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 [(1R)-[1α,2α,2-(1S*,2R*),4α]-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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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,
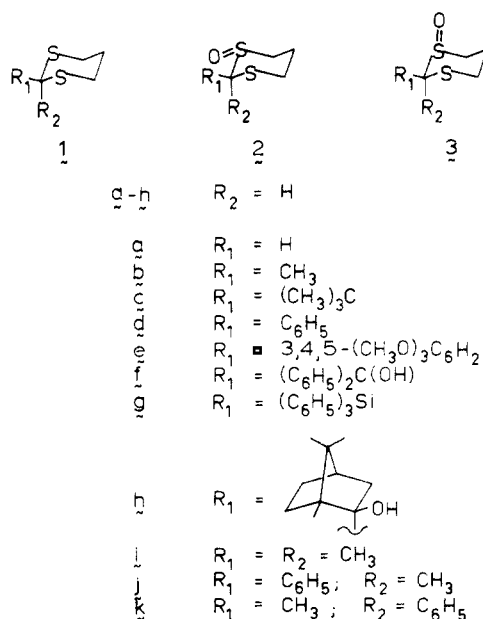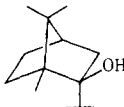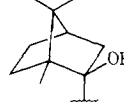

a–h	R_2 = H
a	R_1 = H
b	R_1 = CH_3
c	R_1 = $(CH_3)_3C$
d	R_1 = C_6H_5
e	R_1 = 3,4,5-$(CH_3O)_3C_6H_2$
f	R_1 = $(C_6H_5)_2C(OH)$
g	R_1 = $(C_6H_5)_3Si$
h	R_1 =
i	R_1 = R_2 = CH_3
j	R_1 = C_6H_5; R_2 = CH_3
k	R_1 = CH_3 ; R_2 = C_6H_5
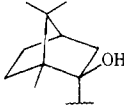
Table I. ^{13}C Chemical Shifts of 1,3-Dithianes

Compd	Registry no.	R$_1$	R$_2$	C(2)	C(4)[a]	C(5)	Other
					Chemical shift, δ		
1a[b]		H	H	32.0	29.9	26.6	
1b[b]		CH$_3$	H	42.2	30.9	25.5	CH$_3$ 21.1
1c[b]		(CH$_3$)$_3$C	H	61.8	31.2	26.0	4 °C 35.7 CH$_3$ 27.8
1d[b]		C$_6$H$_5$	H	51.3	31.9	25.0	
1e	57009-70-8	3,4,5-(CH$_3$O)$_3$C$_6$H$_2$	H	51.4	31.8	24.7	
1f	5849-23-0	(C$_6$H$_5$)$_2$C(OH)	H	58.5	30.4	25.1	
1g	13433-53-9	(C$_6$H$_5$)$_3$Si	H	32.5	31.7	25.7	
1h	63949-54-2	[structure] OH	H	61.3	(30.1) (30.5)	25.4	
1i	6007-22-3	CH$_3$	CH$_3$	45.0	27.0	25.2	CH$_3$ 30.8
1j	6331-22-2	C$_6$H$_5$	CH$_3$	53.7	27.9	24.5	CH$_3$ 32.6

[a] Because of symmetry, C(4) = C(6) in all cases, except 1h. The chemical shifts of C(4) and C(6) in 1h could not be uniquely assigned. [b] Data of E. L. Eliel, V. S. Rao, and F. G. Riddell, *J. Am. Chem. Soc.*, **98**, 3583 (1976).

Table II. ^{13}C Chemical Shifts of 2-Substituted 1,3-Dithiane 1-Oxides

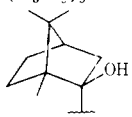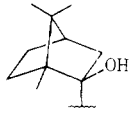| Compd	Registry no.	R$_1$	R$_2$	M[a]	C(2)	C(4)	C(5)	C(6)	Other
						Chemical shift, δ			
2a (3a)	16487-10-8	H	H	1.00	49.9	26.6	27.8	52.3	
2a (3a)		H	H	0.10	50.3	27.1	28.2	52.8	
2a (3a)	60349-89-5	D	D	1.02		26.5	27.7	52.2	
Trans 2-Substituted (Equatorial Oxygen)									
2b	60349-75-9	CH$_3$	H	1.02	59.8	29.3[b]	29.8[b]	53.2	CH$_3$ 14.9
2c	41893-04-3	(CH$_3$)$_3$C	H	1.00	76.8	29.8[b]	30.2[b]	55.4	4 °C 35.9 CH$_3$ 28.3
2d	60349-76-0	C$_6$H$_5$	H	1.00	69.2	29.2	31.0	54.4	
2e	63833-56-7	3,4,5-(CH$_3$O)$_3$C$_6$H$_2$	H	1.05	69.3	29.0[b]	30.9[b]	54.2	
2f	60349-77-1	(C$_6$H$_5$)$_2$C(OH)	H	0.44	74.1	29.4	31.9	54.4	
2g	63383-55-6	(C$_6$H$_5$)$_3$Si	H	0.18	52.0	29.4[b]	30.7[b]	55.4	
2h	63949-97-3	[structure] OH	H		77.9	28.9[b]	30.4[b]	54.0	
Cis 2-Substituted (Axial Oxygen)									
3b	60349-78-2	CH$_3$	H	1.05	52.3	24.6	21.2	44.9	CH$_3$ 11.8
3c	41893-05-4	(CH$_3$)$_3$C	H	0.18	73.8	29.7	14.4	47.7	4 °C 36.0 CH$_3$ 28.3
3d	60349-79-3	C$_6$H$_5$	H	1.00	63.9	29.5	13.2	46.8	
3f	60349-80-6	(C$_6$H$_5$)$_2$C(OH)	H	0.13	68.0	28.5	14.4	47.0	
3h		[structure] OH	H		70.4	28.2	13.9	47.8[c]	
2,2-Disubstituted									
2i (3i)	41893-06-5	CH$_3$	CH$_3$	1.00	57.0	27.8	25.1	46.1	CH$_3$ 16.0, 25.1
2j (3k)	60349-92-0	C$_6$H$_5$	CH$_3$	1.01	64.3	22.6	26.2	45.0	CH$_3$ 18.6
2k (3j)	60349-93-1	CH$_3$	C$_6$H$_5$	0.57	65.5	28.4	27.3	47.0	CH$_3$ 27.8

