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STRUCTURE AND SPECTRAL PROPERTIES OF TWO NOVEL ISOMERIC 2,4-DIMETHYL-2-METHOXY-3,8-DIOXABICYCLO[3.2.1]OCTANES

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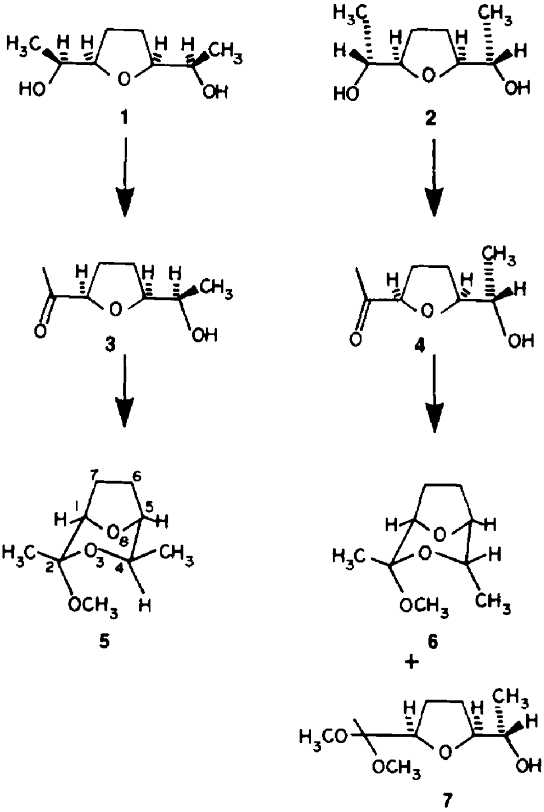
Abstract—The preparation and structure of the novel bicyclic ketals 5 and 6 is reported. A single crystal X-ray structure of compound 5 establishes the structures of 5 and 6. ^{1}H and ^{13}C NMR spectra are interpreted in terms of chair conformations for both 5 and 6, even though an unfavorable syn-diaxial interaction is present in 6. In the ^{1}H spectra, the axial C-4 proton of compound 5 absorbs *downfield* of its equatorial counterpart in 6. This is apparently due to a deshielding effect of the syn-diaxial C-2 methoxy group in compound 5.

In the course of an investigation underway in our laboratories,[1] we required an unambiguous method for proving the relative configurations of tetrahydrofurans 1 and 2†. Our approach was to convert these non-crystalline diols into the rigid [3.2.1] bicyclooctane derivatives 5 and 6 as shown in Scheme 1. Compounds 5 and 6 both proved to be nicely crystalline solids, though 6 melts below room temperature. Our structural problem was solved by single crystal X-ray analysis of 5.

The 3,8-dioxabicyclo[3.2.1] octane system is almost unknown in the literature.[2] Having prepared isomeric derivatives well suited for spectral comparison, we report here on the X-ray crystal structure of 5, and on the ^{1}H and ^{13}C magnetic resonance properties of 5 and 6.

Synthesis. Tetrahydrofurandiethanols 1 and 2 were each prepared stereospecifically in one step from (*Z,Z*)- and (*E,E*)- 2,6-octadiene, respectively.[1] As shown in Scheme 1, the synthesis of bicyclics 5 and 6 proceeded in a straightforward manner from diols 1 and 2. Thus, oxidation of symmetrical diols 1 and 2 with pyridinium chlorochromate in dichloromethane containing sodium acetate[3] afforded ketols 3 and 4, respectively, in moderate yield. Treatment of ketol 3 with trimethylorthoformate in methanol containing a trace of toluenesulfonic acid afforded 2,4-dimethyl-2-methoxy-3,8-dioxabicyclo[3.2.1]octane (5) with the methyl groups at C-2 and C-4 in the equatorial configuration. There was no evidence for formation of axial methyl isomer at C-2, in agreement with the expected enhanced stability of an axial methoxy due to the anomeric effect.

