aromatic), 7.67–7.80 (m, 1 H, aromatic); NMR (180 MHz, $CDCl_3$) δ 1.80–2.04 (m, 2 H, $H_{4,4'}$ anti to $H_{3,3'}$), 2.06–2.26 (m, 2 H, $H_{4,4'}$ syn to $H_{3,3'}$), 3.10–3.30 (m, 6 H, $H_{2,2'}$, $H_{3,3'}$, $H_{5,5'}$ syn to $H_{3,3'}$), 3.40–3.64 (m, 2 H, $H_{5,5'}$ anti to $H_{3,3'}$), 7.14–7.36 (m, 6 H, arom), 7.46 (d of d, 2 H, J = 7, 2.5 Hz, $H_{8,8'}$).[25]

Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found for **22**: C, 83.59; H, 6.43. Found for **23**: C, 83.48; H, 6.42. Found for **24**: C, 83.38; H, 6.38. Found for **25**: C, 83.60; H, 6.23.

(25) From the model of **25**, the carbonyl group is almost perpendicular to the aryl ring. Consequently $H_{8,8'}$ protons are at higher field than in the other three dimers. In **25**, $H_{5,5'}$ protons anti to $H_{3,3'}$ are equatorial and nearly in the plane of the aryl ring and consequently deshielded. The $H_{4,4'}$ protons anti to $H_{3,3'}$ are in pseudoaxial positions and are shielded by the carbonyl group.

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Registry No. **14**, 69456-01-5; **15**, 45998-98-9; **16**, 71975-02-5; **17**, 72028-55-8; **18**, 71975-03-6; **19**, 72028-56-9; **22**, 72028-85-4; **23**, 71975-04-7; **24**, 71975-05-8; **25**, 71975-06-9; 4,5-benzotropone, 4443-91-8.

Supplementary Material Available: Positional and thermal parameters and their standard deviations for the X-ray structures of **18**, **22**, **23**, **24**, and **25** (9 pages). Ordering information is given on any current masthead page.

Conformational Study of 3-Substituted Thietane 1-Oxides. Lanthanide Shift Reagent Approach

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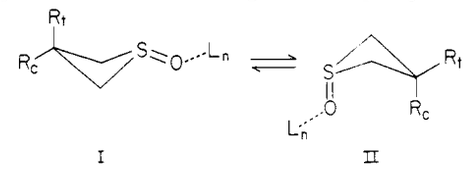
The NMR lanthanide-induced shifts (LIS) for a series of cis and trans 3-substituted thietane 1-oxides and 3,3-disubstituted thietane 1-oxides were measured and interpreted in terms of the ring conformations. The data suggested that all cis 3-substituted thietane 1-oxides (R = CH_3, *t*-Bu, and aryl) exist exclusively in the diequatorial conformation and that the two isomeric 3-methyl-3-phenylthietane 1-oxides exist strongly, if not exclusively, in the equatorial oxygen conformation when they are bound to a shift reagent—$Eu(dpm)_3$ or $Yb(fod)_3$. The data for trans 3-substituted thietane 1-oxides suggested that they all preferred the equatorial oxygen conformation (CH_3, 86%; aryl, 75%; *t*-Bu, 65–75%) when they are bound to a shift reagent.

Relatively little is known about the conformation of four-membered heterocycles such as thietane and its derivatives.[1] Pioneering work by Johnson[2] and co-workers showed that the sulfinyl group of 3-substituted thietane 1-oxides prefers to occupy the equatorial position. In his work 3-*tert*-butyl- and 3-arylthietane 1-oxides were equilibrated to mixtures which were rich (85%) in the cis isomer. Arguments based on the chemical shift of H(3) were presented which suggested that the cis isomers were mainly in the diequatorial conformation and that the trans isomers were mainly in the equatorial R/axial O conformation. More recently one of us (D.J.H.S.) presented proton NMR and X-ray evidence which questioned the latter suggestion.[3] Thus there is some uncertainty about whether the sulfinyl group prefers the equatorial position more than 3-aryl and 3-alkyl substituents.

