

Received November 5, 1977

POLYFLUOROCYCLOALKENES. PART XIV.[1] A NOVEL HYDROLYSIS PRODUCT OF  
DECAFLUOROCYCLOHEPTA-1,4-DIENE. CRYSTAL STRUCTURE OF  
2H,4H-HEXAFLUORO-1,5-DIMETHOXY-8-OXABICYCLO(3,2,1)OCTAN-3-ONE

M.J.HAMOR, T.A.HAMOR, C.M.JENKINS, R.STEPHENS and J.C.TATLOW

Department of Chemistry, University of Birmingham, P.O.Box 363,  
Birmingham B15 2TT (Great Britain)

SUMMARY

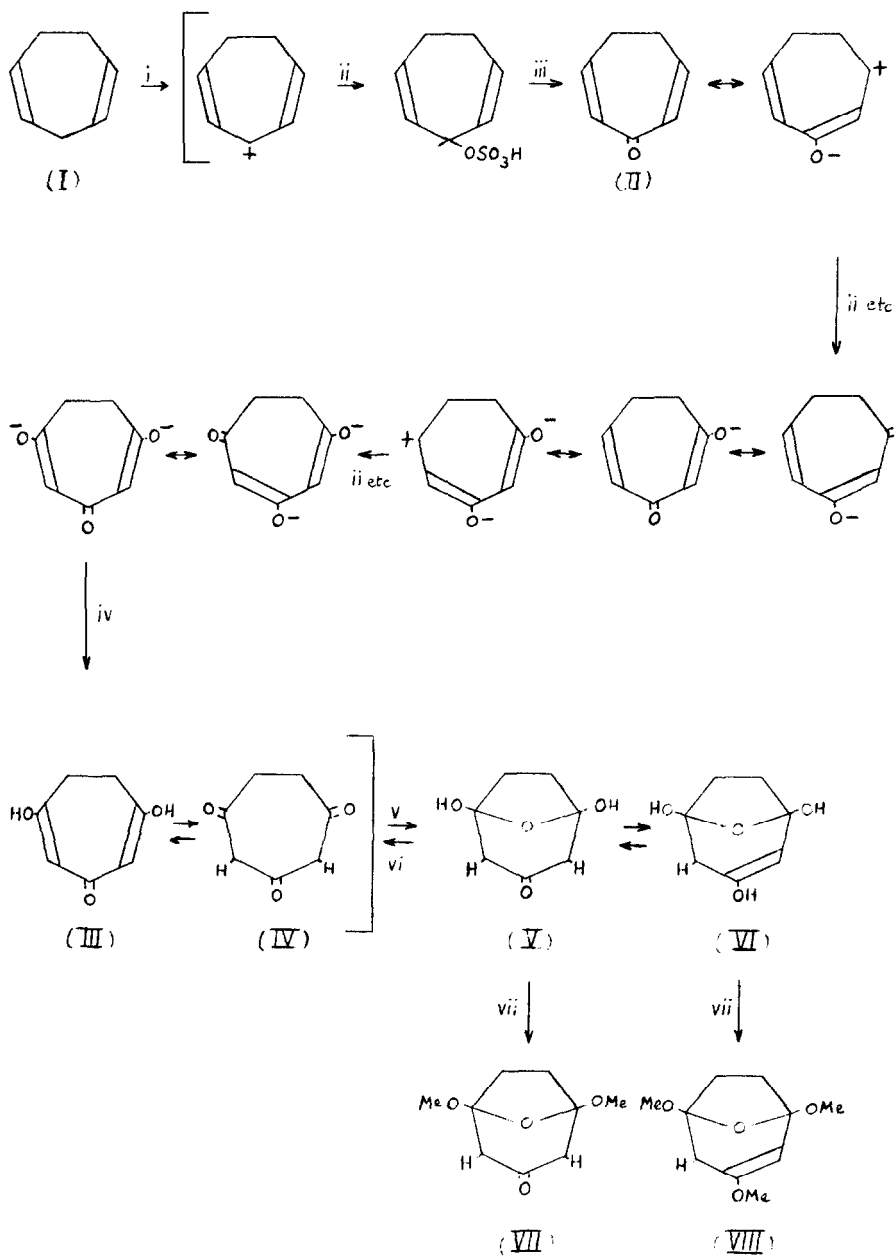
Decafluorocyclohepta-1,4-diene and fuming sulphuric acid at 100° gave a bright yellow solution which was decolourised on dilution with water to give 2H,4H-hexafluoro-1,5-dihydroxy-8-oxabicyclo(3,2,1)octan-3-one. This was methylated with diazomethane in ether to give 2H,4H-hexafluoro-1,5-dimethoxy-8-oxabicyclo(3,2,1)octan-3-one and 2H-hexafluoro-1,3,5-trimethoxy-8-oxabicyclo(3,2,1)oct-3-ene. The crystal and molecular structure of the former compound was determined by a single crystal X-ray analysis from three-dimensional counter data.