When ketol 4 was treated with trimethylorthoformate under identical conditions, two compounds were formed. These were readily separated and identified as the bicyclic ketal 6 and monocyclic hydroxyketal 7, formed in a 1:2 ratio. When purified hydroxyketal 7 was subjected to the same reaction conditions, an identical mixture of 6 and 7 was produced. This result is consistent with the expected greater strain in bicyclic 6 relative to 5 associated with the syn-diaxial interaction present in 6.



Scheme 1

Crystal structure of compound 5. The detailed structure of the rigid [3.2.1] bicyclooctane derivative 5 is shown in Fig. 1 together with the numbering scheme used in the X-ray work. Final positional and thermal parameters are given in Table 1. Figure 2 shows bond lengths and angles derived from these parameters. Examination of these lengths and angles shows no significant variation from expected values. Deviations from planes calculated through atoms C(2), C(3), C(4) and C(5), and through C(1), C(2), C(5) and C(6) show that both groups are only slightly non planar. The dihedral angle between these two planes is 114 deg. Between the planes defined by C(2), C(3), and C(4) and C(5) and by C(2), O(2) and C(5) the dihedral angle is 131 deg. The dihedral angle between the C(1), C(2), C(5) and C(6) plane and the C(1), O(1) and O(6) plane is 133 deg. Thus,

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†All chiral compounds discussed in this work are racemates. For the sake of clarity only the series of enantiomers in which C-5 of compounds 5 and 6 (numbering as shown in Scheme 1) has the S configuration are considered.

Table 1. Final positional and thermal parameters

ATOM	X[A]	Y	Z	B11 OR B,Å^2 [B]	B22	B33	B12	B13	B23
O1	0.8920(6)	0.3090(3)	0.7420(5)	39.9(25)	28.0(24)	22.8(21)	-2.3(19)	-4.6(18)	-1.4(20)
O2	0.7367(7)	0.3757(3)	0.4603(5)	41.9(27)	43.4(28)	29.1(26)	4.3(22)	2.0(20)	5.7(21)
O3	0.9320(7)	0.22034(28)	0.5274(5)	44.9(27)	38.1(29)	29.1(25)	10.3(23)	4.5(21)	-3.1(20)
C1	0.7976(10)	0.2514(4)	0.6346(8)	34.(4)	24.(3)	25.(3)	-1.(3)	1.(3)	-4.(3)
C2	0.6456(9)	0.3035(5)	0.5452(8)	27.(3)	37.(1)	39.(4)	-1.(3)	-2.(3)	11.(3)
C3	0.5018(10)	0.3509(5)	0.6417(8)	25.(4)	41.(4)	56.(5)	8.(3)	6.(3)	1.(3)
C4	0.6017(10)	0.4385(5)	0.6824(8)	39.(4)	35.(4)	47.(4)	3.(3)	4.(3)	0.(3)
C5	0.7849(10)	0.4331(5)	0.5925(8)	43.(4)	34.(4)	28.(4)	1.(3)	-6.(3)	4.(3)
C6	0.9545(10)	0.3913(4)	0.6772(8)	32.(4)	29.(4)	34.(4)	-10.(3)	5.(3)	0.(3)
C7	0.7134(12)	0.1750(5)	0.7259(9)	63.(5)	28.(4)	50.(5)	-8.(3)	10.(4)	0.(3)
C8	1.0427(10)	0.4458(5)	0.8036(6)	42.(4)	37.(4)	53.(5)	-10.(4)	-9.(3)	1.(4)
C9	1.0932(11)	0.1728(6)	0.5954(9)	41.(5)	68.(5)	49.(5)	20.(4)	3.(4)	4.(4)
H1C2	0.576	0.264	0.471	4.5					
H1C3	0.482	0.316	0.735	5.2					
H2C3	0.379	0.359	0.596	5.2					
H1C4	0.627	0.445	0.790	4.9					
H2C4	0.520	0.489	0.653	4.9					
H1C5	0.823	0.492	0.557	4.8					
H1C6	1.059	0.379	0.608	4.0					
H1C7	0.683	0.193	0.826	5.6					
H2C7	0.600	0.151	0.678	5.6					
H3C7	0.808	0.127	0.736	5.6					
H1C8	1.161	0.419	0.839	5.2					
H2C8	1.070	0.505	0.769	5.2					
H3C8	0.956	0.449	0.805	5.2					
H1C9	1.069	0.109	0.586	6.4					
H2C9	1.206	0.183	0.528	6.4					
H3C9	1.124	0.190	0.689	6.4					

