Synthesis, Reactions, and Structural Studies of Two-Carbon Bridged Spiropentanes

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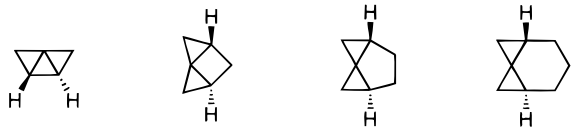
The syntheses of three 4,5-disubstituted derivatives of tricyclo[4.1.0.0^{1,3}]heptane (**3**) are reported. The relative stereochemistry of the oxygen substituents in these compounds was deduced by ^{13}C NMR spectroscopy and unequivocally confirmed by single-crystal X-ray analysis of the thiocarbonate derivative **15**. The experimental results obtained from reaction of the 2,4-diol **6** under Swern conditions and with TPAP were explained by the results of ab initio calculations at the MP2/6-31G* level of theory.

1. Introduction

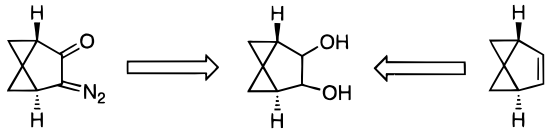
We have been interested in the synthesis and reactions of the bridged spiropentanes **1**−**4**.[1] The low-temperature X-ray structure for **3** has been reported,[2] yet experimental structural data for functionalized derivatives of **3** have not been forthcoming. Herein we report the synthesis, reactions, and structural data for some two-carbon bridged spiropentanes.



1 **2** **3** **4**

2. Synthesis of Functionalized Tricyclo[4.1.0.0^{1,3}]heptanes

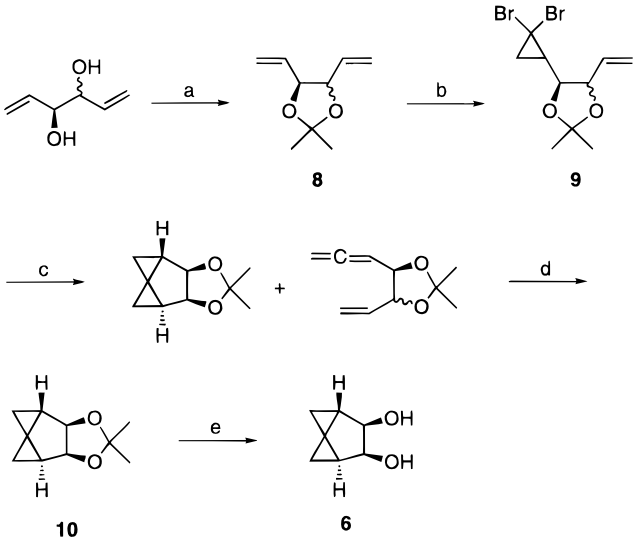
In our studies directed toward the synthesis of **5**[3,4] and **7**,[4] the diol **6** became an attractive intermediate. The synthesis of **6** is outlined in Scheme 1.



5 **6** **7**

The acid-catalyzed reaction of 1,5-hexadiene-3,4-diol with 2,2-dimethoxypropane gave the acetonide **8**.[5] A diastereomeric mixture of **9** was prepared in 20% yield when benzyltriethylammonium chloride was used as the phase-transfer catalyst in the addition of dibromocarbene to **8**. The yield of **9** was much improved (40%) when the procedure recently developed by Dailey and Lynch was used in which pinacol and dibenzo-18-crown-6 are used as the phase-transfer catalysts.[6] When **9** was treated with MeLi in diethyl ether, a brown liquid was obtained after quenching and workup. The ^{1}H NMR spectrum had strong allenic and olefinic signals, in addition to small aliphatic signals. In view of the past difficulty we have encountered in separation of desired tricyclic products from their allenic isomers on an appreciable scale,[8] ozone was passed through a methanolic solution of the crude product. Following workup with Me_2S and purification by silica gel column chromatography, the acetonide of tricyclo[4.1.0.0^{1,3}]heptane- 4,5-diol **10** was obtained as a clear, colorless liquid in 5% yield from **8**.

Scheme 1[a]



10 **6**

[a] Conditions: (a) 2,2-dimethoxypropane, *p*-TsOH−H_2O, CH_2Cl_2; (b) $CHBr_3$, 50% NaOH, pinacol, dibenzo-18-crown-6, 45 °C; (c) MeLi, Et_2O, −78 °C; (d) (1) O_3, MeOH, −78 °C, (2) Me_2S; (e) 13% 1.0 M HCl, THF.

