

residual in this structure is probably associated with the generally higher level of thermal vibration in **2** than in **1**.

In each case, a conventional weighting scheme was used.¹⁵ Scattering curves for the nonhydrogen atoms were taken from Hanson, Herman, Lea, and Skillman,¹⁶ and allowance was made for the real part of the anomalous dispersion terms for Si, S, and O.¹⁷ For hydrogen, the curve of Stewart, Davidson, and Simpson was used.¹⁸ Programs used, other than FAME-MAGIC and ORTEP for which a CDC 6400 computer was used, were written in this laboratory for the Sigma 2 computer.

Registry No.—**1**, 13433-56-2; **2**, 63883-55-6; **4**, 60349-76-0; 2-triphenylsilyl-1,3-dithiane, 13433-53-9.

Supplementary Material Available. Anisotropic thermal parameters, selected nonbonded intramolecular contact distances, intermolecular contacts, and information on least-squares mean planes of interest (3 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) Presented, in part, at the 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974, and at the 10th International Union of Crystallography Congress, Amsterdam, Netherlands, August 1975; see: *Acta Crystallogr., Sect. A*, **31**, S166 (1975).
- (2) F. A. Carey, O. D. Dailey, Jr., O. Hernandez, and J. R. Tucker, *J. Org. Chem.*, **41**, 3975 (1976).
- (3) The directly analogous 2-triphenylsilyl-1,3-dithiane was prepared for comparison with **2**, but crystal twinning prevented a successful x-ray analysis. Use of **1** allows a check on the effect of oxygenation and of triphenylsilyl substitution and throws light on the effect of additional axial substitution at C(2).
- (4) F. A. Carey, P. M. Smith, R. J. Maher, and R. F. Bryan, *J. Org. Chem.*, **42**, 961 (1977).
- (5) For a theoretical treatment, see: N. L. Allinger and J. Kao, *Tetrahedron*, **32**, 529 (1976).
- (6) A. T. McPhail, K. D. Onan, and J. Koskimies, *J. Chem. Soc., Perkin Trans. 2*, 1004 (1976).
- (7) R. F. Bryan, F. A. Carey, O. D. Dailey, Jr., R. Maher, and R. W. Miller, *J. Org. Chem.*, accompanying paper in this issue.
- (8) C. K. Johnson, "ORTEP-II, A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations", ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1976.
- (9) Values of geometrical parameters for 2-phenyl-1,3-dithiane are taken from H. T. Kalf and C. Romers, *Acta Crystallogr.*, **20**, 490 (1966).
- (10) (a) A. Domenicano, A. Vaciago, and C. A. Coulson, *Acta Crystallogr., Sect. B*, **31**, 221 (1975); (b) A. Domenicano, P. Mazzeo, and A. Vaciago, *Acta Crystallogr., Sect. A*, **31**, S117 (1976); (c) A. Domenicano, A. Vaciago, and C. A. Coulson, *Acta Crystallogr., Sect. B*, **31**, 1630 (1975).
- (11) M. Colapietro, A. Domenicano, and A. Vaciago, *Acta Crystallogr., Sect. A*, **31**, S117 (1975).
- (12) A comparable nonbonded interaction occurs intramolecularly in (–)-*o*-carboxyphenyl methyl sulfoxide, but excited no comment. See: B. Dahlén, *Acta Crystallogr., Sect. B*, **30**, 642, (1974).
- (13) A. G. Brook, J. M. Duff, P. F. Jones, and N. R. Davis, *J. Am. Chem. Soc.*, **89**, 431 (1967).
- (14) E. B. Fleischer, R. B. K. Dewar, and A. L. Stone, *Abstr. Am. Crystallogr., Assoc. Atlanta*, **20** (1967).
- (15) D. F. Grant, R. C. G. Killeen, and J. L. Lawrence, *Acta Crystallogr., Sect. B*, **25**, 374 (1969).
- (16) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).
- (17) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
- (18) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1969).

Optically Active 1,3-Dithiane 1-Oxide: Optical Resolution and Absolute Configuration

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Received May 31, 1977

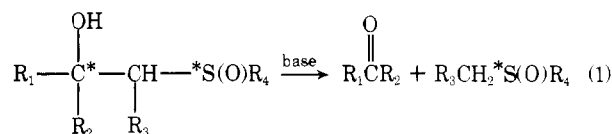
1,3-Dithiane 1-oxide (**1**) has been resolved into its enantiomers by two methods, both based on separation of D(+)-camphor adducts followed by base-catalyzed cleavage back to **1** and camphor. Reaction of the lithio derivative of (±)-**1** with D(+)-camphor gives a mixture of diastereomeric adducts **2** and **3**, either of which may be isolated depending on the temperature at which the reaction is carried out and the isolation procedure adopted. Diastereomer **2** was cleaved to (–)-**1** on treatment with potassium hydroxide in *tert*-butyl alcohol, whereas similar treatment of **3** yielded (+)-**1**. Oxidation of (2*R*)-2-(1,3-dithian-2-yl)isborneol (**4**) with *m*-chloroperoxybenzoic acid gave a mixture of diastereomeric sulfoxides from which **3** could be isolated. The absolute configuration of (–)-**1** is *S* as determined by x-ray crystallographic characterization of its precursor **2**. Crystals of **2** conform to space group *P*₂₁₂₁ with *a* = 23.890 (7), *b* = 9.336 (4), *c* = 6.727 (3) Å, and *Z* = 4. The valence angle of 112.8° found for S–C–S in the dithiane moiety of **2** is identical with that found in *cis*-2-phenyl-1,3-dithiane 1-oxide.

The stereochemical properties of 1,3-dithiane 1-oxide (**1**) and its derivatives are receiving much attention. Questions of conformation have been studied experimentally^{1–3} and probed by molecular mechanics.⁴ These investigations, together with x-ray crystallographic studies,⁵ have revealed significant structural effects associated with cross-ring electrostatic interactions. The stereoselectivity of formation of diastereomeric derivatives of **1** by oxidation of 2-substituted 1,3-dithianes^{1,6} and by the reaction of the 2-lithio derivative of **1** with electrophilic reagents has been determined.⁷

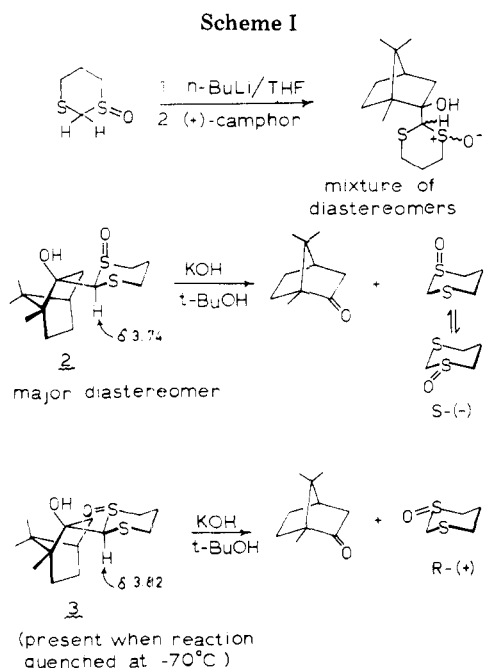
Since **1** is a chiral molecule, other aspects of stereochemistry may be explored as well. Asymmetric synthesis, for example, would use optically active **1** as a chiral carbonyl equivalent group. The synthetic value of carbonyl equivalents in nucleophilic acylation reactions is well established.⁸ Many useful transformations involving 1,3-dithiane⁹ and methyl methylthiomethyl sulfoxide¹⁰ have been described which embody this concept. Considerable success in asymmetric synthesis has also been achieved by Meyers using (4*S*,5*S*) 2-substituted