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. [B] THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: $EXP[-1/4(B11H^2A^{*2} + B22K^2B^{*2} + B33L^2C^{*2} + 2B12HKA^*B^* + 2B13HLA^*C^* + 2B23KLB^*C^*)]$.

THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS X 10^1.

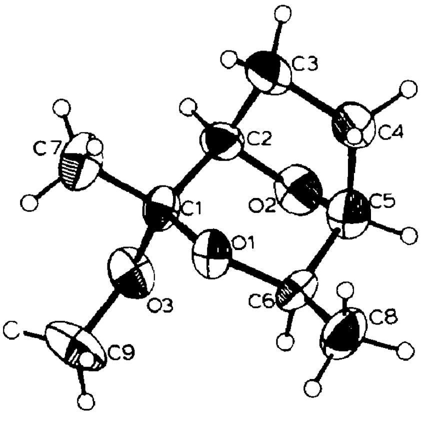

Fig. 1. A perspective view of 2,4-dimethyl-2-methoxy-3,8-dioxabicyclo[3.2.1]octane (5) showing the numbering scheme used in the crystallographic study. Thermal ellipsoids for the non hydrogen atoms are drawn at the 50% probability level. Hydrogen atoms are included on an arbitrary scale for clarity.

the dioxane ring of 5 exists in the expected chair conformation. Table 2 gives torsion angles for 5.

^1H NMR spectra. The ^1H magnetic resonance spectra of 5 and 6 taken at 90 MHz in $CDCl_3$ allow determination of the relevant chemical shift and coupling constant data. Specifically, the ^1H spectrum of 5 shows a doublet at δ1.01 (J = 6.5 Hz) for the equatorial Me at C-4. The signal corresponding to the axial ring proton at C-4 appears as the downfield half of a quartet of doublets centered at δ4.13 ($J_{CH_3} = 6.5$ Hz, $J_{ax\text{-}equ} = 1.8$ Hz), obscured by a multiplet arising from the bridgehead protons. Irradiation of the C-6 and C-7 protons (δ2.0) caused a narrowing of the signal from the bridgehead protons and revealed the third peak of the quartet of doublets. The ^1H spectrum of 6 shows the C-4 axial Me doublet at δ1.48 (J = 6.0 Hz). The C-4 equatorial ring proton of 6 appears as a quartet centered at δ3.54 ($J_{CH_3} = 6.0$Hz, $J_{equ\text{-}equ} =$ 0 Hz).

Some aspects of these spectra deserve comment. The axial C-4 proton in 5 absorbs downfield of the equitorial C-4 proton in 6 (Δδ = 0.59 ppm). In this case the well known generalization that axial protons are more shielded than their equatorial counterparts[4] does not hold. This behavior is common in α-halocyclohexanones.[4c,5] Similar reversals of the general rule have been reported in other systems, [4c,6] including the related 8-oxabicyclo[3.2.1]oct-6-ene-3-ones.[7] The latter observation in interpreted as resulting from the CO bond anistropy.[7] In our case, the syn-diaxial interaction of the axial C-4 proton of 5 could be responsible for its downfield chemical shift relative to the equatorial C-4 proton of 6. The deshielding effect of a syn-diaxial polar substitutent on ring protons in carbocyclic and heterocyclic systems has been stated as a general rule.[4c]