3. Structural Analysis

Since the starting material was a mixture of both *d*,*l* and *meso*-1,5-hexadiene-3,4-diol, the intramolecular at-

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(2) Boese, R.; Bläser, D.; Gomann, K.; Brinker, U. *J. Am. Chem. Soc.* **1989**, *111*, 1501.
(3) Wiberg, K. B.; Snoonian, J. R.; Lahti, P. M. *Tetrahedron. Lett.* **1996**, 8285.
(4) Wiberg, K. B.; Snoonian, J. R. *J. Org. Chem.* **1998**, *63*, 1390.
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(6) Dailey, W. P.; Lynch, K. M. *J. Org. Chem.* **1995**, *60*, 4666.
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(8) Wiberg, K. B., Snoonian, J. R. *Tetrahedron. Lett.* **1995**, 1171.

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tack of the cyclopropylidene upon the double bond could have conceivably yielded both the cis and trans epimers of **10** with respect to the dioxolane stereochemistry. Although both **10-*cis*** and **10-*trans*** could have been formed, it was found that only **10-*cis*** was produced, and this epimer is derived from *meso*-1,5-hexadiene-3,4-diol.

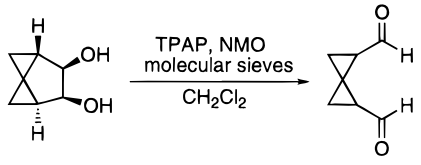
The cis stereochemistry of **10** was determined by ^{13}C NMR spectroscopy. Compound **10-*cis*** lacks a symmetry element and, thus, would be expected to have a distinct resonance in the ^{13}C NMR spectrum for each carbon. Only a single tricyclic compound was detected in this reaction, and it exhibited 10 bands in its ^{13}C NMR spectrum at δ 18.3 (t), 18.9 (d), 19.7 (t), 25.0 (d), 26.0 (q), 27.6 (q), 30.8 (s), 88.4 (d), 92.4 (d), and 112.6 (s) ppm. On the other hand, **10-*trans*** would possess a C_2 axis of symmetry and would, therefore, be expected to have only six resonances in its ^{13}C NMR spectrum.

Product stability may explain the observation that **10-*trans*** was not detected. Both **10-*cis*** and **10-*trans*** contain a substructure that resembles a bicyclo[3.3.0]-octane ring system, and it is known that a trans ring fusion in such a system is more strained than when the ring fusion is cis. *trans*-Bicyclo[3.3.0]octane has a $\Delta H_f = -15.9$ kcal/mol and a strain energy of 15.8 kcal/mol, while *cis*-bicyclo[3.3.0]octane has a $\Delta H_f = -22.3$ kcal/mol and a strain energy of 9.4 kcal/mol.[9] The 6.4 kcal/mol difference in the heats of formation corresponds to over a 50 000/1 ratio of *cis*- to *trans*-bicyclo[3.3.0]octane at 298 K, making the formation of the trans compound negligible. It is reasonable to propose a similar explanation in the case of **10-*cis*** and **10-*trans*** because the only difference between the two structures is the relative stereochemistry of the bridgehead oxygens, and thus, both heterocyclic [3.3.0]octanes should have a geometry very similar to that of their corresponding parent hydrocarbons.

Removal of the acetonide protecting group was best affected by treatment of **10** with 13 vol % of 1.0 M aqueous HCl in THF at ambient temperature.[11] The diol **6** was consistently isolated in yields of 70−75% after recrystallization from hexanes−diethyl ether. The ^{13}C NMR displayed seven chemical shifts at δ 15.7 (t), 20.8 (d), 22.6 (t), 23.8 (d), 25.9 (s), 80.7 (d), and 84.4 (d), which indicates **6** also has a cis relationship of the hydroxyl groups.

Oxidation of **6** with tetra-N-propylammonium perruthenate (TPAP) and *N*-methylmorpholine *N*-oxide (NMO)[12] gave a rapid reaction in which the only product was spiropentane-1,3-dialdehyde. It is known that chromium-based reagents lead to cleavage of vicinal diols,[13] but cleavage with TPAP was somewhat unexpected.

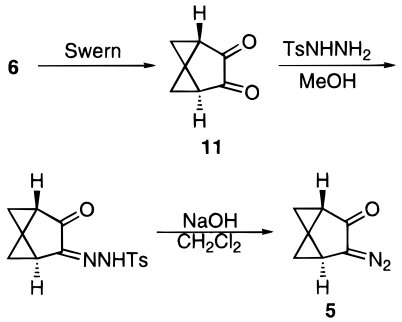
Oxidation of **6** was attempted under Swern conditions.[14] The reaction gave a yellow solution after workup, but the solution rapidly darkened to an orange color even when the solution was kept under argon. Evaporation



6 **16**

of the volatiles gave an orange oil that was insoluble even in methanol and acetone.