INTRODUCTION

As part of a programme to find an improved synthesis of hexafluorotropone from dodecafluorocycloheptanes [2], we unsuccessfully attempted to hydrolyse decafluorocyclohepta-1,3- and -1,4-diene to octafluorocyclohepta-2,4- and -2,6-dienone, respectively. However, a hydrolysis product was obtained from the 1,4-diene which probably involves the 2,6-dienone as an intermediate, and is of sufficient novelty to prompt this report.

RESULTS AND DISCUSSION

It is known that treatment of octafluorocyclohexa-1,4-diene with oleum at 100° followed by the addition of water and subsequent oxidation with nitric acid gives tetrafluoro-p-benzoquinone, and that the fluorine atoms



ALL UNMARKED SUBSTITUENTS ARE FLUORINE

Fig. 1

(i)  $\text{SO}_3$  (ii)  $\text{HSO}_4^-$  (iii)  $-\text{HFSO}_3$  (iv)  $\text{H}_3\text{O}^+$  (v)  $\text{H}_2\text{O}$  (vi)  $\text{P}_2\text{O}_5$  (vii)  $\text{CH}_2\text{N}_2$

in the latter quinone are susceptible to nucleophiles [3]. Therefore, by analogy, decafluorocyclohepta-1,4-diene(I) might be expected to give octafluoro-cyclohepta-2,6-dienone(II). When the diene(I) was treated with fuming sulphuric acid at 100° a bright yellow solution was produced, which became colourless on dilution with water, and afforded a white crystalline solid. However, this was shown by elemental analysis and mass spectrometry to have the formula  $C_7H_4F_6O_4$ . The IR spectrum revealed a strong OH stretching frequency at 3450 as well as a carbonyl stretching frequency at  $1770\text{ cm}^{-1}$ . The proton NMR spectrum consisted of a doublet at  $5.15\delta$  and a broad band at  $7.4\delta$  of equal intensity, consistent with the presence of CHF and OH groups, respectively. The fluorine NMR spectrum consisted of two signals in the relative intensity ratio of 2 : 1; the low field signal was a complex AB doublet and the high field signal ( $205.4\text{ ppm}$ ) had a large doublet coupling characteristic of a CHF group. These observations are consistent with the structure (Fig. 1) 1,5-dihydroxy-2H,4H-hexafluoro-8-oxabicyclo(3,2,1)octan-3-one(V), which was confirmed completely by the X-ray data on the dimethoxy-derivative. Methylation with diazomethane in ether gave 2H,4H-hexafluoro-1,5-dimethoxy-8-oxabicyclo(3,2,1)octan-3-one(VII) with consistent analytical and spectroscopic properties. The crystal and molecular structure of (VII) was determined by X-ray crystallography. The stereochemistry of the molecule is illustrated in Fig. 2, which also shows the atomic numbering scheme used in the Tables of results. With a large excess of diazomethane in ether, 2H-hexafluoro-1,3,5-trimethoxy-8-oxabicyclo(3,2,1) oct-3-ene(VIII) was obtained also, and was characterised by elemental analysis and the standard spectroscopic techniques.