Though in the above discussion we have assumed that 6 exists in a chair conformation, a flattened chair or boat cannot be ruled out *a-priori*. The small equatorial–equatorial coupling constant (0 Hz) found in 6 is similar to that found for equatorial–equatorial couplings in the 8-oxa-3-oxo analogues, where the chair conformation has been assigned to compounds with axial Me substituents at C-2 and C-4.[7] A chair conformation of 6 is also consistent with the relative chemical shifts of the C-4 Me protons of 5 and 6. The axial Me protons of 6 absorb at lower field than their equatorial counterparts in 5 (Δδ = 0.47 ppm). This is in agreement with the general rule, derived from analysis of steroid spectra, that syn-diaxial interaction of a ring methyl group with an electronegative substituent causes deshielding of the Me group of similar magnitude as the deshielding of a ring proton.[4c]

^{13}C Spectra. Though unambiguous assignment of the carbon resonances of 5 and 6 is difficult, analysis of the spectra does lead to some useful conclusions. Assuming that the stereochemical δ effect is small[8] we may tentatively assign all four of the aliphatic carbon resonances. Again, the analysis is consistent with a chair conformation for 6. Thus, C-7 and the C-2 Me absorb at 26.16 and 19.46 ppm, respectively, in 5, and at 25.58 and 19.66 ppm, respectively, in 6 (Δδ × 0.58 for C-7, and 0.2 for the C-2 Me). Whereas the stereochemical δ effect is small, the γ effect is large, as expected. C-6 and the C-4

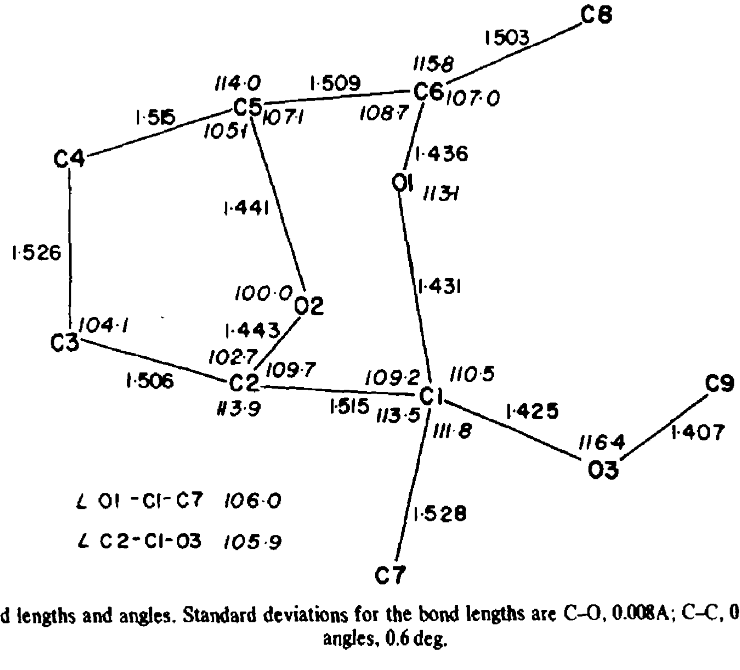

Fig. 2. Bond lengths and angles. Standard deviations for the bond lengths are C–O, 0.008Å; C–C, 0.009Å; and for angles, 0.6 deg.

