and the production of another carbocation, which can go on to give several different products. For example:

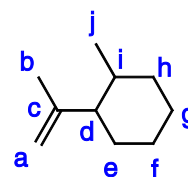


It can sometimes be difficult to work out which atoms become connected in a cyclization reaction, however there is a general strategy which we will outline by considering the reaction to form **Compound 19**. It is important to remember that no C-C single bonds are broken in the reaction.

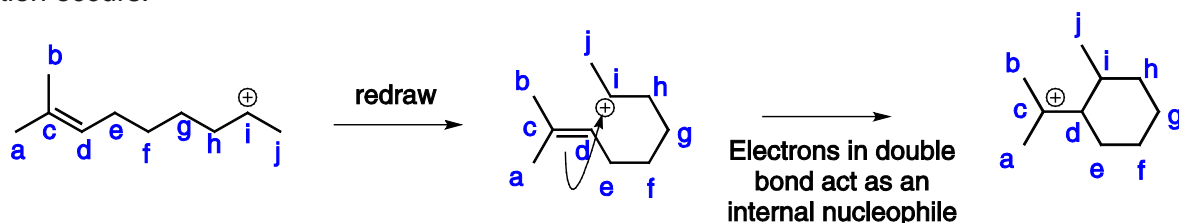
- (1) Look for small groups of atoms in the product that are unchanged in connectivity from the starting material and label them. It is a good idea to start by trying to identify where the atoms at the ends of the starting material appear in the product. In more complex molecules look for features such as rings and methyl groups. Atoms a, b, c, d and j in **Compound 19** can be labelled using this approach.



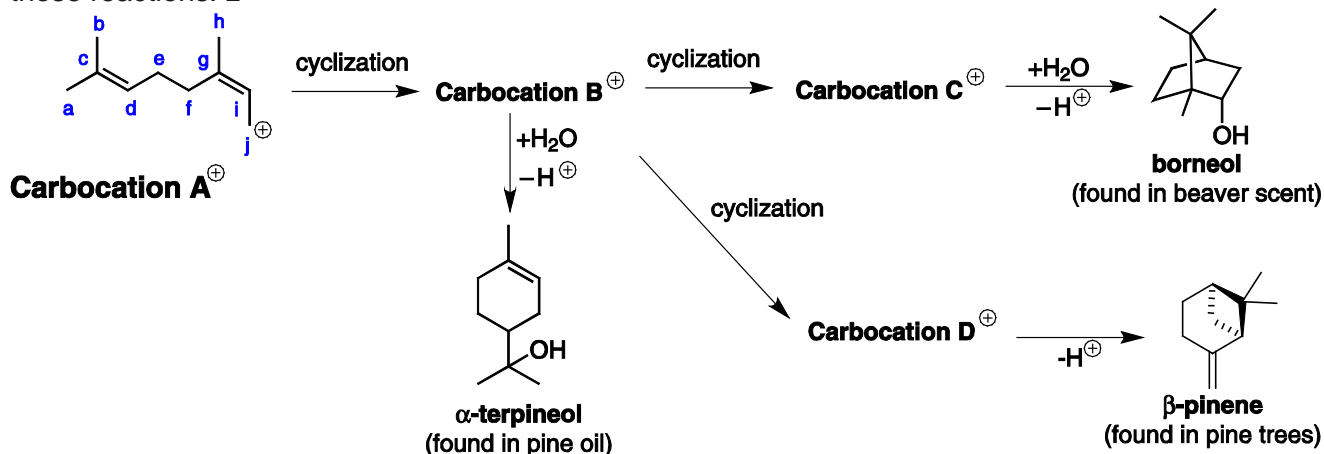
- (2) Start from one of the groups of atoms which you are confident you have identified correctly and see if you are now able to trace out the path to the next group you are confident about.



If we redraw the starting material folded round to resemble the product, it is easy to see how the reaction occurs:



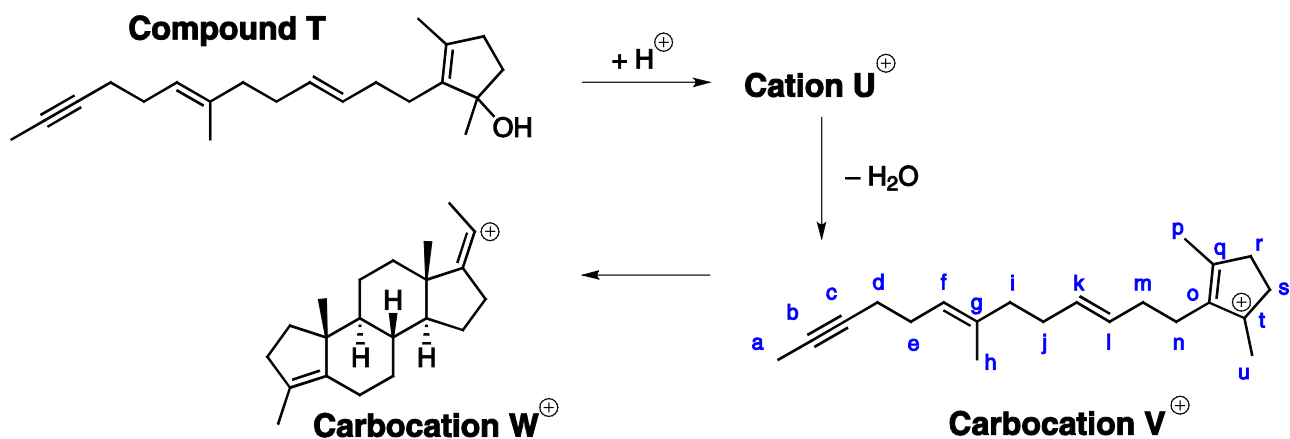
Carbocation A⁺ is readily formed in nature and can react to form various natural products by one or more cyclizations of double bonds onto carbocations. No C-C single bonds are broken in any of these reactions. z