4-methoxymethyl-5-phenyl-2-oxazolines as chiral carbonyl equivalents.¹¹

A number of techniques have been developed for the preparation of optically active sulfoxides.¹² Sulfinyl-group transfers from optically active sulfinate esters on reaction with organometallic reagents have proven particularly useful¹³ but are not appropriate for **1**. Oxidations of unsymmetrical sulfides with optically active peroxy acids have been reported, but normally with low optical yields.¹² We envisioned generation of optically active **1** by base-catalyzed cleavage of a single stereoisomer of a β-hydroxyalkyl sulfoxide (eq 1). The process



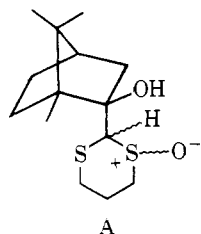
is then one of resolution whereby separation of a mixture of diastereoisomers and subsequent cleavage lead to optically



active sulfoxide. In principle, the technique could be extended to other systems in which the chiral atom is one which can stabilize an adjacent carbanion. This paper reports the successful optical resolution of **1** by this method and the determination of the absolute configurations of its enantiomeric forms by x-ray crystallographic methods, making use of the known absolute configuration of camphor as an internal reference center.¹⁴

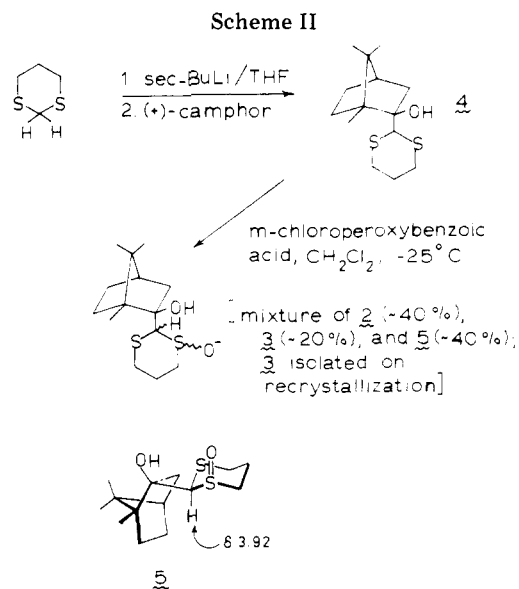
Results and Discussion

Optical Resolution. The β -hydroxyalkyl sulfoxides chosen for study were the stereoisomeric 2-(1,3-dithian-2-yl)isoborneol 1'-oxides having the general structure **A**. Since these



adducts are formed by organometallic addition to D(+)-camphor, highly stereoselective attack from the endo face is assumed. There are then just two chiral centers of variable configuration and four diastereoisomeric forms of **A** to be considered. Two distinct procedures, described in Schemes I and II, were developed for formation of diastereoisomers of **A**. As anticipated, these adducts are labile in base and are readily cleaved to (+)-camphor and the corresponding (+)- or (-)-**1** on treatment with potassium hydroxide in refluxing *tert*-butyl alcohol.

The first route (Scheme I) involves reaction of 2-lithio-1,3-dithiane 1-oxide^{7,15} with D(+)-camphor to yield a mixture of diastereomeric adducts together with unreacted (and partially resolved) **1**. The composition of the product mixture is extremely sensitive to the experimental conditions. When the reaction was carried out at -70°C and allowed to warm to $+15^\circ\text{C}$ before quenching, the recovered unreacted **1** (19%) had a specific rotation of $+75^\circ$. The NMR spectrum of the adduct mixture revealed the presence of two diastereoisomers characterized by signals for the C(2) proton of the dithiane oxide ring at δ 3.74 and 3.92 ppm, with the former present in slightly greater amount. Chromatography and recrystalliza-



tion gave the δ 3.74 material as a pure diastereomer: mp $190.5\text{--}192^\circ\text{C}$; $[\alpha]^{20}_{\text{D}} -74.4^\circ$ (*c* 2.7, ethanol). The structure of this adduct was established as (2*R*)-2-[(1*S*,2*R*)-1,3-dithian-2-yl]isoborneol 1'-oxide (**2**) by single-crystal x-ray analysis. Base-catalyzed cleavage of **2** occurred readily to give (*S*)-(-)-**1**; $[\alpha]^{20}_{\text{D}} -223^\circ$ (*c* 1, ethanol).

If the reaction was both carried out and quenched at -65 to -75°C , then the **1** recovered from the reaction mixture (14%) had a rotation of -111° . The crude product contained, in addition to the two diastereoisomers observed previously, a third adduct having a signal for its C(2) proton at δ 3.82 ppm. As estimated by NMR, the ratio of the δ 3.74, 3.82, and 3.92 diastereomers was 44:37:19. The δ 3.82 diastereomer **3** is the least soluble of these and was obtained in pure form, mp $216\text{--}217.5^\circ\text{C}$ and $[\alpha]^{24}_{\text{D}} +25^\circ$ (*c* 1.3, chloroform), after recrystallization. Base-catalyzed cleavage of **3** gave (+)-**1**, $[\alpha]^{20}_{\text{D}} +230^\circ$ (*c* 1.0, ethanol), in 94% yield.

Structure **3**, (2*R*)-2-[(1*R*,2*R*)-1,3-dithian-2-yl]isoborneol 1'-oxide can be assigned to the δ 3.82 diastereomer both from its cleavage to (*R*)-(+)-**1** and from its NMR (¹³C and ¹H) spectra. The ¹³C chemical shift of C(2') is sensitive to the orientation of the sulfoxide oxygen.¹⁶ For six *trans* 2-substituted 1,3-dithiane 1-oxides (equatorial oxygen) studied, the chemical shifts of C(2) were 15.0–19.5 ppm farther downfield than for C(2) for the corresponding 2-substituted 1,3-dithianes.¹⁷ For four *cis* 2-substituted 1,3-dithiane 1-oxides (axial oxygen), the C(2) chemical shifts were 9.5–12.6 ppm farther downfield than for the corresponding 2-substituted 1,3-dithianes.¹⁷ The ¹³C chemical shift of C(2) of the dithiane ring moiety of 2-(1,3-dithianyl)isoborneol (**4**) is 61.30 ppm. Compound **2** (axial oxygen by x-ray structure determination) has its C(2) signal at 70.38 ppm, corresponding to $\Delta\delta = 9.08$ ppm, whereas compound **3** has its C(2) signal at 77.90 ppm, corresponding to $\Delta\delta = 16.60$ ppm. Therefore, the sulfoxide oxygen must be equatorial in this diastereomer. An equatorial oxygen is also indicated by the proton NMR spectrum which shows a multiplet, assigned to the C(6) equatorial proton of the dithiane ring, at 3.2–3.6 ppm. Evidence has been presented previously that a signal in this region is characteristic of *trans* 2-monosubstituted 1,3-dithiane 1-oxides.^{6,7} The stereoisomer of **A** which has an equatorial sulfoxide oxygen and which is related to (*R*)-(+)-**1** by cleavage can only be **3**.