Table 2. Torsion angles

C(6)-O(1)-C(1)-O(3)	67.5(7)	C(2)-C(3)-C(4)-C(5)	4.4(7)
C(2)	-48.6(7)	H(1C4)	-117.
C(7)	-171.3(6)	H(2C4)	124.
C(1)-O(1)-C(1) C(5)	52.0(7)	H(1C3)-C(3)-C(4)-C(5)	121.
C(8)	177.7(6)	H(1C4)	0
H(1C6)[b]	-68.	H(2C4)	-119.
C(9)-O(3)-C(1)-O(1)	59.1(7)	H(2C3)-C(3)-C(4)-C(5)	-120.
C(2)	177.3(6)	H(1C4)	118.
C(7)	-58.7(8)	H(2C4)	0.
O(1)-C(1)-C(2)-O(2)	60.1(7)	C(3)-C(4)-C(5)-O(2)	26.3(6)
C(3)	-54.4(7)	C(6)	-90.7(7)
H(1C2)	-179.	H(1C5)	146.
O(3)-C(1)-C(2) O(2)	-58.9(7)	H(1C4)-C(4)-C(5)-O(2)	148.
C(3)	-173.3(5)	C(6)	31.
H(1C2)	62.	H(1C5)	-93.
C(7)-C(1)-C(2)-O(2)	178.1(6)	H(2C4)-C(4)-C(5)-O(2)	-92.
C(3)	63.7(8)	C(6)	151.
H(1C2)	-61.1	H(1C5)	27.
O(2)-C(2)-C(3)-C(4)	-33.4(7)	O(2)-C(5)-C(6)-O(1)	-66.1(7)
H(1C3)	-150.	C(8)	173.5(6)
H(2C3)	90.	H(1C6)	53.
C(1)-C(2)-C(3)-C(4)	85.1(7)	C(4)-C(5)-C(6)-O(1)	50.
H(1C3)	-32.	C(8)	-71.
H(2C3)	-151.	H(1C6)	169.
H(1C2)-C(2)-C(3)-C(4)	-150.	H(1C5)-C(5)-C(6)-O(1)	174.
H(1C3)	93	C(8)	54.
H(2C3)	-26.	H(1C6)	-67.

a) The sign of the angle is positive if when looking down from the second atom to the third a clockwise motion of the first atom would superimpose it on the fourth.

b) Errors are not included for angles involving hydrogen atoms because the hydrogen atom positions were not refined.

Me absorb at 21.94 and 16.54 ppm, respectively, in **5**, and at 27.91 and 20.39 ppm respectively, in **6**. Thus the C-6 resonance is shifted upfield by 5.97 ppm in going from **6** to **5**. This is the expected steric gauche γ effect for C-6.[8] The C-4 methyl resonance is also shifted upfield in going from **6** to **5** ($\Delta\delta = 3.84$). We feel the origin of this diamagnetic shift is related to two factors. Firstly, the C-4 Me in **5** is shielded by gauche γ interaction with C-6. More interestingly, the axial Me of **6** is deshielded by the syn-diaxial interaction with the C-2 OMe.[8] In fact, the C-4 Me of **6**, with on β-O atom, absorbs downfield of the C-2 Me with two β-O atoms. The additivity principle would predict an opposite ordering of chemical shifts in the absence of the syn-diaxial interaction. Recently a paper describing an unusually large anti-γ effect of polar substituents was reported for β-substituted bicyclo[3.2.1]octan-8-ones.[9] This effect would also tend to shield the equatorial C-4 Me of **5** relative to the axial C-4 Me of **6**. However, in our system this shielding is expected to be of minor importance.[9]

In conclusion, we have prepared the novel bicyclic compounds **5** and **6**. The X-ray crystal structure of **5** is reported along with some ^{1}H and ^{13}C spectral properties of **5** and **6**. The spectra are most readily interpreted in terms of chair conformations for both **5** and **6**, even though an unfavorable syndiaxial interaction is present in **6**.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on Varian EM 390 and JEOL 100 spectrometers, respectively, with TMS as internal standard. IR spectra were recorded on a Perkin-Elmer model 927 spectrometer. Dry CH_2Cl_2 was freshly distilled from P_2O_5, and dry MeOH was freshly distilled from Mg. All reactions were run under a slightly positive pressure of argon using a silicone oil bubbler.