[a] Concentration (mol/L) in CDCl$_3$. [b] Assignment of signals to C(4) and C(5) may be reversed. [c] The chemical shift of this carbon may be 47.4 ppm. There are two signals in this region one of which is due to C(6) of the dithiane ring, and the other to C(3) of the isoborneol portion of the molecule. For the ^{13}C NMR spectrum of borneol, see: J. Briggs, F. A. Hart, G. P. Moss, and E. W. Randall, *J. Chem. Soc. D.* 364 (1971).

with the exception of **2h**, assigned on the basis of analogous methods of synthesis and physical correlations described earlier.[2b] The stereochemistry of **2h** was not known independently but its ^{13}C NMR spectrum allows its assignment to be made with confidence.

The thorough study by Eliel, Rao, and Riddell[3a] has provided an extensive compilation of chemical-shift data which, taken together with relative intensities, allows peak assignments to be made for the parent 1,3-dithianes. The ^{13}C shifts for the 1,3-dithianes used in this study (**1a–l**) are presented in Table I.[14] Chemical-shift data for the trans 1-oxides, cis

1-oxides, and 2,2-disubstituted 1-oxides appear in Table II. Differential shifts (Δδ values)[15] relating ^{13}C shifts of the oxides to the corresponding 1,3-dithianes are collected in Table III. Peak assignments for the oxides were made on the basis of the following criteria. The two lowest field signals for sp^3 carbons were assigned to C(2) and C(6), since oxidation of sulfur to sulfoxide substantially deshields the α carbons.[4] Off-resonance decoupling served to distinguish between primary, secondary, tertiary, and quaternary carbons in questionable cases. The signal for C(2) in 1,3-dithiane 1-oxide (**2a**) was identified by comparing its ^{13}C NMR spectrum with that of

Table III. ^{13}C-Shift Effects ($\Delta\delta$) of Oxygen Orientation in 1,3-Dithiane 1-Oxides

Compd	R_1	R_2	C(2)	C(4)	C(5)	C(6)
			Shift effect, $\Delta\delta$ [a]			
2a (3a)	H	H	17.9	−3.3	1.2	22.4
	Trans 2-Substituted (Equatorial Oxygen)					
2b	CH_3	H	17.6	−1.6	4.3	22.3
2c	$(CH_3)_3C$	H	15.0	−1.4	4.2	24.2
2d	C_6H_5	H	17.9	−2.7	6.0	22.5
2e	$(CH_3O)_3C_6H_2$	H	17.9	−2.8	6.2	22.4
2f	$(C_6H_5)_2C(OH)$	H	15.6	−1.0	6.8	24.0
2g	$(C_6H_5)_3Si$	H	19.5	−2.3	5.0	23.7
2h	(bornyl-OH structure)	H	16.6	−1.2	5.0	23.5
	Average		17.2	−1.9	5.4	23.3
			±1.2	±0.6	±0.8	±0.7
	Cis 2-Substituted (Axial Oxygen)					
3b	CH_3	H	10.1	−6.3	−4.3	14.0
3c	$(CH_3)_3C$	H	12.0	−1.5	−11.6	16.5
3d	C_6H_5	H	12.6	−2.4	−11.8	14.9
3f	$(C_6H_5)_2C(OH)$	H	9.5	−1.9	−10.7	16.6
3h	(bornyl-OH structure)	H	9.1	−1.9	−11.4	16.9
	Average		10.7	−2.4	−10.0	15.8
			±1.3	±1.2	±2.2	±1.1
	2,2-Disubstituted					
2i (3i)	CH_3	CH_3	12.0	0.8	0.1	19.1
2j	C_6H_5	CH_3	10.6	−5.3	1.7	17.1
2k	CH_3	C_6H_5	11.8	0.5	2.8	19.1

[a] $\Delta\delta = (\delta_{oxide} - \delta_{parent\ dithiane})$. A positive value indicates the carbon atom of the substituted 1,3-dithiane 1-oxide appears at lower field (deshielded) than the carbon of the corresponding 1,3-dithiane derivative. A negative sign is indicative of an upfield shift (shielding) on oxidation.