When the crude reaction mixture immediately following Swern oxidation was treated with a methanolic solution containing 1 equiv of tosylhydrazine based on the theoretical amount of diketone present, a white-orange solid was obtained. A dichloromethane solution of this solid was treated with aqueous NaOH,[15] and 5-diazo-tricyclo[4.1.0.0^{1,3}]heptane-4-one **(5)** was produced.



11 **5**

Since **5** formed by this route is necessarily derived from **11**, this means that the failure of the Swern oxidation was due to the instability of the product diketone, and not the reaction itself. Although **5** could be prepared by this route, the overall yield was not much improved over another synthesis of **5** we have previously reported.[4]

4. Calculations

Tricyclo[4.1.0.0^{1,3}]heptane-4,5-dione (**11**) has some interesting geometrical features that were calculated at the MP2/6-31G* level of theory. The molecule was initially given C_1 symmetry, but the optimized structure was C_2 symmetric. We have shown that it is possible to estimate heats of formation at 298 K from MP2/6-31G* energies,[4] and from these heats of formation values, it is possible to calculate strain energies using Franklin's group equivalent values to define strainless models.[16] The diketone (**11**) has a calculated $\Delta H_f = +8.7$ kcal/mol and a strain energy of 83.3 kcal/mol. A noteworthy geometrical feature of this diketone is that the $O_{14}-C_6-C_7-O_{15}$ torsional angle is 1.3°. A 1,2-diketone normally adopts a conformation such that the torsional angle between the carbonyl oxygens is as large as possible so as to minimize the interaction between the carbonyl group dipoles. However, in the tricyclic structure the carbonyl groups exist in a nearly planar conformation since their incorporation into the tricyclic ring system restricts rotation about the C_6-C_7 bond.

The instability of **11** is not the result of having two adjacent sp^2-hybridized centers on the ethano bridge. If this were the case, then **12**, which we have reported

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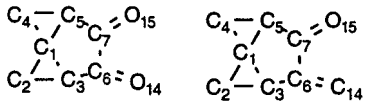
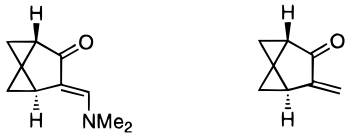
(16) Franklin, J. L. *Ind. Eng. Chem.* **1949**, *41*, 1070.

Table 1. Geometries of 11 and 13 Optimized at the MP2/6-31G* Level of Theory



bond lengths (Å)	**11**	**13**
C_1-C_2	1.466	1.472
C_1-C_3	1.490	1.493
C_2-C_3	1.552	1.545
C_3-C_6	1.498	1.487
C_6-C_7	1.569	1.517
C_7-O_{15}	1.221	1.225
bond angles (deg)	**11**	**13**
$C_1-C_2-C_3$	59.1	59.3
$C_1-C_3-C_2$	57.6	57.9
$C_1-C_3-C_6$	106.6	106.4
$C_2-C_1-C_3$	63.3	62.8
$C_2-C_1-C_4$	160.2	161.2
$C_3-C_1-C_5$	111.7	110.6
$C_3-C_6-C_7$	107.2	108.4
$C_3-C_6-O_{14}$	129.0	126.8
$C_7-C_6-O_{14}$	123.6	125.6

to be quite stable,[4] would also be expected to be an unstable compound. To gain further insight into the origin of the instability of the tricyclic diketone, the hypothetical methylene compound **13** was also studied at the MP2/6-31G* level of theory. This compound should have a geometry very similar to that of the experimentally known α-enamino ketone, **12**, but **13** was more practical to study by ab initio methods since it contains fewer heavy atoms than **12**.[5]

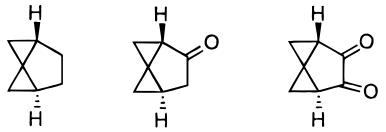


12 **13**

There is little difference between **11** and **13** in terms of spiropentyl distortion. Table 1 gives the calculated data and shows that the $C_3-C_1-C_5$ angle in **11** is 111.7° and that this same angle is 110.6° for **13**. The difference between the $O_{15}-C_7-C_6-O_{14}$ torsional angle in **11** and the corresponding $O_{15}-C_7-C_6-C_{14}$ angle in **13** is not significant, as it is 1.3° in the former and 0.6° in the latter. Furthermore, **13** had a calculated $\Delta H_f = +48.1$ kcal/mol and a strain energy of 74.1 kcal/mol. Thus, the strain energy of **11** is estimated to be 9 kcal/mol higher than **13**. Since the torsional angle between the bridge substituents and spiropentyl distortion are essentially the same in both compounds, another geometrical feature must be the source of the diketone's instability.