(5S, 1' R; 5R, 1'S)-cis-2-*Acetyl-5-(1'-hydroxyethyl)-tetrahydrofuran* (**4**). To a stirred suspension of 85 mg (0.39 mmol) of pyridinium chlorochromate[3] and 64 mg (0.08) NaOAc acetate in 1 ml dry CH_2Cl_2 was added a soln of 63 mg (0.39 mmol) of **1** in 2 ml CH_2Cl_2. After 1.5 hr the black mixture was loaded directly onto a column of 15 g of silica gel packed in CH_2Cl_2 . The column was elluted with 10 ml CH_2Cl_2 then with 50 ml EtOAc to give 32 mg (51%) of **3** as a slightly yellow liquid. The proton NMR spectrum of this material indicates that it exists as a mixutre of **3** and two epimeric bicyclic hemi-ketals equilibrating slowly on the NMR timescale: NMR ($CDCl_3$)δ1.0 (s, 0.2 H, hemiketal $C\underline{H}_3$), 1.12(d, 3H, $J = 6.0$ Hz, $R_2CH-C\underline{H}_3$), 1.28(s, 0.9 H, hemiketal $C\underline{H}_3$, 2.18 (s, 2H, $RCO-C\underline{H}_3$), 1.6 – 2.5 (m, 4H, $RC\underline{H}_2C\underline{H}_2R$), 3.8 – 4.3 (m, 3H, $(RO)R_2C\underline{H}$ and $O\underline{H}$), 4.60 (m, 0.8H, R(C)) CHOR): IR ($CHCl_3$) 3400 (OH), 2960 (CH), 1760, 1710 (CO) cm^{-1}; $R_f = 0.33$ (ethyl acetate). Bulb to bulb distillation at 1 mm gave analytically pure material: (Found: C, 60.76: H, 8.93 Calc. for $C_8H_{14}O_3$: C, 60.74: H, 8.92%).

(5S, 1'S: 5R, 1'R)-cis-2-*Acetyl-5 (1'-hydroxyethyl)-tetrahydrofuran* (**4**). Ketol **4** was prepared in a manner identical to that used for preparation of **3**. Flash chromatography[10] of the mixture on silica gel, elluting with 8% acetone/EtOAc gave **4** in 44% yield:

^{1}H NMR $(CDCl_3)\delta 1.22$(d, 3H, J = 6.6Hz, $R_2CHC\underline{H}_3$), 2.25(s, 3H, $R(CO)C\underline{H}_3$), 1.6 – 2.6(m, 4H, $RC\underline{H}_2C\underline{H}_2R$), 3.31(D, 1H, J = 5Hz, $RO\underline{H}$), 3.5 – 4.1(m, 2H, $(RO)R_2C\underline{H}$, 4.5(m, 1H, $R(CO)C\underline{H}OR$); ^{13}C NMR $(CDCl_3)\delta 19.78$, 25.97, 27.00, 29.12, 69.17, 83.30, 85.36, 210.04; IR$(CHCl_3)$ 3450(OH), 2975, 2875, 1770, 1708(CO) cm^{-1}; $R_f = 0.36$(8% acetone/ethyl acetate). Bulb to bulb distillation afforded analytically pure material: (Found: C, 60.97; H, 8.74. Calc. for $C_8H_{14}O_3$: C, 60.74; H, 8.92%).