Table IV. ^{13}Chemical Shifts and $\Delta\delta$ Values of Thiane 1-Oxides [a]

Compd	C(2)	C(3)	C(4)	Ref
	Equatorial Oxides			
Unsubstituted[b]	52.1 (22.8)	23.3 (−4.9)	24.7 (−2.2)	4a
trans-4-Methyl	50.7	30.0	30.5	10a
trans-4-Isopropyl	52.3 (22.2)	26.0 (−5.8)	42.8 (−1.6)	4b
trans-4-*tert*-Butyl	52.4	24.4	48.0	7b
	Axial Oxides			
Unsubstituted[b]	45.1 (15.8)	15.5 (−12.7)	24.7 (−4.9)	4a
cis-4-Methyl	45.7	23.7	30.9	10a
cis-4-Isopropyl	46.7	19.1 (−12.7)	43.0 (−1.4)	4b
cis-4-*tert*-Butyl	46.9	16.9	47.3	7b

[a] $\Delta\delta$ Values are in parentheses. [b] Determined from low-temperature spectrum.

C(2), C(5), and C(6) are each sensitive to the stereochemistry of the sulfoxide group. In all of the 2-monosubstituted compounds where direct comparison of diastereomers is possible (**b,c,d,f**), C(2) and C(6) are more shielded in the cis isomer (axial oxygen) than in the trans isomer (equatorial oxygen). The ^{13}C shifts of C(6) can be used to determine stereochemistry, even if only one diastereomer is available. The seven trans oxides **2b–h** all had their C(6) signals in the range 53.2–55.4 ppm, while the corresponding signals for the five cis oxides **3b–d,f,h** were 44.9–47.8 ppm. The $\Delta\delta$ values for C(6) in each series (Table III) were also diagnostic of sulfoxide stereochemistry. The cis oxides had $\Delta\delta$ values in the range 14.0–16.9 ppm and the trans 22.3–24.2 ppm. The chemical shifts and $\Delta\delta$ values for C(6) correspond quite well to published data for the α carbon [C(2)] of thiane 1-oxide and its derivatives (Table IV). The chemical shifts and $\Delta\delta$ values for C(2) of 1,3-dithiane 1-oxides are significantly smaller than those for C(6) or for the α carbons of thiane oxides. The C(2) $\Delta\delta$ values for the cis (9.1–12.6 ppm) and trans (15.0–19.5 ppm) series are free of overlaps and are sufficiently different from each other to again permit stereochemical assignments to be made with confidence.

The carbon which is β to the sulfoxide group in dithiane oxides is C(5) and its pattern of $\Delta\delta$ values is different for the cis and trans series. The cis series, in which oxygen is axial, appears to be normal in that large upfield shifts are found relative to the parent dithianes. These $\Delta\delta$ values average −10.0 ppm and, with the exception of **3b**, are very similar to those observed for the β carbons C(3) and C(5) of thiane oxide (Table IV).[15] Interestingly, C(5) in the trans series has been shifted downfield relative to the dithianes. This effect is opposite to that which occurs in equatorial thiane oxides where $\Delta\delta$ values of ca. −5.0 ppm have been observed.

The signal for C(4) shifts upfield by about 2 ppm when either an axial or equatorial oxygen is attached to sulfur and is not useful for assigning sulfoxide stereochemistry.

Dynamic proton NMR studies have established that the equatorial oxide conformation of **2a** is 0.6 kcal/mol more stable than the axial oxide conformation.[2a,16] Qualitatively, we see from ^{13}C NMR that the chemical shifts and $\Delta\delta$ values are close to those exhibited by the trans series and indicative of an equatorial oxide. In the case of 1,3,5-trithiane 1-oxide (4), low-temperature proton NMR detected the presence of only a single conformation which was assumed to be the equatorial oxide by analogy with **2a**.[2a] The ^{13}C NMR results for **4**

its 2,2-dideuterio analogue. The signal which was absent in the spectrum of the dideuterated compound was assigned to C(2) of **2a**. In order to distinguish between C(4) and C(5) in **2a**, the trans oxides **2d** and **2f**, and in the 2,2-disubstituted oxides **2i–k**, gated decoupling was employed. The signal with the greater multiplicity was assigned to C(5) and was the more deshielded in **2a, d**, and **f**. Accordingly, the lower field signal in the other trans 2-monosubstituted oxides **2b,c,e,g**, and **h** was also assigned to C(5). In the cis oxides the signal appearing at highest field was assigned to C(5), since an axial oxygen substituent on sulfur is known to exert a significant shielding effect on carbons oriented synclinal to it.[4–9]

The solvent was CDCl$_3$ and concentrations were 1 M in most cases. In order to ensure that concentration effects were not large, since we were sometimes sample or solubility limited, the ^{13}C NMR spectrum of **2a** was determined at 0.10 and 1.0 M. The chemical shifts differed by ca. 0.5 ppm in the two runs. As is evident from the tables, this variation is small compared with differences resulting from structural factors.