The C_6-C_7 bond in **11** is 1.569 Å. This is 0.052 Å longer than the C_6-C_7 bond in **13**. As a result of being locked into a conformationally rigid structure, **11** is unable to minimize the dipole−dipole interaction between the carbonyl groups by creating an appreciable $O_{15}-C_7-C_6-O_{14}$ torsional angle. An alternative way of reducing the repulsive interaction between the carbonyl groups, however, is to lengthen the distance between the sp^2 carbons to which the carbonyl oxygens are attached. This unusually long, bridging bond in **11** may lead to its high instability. This conclusion, as based on the calculated results, is in agreement with the experimental observation that cleavage of the C_6-C_7 bond is observed in the attempted synthesis of **11** by oxidation of **6** with TPAP.

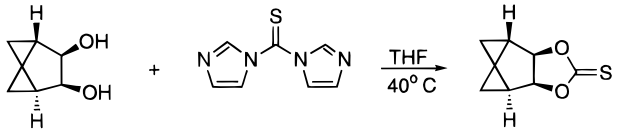
The calculated strain energies of tricyclo[4.1.0.0^{1,3}]-heptane **(3)**,[17] tricyclo[4.1.0.0^{1,3}]heptane-4-one **(14)**[18], and tricyclo[4.1.0.0^{1,3}]heptane-4,5-dione **(11)** illustrates how different structural features can affect strain in a molecule.[19] The calculated 1.9 kcal/mol reduction in strain



	3	**14**	**11**
strain energy (kcal/mol)	79.2	77.3	83.3

in **14** as compared to **3** may be attributed to removal of three eclipsing hydrogen−hydrogen interactions in **14**. Extension of this reasoning would predict that **11** should have a strain energy *lower* than that of both **3** and **14** because a hydrogen−hydrogen eclipsing interaction that exists in **14** is absent in **11**. This, however, is not the case, as the strain energy of **11** is *higher* than that of both **3** and **14**. Here the removal of a hydrogen−hydrogen interaction is not sufficient to offset the repulsive, nonbonded interaction between the lone-pairs on the carbonyl oxygens in **11**.

Another use for the diol, **6**, was found. The preparation of **6** opened the possibility that deoxygenation could give **7**. One approach to the preparation of **7** involved the Corey−Winter reaction[20] of thiocarbonate **15**. The chemistry of **15** and other derivatives used in our attempts to prepare **7** are reported elsewhere.[4] Reaction of **6** with



6 **15**

(thiocarbonyl)diimidazole at 40 °C in THF gave **15** in 80% yield as hexagonal columns after recrystallization from hexanes−diethyl ether. Like **6** and **10**, the thiocarbonate **15** had cis stereochemistry as first determined by ^{13}C NMR spectroscopy and was unequivocally confirmed by X-ray crystallography (Figure 1).

The geometries of a number of the bridged spiropentanes prepared in our laboratory have been calculated by ab initio molecular orbital theory,[1,4,21] and it was of interest to compare the experimental geometry of **15** to that calculated at the MP2/6-31G* level of theory. The experimental and calculated data are given in Table 2. The agreement between bond angles is quite good (Figure 3). Most of the bond lengths are well correlated with a slope close to unity (Figure 2). The exceptions are the

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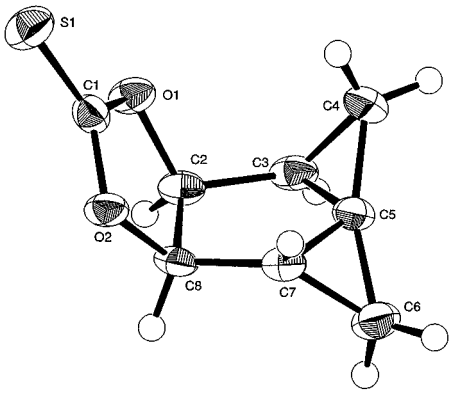
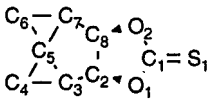


Figure 1. Structure of the thiocarbonate **15** as determined by X-ray crystallography.