Results and Discussion

In this paper we shall discuss lanthanide-induced shift (LIS) data for a series of thietane 1-oxides (**1**–**11**) in terms of the conformational equilibrium shown in eq 1, where Ln represents the shift reagent $Eu(dpm)_3$ or $Yb(fod)_3$.



I II (1)

Chloroform solutions of the sulfoxides were doped with increasing amounts of $Eu(dpm)_3$ or $Yb(fod)_3$, and the proton (and in some cases carbon) NMR spectra were recorded as a function of shift reagent concentration. From these data the relative LIS for most protons (and carbons) could be determined (Table I). Previous work[4] has shown that the shift reagent coordinates with the sulfoxide oxygen. If the location of the shift reagent relative to the sulfoxide is known, then it should be possible to calculate the relative LIS for comparison with the experimentally determined ones. Good agreement implies that the shift reagent has been properly located, that the substrate's structure is correct, and that the NMR spectrum is properly assigned.[5] In our study we have assumed that all the thietane 1-oxides have the same shape, namely that reported for thiethane 1-oxide (**14**).[6] This is probably a good

(1) For a review see: Moriarty, R. M. *Top. Stereochem.* **1974**, *8*, 271–421.

(2) (a) Johnson, C. R.; Siegl, W. O. *J. Am. Chem. Soc.* **1969**, *91*, 2796. (b) *Tetrahedron Lett.* **1969**, 1879. (c) Siegl, W. O.; Johnson, C. R. *Tetrahedron* **1971**, *27*, 341. (d) *J. Org. Chem.* **1970**, *35*, 3657.

(3) Barlow, J. H.; Hall, C. R.; Russell, D. R.; Smith, D. J. H. *J. Chem. Soc., Chem. Commun.* **1975**, 133.

(4) (a) Uebel, J. J.; Wing, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 8910. (b) Wing, R. M.; Uebel, J. J.; Andersen, K. K. *Ibid.* **1973**, *95*, 6046.

(5) For a review of the lanthanide-induced-shift technique and its application in conformational analysis see: Hofer, O. *Top. Stereochem.* **1976**, *9*, 111–97.

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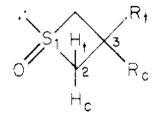
Table I. Chemical Shifts and Lanthanide-Induced Shifts (LIS) (ppm) for



compd (R_c/R_t)	^1H shifts/relative LIS (Eu(dpm)$_3$) H_c	H_t	R_c	R_t	I/II	$10^2/R^a$
1 (CH_3/CH_3)	3.00/100	3.50/58	1.29/27	1.22/33	100/0	0.1
2 (H/CH_3)	3.2[b]/100	3.2[b]/63	3.0[b]/56	1.25/32	86/14	0.4
3 (CH_3/H)	2.80/100	3.65/66	1.22/27	2.32/49	100/0	5.8
4 (H/*t*-Bu)	3.3[a]/100	3.3[b]/65	3.1[b]/63	0.90/22	68/32	6.8
5 (*t*-Bu/H)	2.92/100	3.92/64	0.92/24	1.93/61	100/0	6.0
6 (H/Ph)	3.62[b]/100	3.62[b]/74	4.39/65	7.1/17	75/25	5.3
7 (Ph/H)	3.3[b]/100	3.90/68	7.3/17	3.3[b]/63	100/0	5.1
8 (H/4-BrPh)	3.6[b]/100	3.6[b]/61[c]	4.38/63[c]	7.10, 7.49/17[c]	74/26	4.5
9 (4-BrPh/H)	3.2[b]/100	3.86/66	7.08, 7.44/24[c]	3.2[b]/59	100/0	0.1
10 (Ph/CH_3)	3.46/100[d]	3.86/50[d]	7.21/. . .	1.48/25[d]	100[e]/0	6.0[e]
11 (CH_3/Ph)	3.3/100	4.0/56	1.68/36	7.2/13	100/0	0.2

compd (R_c/R_t)	C-13 shifts/relative LIS (Yb(fod)$_3$) C_2	C_3	R_c	R_t
1 (CH_3/CH_3)	63.8/100[f]	28.6/69[f]	32.0/34[f]	29.2/37[f]
10 (Ph/CH_3)	63.3/100	34.4/69		30.4/36
11 (CH_3/Ph)	62.7/100	37.1/81	34.3/48	