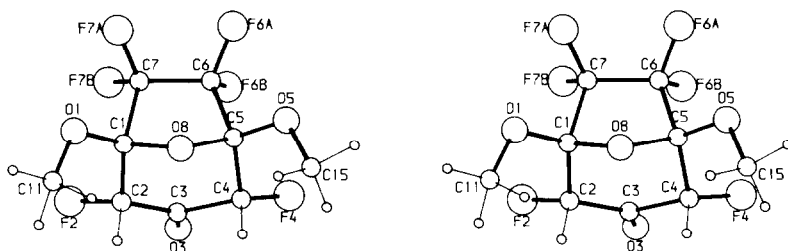


Figure 2. Stereoscopic view of the molecule(VII).

In agreement with the structure established above, treatment of (V) with potassium permanganate in acetone gave tetrafluorosuccinic acid. Treatment with aqueous potassium hydroxide followed by acidification also gave tetrafluorosuccinic acid, as expected from such a 1,3,5-triketone.

As with the analogous cyclohexa-1,3-diene system [3], decafluorocyclohepta-1,3-diene and oleum did not give the ketone; under the conditions that hydrolysed the 1,4-diene(I) an intractable brown oil and largely unchanged 1,3-diene (60%) were obtained.

The formation of 2H,4H-hexafluoro-1,5-dihydroxy-8-oxabicyclo(3,2,1)octan-3-one(V) from decafluorocyclohepta-1,4-diene and oleum probably arises via the sequence depicted in Fig. 1 involving the initial formation of the 2,6-dienone(II). This could arise from the perfluorocarbonium ion generated by sulphur trioxide in sulphuric acid, in a manner analogous to the generation of the heptafluoroarenonium ion from octafluorocyclohexa-1,4-diene and  $\text{SbF}_5$  (from which the hexafluorocyclohexadienone is produced by quenching with water [4]). However, the dienone(II) is unusual in that it is not isolated but apparently reacts readily with oleum, in a sequence like that in Fig. 1, to give the tautomeric hexafluorotriketone (IV). On quenching with water the latter should readily hydrate in the manner of polyfluoro-ketones. However, the triketone(IV) structure allows facile intramolecular hemi-ketal formation to give the oxabicyclooctanone(V); a process analogous to that in which 2,6-dimethyl-hexafluoropyran-2,6-diol arises from 3,3,4,4,5,5-hexafluoro-hepta-2,6-dione [5]. An attempt to prepare the triketone(IV) from the dihydroxy-ketone(V), by sublimation from phosphoric oxide after 1 hr at  $100^\circ$ , gave an intractable yellow oil which regenerated (V) on exposure to the atmosphere.

Although the stereochemistry of the crystalline dimethoxy-ketone(VII) is unequivocally established (Fig. 2), the tautomeric nature of the dihydroxy-ketone(V) prevents a precise structural allocation of this compound or of that of the trimethoxy compound (VIII) produced from it with an excess of diazomethane. However, the structure of (VII), established by the X-ray analysis, suggests that the oxo-bridge fluorine interaction is unfavourable and that the dihydroxy-ketone(V) is similarly disposed.

Atomic coordinates for (VII) obtained from the X-ray analysis are listed in Table 1 and the thermal parameters are in Table 2. Bond lengths, bond angles and torsion angles are listed in Table 3. Mean estimated standard deviations for these are  $0.03 \text{ \AA}$ ,  $2^\circ$  and  $3^\circ$ , respectively

TABLE 1

Atomic coordinates expressed as fractions ( $\times 10^4$ ) of the unit cell lengths