The second route (Scheme II) uses the dithiane (**4**), prepared from 2-lithio-1,3-dithiane and D(+)-camphor. Oxidation of **4** with *m*-chloroperoxybenzoic acid in dichloromethane at -25°C yields a mixture of three diastereomeric oxides in a ratio of about 2:1:2, as determined by integration of the

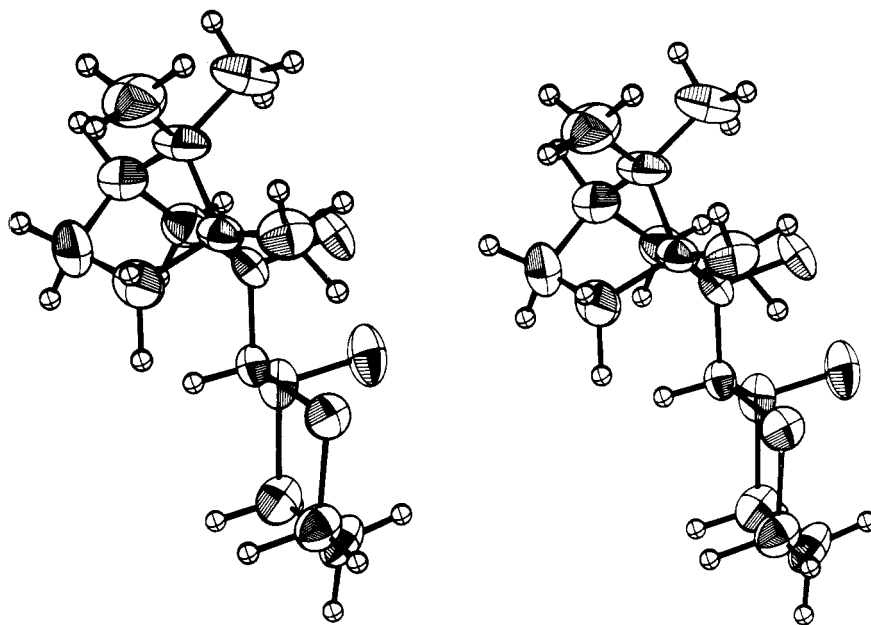


Figure 1. ORTEP drawing of the structure of **2**. Thermal ellipsoids for S, O, and C are drawn with the 50% probability level as boundary surface. Hydrogen atoms, where located, are represented by spheres of arbitrary radius.

NMR signals at δ 3.92 (**5**), 3.82 (**3**), and 3.74 (**2**), respectively. Direct base-catalyzed cleavage of this mixture yielded **1** having $[\alpha]_D +38^\circ$. Since **2** is related to (–)-**1** and **3** to (+)-**1**, the δ 3.92 component must yield (+)-**1** on cleavage and therefore has the *R* configuration at sulfur. Structure **5**, (*R*)-2-[(1*R*,2*S*)-1,3-dithian-2-yl]isborneol 1'-oxide, may therefore be assigned to the δ 3.92 diastereomer.

Recrystallization of the crude mixture of **2**, **3**, and **5** leads to the isolation of **3** (the least soluble component), mp 215–217 °C. Base-catalyzed cleavage of **3** gave (+)-**1**, $[\alpha]^{21}_D +225^\circ$ (*c* 1.3, ethanol).

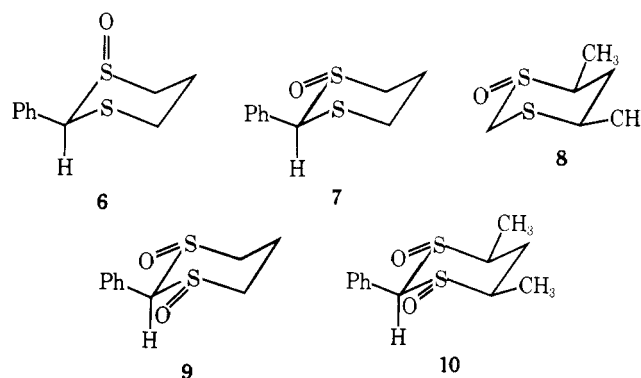
The procedure in Scheme II is not as efficient as either of the modifications of Scheme I. Condensation of 2-lithio-1,3-dithiane with (+)-camphor proceeds in only 49% yield to **4**. The corresponding reaction of 2-lithio-1,3-dithiane 1-oxide with (+)-camphor gives yields of 56–83%, depending on the conditions used, along with recovered (and optically active) **1**. Moreover, the diastereoisomer which is obtained on recrystallization corresponds to only about 20% of the mixture of oxides formed by oxidation of **4**. A considerable degree of flexibility exists in that not only does Scheme I allow the isolation of either (*R*)- or (*S*)-**1**, depending on conditions, but also the commercial availability of both enantiomers of camphor permits the isolation of (*R*)- or (*S*)-**1** by proper choice of starting materials.

Absolute Configuration. Because cleavage of **2** to (–)-**1** is a process which does not involve the chiral sulfoxide group, the absolute configuration of (–)-**1** may be determined by relation to the structure of **2**. The absolute configuration of (+)-camphor is known, and its use as a potential internal reference center in the x-ray determination of absolute configuration has been explicitly mentioned.¹⁸ The assignment of absolute configuration to **2** made in this way has also been independently confirmed by taking into account the anomalous scattering terms for sulfur in separate structure factor calculations for each of the two enantiomers of **2** where a clear preference for the enantiomer embodying the (+)-camphor structure emerged.¹⁹

An ORTEP²⁰ view of **2** is shown in Figure 1. Positional and thermal parameters are given in Table I, and the numbering scheme, bond lengths, valence angles, and torsion angles in **2** are illustrated in Figure 2.²¹ The configuration of the sulfoxide group is *S*. The dithiane ring is in a chair conformation

with the sulfoxide oxygen axial and the 2-hydroxyl-1,7,7-trimethylbicyclo[2.2.1]heptyl group equatorial.

It is of interest to compare certain structural features of **2** with other derivatives of **1** for which x-ray crystallographic data have been reported. These include: the axial sulfoxide, *cis*-2-phenyl-1,3-dithiane 1-oxide (**6**);^{5b} two equatorial oxides, *trans*-2-phenyl-1,3-dithiane 1-oxide (**7**)^{5b} and *r*-4,*c*-6-dimethyl-1,3-dithiane *t*-1-oxide (**8**);^{5a} and two diequatorial dioxides, 2-phenyl-1,3-dithiane *trans*-1,*trans*-3-dioxide (**9**)^{5b} and *r*-4,*c*-6-dimethyl-1,3-dithiane *t*-1,*t*-3-dioxide (**10**).^{5a} The



axial oxides **2** and **6** are slightly less puckered (sum of torsion angles = 371° and 375°, respectively) than the equatorial oxides **7** (381°), **8** (382°), **9** (389°), and **10** (400°) (Table II). All of the oxides are more puckered than 2-phenyl-1,3-dithiane (**11**, 348°)²² or *r*-4,*c*-6-dimethyl-1,3-dithiane (**12**, 366°).^{5a}

Electrostatic interactions between the sulfoxide group and the cross-ring sulfur, as reflected in the S(1)–C(2)–S(3) valence angle, have been discussed previously.⁵ This angle in **2** (112.8°) is identical, within the limits of error, with that found for the other axial oxide **6** (112.9°). Both are larger than the angles found in the equatorial oxides **7** (109.6°) and **8** (110.0°).