[a] Agreement factor, $[\Sigma(\text{obsd} - \text{calcd})^2/\Sigma(\text{obsd})^2]^{1/2}$. [7,9] [b] Estimated chemical shift. Spectrum unresolved. [c] Shift as measured from center of AA'BB' pattern. [d] Yb(fod)$_3$-induced shifts. [e] Results obtained by combining proton and carbon LIS data. [f] Yb(dpm)-induced shifts; private communication from M. R. Willcott.

approximation since **1**,[6] **8**,[3] **9**,[3] and **14**[6] all have about the same dihedral ring angles—33 ± 2°.

The location of the lanthanide shift reagent and the ratio (I/II) were treated as unknowns. They therefore were varied to obtain the best agreement[7] between calculated and observed LIS. Only chemically reasonable solutions were allowed. The lanthanide was positioned within the OSC(3) plane, syn to sulfur's lone electron pair, at a distance of 2.5 ± 0.5 Å from the oxygen, with a Ln–O–S angle of 110–170°. Using these restrictions, we found (Table I) that all the cis sulfoxides (**3**, **5**, **7**, and **9**) gave their best correlations with the substituents in the diequatorial conformation, i.e., conformation I. Attempts to mix in small amounts of the diaxial conformation always led to considerably poorer results. The best correlations tended to have the lanthanide located 2.0–2.4 Å away from the oxygen, with an average Ln–O–S angle of 160 ± 10°. Similarly, all three 3,3-disubstituted compounds strongly prefer the equatorial oxygen conformation, i.e., conformation I. Once again the best correlations tended to have the lanthanide located relatively close to the oxygen (2.1–2.5 Å), but the average Ln–O–S angle was more acute (120 ± 4°). The variations observed in the location of the lanthanide reflect uncertainties in the LIS data, undoped chemical shifts, and the geometry of the ring.

The more interesting and more difficult questions concern the trans 3-substituted thietane 1-oxides (**2**, **4**, **6**, and **8**). The best correlations for all these compounds tended to have a somewhat longer Ln–O distance (2.5–3.0 Å) with fairly acute Ln–O–S angles (100–125°). These metal locations are again reasonable. Every trans isomer preferred the equatorial oxygen conformation to various degrees (Table I, compounds **2**, **4**, **6**, and **8**, or Table II, method A). The trends shown in Table II are reasonable and are in line with the steric requirements of these groups when they are attached to a cyclohexane ring.[8] Plots of the % *R* factors vs. mole fraction of the equatorial oxygen conformation (Figure 1) show the sensitivity of the correlations to the conformational equilibrium. The methyl and *p*-bromophenyl cases are the most sensitive, and the *tert*-butyl and phenyl cases are the least. The ranges given

Table II. Substituent Effects on the Conformations of *trans*-3-Substituted-Thietane 1-Oxides

substituent	% equatorial oxygen conformation (I) method A[a]	method B[a]
CH_3	86 ± 2	87
C_6H_5	75 ± 20	76
p-BrC_6H_4	74 ± 3	75
t-Bu	68 ± 20	74

[a] Consult text for explanation.

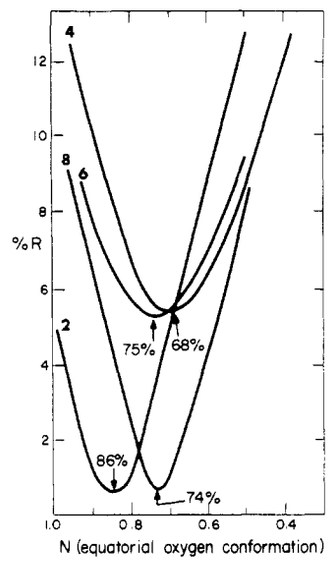


Figure 1. Plots of calculated agreement factors (% *R*) for trans sulfoxides **2**, **4**, **6**, and **8** as a function of the mole fraction of the equatorial oxygen conformer (I, eq 1).