	x	y	z
C(1)	1902(16)	3831(28)	3795(12)
C(2)	1746(13)	3697(26)	3027(11)
C(3)	2509(18)	4319(20)	2655(12)
C(4)	3465(15)	3635(26)	3048(11)
C(5)	3482(13)	3900(24)	3826(12)
C(6)	3257(16)	5587(25)	4077(12)
C(7)	2234(12)	5578(29)	4098(13)
C(11)	840(14)	1762(31)	3973(13)
C(15)	4560(14)	1682(31)	4110(13)
F(2)	996(9)	4595(20)	2758(7)
F(4)	4143(7)	4476(18)	2806(6)
F(6a)	3680(8)	6101(15)	4676(8)
F(6b)	3457(9)	6764(16)	3603(8)
F(7a)	2031(8)	5878(17)	4726(8)
F(7b)	1775(8)	6804(15)	3689(9)
O(8)	2715(8)	2904(13)	4020(7)
O(1)	1231(9)	3303(20)	4166(8)
O(3)	2477(11)	5123(16)	2169(8)
O(5)	4280(10)	3387(19)	4229(9)
H[C(2)]	1621	2353	2910
H[C(4)]	3422	2368	2960
H <sup>1</sup> [C(11)]	301	1400	4258
H <sup>2</sup> [C(11)]	1366	780	4042
H <sup>3</sup> [C(11)]	549	1667	3398
H <sup>1</sup> [C(15)]	5230	1466	4480
H <sup>2</sup> [C(15)]	4701	1514	3603
H <sup>3</sup> [C(15)]	4085	851	4269

A view of the contents of the unit cell projected along the  $y$  axis is shown in Fig. 3.

There are two short intermolecular contacts of 2.27 and 2.25 Å between the carbonyl oxygen atom O(3) and the hydrogen atoms linked to C(2) and C(4) of the molecule related to the standard molecule (atomic coordinates

TABLE 2

Anisotropic thermal parameters ( $\text{\AA}^2 \times 10^4$ ) for the heavier atoms. Temperature factors are in the form:

$$T = \exp[-2\pi^2(U_{11}h^2a^*2 + \dots + 2U_{12}hka^*b^* + \dots)]$$

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
C(1)	486	961	828	212	-366	18
C(2)	214	1029	808	181	208	0
C(3)	1024	316	711	-289	-273	143
C(4)	390	1110	451	162	-28	-159
C(5)	394	781	866	31	104	455
C(6)	872	722	836	-639	233	-533
C(7)	71	1100	955	-165	60	-106
C(11)	251	1329	1228	-418	-106	-155
C(15)	375	1248	1267	190	140	399
F(2)	709	1392	1174	540	-172	135
F(4)	347	1330	1113	-335	259	255
F(6a)	593	1036	1352	-168	-88	-848
F(6b)	879	865	1487	-475	36	-204
F(7a)	493	1428	1365	-50	325	-542
F(7b)	430	890	2228	81	-4	-10
O(8)	229	723	733	204	127	1
O(1)	149	1312	893	-50	75	-421
O(3)	770	791	845	163	-1	203
O(5)	320	1062	1431	56	-38	18

TABLE 3

## Molecular dimensions

(a) Bond lengths ( $\text{\AA}$ ) with standard deviations ( $\times 10^2$ ) in parentheses			
C(1) - C(2)	1.47(3)	0(1) - C(11)	1.40(3)
C(2) - C(3)	1.51(3)	C(2) - F(2)	1.37(2)
C(3) - C(4)	1.61(3)	C(3) - O(3)	1.14(2)
C(4) - C(5)	1.51(3)	C(4) - F(4)	1.35(2)
C(5) - C(6)	1.50(3)	C(5) - O(5)	1.39(2)
C(6) - C(7)	1.53(3)	O(5) - C(15)	1.47(3)
C(7) - C(1)	1.58(3)	C(6) - F(6a)	1.31(2)
C(1) - O(8)	1.44(2)	C(6) - F(6b)	1.38(2)
C(5) - O(8)	1.49(2)	C(7) - F(7a)	1.31(2)
C(1) - O(1)	1.38(3)	C(7) - F(7b)	1.39(2)
(b) Bond angles ( $^\circ$ ) with standard deviations in parentheses			
C(2) - C(1) - C(7)	116(2)	C(6) - C(5) - O(8)	102(2)
C(2) - C(1) - O(8)	106(2)	C(6) - C(5) - O(5)	108(2)
C(2) - C(1) - O(1)	119(2)	O(8) - C(5) - O(5)	109(1)
C(7) - C(1) - O(8)	99(2)	C(5) - C(6) - C(7)	106(2)
C(7) - C(1) - O(1)	107(2)	C(5) - C(6) - F(6a)	118(2)
O(8) - C(1) - O(1)	109(2)	C(5) - C(6) - F(6b)	110(2)
C(1) - C(2) - C(3)	116(2)	C(7) - C(6) - F(6a)	110(2)
C(1) - C(2) - F(2)	110(2)	C(7) - C(6) - F(6b)	109(2)
C(3) - C(2) - F(2)	106(2)	F(6a) - C(6) - F(6b)	104(1)
C(2) - C(3) - C(4)	109(2)	C(6) - C(7) - C(1)	105(2)