Table 2. Geometry of the Thionocarbonate of *cis*-Tricyclo[4.1.0.0^{1,3}]heptane-4,5-diol (15) Determined by X-ray Crystallography as Compared to the Geometry Calculated at the MP2/6-31G* Level of Theory[a]



bond lengths	X-ray	MP2/6-31G*	bond lengths	X-ray	MP2/6-31G*
C_1-O_1	1.325	1.356	C_3-C_5	1.482	1.487
C_1-O_2	1.330	1.359	C_4-C_5	1.471	1.472
C_1-S_1	1.628	1.621	C_5-C_6	1.470	1.475
C_2-O_1	1.469	1.451	C_5-C_7	1.478	1.482
C_2-C_8	1.537	1.546	C_6-C_7	1.529	1.536
C_2-C_3	1.500	1.514	C_7-C_8	1.519	1.528
C_3-C_4	1.531	1.537	C_8-O_2	1.455	1.441
bond angles	**X-ray**	**MP2/6-31G***	**bond angles**	**X-ray**	**MP2/6-31G***
$C_1-O_1-C_2$	110.8	110.2	$C_4-C_3-C_5$	58.4	58.2
$C_1-O_2-C_8$	109.8	108.6	$C_5-C_6-C_7$	59.0	58.9
$C_2-C_3-C_4$	123.5	122.1	$C_5-C_7-C_6$	58.5	58.5
$C_2-C_8-O_2$	103.8	103.3	$C_5-C_7-C_8$	107.2	106.9
$C_2-C_8-C_7$	105.9	104.6	$C_6-C_7-C_8$	124.9	123.0
$C_2-C_3-C_5$	107.1	106.1	$C_6-C_5-C_7$	62.5	62.6
$C_3-C_4-C_5$	59.1	59.2	$C_7-C_8-O_2$	109.0	110.5
$C_3-C_5-C_4$	62.5	62.6	$C_8-C_2-O_1$	102.0	101.3
$C_3-C_2-O_1$	113.0	114.3	$O_1-C_1-O_2$	112.2	110.8
$C_3-C_5-C_7$	110.3	110.2	$O_1-C_1-S_1$	123.6	124.6
$C_4-C_5-C_6$	162.5	160.5	$O_2-C_1-S_1$	124.2	124.6

[a] Bond lengths are in Angstroms and bond angles are in degrees. The numbering scheme is that which was assigned to the X-ray Structure.

C−O bond lengths in which the calculated C−O bond lengths from the tricyclic system are too short and the C−O bond lengths to the C=S group are too long. The average absolute error between the calculated and experimental value for the bonds in **15** is 0.012 Å or 0.8%.

It was also interesting to make a direct comparison between the X-ray data for **15** with those previously reported for **3**. The C_2-C_8 bond is slightly shorter in **15** than in **3**, which leads to a slightly larger $C_4-C_5-C_6$ bond angle in **15** as compared to **3**. Otherwise, the geometry of the tricyclo[4.1.0.0^{1,3}]heptane ring system is not greatly affected by the oxygen atoms bonded to the bridging carbons.

5. Conclusions

This work has described the synthesis of some derivatives of tricyclo[4.1.0.0^{1,3}]heptane **(3)**. The cis stereochemistry of **6**, **10**, and **15** was deduced by ^{13}C NMR spectroscopy and unequivocally confirmed by the first known X-ray crystal structure of a functionalized derivative of **3**. In conjunction with experimental observations, a computational study of **11** and **13** suggests that the long C_6-C_7 bond, resulting from the geometrical constraints imposed on this molecule and repulsive interaction between the lone pairs on the vicinal carbonyl groups, is responsible for its observed instability. The preparation of **6** may be of use in the synthesis of other functionalized bridged spiropentanes.

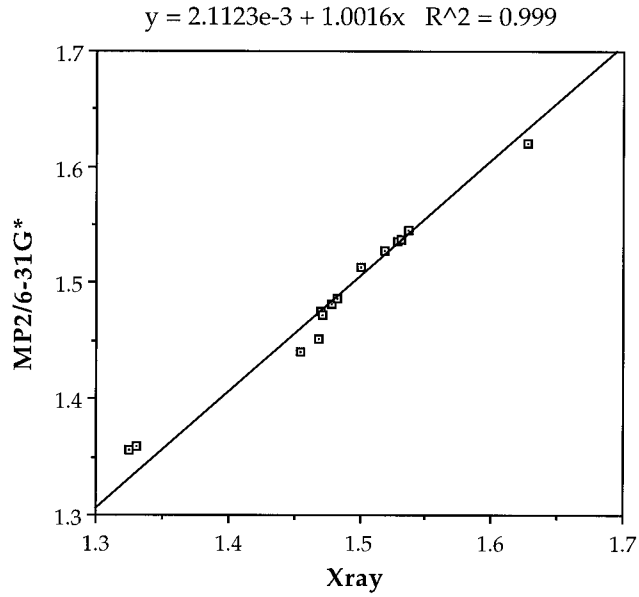
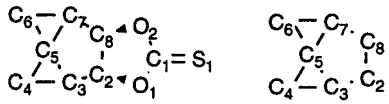


Figure 2. Correlation between the experimental and calculated (MP2/6-31G*) bond lengths in **15**. The line was forced to go through the origin.