The pattern of S–C bond distances (Table III) follows that seen in **6**, **7**, and **9**, where it was observed that the S(1)–C(2) distance is significantly longer than the S(1)–C(6) distance (1.842 vs. 1.803 Å in **2**). The situation is reversed in **8** and **10**, where S(1)–C(2) is shorter than S(1)–C(6) (1.805 Å vs. 1.828 Å in **8** and 1.812 Å vs. 1.821 Å in **10**). McPhail^{5a} has suggested

Table I. Atomic Parameters for 2^a

Atom	x	y	z	B
S(1')	-138.2 (5)	2298.6 (13)	6851.4 (18)	3.46
S(3')	182.9 (5)	3193.8 (13)	2653.3 (20)	3.68
C(2')	382 (2)	2181 (5)	4839 (7)	2.62
C(4')	-479 (2)	2359 (6)	2054 (8)	4.24
C(5')	-900 (2)	2503 (6)	3704 (10)	4.58
C(6')	-742 (2)	1643 (6)	5524 (9)	4.15
C(1)	1479 (2)	2578 (5)	4342 (8)	3.44
C(2)	940 (2)	2714 (5)	5710 (7)	2.87
C(3)	1111 (2)	1825 (6)	7545 (8)	4.00
C(4)	1688 (2)	1205 (6)	6992 (11)	5.14
C(5)	1589 (3)	80 (6)	5343 (13)	6.19
C(6)	1462 (2)	1023 (6)	3535 (10)	4.80
C(7)	1964 (2)	2452 (7)	5898 (9)	4.74
C(8)	2074 (3)	3790 (8)	7150 (11)	6.10
C(9)	2537 (3)	2073 (8)	4931 (13)	6.94
C(10)	1553 (2)	3734 (7)	2768 (9)	4.95
O(1')	-230 (2)	3849 (4)	7252 (6)	4.95
O(2)	877 (2)	4216 (3)	6167 (6)	4.17

^a Positional parameters (for hydrogen atoms are provided in the microfilm edition; see footnote on supplementary material) are given as fractions of the unit cell edges ($\times 10^4$) with esd's, in parentheses on the same scale. Equivalent isotropic thermal parameters are given in \AA^2 . (Anisotropic thermal parameters for S, O, and C and isotropic B values for hydrogen atoms are given in the microfilm edition.)

Table II. Endocyclic Torsion Angles for 1,3-Dithiane Systems (Deg)

Central bond	Compound							
	11 ^a	2	6 ^b	7 ^b	9 ^b	12 ^c	8 ^c	10 ^c
S(1)-C(2)	57	57	59	63	61	62	68	67
C(2)-C(3)	-57	-58	-61	-63	-60	-62	-67	-67
S(3)-C(4)	56	60	62	61	61	57	58	62
C(4)-C(5)	-63	-68	-68	-64	-72	-64	-62	-72
C(5)-C(6)	61	69	67	67	73	64	65	72
C(6)-S(1)	-54	-59	-58	-63	-62	-57	-63	-62

^a Data of Kalff and Romers; see ref 22. ^b See ref 5b. ^c Data of McPhail et al., see ref 5a.

that the bond-length differences in 8 and 10 simply depend on the degree of substitution at the carbon atoms involved—the shorter bonds always involving the methylene carbon atom. All of the results, including those not known to McPhail at the time his suggestion was made, are consistent with this generalization; 2, 6, 7, and 9 are unsubstituted at C(6), whereas 8 and 10 are unsubstituted at C(2).

Turning briefly to the bicyclo[2.2.1]heptyl moiety, the distortion which results from substitution at C(2) can be considered as a partial pseudorotation of a cyclopentane envelope. This is conveniently described in Figure 3 after the work of Altona and Sundaralingam.²³ The synchro (-, -) twist observed in 2 is also seen in (+)-10-bromo-2-*exo*-chloro-2-nitrosocamphane²⁴ and in (-)-2-*exo*-bromo-2-nitrosocamphane,²⁵ the only two reported camphane structures substituted at C(2). Particularly unfavorable gauche interactions about the C(1)-C(2) bond lead to opening of the C(1)-C(2)-C(2') and S(3')-C(2')-C(2) valence angles to 117.1° and 111.6°, respectively, as opposed to the corresponding C(3)-C(2)-C(2') and S(1')-C(2')-C(2) angles of 111.7° and 106.6°. For the same reason the C(1)-C(2) bond is lengthened to 1.588 Å. A similar situation is found in 1,3-biapocamphane,²⁶ leading, in that compound, to a value of 119.6° for the corresponding C-C-C angle and to a C-C bond length of 1.584 Å. The remaining features of the camphane system in 2 are comparable to those found in related structures²⁷ (though our

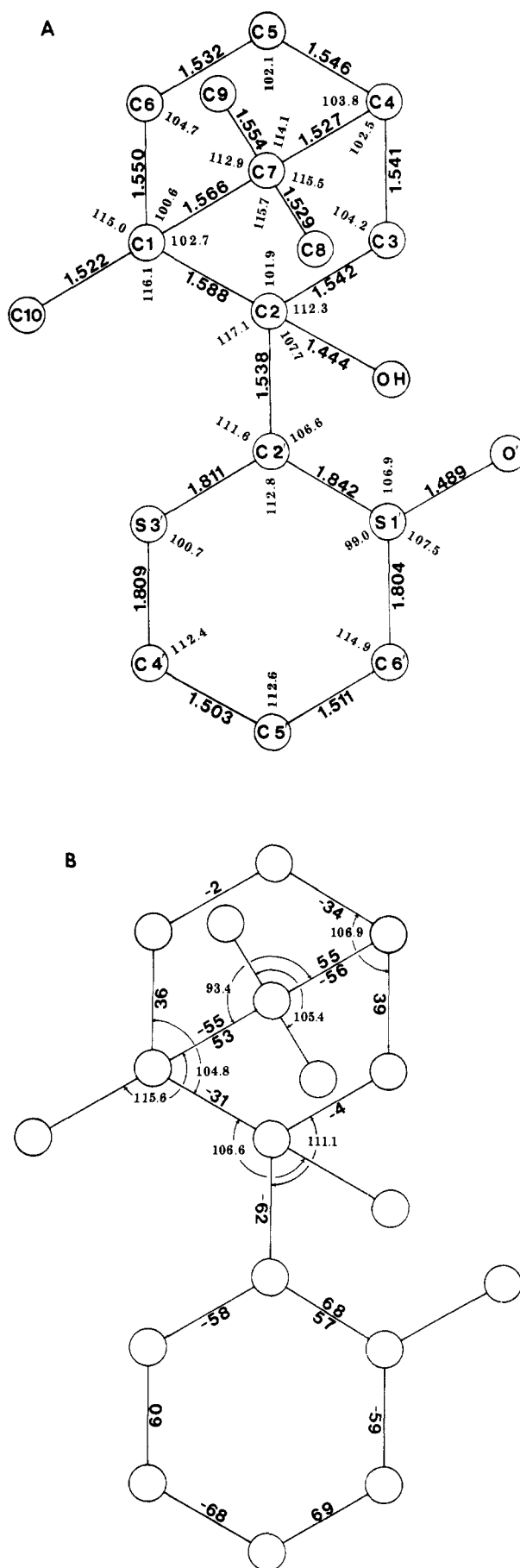


Figure 2. (a) Bond lengths (Å) and bond angles (deg) in 2. Esd's are S-C 0.005 Å, S-O 0.003 Å, C-C 0.010 Å, S-C 0.2°, C-S-O 0.2°, S-C-S 0.2°, S-C-C 0.4°, C-C-C 0.6°. (b) Torsion angles in 2 and remaining bond angles.