Discussion

(A) Assignment of Stereochemistry to 1,3-Dithiane 1-Oxides. We have previously described proton NMR correlations which were helpful in deducing whether a particular 2-substituted 1,3-dithiane 1-oxide diastereomer belonged to the cis or trans series.[2b] The present study supersedes that work and clearly establishes that ^{13}C NMR is the method of choice for making such assignments. The chemical shifts of

Figure 1. Proposed interaction of sulfoxide 3p orbital with σ^* orbitals of C(5)–C(6) and C(2)–S(3) fragments is better when the lone pair is equatorial and the oxygen is axial.

strongly support this assertion. The α carbons of the oxide have chemical shifts which are 17.2 ppm downfield from 1,3,5-trithiane (**5**). The environment of C(2) in **4** resembles the environment of C(2) in dithiane oxides and the $\Delta\delta$ value of 17.2 ppm is exactly the same as the average of the seven trans oxides in Table III.

(B) Relation of Chemical Shifts to Structure.[17] In attempting to understand the increased shielding of the α carbon in an axial sulfoxide compared to an equatorial one, structural relationships between the diastereomeric pair *trans*- (**2d**) and *cis*-2-phenyl-1,3-dithiane 1-oxide (**3d**) were examined. A simple explanation for decreased shielding in the equatorial oxides would be available if the electronegativity of an equatorially oriented sulfoxide group exceeded that of an axial one. Conceivably, this would be reflected in the C(2)–S(1)–C(6) valence angles and in the S(1)–O bond lengths. A larger C–S–C valence angle would indicate an increased amount of *s* character in the orbitals used by S(1) to bond to C(6) and C(2), deshielding the α carbon by shifting the center of electron density away from carbon and toward sulfur. A longer S–O distance would indicate more single bond character and more positive charge at sulfur. The anticipated greater electron-withdrawing effect of this group would lead to decreased shielding of the α carbon. Neither of these structural effects was evident. The C(2)–S(1)–C(6) valence angles are similar: 98.2° in the equatorial oxide **2d** and 98.7° in the axial oxide **3d**.[2d] The small difference is, in fact, in the wrong direction to provide an explanation for the chemical shifts. The S–O distances in **2d** and **3d**, after correcting for a pronounced thermal anisotropy, are virtually identical: 1.512 Å in **2d**, and 1.509 Å in **3d**.[2d]

A second possibility lies in an interaction of the sulfur lone-pair orbital with the σ^* orbitals associated with C(5)–C(6) and C(2)–S(3). Assuming directional properties for the sulfur 3p orbital,[18] interaction with the σ^* orbitals will be effective only when the sulfoxide oxygen is axial (lone pair equatorial) (Figure 1). Electron release from the sulfur lone pair will populate the antibonding orbitals, weaken the C(5)–C(6) and C(2)–S(3) bonds, and increase the electron density at carbons 2, 5, and 6 in the axial oxides. Again, this is not borne out by the structural evidence. The C(2)–S(3) bond in the axial oxide **3d** is shorter, not longer, than in the equatorial oxide **2d** (1.797 vs. 1.814 Å). The C(5)–C(6) distances in **2d** and **3d** (1.519 and 1.512 Å) are not significantly different from each other.[2d]

A semiquantitative rationalization of this question in terms of an electric-field effect has been presented by Buchanan and Durst.[7b] The sulfoxide oxygen is considered a point charge which polarizes the electron distribution in all the bonds to the α carbon. The shielding effect is a function of the spatial orientation (distance, angle) of these bonds with respect to the perturbing oxygen and their longitudinal polarizability. Qualitatively, the difference in shielding may be attributed to the S–O bond existing in a gauche relationship to the C_α–C_β bonds in the axial oxide (anti in the equatorial oxide) compared with a gauche relationship between S–O and the C_α–H_{ax} bond in the equatorial oxide (Figure 2). Since the longitudinal polarizability of a C–C bond is ca. 50% greater than that of a C–H bond,[19] the shift of electron density toward the α carbon is greater in the axial oxide.[20]
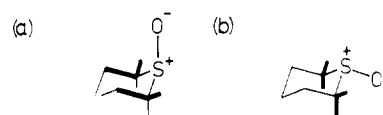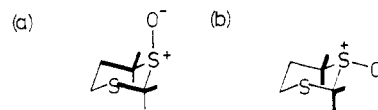
Figure 2. Bonds to α carbons subject to most pronounced polarization by electric-field associated with oxygen are thickened.

The electric-field explanation is consistent with the decreased sensitivity of the C(2) shifts to oxidation at sulfur in the 1,3-dithiane system. In the axial oxide, the most significant polarizations would involve C(5)–C(6) and C(2)–S(3). The greater polarizability of the C(2)–S(3) bond leads to increased shielding of C(2) relative to C(6) and smaller values of $\Delta\delta$. However, since the differential C(2) shifts are smaller than the C(6) shifts in the equatorial oxides as well, this cannot be the only factor. The interaction of an equatorial oxygen with the C(2)–S(3) bond must be small because of their antiperiplanar relationship.[21] What is probably a more important contributor to the decreased sensitivity of C(2) to oxidation at sulfur is its attachment to S(3). Since C(2) is already bonded to an electronegative substituent,[21] the inductive electron withdrawal by the sulfoxide group will be attenuated.