- (e) (i) Write down the letters (from **A⁺**) of the pair of carbon atoms that are connected in order to form **α-terpineol**.
 (ii) Suggest a structure for intermediate **Carbocation B⁺**.
- (f) (i) Write down the letters (from **A⁺**) of the pair of carbon atoms that are connected in order to form **borneol** from the cyclization of **Carbocation B⁺**.
 (ii) Suggest a structure for intermediate **Carbocation C⁺**.
- (g) (i) Write down the letters (from **A⁺**) of the pair of carbon atoms that are connected in order to form **β-pinene** from the cyclization of **Carbocation B⁺**.
 (ii) Suggest a structure for intermediate **Carbocation D⁺**.

The biological synthesis of steroid hormones was mimicked in the conversion of **Compound T** into the hormone Progesterone. The reaction starts with the treatment of **Compound T** with acid to give **Cation U⁺**, which then loses water to form **Carbocation V⁺**.

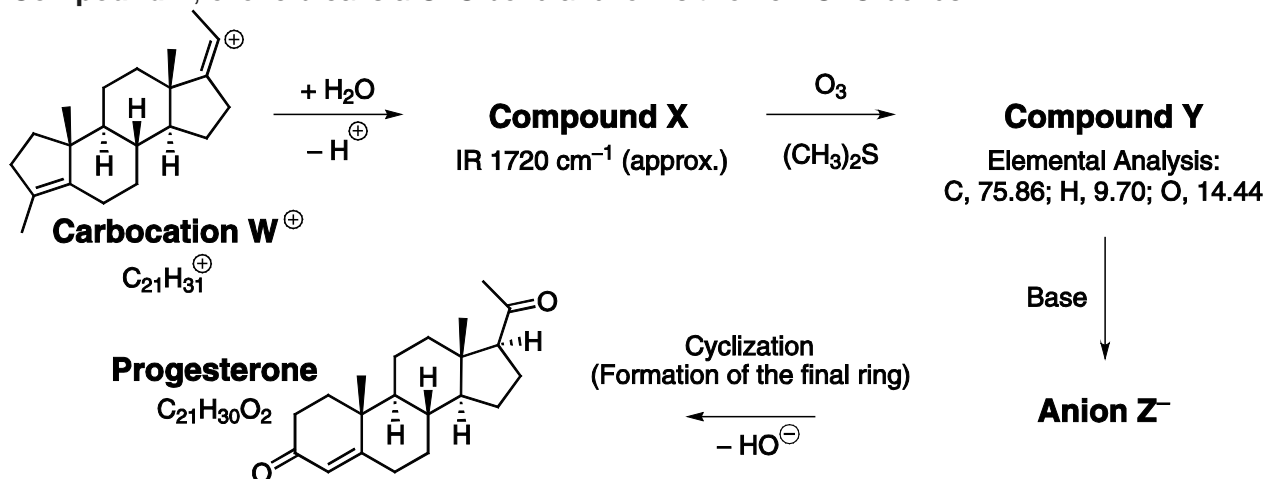
- (h) Draw the structure of **Cation U⁺**.



Carbocation V⁺ then undergoes cyclization to form **Carbocation W⁺**. No C–C single bonds are broken in this process.

- (i) Write down the letters of the pairs of carbon atoms that are connected in the cyclization of **Carbocation V⁺** to **Carbocation W⁺**.

Carbocation W⁺ can then be converted into Progesterone in three steps. Note that in forming **Compound Y**, ozone breaks a C=C bond and forms two new C=O bonds.



- (j) Draw the structures of **Compound X**, **Compound Y** and **Anion Z⁻**.

Acknowledgements

We would like to thank those who support C3L6:

aramco



The Royal Society of Chemistry

University of Cambridge Department of Chemistry

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References for Question 1

Drinks claiming to contain O₄ are available in Canada and the USA.

The picture of the preparation of oxygen taken from *Chemische Abhandlung von der Luft und dem Feuer*, Carl Wilhelm Scheele, 1777.

Journal of Chemical Theory and Computation, **9**, 2013, 247-262

"Structure, Energy, and Vibrational Frequencies of Oxygen Allotropes O_n (n ≤ 6) in the Covalently Bound and van der Waals Forms: Ab Initio Study at the CCDC(T) Level"

Oleg B. Gadzhiev *et al.*

Angew. Chem. Int. Ed., **40**, 2001, 4062-4065

"Experimental Detection of Tetraoxygen"

J. Lindsay Oaks *et al.*

References for Question 2

Journal of the American Chemical Society, **100**, 1978, 4274-4282

"Acetylenic bond participation in biomimetic polyene cyclizations. Model studies directed toward the synthesis of 20-keto steroids. Synthesis of dl-progesterone and dl-DELTA.4-androstene-3,17-dione"

Michael B. Gravestock