Table III. 1,3-Dithiane Ring Bond Lengths (Å)

Bond	Compound							
	11 ^a	2	6 ^b	7 ^b	9 ^b	12 ^c	8 ^s	10 ^c
S(1)-C(2)	1.79	1.842 (4)	1.843 (3)	1.830 (2)	1.834 (5)	1.791 (5)	1.805 (3)	1.812 (5)
S(3)-C(2)	1.80	1.811 (4)	1.797 (3)	1.814 (2)	1.833 (4)	1.792 (5)	1.797 (3)	1.821 (6)
S(1)-C(6)	1.81	1.804 (5)	1.803 (3)	1.806 (2)	1.803 (5)	1.825 (4)	1.828 (2)	1.821 (5)
S(3)-C(4)	1.83	1.809 (5)	1.812 (3)	1.808 (2)	1.787 (5)	1.822 (4)	1.823 (3)	1.819 (5)
C(4)-C(5)	1.46	1.503 (7)	1.508 (4)	1.506 (3)	1.513 (8)	1.523 (5)	1.522 (3)	1.524 (7)
C(5)-C(6)	1.51	1.511 (8)	1.512 (4)	1.519 (2)	1.513 (6)	1.513 (6)	1.527 (4)	1.505 (8)

^a Data from ref 22. ^b Data from ref 5b. ^c Data from ref 5a.

Table IV. Endocyclic Valence Angles (Deg) for 1,3-Dithiane Systems

Central atom	Compound							
	11 ^a	2	6 ^b	7 ^b	9 ^b	12 ^c	8 ^c	10 ^c
S(1)	101	99.0 (2)	98.7 (2)	98.2 (2)	96.9 (2)	99.0 (2)	97.1 (1)	96.4 (2)
S(3)	99	100.7 (2)	99.2 (2)	100.5 (2)	97.0 (2)	99.4 (2)	99.7 (1)	96.7 (2)
C(2)	115	112.8 (2)	112.9 (2)	109.6 (2)	114.2 (3)	114.5 (3)	110.0 (1)	112.5 (3)
C(4)	116	112.4 (4)	112.6 (2)	113.0 (2)	113.4 (4)	112.7 (3)	112.2 (2)	109.1 (3)
C(5)	117	112.6 (4)	113.0 (3)	113.3 (2)	111.2 (4)	116.7 (3)	116.3 (2)	115.5 (4)
C(6)	115	114.9 (4)	114.6 (2)	114.0 (2)	112.0 (3)	112.9 (3)	111.9 (2)	109.8 (3)

^a Data of ref 22. ^b Data of ref 5b. ^c Data of ref 5a.

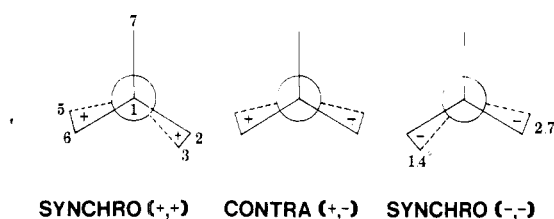


Figure 3. Projections along the C(1)---C(4) axis of the camphane moiety showing possible modes of twist and the values observed for 2.

results appear to be the most accurate thus far obtained for this system) and are not discussed further.

All intermolecular distances correspond to normal van der Waals separations. The S-O bonds of neighboring molecules have their dipoles aligned, but the nonbonded S...O separations of 3.39 Å are greater than the sum of the van der Waals radii of the atoms involved (3.22 Å).²⁷ The sulfoxide oxygen atom appears to act as an acceptor in an intramolecular O-H...O hydrogen bond involving the isborneol hydroxy group (O...O 2.77 Å) but the hydrogen atom involved has not been definitively located.

Experimental Section

Infrared spectra (IR) were obtained on a Perkin-Elmer 337 grating spectrometer as KBr disks or thin films and were calibrated with either the 1601- or 1028-cm⁻¹ band of polystyrene. Melting points are corrected and were measured on a Thomas-Hoover apparatus. Optical rotations were measured at ambient temperatures on a Perkin-Elmer 141 polarimeter using a 1-dm tube. Microanalyses were performed by Atlantic Microlab, Inc., Atlanta, Georgia, and by Alfred Bernhardt, Engelskirchen, West Germany. Mass spectra were recorded on a Hitachi-Perkin-Elmer RMU-6E spectrometer at 70 eV. Carbon-13 NMR spectra were recorded using a JEOL-PS 100P/EC-100 Fourier transform spectrometer. The operating conditions are described in ref 17. Proton NMR spectra were obtained at 60 MHz using a Hitachi-Perkin-Elmer R-20 instrument.

All metalation reactions were carried out under nitrogen in a three-necked flask equipped with thermometer, serum cap, nitrogen inlet, and drying tube (Drierite). Tetrahydrofuran (THF) and diisopropylamine were distilled from calcium hydride and stored over 4 Å molecular sieves under argon. *n*-Butyllithium in *n*-hexane and *sec*-butyllithium in *n*-hexane were supplied by Alfa Inorganics.

(2R)-2-[(1S,2R)-1,3-Dithian-2-yl]isborneol 1'-Oxide (2).²⁸ A slurry of 6.81 g (50.0 mmol) of 1,3-dithiane 1-oxide (1) in 125 mL