(2S, 4R; 2R, 4S) 2,4-*Dimethyl1-2-methoxy-3,8-dioxabicyclo*-[3.2.1] *octane* (**5**). To a soln of 82 mg (0.52 mmol) of **3** in 1 ml MeOH was added 114 μl (110 mg, 1.04 mmol) trimethylorthoformate and a small crystal of *p*-toluenesulfonic acid monohydrate. After 5 hr the reaction was quenched by addition of a small amount of anhyd K_2CO_3. The resulting mixture was concentrated on a rotary evaporator. Flash chromatography[10] of the residue, elluting with 40 ml 40% hexanes/EtOAc, gave 45 mg (50%) colorless liquid which crystallized on standing at room temp and sublimed in the container at ambient temp and pressure (630 mm in Boulder): m.p. 55–56° (vac); ^{1}H NMR $(CDCl_3)\delta 1.01$ (d, 3H, J = 6.5 Hz, C-4 $C\underline{H}_3$), 1.18(s, 3H, C-2 $C\underline{H}_3$), 2.95 (m, 4H, $RC\underline{H}_2C\underline{H}_2R$), 3.31 (s, 3H, $OC\underline{H}_3$), 4.01(m, 2H, c-1 and C-5 H), 4.13(q of ds, J = 1.8, 6.5Hz, C-4 H); ^{13}C NMR $(C_6D_6)\delta 16.55$, 19.46, 21.94, 26.16, 47.42, 69.41, 77.42, 78.48, 98.53; IR$(CHCl_3)$ 2960, 1460, 1380, 1165, 1105, 1060 cm^{-1}; $R_f = 0.42$(EtOAc). A crystal of this material was analyzed by X-ray diffraction as described below.

(2S, 4S; 2R, 4R) 2,4-*Dimethyl-2-methoxy-3,8-dioxabicyclo*[3.2.1]-*octane* (**6**). Ketol **4** (162 mg, 1.03 mmol) was treated with trimethylorthoformate under the conditions described for preparation of **5**. Flash chromatography[10] of the crude product, elluting with 120 ml 60% hexanes/EtOAc afforded 52 mg (29%) of **6** as a colorless liquid which freezes at approximately −20°: ^{1}H NMR $(CDCl_3)\delta 1.17$ (s, 3H, C-2 $C\underline{H}_3$), 1.48 (d, 3H, J = 6.0Hz, C-4 $C\underline{H}_3$), 1.98(m, 4H, $RC\underline{H}_2C\underline{H}_2R$), 3.34(s, 3H, $OC\underline{H}_3$), 3.54(q, 1H, J = 6.0Hz, C-4H), 4.06(m, 2H, C-1 and C-5H); ^{13}C NMR $(C_6D_6)\delta 19.68$, 20.39, 25.58 27.91, 48.44, 74.31, 76.69, 79.70, 98.04; IR$(CHCl_3)$ 2950, 1450, 1375, 1160, 1130, 1115 cm^{-1}; $R_f = 0.34$(60% hexanes/EtOAc). Bulb to bulb distillation (70° at 20 mm) gave analytically pure material: (Found: C, 62.64; H, 9.44. Calc. for $C_9H_{16}O_3$: C, 62.77; H, 9.36;).

Continuing the flash chromatography elluting with 70 ml 8% acetone/EtOAc gave 119 mg (56%) of unstable **7**, identified by its ^{1}H and ^{13}C NMR spectra: colorless oil; ^{1}H NMR $(CDCl_3)\delta 1.15$ (d, 3H, J = 6.0Hz, $R_2CHC\underline{H}_3$), 1.23(s, 3H, $(OCH_3)_2$ $RC\underline{H}_3$), 1.7 – 2.0(m, 4H, $RC\underline{H}_2C\underline{H}_2R$), 2.9(broad s, 1H, $O\underline{H}$), 3.28(s, 6H, $OC\underline{H}_3$), 3.55 – 3.9(m, 2H, C-5 and C-1'H), 4.0 – 4.2(m, 1H, C-2H); ^{13}C NMR $(C_6D_6)\delta 17.81$, 19.66, 27.76, 27.91, 48.25, 48.73, 70.43, 81.01, 84.89, 10.27; IR$(CHCl_3)$ 1765, 1445, 1380 cm^{-1} $R_f = 0.16$ (60% hexanes EtOAc). Treatment of purified **7** with trimethylorthoformate under the conditions described above afforded identical isolated yields of bicyclic **6** and **7** after flash chromatography.

X-Ray crystallography.