Table 3. Comparison of the Experimental Geometries of 15 and 3[2]



	15	**3**
bond lengths (Å)	**15**	**3**
C_3-C_5	1.482	1.477
C_5-C_6	1.470	1.481
C_2-C_8	1.537	1.550
C_6-C_7	1.529	1.537
C_2-C_3	1.500	1.526
bond angles (deg)	**15**	**3**
$C_2-C_8-C_7$	105.9	103.4
$C_6-C_5-C_7$	62.5	62.6
$C_3-C_5-C_7$	110.3	110.1
$C_4-C_5-C_6$	162.5	158.2

6. Experimental Section

General Information. The basic information is given in the preceding paper.[4] All calculations were performed using the developmental version of GAUSSIAN 95.[23] Unless otherwise stated, all of the calculated energy values and geometrical

(22) Hehre, W. J.; Radom, L.; Schleyer, P.v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley and Sons: New York, 1986.

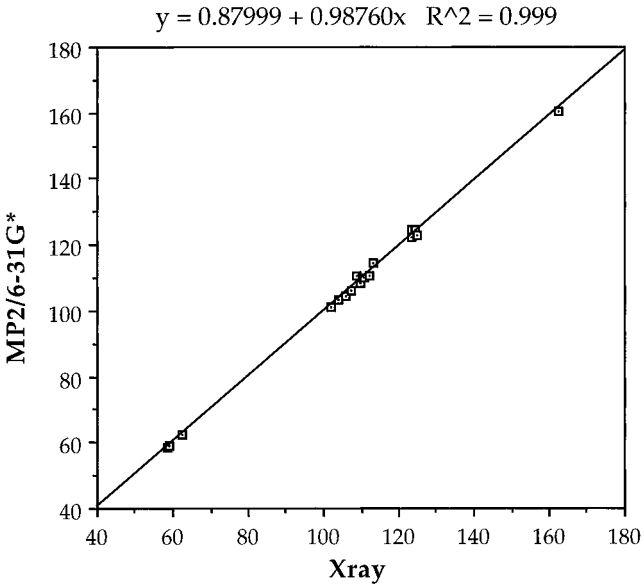


Figure 3. Correlation between the experimental and calculated (MP2/6-31G*) bond angles in **15**. The slope is 0.99 and $r^2 = 0.999$.

parameters were obtained by using the FOPT option at the MP2[24] level of theory, the 6-31G* basis set,[25] and the frozen core approximation.[26] The measurements for the crystal structure of **15** were made using an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo Ka radiation, and the structure was solved using the SHELXS method[27] with the TEXAN-TEXRAY structural analysis programs.[28]

***d,l*- and *meso*-2,2-Dimethyl-4,5-divinyl-1,3-dioxolane (8).** To a solution of 325 g of 1,5-hexadiene-3,4-diol (2.85 mol) and 593 g (5.69 mol) of 2,2-dimethoxypropane in 300 mL of CH_2Cl_2 was added 15.0 g of *p*-TsOH−H_2O in small portions over 5 min. After 8 h, the solution was diluted with 600 mL of CH_2Cl_2. The CH_2Cl_2 solution was washed with 1.0 L of 1.0 M NaOH, and the aqueous layer was then extracted with 200 mL of CH_2Cl_2. The total organic solution was fractionally distilled at ambient pressure to remove the CH_2Cl_2, followed by fractional vacuum distillation to afford 387 g (88% yield) of the product as a mixture of the *d,l*- and *meso*-dioxolanes (bp 46−49 °C, 15 Torr). All spectral data were identical with that reported in the literature.[5]