Gorenstein[22] has analyzed ^{13}C, ^{31}P, and ^{19}F chemical shifts in V–X–Y–Z systems where V, X, and Y are component atoms of a six-membered ring and Z is an axial or equatorial substituent. He notes that torsional relationships and bond angles are not independent and proposes that atoms belonging to a gauche array (Z axial) are more shielded than when part of an anti array (Z equatorial) because the ring valence angles around the atoms are larger in the gauche. Downfield shifts are associated with increases in C–X–C bond angles. The proposal apparently applies to all the atoms in the array even though presented as an alternative to the steric polarization suggested by Grant and Cheney[23] which is often used to rationalize the upfield shift of the α carbons in axially substituted six-membered rings, including C(3) of thiane oxides.[24] The ^{13}C and structural data for **2d** and **3d** provide an opportunity to test Gorenstein's proposal. Indeed, the signal for C(2) in the equatorial oxide **2d** appears at 5.3 ppm lower field than in the axial oxide **3d**, and the S(1)–C(2)–S(3) angle is smaller in the equatorial oxide (109.6°) than in the axial (112.9°).[2d] At C(6) the equatorial ^{13}C shift is 7.6 ppm to lower field than the axial, but the C(5)–C(6)–S(1) angle is now only slightly smaller in the equatorial (114.0 ± 0.2°) than in the axial oxide (114.6 ± 0.2°). The largest difference in chemical shift involves C(5) which is γ to the oxygen substituent. Here the signal for C(5) is 17.8 ppm to lower field in the equatorial than in the axial oxide, yet the C(4)–C(5)–C(6) valence angles are not significantly different, being 113.3 ± 0.2° in **2d** vs. 113.0 ± 0.3° in **3d**.

(C) Ring Deformation in 2,2-Disubstituted 1,3-Dithiane 1-Oxides. Equilibration of diastereomeric alkyl derivatives of 1,3-dithiane has provided evidence that the free-energy difference between chair and twist forms lies in the range 1.8–2.6 kcal/mol.[25] Since this is comparable to the conformational energy of a C(2)-axial methyl group (1.8 kcal/mol),[25] 2,2-disubstituted 1,3-dithianes and their oxides might be anticipated to contain significant amounts of twist confor-

mations. A proton NMR study of *trans*-2-*tert*-butyl-*cis*-2-methyl-1,3-dithiane 1-oxide in which conformational distortion in the C(4)–C(5)–C(6) portion of the ring was probed by analysis of vicinal H···H coupling constants did not provide evidence capable of distinguishing between a flattened chair form or the presence of twist forms.[26] As was noted, however, in a previous paper by the same group,[27] this method is insensitive to distortions occurring in the S(1)–C(2)–S(3) portion of the ring. The ^{13}C NMR spectra of the 2,2-disubstituted oxides **2i–k** provides complementary information and clearly indicates important contributions from twist conformations.[28]

The pattern of ^{13}C shifts and $\Delta\delta$ values in the three 2,2-disubstituted 1,3-dithiane 1-oxides **2i–k** is different from that of both the trans and cis 2-monosubstituted series. For C(2), $\Delta\delta$ values range from 10.6 to 12.0 ppm and resemble axial oxides. The $\Delta\delta$ values for C(6) are intermediate between those of axial and equatorial oxides. Since, however, the ca. 11 ppm upfield shift of C(5) characteristic of axial oxides is *not* observed in any of the three, including the diastereomeric pair **2j,k**, oxygen cannot be axial. These data point to the involvement of the twist form **A** in which the sulfoxide oxygen occupies an isoclinal[29] site and the substituents at C(2) are pseudoaxial or pseudoequatorial. As seen from a model, the geometric relationship of oxygen to the C(2)–S bond in **A** is similar to that of an axial oxide (see part B for discussion of electric-field effects on ^{13}C shifts), yet antiperiplanar rather than synclinal to C(5), consistent with the ^{13}C NMR results.

In 2,2-dimethyl-1,3-dithiane 1-oxide (**2i**) the diastereotopic methyl groups have much different chemical shifts. One is at 16.0 ppm ($\Delta\delta$ −14.8 ppm) and the other at 25.1 ppm ($\Delta\delta$ −5.7 ppm). The signal at higher field is assigned to the methyl group cis to the sulfoxide oxygen based on the premise that the torsional relationship between these groups would lead to a larger γ-gauche upfield shift than that experienced by the methyl trans to oxygen.[6a,12] The diastereomeric pair **2j,k** have similar shifts for the ring carbons but the methyl signal of **2j** which is cis to oxygen is more shielded (18.6 ppm, $\Delta\delta$ −14.0 ppm) than that of **2k** which is trans to oxygen (27.8 ppm, $\Delta\delta$ −4.8 ppm).