Crystal data. $C_9H_{16}O_3$, M = 156.1 amu, Monoclinic, $a = 6.896(2)$, $b = 15.044(3)$, $c = 8.860(2)$Å, $\beta = 91.62(2)°$., U = 918.8(4) Å^3, Z = 4, $D_c = 1.128$ gcm^{-3}, F(000) = 376. MoK$_\alpha$ radiation, $\lambda = 0.71069$, μ(MoKα) = 0.991 cm^{-1}, space group $P2_1/n$ from systematic absences 0k0 when $K \neq 2n$ and h0l when $h + 1 \neq 2n$.

Crystallographic measurements. The crystals used for data collection formed in a sealed vessel from a neat soln of the compound at room temp. A crystal (0.29 × 0.33 × 0.50; clear colorless paralellpiped) was wedged in a glass capillary and sealed. This procedure was necessary because exposed crystals sublimed at room temp. The cell parameters were determined on the diffractometer and refined by least-squares fit of the parameters to 15 centered reflections ($14° < 2\theta < 24°$). Data were collected on a Syntex P$\bar{1}$ autodiffractometer using graphite monochromaticized MoK$_\alpha$ radiation and θ-2θ scan techniques. Data were collected at a scan rate of 2.0 deg/min over the range $3.0° < 2\theta < 40°$. Background measurements were made at the beginning and end of each measurement cycle. Intensities for the four standard reflections, monitored every 100 measurement cycles, showed a decline of 28% in observed intensity. The data were corrected for this and for Lorentz and polarization effects, but not for absorption. Of the 1558 reflections measured, 637 determined to be significant† and were used for the soln and refinement of the structure.

Structure analysis. The structure was solved by routine application of MULTAN 78.[11] The correct E-map showed the positions of the twelve non-H atoms as the top twelve peaks. The model was refined using isotropic thermal parameters to R = 0.11 and wR = 0.13.‡ H atoms were located in the resulting 3-dimensional difference map. These were included in fixed idealized positions with isotropic thermal parameters set to be 1.0 greater than the thermal parameter of the atom to which they were attached. Full-matrix least-square refinement with non-H atoms treated anisotropically converged with no shift in any parameter exceeding 2% of the corresponding e.s.d. The final residuals are R = 0.061 and wR = 0.061. The ratio of observations to parameters is 6:1. The final difference map was featureless. The scattering factors used were for neutral atoms.[12] All calculations were carried out on the University of Colorado's dual CDC 6400 computers using programs contained in or derived from Northwestern University crystallographic Library of Dr. J. A. Ibers, the MULTAN 78 package, and a data reduction program written in this laboratory.

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†A reflection was taken as significant when $F_0^2 > 3.0\sigma(F_0^2, \sigma(F_0^2) = RLP\{TSC + BACK + [P(TSC\text{-}BACK)]^2\}^{1/2}$, where TSC is the total number of counts accumulated the measurement scan, BACK is the total number of counts accumulated during the background measurement, P, a damping factor, was given a value of 0.04, and $RLP = 1/LP = (2 \sin\theta \cos\theta)/\{0.5[(\cos^2 2\theta_m + \cos^2 2\theta)/(1 + \cos^2 2\theta_m)] + 0.5[(\cos 2\theta_m + \cos^2 2\theta)/(1 + \cos 2\theta_m)]\}$, where θ and θ_m are the Bragg angles for the crystals and the monochromator ($2\theta_m = 26.6$). The fractional mosaicity of the monochromator is assumed to be 0.5.

‡$R = \Sigma|\,|F_0| - |F_c|\,|/\Sigma|F_0|$ and $wR = \{\Sigma w(|F_0| - |F_c|)^2/\Sigma w(F_0)^2\}^{1/2}$. The function minimized in the least-square procedure is $w(|F_0| - |F_c|)^2$. W is defined as $1.0/\sigma^2(F_0) = 4.0\,F_0^2/\sigma^2(F_0^2)$.

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