of THF was treated with 21 mL (50 mmol) of 2.4 M *n*-butyllithium at -70 to -60 °C. After stirring for 1 h at -70 °C, 7.61 g (50.0 mmol) of D(+)-camphor dissolved in 20 mL of THF was added rapidly via a dropping funnel. The mixture was stirred for 1 h, then allowed to warm to 15 °C, and quenched with 25 mL of saturated ammonium chloride solution. The THF was evaporated, 100 mL of saturated ammonium chloride was added to the residue, and the product was extracted in chloroform (two 100-mL portions). The combined chloroform layers were washed with 100 mL of brine and dried over sodium sulfate. After removal of solvent, the crude product was purified by column and thin-layer chromatography to give 8.134 g (56%) of a mixture of diastereomeric adducts along with 1.276 g (18.7%) of recovered 1, mp 82-91 °C, [α]_D²⁰ +74.8° (c 3.2, ethanol). Recrystallization of crude 1 from cyclohexane/dichloromethane gave material melting at 89.5-94 °C and with [α]_D²⁰ +92.2° (c 1.05, ethanol). The NMR spectrum of the crude mixture of diastereomers showed singlets at δ 3.74 and 3.92, corresponding to the C(2) proton on the dithiane ring. The mixture of diastereomers was recrystallized five times from dichloromethane/ether and twice from ethanol, yielding 546 mg of pure 2: mp 194.5-195 °C; [α]_D²⁰ -74.4° (c 2.7, ethanol); IR (KBr) 3365 (OH) and 1025 cm⁻¹ (S=O); NMR (CDCl₃) δ 0.83 (s, 3, CH₃), 1.06 (s, 3, CH₃), 1.08 (s, 3, CH₃), 1.2-2.0 (m, 7, remaining isborneol skeletal H), 2.1-3.4 (m, 7, dithiane ring protons and OH), and 3.74 ppm [s, 1, C(2') H]; mass spectrum *m/e* (rel intensity) 288 (17), 271 (35), 166 (100), 165 (51), 151 (45), 137 (57), 123 (64), 109 (65), 95 (87), 81 (80).

Anal. Calcd for C₁₄H₂₄O₂S₂: C, 58.29; H, 8.39; S, 22.23. Found: C, 58.32; H, 8.39; S, 22.29.

Base-Catalyzed Cleavage of 2. A 450-mg (1.56 mmol) portion of 2 was treated with 104 mg (1.58 mmol) of 85% potassium hydroxide in refluxing *tert*-butyl alcohol under nitrogen for 3 h. After cooling, saturated ammonium chloride was added to the reaction mixture. The *tert*-butyl alcohol was removed in vacuo, and the residue was partitioned between brine and chloroform. The layers were separated, and the aqueous phase was extracted with a second portion of chloroform. The combined chloroform layers were dried over sodium sulfate. Removal of solvent provided a mixture of (-)-1 and (+)-camphor which was washed with cyclohexane to remove the camphor. The residual (-)-1 (201 mg, 95%) had mp 103-105 °C, [α]_D²⁰ -192° (c 2.1, ethanol). Recrystallization from cyclohexane/dichloromethane gave white crystals: mp 108.2-109.4 °C, [α]_D²⁰ -224° (c 0.85, ethanol).

(2R)-2-[(1R,2R)-1,3-Dithian-2-yl]isborneol 1'-Oxide (3). *n*-Butyllithium (50.0 mmol) was added to a slurry of 6.81 g (50.0 mmol) of 1 in 125 mL of THF at -75 to -65 °C. After stirring at -75 °C for 1 h, a solution of D(+)-camphor (50.1 mmol) in 20 mL of THF was added dropwise over a 10-min period (temperature never exceeding -68 °C). After stirring at -75 °C for 1 h, 25 mL of saturated ammonium chloride solution was added and the mixture allowed to warm up to room temperature overnight. Workup furnished 16.36 g of creamy white solid, containing 44% 2 and 37% 3, which was placed

on a column containing 90 g of silica gel 60. Unreacted camphor and nonpolar impurities were eluted with 300 mL of carbon tetrachloride, 550 mL of 2% 2-propanol/carbon tetrachloride, and 375 mL of 3% 2-propanol/carbon tetrachloride. Elution with 850 mL of 5% 2-propanol/carbon tetrachloride afforded 7.68 g of product. Further elution with 700 mL of 8% 2-propanol/carbon tetrachloride gave 1.53 g of diastereomers and unreacted 1. Pure 1,3-dithiane 1-oxide (757 mg) was obtained upon elution with 250 mL of 8% 2-propanol/carbon tetrachloride, 775 mL of 10% 2-propanol/carbon tetrachloride, and 250 mL of 20% 2-propanol/carbon tetrachloride. A quantity of diastereomer 3 (1.72 g, mp 190–192 °C) failed to dissolve in the solvent used for loading the column.

Purification of fractions containing 1, diastereomers, and impurities by TLC (silica gel; 20% 2-propanol/carbon tetrachloride) yielded an additional 225 mg of 1, 501 mg of a mixture of diastereomers, and 726 mg of pure 3, mp 214–217 °C. Recrystallization of the mixture of diastereomers (8.18 g) from ether/dichloromethane afforded 2.452 g of 3, mp 216–217.5 °C. The isolated 3 (4.90 g total, 34%) was further purified by recrystallization from ethanol giving 3.53 g (24.5%) of pure material melting at 216–218 °C: $[\alpha]_D^{20} +25.9^\circ$ (*c* 1.3, CHCl₃); IR (KBr) 3215 (OH) and 1010 cm⁻¹ (S=O); NMR (CDCl₃) 0.83 (s, 3, CH₃), 1.06 (s, 3, CH₃), 1.09 (s, 3, CH₃), 1.2–3.1 (m, 13), 3.1–3.6 [m, 1, C(6') eq H], and 3.82 ppm [s, 1, C(2') H]; mass spectrum *m/e* (rel intensity) 288 (14), 271 (23), 166 (100), 165 (50), 151 (53), 137 (56), 123 (74), 109 (58), 95 (45), 90 (52), 81 (58).

Anal. Calcd for C₁₄H₂₄O₂S₂: C, 58.29; H, 8.39; S, 22.23. Found: C, 58.25; H, 8.41; S, 22.29.

The unreacted 1,3-dithiane 1-oxide (982 mg) isolated had $[\alpha]_D^{24} -111^\circ$ (*c* 1.2, ethanol).

Base-Catalyzed Cleavage of 3. Using the procedure previously described for 2, 3.14 g (10.9 mmol) of 3 gave 1.40 g (94%) of (*R*)-(+)-1: mp 108.4–109.3 °C, $[\alpha]_D^{24} +227^\circ$ (*c* 1.0, ethanol). After recrystallization from cyclohexane/dichloromethane, material with mp 108–111 °C and $[\alpha]_D^{20} +230^\circ$ (*c* 1.0, ethanol) was obtained.

(2*R*)-2-(1,3-Dithian-2-yl)isborneol (4). To a solution of 6.01 g (50.0 mmol) of 1,3-dithiane in 75 mL of THF was added 38.5 mL (50 mmol) of 1.3 M *sec*-butyllithium at –50 to –30 °C. The reaction mixture was stirred at –30 to –20 °C for 1 h and then warmed to –10 °C. Thereupon, 7.61 g (50.0 mmol) of D(+)-camphor dissolved in 20 mL of THF was added at –10 to 0 °C. The reaction mixture was stirred at 0 to 20 °C for 12 h, and following the usual workup 13.06 g of crude product was obtained. The NMR spectrum of this material indicated that the reaction was 49% complete. A combination of recrystallization from cyclohexane and sublimation at 100 °C and 0.35 Torr afforded 5.54 g (41%) of purified 4 (mp 122 °C). Recrystallization from ether gave the analytical sample: mp 125.5–127 °C; $[\alpha]_D^{20} +2.9^\circ$ (*c* 1.5, ethanol); IR (KBr) 3500 cm⁻¹ (OH); NMR (CDCl₃) δ 0.82 (s, 3, CH₃), 1.05 (s, 3, CH₃), 1.08 (s, 3, CH₃), 1.20–2.23 (m, 9), 2.31 (s, 1, OH), 2.7–3.1 [m, 4, C(4') and C(6') H], and 4.22 ppm [s, 1, C(2') H]; mass spectrum *m/e* (rel intensity) 272 (6), 254 (6), 153 (100), 135 (65), 120 (98), 119 (90), 109 (60), 97 (69), 95 (71), 69 (67), 55 (57), 41 (86).