An alternative twist conformation **B** seems sterically as reasonable as **A** but does not fit the ^{13}C NMR results as well. A more detailed analysis of the conformations of these systems must await the results of dynamic ^{13}C NMR studies and x-ray crystallographic analysis of the putative twist forms.
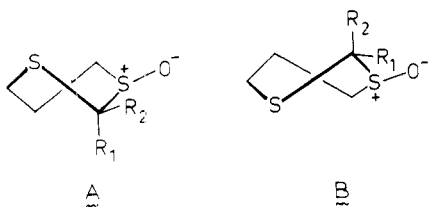
Experimental Section

Carbon-13 NMR spectra were recorded using a JEOL-PS100P/EC-100 Fourier transform spectrometer. Measurements were made at 25.2 MHz with a probe temperature of 23 °C using a 5-KHz rf crystal filter. Typically, a 45° pulse width was used (10 s) with a pulse repetition rate of 1 s; 8K data points were employed in the time domain. Carbon-13 chemical shifts were referenced to the center of the CDCl$_3$ multiplet using a value of $\delta_{Me_4Si} = \delta_{CDCl_3} + 76.91$ ppm.[30]

The preparation of oxides **2a,b,d,f,i–k** and **3b,d,f** have been described previously[2b,c] as have **2c** and **3c**.[31] Oxides **2g**, **2h**, and **3h** were available from another study and will be reported separately.[13] 2-(3′,4′,5′-Trimethoxyphenyl)-1,3-dithiane and its oxide were obtained from Dr. O. Hernandez.[32] The parent dithianes **1f**,[2b] **1g**,[33] **1h**,[13b] and **1j**[34] have been reported. Trithiane 1-oxide was available from a previous study.[2a]

References and Notes

(1) (a) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972; (b) N. K. Wilson and J. B. Stothers, *Top. Stereochem.*, **8**, 1 (1974).

(2) (a) S. A. Khan, J. B. Lambert, O. Hernandez, and F. A. Carey, *J. Am. Chem. Soc.*, **97**, 1468 (1975); (b) F. A. Carey, O. D. Dailey, Jr., O. Hernandez, and J. R. Tucker, *J. Org. Chem.*, **41**, 3975 (1976); (c) F. A. Carey, O. D. Dailey, Jr., and O. Hernandez, *ibid.*, **41**, 3979 (1976); (d) F. A. Carey, P. M. Smith, R. J. Maher, and R. F. Bryan, *ibid.*, **42**, 961 (1977).

(3) (a) E. L. Eliel, V. S. Rao, and F. G. Riddell, *J. Am. Chem. Soc.*, **98**, 3583 (1976); (b) R. L. Willer and E. L. Eliel, *ibid.*, **99**, 1925 (1977).

(4) (a) J. B. Lambert, D. A. Netzel, H.-n. Sun, and K. L. Lilianstrom, *J. Am. Chem. Soc.*, **98**, 3778 (1976); (b) G. Barbarella, P. Dembeck, A. Garbesi, and A. Fava, *Org. Magn. Res.*, **8**, 108 (1976).

(5) Sulfoxides incorporated into rigid bicyclic systems: (a) H. J. Reich and J. E. Trend, *J. Org. Chem.*, **38**, 2637 (1973); (b) J. R. Wiseman, H. O. Krabbenhoft, and B. R. Anderson, *ibid.*, **41**, 1518 (1976).

(6) Penicillin sulfoxides: (a) R. A. Archer, R. D. G. Cooper, P. V. Demarco, and L. F. Johnson, *J. Chem. Soc., Chem. Commun.*, 1291 (1970); (b) K. Tori, T. Tsushima, Y. Tamura, H. Shigemoto, T. Tsuji, H. Ishitobi, and H. Tanida, *Tetrahedron Lett.*, 3307 (1975).

(7) Thiane oxides: (a) see ref 4; (b) G. W. Buchanan and T. Durst, *Tetrahedron Lett.*, 1683 (1975).

(8) Oxathiane oxides: (a) D. M. Frieze and S. A. Evans, *J. Org. Chem.*, **40**, 2690 (1975); (b) W. A. Szarek, D. M. Vyas, A.-M. Sepulchre, S. D. Gero, and G. Lukacs, *Can. J. Chem.*, **52**, 2041 (1974); (c) G. W. Buchanan, N. K. Sharma, F. de Reinack-Hirtzbach, and T. Durst, *Can. J. Chem.*, **55**, 44 (1977).

(9) Cyclic sulfites: G. W. Buchanan, J. B. Stothers, and G. Wood, *Can. J. Chem.*, **51**, 3746 (1973).

(10) Thiane and 1,3-dithiane imides: (a) P. K. Claus, W. Rieder, F. W. Vierhapper, and R. L. Willer, *Tetrahedron Lett.*, 119 (1976); (b) P. K. Claus, F. W. Vierhapper, and R. L. Willer, *J. Chem. Soc., Chem. Commun.*, 1002 (1976); (c) R. B. Greenwald, D. H. Evans, and J. R. De Member, *Tetrahedron Lett.*, 3885 (1975).