TABLE 3 (continued)

C(2) - C(3) - O(3)	129(2)	C(6) - C(7) - F(7a)	113(2)
C(4) - C(3) - O(3)	121(2)	C(6) - C(7) - F(7b)	113(2)
C(3) - C(4) - C(5)	108(2)	C(1) - C(7) - F(7a)	114(2)
C(3) - C(4) - F(4)	108(2)	C(1) - C(7) - F(7b)	109(2)
C(5) - C(4) - F(4)	111(2)	F(7a) - C(7) - F(7b)	104(2)
C(4) - C(5) - C(6)	118(2)	C(1) - O(8) - C(5)	106(2)
C(4) - C(5) - O(8)	105(2)	C(1) - O(1) - C(11)	116(2)
C(4) - C(5) - O(5)	114(2)	C(5) - O(5) - C(15)	116(2)
(c) Torsion angles ( $^{\circ}$ ); estimated standard deviations <u>ca</u> $3^{\circ}$			
seven-membered ring			
C(1) - C(2) - C(3) - C(4)	46	C(5) - C(6) - C(7) - C(1)	-4
C(2) - C(3) - C(4) - C(5)	-46	C(6) - C(7) - C(1) - C(2)	-82
C(3) - C(4) - C(5) - C(6)	-51	C(7) - C(1) - C(2) - C(3)	50
C(4) - C(5) - C(6) - C(7)	91		
six-membered ring			
C(1) - C(2) - C(3) - C(4)	46	C(4) - C(5) - O(8) - C(1)	-78
C(2) - C(3) - C(4) - C(5)	-46	C(5) - O(8) - C(1) - C(2)	73
C(3) - C(4) - C(5) - O(8)	62	O(8) - C(1) - C(2) - C(3)	-58
five-membered ring			
C(1) - O(8) - C(5) - C(6)	46	C(6) - C(7) - C(1) - O(8)	30
O(8) - C(5) - C(6) - C(7)	-23	C(7) - C(1) - O(8) - C(5)	-47
C(5) - C(6) - C(7) - C(1)	-4		