Anal. Calcd for C₁₄H₂₄O₂S₂: C, 61.71; H, 8.88; S, 23.54. Found: C, 61.87; H, 8.95; S, 23.37.

***m*-Chloroperoxybenzoic Acid Oxidation of 4.** A solution of 4.80 g (23.6 mmol) of 85% *m*-chloroperoxybenzoic acid in 80 mL of dichloromethane was added dropwise at –25 to –15 °C to a solution of 6.40 g (23.5 mmol) of 4 in 120 mL of dichloromethane over a 1-h period. The resultant slurry was stirred at –25 °C for 1 h and then stored at –25 °C overnight. The reaction mixture was washed with 100 mL of 10% sodium carbonate solution and 100 mL of brine, and the organic solution was dried over sodium sulfate. Removal of solvent yielded 6.69 g (98.8%) of white solid, mp 147–159 °C. The NMR spectrum showed singlets at 3.74, 3.82 (minor constituent), and 3.91 ppm, corresponding to the C(2) proton of the dithiane ring. The crude product showed $[\alpha]_D^{20} -3.6^\circ$ (*c* 2.6, ethanol). Successive recrystallizations from dichloromethane/ether, ethanol, dichloromethane/ether, and ethanol afforded 357 mg of 3: mp 215–217 °C; $[\alpha]_D^{21} +24.4^\circ$ (*c* 1.27, CHCl₃).

When 196.5 mg (0.68 mmol) of the crude mixture of diastereomers was subjected to base-catalyzed cleavage under the conditions previously described, 85.1 mg (92%) of 1,3-dithiane 1-oxide was obtained. After purification by preparative TLC on silica gel (15% 2-propanol in CCl₄), 57.5 mg of 1 was obtained, mp 84–88 °C, $[\alpha]_D^{20} +38^\circ$ (*c* 2, ethanol).

Carbon-13 NMR Spectra. ¹³C chemical shift data for 3, 4, and 5 are given in the microfilm edition of the Journal. (See note on Supplementary Material.)

Crystal Data. Preliminary cell dimensions were derived from 25° precession photographs taken with Mo Kα radiation. Systematic

absences of axial reflections of odd order in *h*00, 0*k*0, and 00*l* define the space group for this orthorhombic crystal as *P*₂₁₂₁. Accurate cell dimensions were obtained by a least-squares fit to the diffractometer values of ±2θ measured for 20 strong general reflections (λ = 1.5418 Å) and are *a* = 23.890 (7), *b* = 9.336 (4), and *c* = 6.727 (3) Å. The measured crystal density (floatation in ZnCl₂ solution) of 1.28 g cm⁻³ is identical with that calculated assuming four molecules of 2 in the unit cell. The absorption coefficient for the crystal for Cu Kα radiation is 39 cm⁻¹ and the dimensions of the crystal used 0.70 × 0.17 × 0.40 mm. No absorption corrections were made, and most of the residual error is attributable to this neglect.

Intensity Data. These were measured using a Picker four-circle diffractometer controlled by an XDS Sigma 2 computer. Monochromatic Cu Kα radiation was used to survey a single octant of reciprocal space containing 1268 independent reflections (2θ < 12.0°) of which 1117 showed intensity significantly above background [*I* > 3σ(*I*)]. The θ–2θ scan method was used at a scan rate of 2° min⁻¹ and scan widths 2.5–3.0°. Background measurements were made with both crystal and counter stationary for 15 s at either end of the scan ranges. Stability of the experimental conditions was monitored by measurement of a single reference reflection after every five measurement cycles, the rms deviation about the mean intensity for this reference being 1.5%. Structure amplitudes and normalized structure amplitudes were derived in the usual ways.

Structure Determination and Refinement. The structure was solved by direct methods by use of the program MULTAN²⁹ and refined by block-diagonal least-squares methods with a conventional weighting scheme adopted.³⁰ Anisotropic thermal parameters were used for S, O, and C atoms. All hydrogen atoms, except H(5b) and the hydroxy proton, were identified from difference electron-density maps and included in the refinement with isotropic B values assumed. At convergence, no calculated shift in any parameter exceeded 0.35 σ. The final conventional unweighted and weighted residuals were 0.046 and 0.057. The scattering functions used were taken from ref 31. With the exception of ORTEP and MULTAN, all programs used were written in this laboratory for the XDS Sigma 2 computer.

Acknowledgments. The Fourier transform NMR spectrometer was purchased with assistance from a major instrument grant from the National Science Foundation. We thank Mr. William C. Hutton for measuring the ¹³C NMR spectra.

Registry No.—1, 63903-43-5; (*R*)-(+)-1, 63865-79-2; (*S*)-(–)-1, 63865-78-1; 2, 63903-42-4; 3, 63865-80-5; 4, 63865-77-0; D(+)-camphor, 464-49-3; 1,3-dithiane, 505-23-7; *sec*-butyllithium, 598-30-1.

Supplementary Material Available. Listings of complete bond length and angle calculations, information on least-squares mean planes of interest, intermolecular contact distances, and ¹³C chemical shift data for 3, 4, and 5 (8 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) (a) M. J. Cook and A. P. Tonge, *Tetrahedron Lett.*, 849 (1973); (b) M. J. Cook and A. P. Tonge, *J. Chem. Soc., Perkin Trans. 2*, 767 (1974); (c) K. Bergesen, M. J. Cook, and A. P. Tonge, *Acta Chem. Scand. Ser. A*, **30**, 574 (1976).
- (2) L. Van Acker and M. Anteunis, *Tetrahedron Lett.*, 225 (1974).
- (3) S. A. Khan, J. B. Lambert, O. Hernandez, and F. A. Carey, *J. Am. Chem. Soc.*, **97**, 1468 (1975).
- (4) N. L. Allinger and J. Kao, *Tetrahedron*, **32**, 529 (1976).
- (5) (a) A. T. McPhail, K. D. Onan, and J. Koskimies, *J. Chem. Soc., Perkin Trans. 2*, 1004 (1976); (b) F. A. Carey, P. M. Smith, R. J. Maher, and R. F. Bryan, *J. Org. Chem.*, **42**, 961 (1977).
- (6) F. A. Carey, O. D. Dailey, Jr., O. Hernandez, and J. R. Tucker, *J. Org. Chem.*, **41**, 3975 (1976).
- (7) F. A. Carey, O. D. Dailey, Jr., and O. Hernandez, *J. Org. Chem.*, **41**, 3979 (1976).
- (8) (a) D. Seebach and M. Kolb, *Chem. Ind. (London)*, 687 (1974); (b) D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **8**, 639 (1969); (c) O. W. Lever, Jr., *Tetrahedron*, **32**, 1943 (1976).
- (9) D. Seebach and E. J. Corey, *J. Org. Chem.*, **40**, 231 (1975).
- (10) K. Ogura, M. Yamashita, M. Suzuki, and G. Tsuchihashi, *Tetrahedron Lett.*, 3653 (1974), and preceding papers in this series.
- (11) (a) A. I. Meyers and C. E. Whitten, *J. Am. Chem. Soc.*, **97**, 6266 (1975); (b) A. I. Meyers, G. Knaus, K. Kamata, and M. E. Ford, *ibid.*, **98**, 567 (1976); (c) A. I. Meyers and E. D. Mihelic, *J. Org. Chem.*, **40**, 1186 (1975).
- (12) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions", Prentice-Hall, Englewood Cliffs, N.J., 1971, pp 335–365.
- (13) (a) K. Mislow, M. M. Green, P. Laur, J. T. Mellillo, T. Simmons, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **87**, 1958 (1965); (b) M. Axelrod, P. Bickart, J. Jacobus, M. M. Green, and K. Mislow, *ibid.*, **90**, 4835 (1968); (c) K. K. Andersen, *Tetrahedron Lett.*, 93 (1962); (d) K. K. Andersen, W. Gaffield, N. Papanikolaou, J. W. Foley, and R. I. Perkins, *J. Am. Chem. Soc.*, **86**,