(6) Bevan, J. W.; Legon, A. C.; Miller, D. J. *J. Chem. Soc., Chem. Commun.* **1974**, 659.
(7) Davis, R. E.; Willcott III, M. R. *J. Am. Chem. Soc.* **1972**, *94*, 1744.
(8) Hirsch, J. A. *Top. Stereochem.* **1967**, *1*, 199–222.

Scheme I

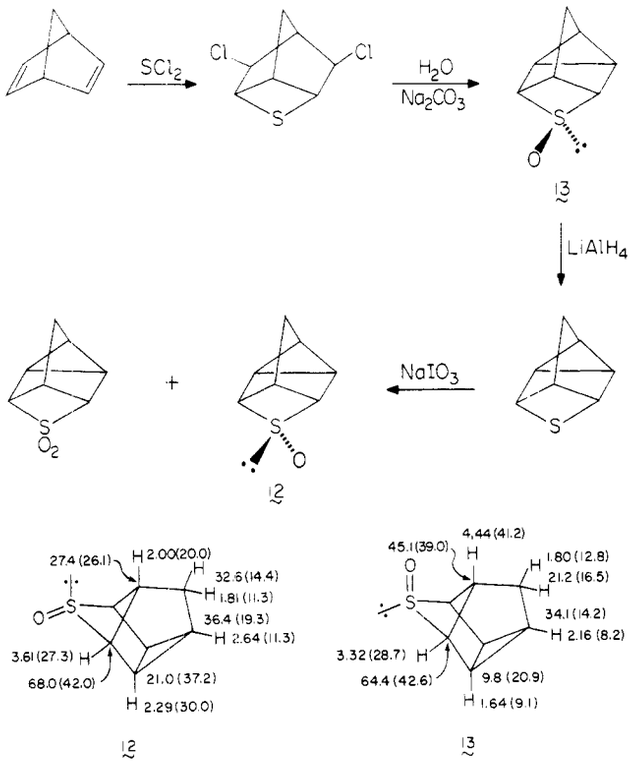


Figure 2. Proton and carbon chemical shifts (in parts per million downfield from Me_4Si) and the relative LIS induced by $Yb(fod)_3$ (in parentheses) for **12** and **13**. The proton and carbon LIS are roughly scaled to one another. For **12**, using the proton LIS, we calculate r (Yb–O) = 2.0 Å, θ (Yb–O–S) = 120°, and R = 3.4% and, using the carbon LIS, r = 2.0 Å, θ = 130°, and R = 2.7%. For **13**, using the proton LIS, we calculate r = 2.3 Å, θ = 161°, and R = 2.6% and, using the carbon LIS, r = 2.0 Å, θ = 152°, and R = 2.9%.

under method A represent the amount a conformational fraction must be changed to cause the R factor[7] to increase by 1.7. A change of 1.7 represents the 95% confidence level for a hypothesis test of order (4,1) using Hamilton[9] statistics. In method A the lanthanide was positioned so as to obtain the best correlation. The location of the metal was assumed to be the same in both conformations. Models suggested that this was a reasonable approximation. However, in an effort to test this and at the same time obtain models of equatorial and axial locked thietane 1-oxides, sulfoxides **12** and **13** were prepared (Scheme I). Sulfoxide **13** was previously prepared by Lautenschlaeger[10] using the method outlined in Scheme I.