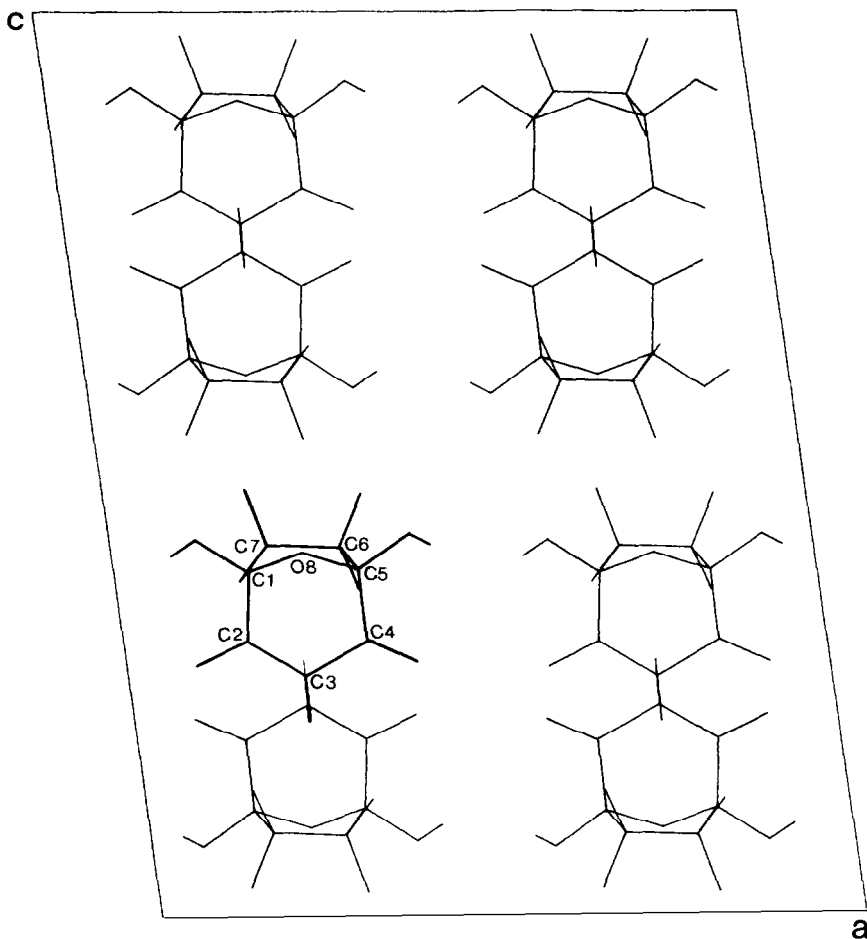


Figure 3. The contents of the unit cell projected along the crystallographic  $y$  axis.

as listed in Table 1) by the operation of the 2-fold screw axis at  $x = \frac{1}{4}$ ,  $z = \frac{1}{4}$ . The corresponding C ... O distances are O(3) ... C(2), 3.16 Å and O(3) ... C(4), 3.17 Å. These distances are consistent with C-H ... O hydrogen bonding [6]. Such an interaction would be favoured by the presence of the highly electronegative fluoro-substituents at the 2- and 4- positions. None of the other intermolecular contact distances is shorter than the sum of the van der Waals radii of the atoms concerned.

The molecule possesses an approximate mirror plane of symmetry passing through O(3), C(3), O(8) and the mid-point of the C(6)-C(7) bond. The six-membered ring adopts a somewhat distorted chair conformation wherein the ring pucker is increased at O(8) and decreased at the carbonyl carbon atom, C(3). The five-membered ring is in the envelope conformation. Atoms C(1), C(5), C(6) and C(7) are coplanar to within  $\pm 0.02 \text{ \AA}$ , and O(8) is displaced by  $0.65 \text{ \AA}$  from the plane of these four atoms. The overall shape of the seven-membered ring resembles the boat conformation postulated by Hendrickson [7] as one of the possible geometries for cycloheptane. The bridging oxygen atom is oriented axial to C(1) and C(5) and thus eliminates the extremely unfavourable H  $\cdots$  H interaction which occurs across the corresponding axial positions in the boat form of cycloheptane [7].

Bond lengths and angles generally agree to within the limits of experimental accuracy with standard values. The accuracy of the analysis is not, however, sufficiently high to discuss these in detail.

#### EXPERIMENTAL

##### 2H,4H-Hexafluoro-1,5-dihydroxy-8-oxabicyclo(3,2,1)octan-3-one (V)

Decafluorocyclohepta-1,4-diene (I) (7.0 g) and fuming sulphuric acid (23% SO<sub>3</sub>; 30 ml) were shaken together in a sealed Pyrex glass tube at 100° for 2 hr., then poured onto ice (ca. 200 g) and continuously extracted with ether for 48 hr. The ethereal extract was dried (MgSO<sub>4</sub>) and evaporated to give a brown solid which was dissolved in dry ether (40 ml) and filtered. Evaporation of the filtrate gave a solid (4.7 g) which was sublimed (150°, 20 mm) to give a white crystalline solid (4.3 g). Recrystallisation of a portion of the solid (0.17 g) from carbon tetrachloride gave 2H,4H-hexafluoro-1,5-dihydroxy-8-oxabicyclo(3,2,1)octan-3-one (V) (nc) (0.14 g) m.p. 182° (Found: C, 31.6; H, 1.4; F, 42.5).