***d,l*- and *meso*-4-(2′,2′-Dibromocyclopropyl)-2,2-dimethyl-5-vinyl-1,3-dioxolane (9).** To 143 g (0.93 mol) of **8**, 423 g (1.67 mol) of bromoform, 4.6 g (39 mmol) of pinacol, and 3.4 g (9.3 mmol) of dibenzo-18-crown-6 was added 300 g of NaOH dissolved in 300 g of H_2O (50% NaOH by weight) in one portion. The initially clear reaction mixture became orange, then brown, and then black-brown 25 min after addition of the NaOH, and the reaction temperature rose to 49 °C, at which time the temperature of the reaction was maintained at 45−49 °C by periodic cooling of the flask walls with ice. When the temperature dropped to 42 °C without the need for external cooling, a heating mantle was placed under the flask to maintain the internal reaction temperature at 45−47 °C for 48 h. The brown, viscous mixture was then cooled to ambient temperature and poured into a 2 L Erlenmeyer flask containing 150 g of Celite. One liter of water was added, and the flask was swirled periodically over a 30 min period. The mixture was then suction filtered through a coarse-fritted funnel. The aqueous filtrate may be discarded. The Celite pad was washed repeatedly with 500 mL portions of 1:1 pentane:acetone using vacuum filtration until the filtrate passing into the flask was colorless. This required approximately 4 L of 1:1 pentane−acetone. The volatiles were removed by rotary evaporation, and the resultant brown oil was vacuum distilled (bp = 95−115 °C, 0.7 Torr) to give 121 g of the dibromide (40% yield) as a clear, pale yellow liquid. The product is a mixture of four diastereomeric pairs, and no attempts were made to separate these diastereomers.

9: ^{1}H NMR δ 1.18−1.94 (m, cyclopropyl), 1.39 (s, CH_3), 1.53 (s, CH_3), 1.54 (s, CH_3), 3.38−3.44 (t, 1H), 3.61−3.66 (t, 1H), 3.83−3.88 (d of d 1H), 3.91−3.96 (d of d, 1H), 4.30−4.35 (t, 1H), 4.37−4.42 (t, 1H), 4.56−4.63 (q, 1H), 4.72−4.74 (d, 1H), 4.80−4.84 (t, 1H), 5.26−5.68 (m, 4H), 5.74−6.27 (m, 2H); CIMS 329(21), 327(42), 325(25), 271(26), 269(50), 267(29), 191(67), 189(100); HRMS calcd for $C_{10}H_{14}Br_2O_2$ CI, (M + 1) 326.9418, found 326.9429.

Acetonide of *cis*-tricyclo[4.1.0.0^{1,3}]heptane-4,5-diol (10). To 100 mL of a 1.4 M, salt-free, diethyl ether solution of MeLi at −78 °C was added dropwise a 40.0 g (12.3 mmol) mixture of *d,l*- and *meso*-**9** dissolved in 400 mL of Et_2O over 7 h. The solution was stirred at −78 °C for an additional 2 h and then allowed to warm to 0 °C. Excess MeLi was decomposed by careful addition of water. The quenched solution was washed with two 200 mL portions of saturated NH_4Cl and one 100 mL portion of saturated NaCl and concentrated in vacuo. The resultant yellow-brown residue was dissolved in 75 mL of absolute MeOH and treated with O_3 at −78 °C until a bright yellow color persisted (this solution never became blue when saturated with ozone). After the solution was purged of excess O_3, Me_2S was added at −78 °C. The solution was allowed to warm to ambient temperature, and the MeOH and excess Me_2S were removed in vacuo. The residue was poured into 200 mL of pentane and washed with 100 mL of saturated $NaHSO_3$. The pentane solution was washed with two additional 100 mL portions of saturated $NaHSO_3$ and then the total aqueous layer was extracted with two 100 mL portions of pentane. The total pentane solution (400 mL) was dried over Na_2SO_4 and concentrated in vacuo. Silica gel column chromatography using 4:1 pentane:Et_2O as the eluant gave the pure acetonide (R_f = 0.80) as a clear, colorless liquid.

10: ^{1}H NMR δ 0.98−1.05 (m, 2H), 1.25 (s, 3H), 1.39−1.43 (t of d, 1H), 1.47 (s, 3H), 1.64−1.68 (AB, 1H), 1.83−1.87 (d of d, 1H), 2.18−2.21 (t of d, 1H), 4.72−4.78 (d of t, 2H); ^{13}C NMR δ 18.28 (t), 18.91 (d), 19.68 (t), 24.97 (d), 26.02 (q), 27.62 (q), 30.76 (s), 88.39 (d), 92.42 (d), 112.57 (s); GC/MS 151 (3), 107 (13), 91 (15), 79 (100), 43 (30), 39 (30); CIMS 167 (41), 109 (97), 81 (100); HRMS calcd for $C_{10}H_{14}O_2$ CI, (M + 1) 167.1072, found 167.1068.

***cis*-Tricyclo[4.1.0.0^{1,3}]heptane-4,5-diol (6).** To a solution of 0.74 g (4.4 mmol) of **10** in 9 mL of THF was added 1.4 mL of 1.0 M aqueous HCl. After 36 h, the THF was removed in vacuo, and the residue was passed through a short column of silica gel using Et_2O as the eluant (R_f = 0.59). Removal of the Et_2O in vacuo (caution−use an oversized flask due to bumping) gave the product as a white solid that was recrystallized from 1:1 Et_2O:hexanes to give 0.45 g (82% yield) of the diol as clear, colorless, rhombic crystals (mp 55.0−56.6 °C).