The ^1H and ^{13}C LIS data (Figure 2) correlate very well with these structures. The lanthanide–oxygen distances are nearly the same (ca. 2.0–2.3 Å) for either compound, whereas the Ln–O–S angle for **12** is somewhat larger (150–160°) than for **13** (120–130°). Larger angles were also observed for the equatorial locked cis 3-substituted thietane 1-oxides (**3**, **5**, **7**, and **9**) and the 3,3-disubstituted compounds (**10** and **11**). These results support the previous assumption that the lanthanide is similarly located in either conformation. They also suggest an alternative approach to the conformational analysis of the trans sulfoxides. The lanthanide locations found for **12** and **13** could be assumed to hold for the respective conformations of the trans sulfoxides. The conformational percentages which gave the best fits using these metal locations are listed under method B in Table II. The results of both methods compare quite favorably.

These conformational estimates are, of course, valid only for the lanthanide-bound sulfoxides (I·L ⇌ II·L) and therefore they represent an estimate of K_c. The extent to which K, the conformational equilibrium constant for the thietane 1-oxides (I ⇌ II), is perturbed by coordination to the lanthanide shift reagent is under investigation.

$$\text{L·I} \overset{K}{\rightleftharpoons} \text{II·L}$$

$$\text{I·L} \overset{K_c}{\rightleftharpoons} \text{II·L}$$

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 237 grating spectrometer or a Perkin-Elmer 580 grating spectrometer. Proton NMR spectra were recorded on a Varian T60 or a JEOL-PS100 spectrometer using deuteriochloroform as solvent and tetramethylsilane (Me_4Si) as internal standard. Carbon-13 NMR spectra were recorded on a JEOL FX60 spectrometer operating at 15 MHz in the FT mode with Me_4Si as internal standard and deuteriochloroform as solvent. Chloroform solutions of the sulfoxides (ca. 50 mg/mL) were doped with increasing amounts of $Eu(dpm)_3$ or $Yb(fod)_3$ and the NMR spectra were recorded as a function of shift reagent concentration up to a molar ratio of about 0.2 (shift reagent/sulfoxide). The relative LIS were determined from the linear plots of the induced shifts vs. amount of added shift reagent. The relative LIS were analyzed in terms of equilibrium 1 with the aid of a modified version of a previously described computer program.[4]

The thietane 1-oxides (1–11) were prepared from the appropriate thiete sulfones.[2d] Reduction to the thietane sulfones was achieved using sodium borohydride[2d] or (for 3-*tert*-butyl-, 3-phenyl-, and 3-(*p*-bromophenyl)thietane sulfones) by catalytic hydrogenation using 10% palladium on barium carbonate.

The thietane sulfones were reduced to the sulfides, using lithium aluminum hydride, and reoxidized to the isomeric sulfoxides by stirring overnight at room temperature with an equivalent amount of *m*-chloroperoxybenzoic acid dissolved in dichloromethane.

Careful chromatography of this mixture of isomers (typically 1.2 g) on silica (50 g) and eluting with ether gave the cis isomer first, closely followed by the trans isomer. Confirmation of the stereochemical assignments of these compounds was based on NMR spectra described previously.[2]

Preparation of the 3-(*p*-Bromophenyl)thietane 1-Oxides (8 and 9). 3-(*p*-Bromophenyl)thiete 1,1-Dioxide. A mixture of *p*-bromoacetophenone (80 g, 0.4 mol), morpholine (52.5 g, 0.6 mol), *p*-toluenesulfonic acid (0.1 g), and benzene (250 mL) was refluxed in a water separator until no more water separated (5 days). The solvent was removed under reduced pressure to give *p*-bromo-α-morpholinostyrene as a yellow oil. Methanesulfonyl chloride (47.6 g, 0.4 mol) was slowly added to an ice-cooled solution of the crude enamine (0.4 mol) and triethylamine (41.9 g, 0.4 mol) in benzene (250 mL). The mixture was allowed to warm to room temperature and stirred overnight. The product was filtered, washed with water to remove triethylamine hydrochloride, and dried.