C<sub>7</sub>H<sub>4</sub>F<sub>6</sub>O<sub>4</sub> requires C, 31.6; H, 1.5; F, 42.9%), m/e 266 (C<sub>7</sub>H<sub>4</sub>F<sub>6</sub>O<sub>4</sub><sup>+</sup>),  $\nu_{\max}$  3450 (OH) and 1770 cm<sup>-1</sup>. (C=O); its <sup>1</sup>H NMR spectrum in hexadeuteroacetone consisted of a doublet (J<sub>HF</sub> 45 Hz) centred at 5.15 p.p.m. (>CHF) and a broad band at 7.4 p.p.m. (OH) in the relative intensity ratio of 1:1; its <sup>19</sup>F NMR spectrum in hexadeuteroacetone consisted of bands at 126.5, 126.7 (collapsed AB, AB low field arm complex, high field arm a

single peak) and a complex doublet of triplets centred at 205.4 p.p.m. (J 45 and 11.3 Hz) (CHF) in the relative intensity ratio of 2:1.

The bicyclic ketone (0.2 g), potassium permanganate (0.25 g) and dry acetone (30 ml) in the usual way afforded dianilinium tetrafluoro-succinate (0.15 g) (from ethanol/chloroform) m.p. 222-224<sup>o</sup>, with a correct NMR spectrum.

The bicyclic ketone (1.7 g) and 5 N-potassium hydroxide (10 ml) were kept at 80<sup>o</sup> for 1 hr. acidified with 4 N HCl and continuously extracted with ether for 24 hr. A portion (0.35 g) of the brown oil (2.4 g) so obtained gave, in the usual way, dianilinium tetrafluorosuccinate (0.19g) (from ethanol/chloroform) m.p. 221-224<sup>o</sup> with a correct NMR spectrum.

Methylation of 2H,4H-hexafluoro-1,5-dihydroxy-8-oxabicyclo(3,2,1)-octan-3-one

(a) An ethereal solution of diazomethane was added dropwise to a solution of the ketone (V) (0.3 g) in dry ether (20 ml) at 0<sup>o</sup> until a yellow colouration persisted. The flask was left open for 15 hr. to allow excess diazomethane to escape and the ether evaporated to leave a white solid (0.22 g) which was recrystallised twice from carbon tetrachloride to give 2H,4H-hexafluoro-1,5-dimethoxy-8-oxabicyclo(3,2,1)octan-3-one (VII) (nc) (0.15 g) m.p. 89-91<sup>o</sup> (Found: C, 36.4; H, 2.9 C<sub>9</sub>H<sub>8</sub>F<sub>6</sub>O<sub>4</sub> requires C, 36.7; H, 2.7%),  $\nu_{\max}$  1765 cm<sup>-1</sup> (>C=O), m/e 294 (C<sub>9</sub>H<sub>8</sub>F<sub>6</sub>O<sub>4</sub><sup>+</sup>); its <sup>1</sup>H NMR spectrum in hexadeuteroacetone consisted of a single band at 3.7 p.p.m. (OCH<sub>3</sub>) and a complex doublet (J<sub>HF</sub> 45 Hz) centred at 5.32 p.p.m. in the relative intensity ratio of 3:1; its <sup>19</sup>F NMR spectrum consisted of bands at 124.5 and 127.7 (AB, J 250 Hz, low field arm shows doublet coupling of 22.5 Hz) and a doublet of doublets (J 45 and 22.5 Hz) centred at 206.3 p.p.m. in the relative intensity ratio of 1:1:1.

(b) A large excess of an ethereal solution of diazomethane was added to the ketone (V) (0.5 g) in dry ether (30 ml) and the solution kept for 16 hr. at room temperature, dried (MgSO<sub>4</sub>) and the ether evaporated to leave a pale yellow oil (0.7 g) which was separated by GLC (silicone gum (Si 301)/celite 1:6; 180<sup>o</sup>; N<sub>2</sub> ca. 1.5 l/hr.) to give: (i) ether (trace); (ii) 2H-hexafluoro-1,3,5-trimethoxy-8-oxabicyclo(3,2,1)oct-3-ene (VIII) (nc) (0.3 g) m.p. 50-51<sup>o</sup> (Found: C, 38.8; H, 3.3; F, 37.1 C<sub>10</sub>H<sub>10</sub>F<sub>6</sub>O<sub>4</sub> requires C, 39.0; H, 3.2; F, 37.0%),  $\nu_{\max}$  1710 cm<sup>-1</sup> (C=C), m/e 308