(11) *S*-Methylthianium salts: see ref 4 and (a) E. L. Eliel, R. L. Willer, A. T. McPhail, and K. D. Onan, *J. Am. Chem. Soc.*, **96**, 3021 (1974); (b) E. L. Eliel and R. L. Willer, *ibid.*, **99**, 1936 (1977).

(12) Thiolane oxides: R. T. LaLonde, C. F. Wong, A. I.-M. Tsai, J. T. Wróbel, J. Ruszkowska, K. Kabzinska, T. I. Martin, and D. B. MacLean, *Can. J. Chem.*, **54**, 3860 (1976).

(13) (a) R. F. Bryan, F. A. Carey, O. Hernandez, and I. F. Taylor, Jr., *J. Org. Chem.*, submitted; (b) R. F. Bryan, F. A. Carey, O. D. Dailey, Jr., R. J. Maher, and R. W. Miller, *J. Org. Chem.*, **42**, 961 (1977); (c) A. T. McPhail, K. D. Onan, and J. Koskimies, *J. Chem. Soc., Perkin Trans.* **2**, 1004 (1976).

(14) All chemical shifts are reported in units of ppm downfield from internal tetramethylsilane. The convention used in this paper for reporting "differential shifts" ($\Delta\delta$ values) subtracts the chemical shift of the corresponding 1,3-dithiane (1) from the 1,3-dithiane 1-oxide. A positive value of $\Delta\delta$ corresponds to a downfield shift in the oxide, a negative value to an upfield shift.

(15) As noted by one of the reviewers, the C(5) chemical shift of **3b** (21.2 ppm) is significantly different from that predicted on the basis of data available on the equatorial/axial preferences of various substituents on 1,3-dithiane rings. Assuming a 2-methyl substituent favors an equatorial orientation by 1.8 kcal/mol and a 1-oxide by 0.6 kcal/mol, then the equatorial CH$_3$-axial oxide conformation should dominate over the axial CH$_3$-equatorial oxide by 87:13 (1.2 kcal/mol). Based on the C(5) chemical shifts of *trans*- and *cis*-2-*tert*-butyl-1,3-dithiane 1-oxide (**2c** and **3c**) as models, C(5) in **3b** should appear at 16.5 ppm. We believe this large discrepancy results from nonadditivity of conformational energies of substituents in oxides of 1,3-dithiane and that at equilibrium much more of the axial CH$_3$-equatorial oxide conformer is present than predicted. The basis for the nonadditivity may lie in the comparative ease of distortion of the C(2)–S(1) bond . Structural studies[2d,13] reveal significant bond lengthening in the oxides which would have the effect of reducing the ΔG value for a C(2) methyl group owing to decreased syn-axial repulsions in the axial orientation.

(16) (a) M. J. Cook and A. P. Tonge, *Tetrahedron Lett.*, 849 (1973); (b) L. Van Acker and M. Anteunis, *ibid.*, 225 (1974); (c) M. J. Cook and A. P. Tonge, *J. Chem. Soc., Perkin Trans.* **2**, 767 (1974).

(17) For critical analyses of substituent effects on ^{13}C shifts, see ref 1a and G. E. Maciel, *Top. Carbon-13 NMR Spectrosc.*, **1**, 53 (1974).

(18) J.-M. Lehn and G. Wipff, *J. Am. Chem. Soc.*, **98**, 7498 (1976).

(19) The longitudinal bond polarizabilities (in units of Å^3) are: C–H, 0.64; C–C, 0.99; and C–S, 1.88. See: R. J. W. LeFévre, *Adv. Phys. Org. Chem.*, **3**, 1 (1965). These polarizabilities differ substantially from those cited by Buchanan and Durst in ref 7 but are of more recent origin and are similar to those cited by others (e.g., ref 18). Indeed, the C–S bond polarizability used by Buchanan and Durst does not appear to come from the reference they cite.

(20) The Buchanan–Durst analysis has been questioned (ref 4b) on the grounds that the effect is a much more general one and is observed as well when the perturbing substituent is not highly polar and even for axial vs. equatorial methyl substitution in cyclohexanes. It should be pointed out, however, that this does not invalidate their reasoning, since the physical bases for similar observable effects need not be the same for all cases.

(21) The electronegativity of sulfur has recently been estimated to be 2.52 and is therefore more electronegative than carbon which is 2.35 on this scale: G. Simons, M. E. Zandler, and E. R. Talaty, *J. Am. Chem. Soc.*, **98**, 7869 (1976).