- 5637 (1964); (e) F. Wudl and T. B. K. Lee, *ibid.*, **95**, 6349 (1973); (f) D. N. Harpp, S. M. Vines, J. P. Montillier, and T. H. Chan, *J. Org. Chem.*, **41**, 3987 (1976); (g) J. C. Martin and T. M. Balthazor, *J. Am. Chem. Soc.*, **99**, 152 (1977).
- (14) A. McL. Mathieson, *Acta Crystallogr.*, **9**, 317 (1956).
- (15) R. M. Carlson and P. M. Helquist, *J. Org. Chem.*, **33**, 2596 (1968).
- (16) For data on the dependence of ^{13}C shifts on sulfoxide stereochemistry, see: (a) G. W. Buchanan and T. Durst, *Tetrahedron Lett.*, 1683 (1975); (b) G. Barberella, P. Dembech, A. Garbesi, and A. Fava, *Org. Magn. Reson.*, **8**, 108 (1976); (c) D. M. Frieze and S. A. Evans, *J. Org. Chem.*, **40**, 2690 (1975).
- (17) F. A. Carey, O. D. Dailey, Jr., and W. C. Hutton, *J. Org. Chem.*, following paper in this issue.
- (18) F. H. Allen and D. Rogers, *J. Chem. Soc. B*, 632 (1971).
- (19) (a) A. F. Peerdeman, A. J. van Bommel, and J. M. Bijvoet, *Proc. K. Ned. Akad. Wet. Ser., B*, **54**, 16 (1951); W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).
- (20) C. K. Johnson. "ORTEP-II. A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations. ORNL-5138," Oak Ridge National Laboratory, Oak Ridge, Tenn. (1976).
- (21) See paragraph at end of paper regarding supplementary material.
- (22) H. T. Kalff and C. Romers, *Acta Crystallogr.*, **20**, 490 (1966).
- (23) C. Altona and M. Sundaralingam, *J. Am. Chem. Soc.*, **92**, 1995 (1970).
- (24) G. Ferguson, C. J. Fritchie, J. M. Robertson, and G. A. Sim, *J. Chem. Soc.*, 1976 (1961).
- (25) D. A. Breuckner, T. A. Hamor, J. M. Robertson, and G. A. Sim, *J. Chem. Soc.*, 799 (1962).
- (26) R. A. Alden, J. Kraut, and T. G. Traylor, *J. Am. Chem. Soc.*, **90**, 74 (1968).
- (27) A. Bondi, *J. Phys. Chem.*, **68**, 471 (1964).
- (28) We have been advised by K. L. Loening, Nomenclature Director of Chemical Abstracts Service, that the naming system used in this article is acceptable. The current Chemical Abstracts name for **2** is [(1*R*)-[1 α ,2 α ,2-(1*S**,2*R**) α]-2-(1,3-dithian-2-yl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol *S*-oxide.
- (29) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. B*, **26**, 274 (1970).
- (30) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
- (31) (a) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964); (b) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

Structural Dependence of Carbon-13 Chemical Shifts in Oxides of 1,3-Dithiane

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Received May 31, 1977

A carbon-13 nuclear magnetic resonance study was carried out on a series of 2-substituted derivatives of 1,3-dithiane 1-oxide (**2a**). The series included seven *trans* and five *cis* 2-monosubstituted 1,3-dithiane 1-oxides (**2b-h** and **3b-d,f,h**) and three 2,2-disubstituted 1,3-dithiane 1-oxides. In the monosubstituted compounds C(6) experiences a larger downfield shift than C(2) on oxidation of a 1,3-dithiane. The ^{13}C shifts of C(2), C(5), and C(6) are at higher field in an axial oxide than an equatorial oxide. The results are discussed with respect to: (a) assignment of stereochemistry to 1,3-dithiane 1-oxides; (b) relation of ^{13}C shifts to structure; and (c) ring deformation in 2,2-disubstituted 1,3-dithiane 1-oxides. Assignments of sulfoxide stereochemistry can be made with confidence by ^{13}C NMR. The preferred conformation of 1,3,5-trithiane 1-oxide was determined to have oxygen equatorial. Comparison of chemical shifts with structural parameters available from x-ray crystallography allowed theories of chemical shifts to be evaluated; electric field effects may be important. Twist conformations appear to be significant in 2,2-disubstituted 1,3-dithiane 1-oxides.

Carbon-13 nuclear magnetic resonance spectroscopy has developed rapidly as a structural probe to where it has become a powerful addition to those techniques employed as a matter of routine in stereochemical studies.¹ In the course of a detailed investigation into the stereochemical features of ground-state properties and chemical reactivity of sulfoxides derived from 1,3-dithiane (**1a**),² many derivatives of rigorously established structure have become available, presenting an opportunity to extend and complement recent systematic ^{13}C NMR studies reported on sulfur-containing heterocycles.^{3,4} It was felt that such an extension would be appropriate, since numerous examples have already appeared which relate ^{13}C chemical shifts to stereochemistry at tricoordinate sulfur.⁴⁻¹² Further, because precise structural parameters have been determined for several key compounds,^{2d,13} we hoped that structural features which might be considered as potentially significant in influencing ^{13}C shieldings could be examined explicitly.

Results

Three groups of 2-substituted 1,3-dithiane 1-oxides (*trans*, *cis*, and 2,2-disubstituted) form the basis of the present study. X-ray crystallographic methods have shown that the chair conformation of the dithiane ring is adopted in the solid state for both the *trans* and *cis* series of 2-substituted derivatives.^{2d,13} The sulfoxide oxygen is equatorial in the *trans* and axial in the *cis*. It will be seen from analysis of the ^{13}C NMR data that the 2,2-disubstituted 1,3-dithiane 1-oxides are

subject to a distortion which causes them to be conformationally distinct from the monosubstituted series. These will be treated separately in the Discussion. The structures of four of the oxides (**2d**, **2g**, **3d**, and **3h**) have been rigorously established by x-ray crystallographic methods^{2d,13a,b} and the others,