6: ^{1}H NMR δ 1.04−1.08 (m, 1H), 1.17−1.22 (m, 1H), 1.48−1.51 (m, 1H), 1.67−1.71 (d of d, 1H, J = 4.4 Hz), 1.85−1.89 (t, 1H), 1.91−1.94 (m, 1H), 2.07 (s, 2H, broad), 3.91−3.94 (t, 1H), 4.36−4.39 (t of d, 1H); ^{13}C NMR δ 15.69 (t), 20.83 (d), 22.59 (t), 23.84 (d), 25.87 (s), 80.68 (d), 84.41 (d); CIMS 127 (11), 109 (47), 81 (100); HRMS calcd for $C_7H_{10}O_2$ CI, (M + 1) 127.0759, found 127.0758.

(23) Gaussian 95, Development Version (Revision D.2): Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Strain, M. C.; Burant, J. C.; Stratman, E.; Petersson, G. A.; Montgomery, J. A.; Zakrzewski, V. G.; Keith, T.; Raghavachari, K.; Al-Laham, M. A.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Gonzalez, C.; Head-Gordon, M.; Gill, P. M. W.; Johnson, B. G.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1996.

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(27) Sheldrick G. M.; Egert, E. *General Direct Methods and Automatic Patterson*; University of Goettingen, 1984.

(28) TEXSAN−TEXRAY Structure Analysis Package, Molecular Structure Corporation, 1989.

Reaction of 6 with TPAP. To a solution of 5.0 mg (0.040 mmol) of **6** and 5.3 mg (0.045 mmol) of *N*-methylmorpholine *N*-oxide in 4 mL of CH_2Cl_2, containing eight 4 Å molecular sieves, was added 0.7 mg (0.002 mmol) of tetra-*N*-propylammonium perruthenate (TPAP) in one portion. The initially pale-yellow solution turned brown-black, and 5 min after addition of the TPAP, TLC (Et_2O), showed that **6** had been consumed. The mixture was diluted with CH_2Cl_2 to a volume of 25 mL and was washed with 10 mL of saturated Na_2SO_3, 10 mL of saturated NaCl, and then 10 mL of saturated $CuSO_4$. The CH_2Cl_2 solution was dried over Na_2SO_4 and then concentrated in vacuo to give about 4 mg of a white solid, which proved to be the cleavage product, spiropentane-1,3-dialdehyde (**16**).

16: IR 1708 cm^{-1}; ^1H NMR δ 1.61−1.69 (m, 4H), 2.45−2.51 (m, 2H), 9.18 (d, 2H, $J = 4.7$ Hz); GC/MS 95 (100), 67 (49), 39 (82).

Thiocarbonate of *cis*-Tricyclo[4.1.0.0^{1,3}]heptane-4,5-diol (15). A solution of 0.25 g (2.0 mmol) of **6** and 1.0 g of 90% (thiocarbonyl)diimidazole (5.1 mmol of reagent) in 16.5 mL of THF was heated at 40 °C for 5 h. The orange solution was cooled to ambient temperature, and the THF was removed in vacuo. The residue was dissolved in 100 mL of CH_2Cl_2 and washed with two 50 mL portions of water, dried over Na_2SO_4, and concentrated in vacuo. The residue was passed through a short column of florisil using Et_2O as the eluant ($R_f = 0.77$, silica plate). Removal of the Et_2O in vacuo gave a white solid which was recrystallized from 4:1 Et_2O−hexanes to give 0.27 g (80% yield after recrystallization) of the desired thiocarbonate as hexagonal columns (mp 77.6−78.4 °C).

15: IR 1280 cm^{-1}; ^1H NMR δ 1.33−1.41 (m, 2H), 1.79−1.82 (t of d, 1H), 2.02−2.06 (t, 1H), 2.14−2.18 (t, 1H), 2.28−2.32 (t of d, 1H), 5.33−5.41 (d of t, 2H); ^{13}C NMR δ 20.2, 20.9, 21.7, 24.4, 31.5, 94.0, 94.6, 191.2; GC/MS 168 (9), 91 (100), 79 (75); CIMS 169 (66), 109 (27), 91 (100), 81 (79), 79 (33); HRMS calcd for $C_8H_8O_2S$ 168.0245, found 168.0244.

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Supporting Information Available: X-ray crystallographic data for the thiocarbonate, **15**, and NMR spectra for compounds **6**, **9**, **10**, and **16** (20 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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