(22) D. G. Gorenstein, *J. Am. Chem. Soc.*, **99**, 2254 (1977).
(23) D. M. Grant and B. V. Cheney, *J. Am. Chem. Soc.*, **89**, 5315 (1967).
(24) The physical basis of steric shifts in hydrocarbons has been recently evaluated and modified; see: K. Seidman and G. E. Maciel, *J. Am. Chem. Soc.*, **99**, 659 (1977).
(25) (a) K. Pihlaja, *J. Chem. Soc., Perkin Trans. 2*, 890 (1974); (b) E. L. Eliel and R. O. Hutchins, *J. Am. Chem. Soc.*, **91**, 2703 (1969).
(26) K. Bergesen, M. J. Cook, and A. P. Tonge, *Acta Chem. Scand., Ser. A*, **30**, 574 (1976).
(27) K. Bergesen, B. M. Carden, and M. J. Cook, *J. Chem. Soc., Perkin Trans. 2*, 345 (1976).
(28) For molecular mechanics calculations of conformations of 1,3-dithiane

1-oxides, see: N. L. Allinger and J. Kao, *Tetrahedron*, **32**, 529 (1976).
(29) For a discussion of nonchair conformations of six-membered rings and terminology, see: G. M. Kellie and F. G. Riddell, *Top. Stereochem.*, **8**, 225 (1974).
(30) G. C. Levy and J. D. Cargioli, *J. Magn. Reson.*, **6**, 143 (1972).
(31) M. J. Cook and A. P. Tonge, *J. Chem. Soc., Perkin Trans. 2*, 767 (1974).
(32) O. Hernandez, Ph.D. Thesis, University of Virginia, 1974.
(33) (a) A. G. Brook, J. M. Duff, P. F. Jones, and M. R. Davis, *J. Am. Chem. Soc.*, **89**, 431 (1967); (b) E. J. Corey, D. Seebach, and R. Freedman, *ibid.*, **89**, 434 (1967).
(34) H. T. Kalff and E. Havinga, *Recl. Trav. Chim. Pays–Bas*, **85**, 467 (1966).

Base-Induced Rearrangements of Mesityl Thienyl Sulfones[1]

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Two mesityl thienyl sulfones (5-mesitylsulfonyl-2-methylthiophene and 2-mesitylsulfonylthiophene) undergo the Truce–Smiles rearrangement. However, the thienyl unit (in contrast to the previously studied naphthyl and substituted phenyl groups) migrates with a change in orientation regardless of the base/solvent system used. The chemistry of 2-mesitylsulfonylthiophene is complicated by the acidity of the open α position, with 2 equiv of base being required for rearrangement. (The monometalated species, on the other hand, slowly decomposes to give mesitylenesulfinic acid as the only isolable product.) A modified Michael addition–β-elimination mechanism has been proposed to explain these results.

Aryl sulfones containing an ortho methyl group rearrange to *o*-benzylbenzenesulfinic acids when treated with *n*-butyllithium in ether[2] or potassium *tert*-butoxide in Me₂SO.[3] The three isomeric mesityl tolyl sulfones all give sulfinic acids with retained tolyl orientation regardless of which of these two base/solvent systems is used. In contrast to this, mesityl α-naphthyl sulfone can be caused to rearrange via two different pathways. In *n*-butyllithium/ether, rearrangement proceeds via direct displacement and retained naphthyl orientation. However, in potassium *tert*-butoxide/Me₂SO an addition–β-elimination sequence occurs, resulting in 2-(2'-naphthylmethyl)-4,6-dimethylbenzenesulfinic acid.[4]

Results and Discussion

It has now been found that treatment of 5-mesitylsulfonyl-2-methylthiophene (1) with either *n*-butyllithium/ether or potassium *tert*-butoxide/Me₂SO yields sulfinic acid 2 via an addition–elimination sequence.

1

2
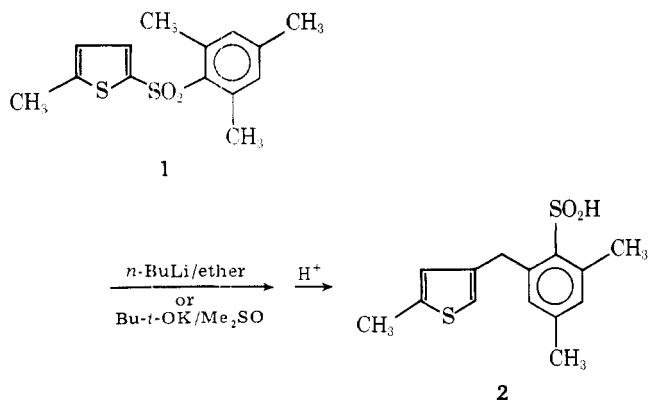
That the same sulfinic acid is produced in both base/solvent systems was shown by the identity of IR and NMR spectra as well as the melting point and mixture melting point of their 2-hydroxy-3,5-dichlorobenzyl sulfone derivative. The structure proposed for **2** is supported by the following series of reactions. Sulfinic acid 2 was treated with Raney nickel to reduce

the thiophene ring to a saturated hydrocarbon unit, and to remove the sulfinate moiety. The two possible hydrocarbon products, 1-(3,5-dimethylphenyl)hexane (**3**) and 1-(3,5-dimethylphenyl)-2-methylpentane (**4**), were alternatively synthesized from 3,5-dimethylbenzyl bromide by treatment with the appropriate organometallic compounds. The Raney nickel reduction product had physical and spectral properties which matched those of hydrocarbon 4. The spectral properties of 3 did not correlate, thus confirming 2 as the correct structure for the sulfinic acid product.

2-Mesitylsulfonylthiophene (**5**) has been found to rearrange

5

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