(C<sub>10</sub>H<sub>10</sub>F<sub>6</sub>O<sub>4</sub><sup>+</sup>); its <sup>1</sup>H NMR spectrum in deuteriochloroform consisted of a singlet at 3.6 p.p.m. superimposed on a doublet (J 1 Hz), a doublet (J 4 Hz) centred at 3.97 p.p.m. and a complex doublet (J 51 Hz) centred at 5.26 p.p.m. in the relative intensity ratio of 3:3:3:1; its <sup>19</sup>F NMR spectrum consisted of bands at 110.9 (J 18 Hz), 127.1 (AB, J<sub>AB</sub> 254 Hz), 131.1 and 131.2 (AB, J<sub>AB</sub> 240 Hz), 156.0 (CF) and a doublet of doublets (J 51 and 18 Hz) at 206.4 p.p.m. (>CHF) of equal relative intensities; (iii) an unidentified component (trace); (iv) 2H,4H-hexafluoro-dimethoxy-8-oxabicyclo(3,2,1)octan-3-one (VII) (0.1 g) with a correct IR spectrum.

#### X-Ray measurements

The crystals of (VII) were in the form of thin needles and examination by photographic methods showed that they were of poor quality for X-ray work. Due to crystal imperfections the spots on the Weissenberg films were considerably elongated and there was a rapid fall-off in intensities with increasing angle of reflection. Nevertheless it was felt that sufficient data would be available to determine the structure, although high accuracy could not be expected.

A crystal of dimensions 0.55 x 0.1 x 0.1 mm was mounted inside a Pantak capillary tube and aligned about the crystallographic y axis. The intensities of the reflections were measured on a Stoe two-circle computer-controlled diffractometer with graphite-monochromated Mo Kα radiation and a scintillation counter. The diffractometer was operated in the ω - 2θ scan mode with a scan rate of 0.15° min<sup>-1</sup> and a scan range of 0.75° (both in ω). Backgrounds were measured for 30s at each end of the scan. To monitor the stability of the system, the intensities of four reflections on the zero layer were checked after each layer of data collection. Of 1314 reflections scanned within the range 0.1 < sin θ/λ < 0.48, 451 having intensities, I, greater than 2.5 σ (I) were considered to be observed and were used in the structure analysis.

#### Crystal data

Monoclinic, a = 14.85 (1), b = 8.10 (1), c = 19.31 (1) Å, β = 98.08 (1)°, U = 2300 Å<sup>3</sup>, Z = 8, D<sub>c</sub> = 1.70 g cm<sup>-3</sup>. Systematic absences: h k l, h + k odd; h0l, l odd; space group Cc or C2/c. C2/c established as a result of the structure analysis. Absorption coefficient for Mo Kα radiation (λ = 0.71069 Å) = 1.38 cm<sup>-1</sup>.

### Structure determination

The structure was solved by direct methods [8] with the SHELX programs [9]. Phases (0 or 180°) were determined for the 205 reflections with  $E > 1.1$  and from the E map calculated with these phases the positions of all the heavier atoms, except one, could be located. This atom, C(15) of one of the methoxy groups, was located from a difference synthesis and the coordinates of the atoms were now adjusted by four cycles of Fourier refinement. Final refinement of positional and anisotropic thermal parameters was carried out by the method of least-squares. Owing to the paucity of data it was not possible to refine all parameters simultaneously and accordingly coordinates and temperature factors were refined in alternate cycles of least-squares calculations. Hydrogen atoms were placed in geometrically reasonable positions and were included in the calculations with isotropic temperature factors but their parameters were not adjusted. The refinement process was terminated when all calculated shifts were  $< 0.1 \sigma$  and the conventional discrepancy  $R$  was 12.39%. A final difference synthesis showed no features greater than  $\pm 0.5 e \text{ \AA}^{-3}$ . Lists of observed and calculated structure factors can be obtained from the authors.

All computations were carried out on the Birmingham University ICL 1960A computer with the SHELX programs together with local ancillary programs.

### ACKNOWLEDGEMENTS

We are indebted to the University of Birmingham for funds to purchase the diffractometer and for the award of Research Studentships (to M.J.H. and C.M.J.).

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