The crude product was oxidized and the amine oxide was pyrolyzed as described by Johnson[2d] for the preparation of 3-phenylthiete 1,1-dioxide. Recrystallization of the crude product from ethanol gave 3-(*p*-bromophenyl)thiete 1,1-dioxide (62 g, 60%) as white crystals: mp 228–230 °C (from ethanol); IR ν_{max} (chloroform) 1600, 1312, 1209, 1130, 785 cm^{-1}; NMR δ 7.53 (2 H, d, J = 9 Hz), 7.20 (2 H, d, J = 9 Hz), 6.87 (1 H, s), 4.70 (2 H, s); MS m/e 260, 258, 212, 210, 196, 194, 183, 181, 131, 115. Anal. Calcd for $C_9H_7BrO_2S$: C, 41.7; H, 2.7; S, 12.35. Found: C, 41.6; H, 2.75; S, 12.5.

3-(*p*-Bromophenyl)thietane 1,1-Dioxide. Procedure A. The thiete sulfone above (22 g, 0.09 mol) was added in small portions over 2 h to a mixture of sodium borohydride (15 g, 0.4 mol) and isopropyl alcohol (50 mL) at 60 °C. The mixture was stirred for 4 days. A further 5 g (0.13 mol) of sodium borohydride was added after the first 2 days. The mixture was cooled and made slightly acidic by dropwise addition of dilute sulfuric acid. The solvent was removed under reduced pressure and the residue

(9) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.
(10) Lautenschlaeger, F. *J. Org. Chem.* **1969**, *34*, 3998.

was extracted with hot ethyl acetate. Removal of the solvent gave 3-(*p*-bromophenyl)thietane 1,1-dioxide (11 g, 50%): mp 154–155 °C (from methanol); IR ν_{max} (chloroform) 1495, 1325 (s), 1220, 1140 (s), 1015, 825 cm^{-1}; NMR δ 7.32 (2 H, d, J = 9 Hz), 3.28–4.65 (5 H, m); *m/e* 262, 260, 198, 197, 196, 194, 182, 133, 118, 117, 116, 115, 103, 102. Anal. Calcd for $C_9H_9BrO_2S$: C, 41.4; H, 3.45; S, 12.25. Found: C, 41.3; H, 3.5; S, 12.3.

Procedure B. The thiete sulfone (5 g, 0.02 mol) and 10% palladium on barium carbonate (1 g) were stirred in ethanol (50 mL) in an atmosphere of hydrogen overnight. The solution was filtered and the solvent was removed under reduced pressure to give a product identical with the above (4.5 g, 90%).

3-(*p*-Bromophenyl)thietane. 3-(*p*-Bromophenyl)thietane 1,1-dioxide was reduced with lithium aluminum hydride, as described by Johnson[2d] for the preparation of 3-phenylthietane, to give 3-(*p*-bromophenyl)thietane (35%).

3-(*p*-Bromophenyl)thietane 1-Oxides (8 and 9). A solution of *m*-chloroperoxybenzoic acid (1.07 g, 5.2 mol) in dichloromethane (30 mL) was slowly added to an ice-cooled solution of 3-(*p*-bromophenyl)thietane (1.1 g, 4.8 mmol) in dichloromethane (35 mL). After 3 h the solution was allowed to warm to room temperature and filtered. The filtrate was washed with aqueous sodium carbonate. Removal of the solvent under reduced pressure gave a clear oil (1 g). Chromatography on silica (50 g) and elution with ether–methanol (50:1) gave *cis*-3-(*p*-bromophenyl)thietane 1-oxide (0.45 g, 38%): mp 108–109 °C (from chloroform–petroleum ether); IR ν_{max} (chloroform) 1495, 1142, 1065 (br), 1012, 820 cm^{-1}; IR ν_{max} (Nujol) 1490, 1138, 1060 (br), 1012, 823 cm^{-1}; NMR δ 7.37 (2 H, d, J = 8.5 Hz), 6.98 (2 H, d, J = 8.5 Hz), 3.17–4.00 (5 H, m); MS *m/e* 246, 244, 197, 195, 184, 182, 171, 169, 117, 116, 115, 103, 77. Anal. Calcd for C_9H_9BrOS: C, 44.1; H, 3.65; S, 13.05. Found: C, 43.8; H, 3.65; S, 13.1. *trans*-3-(*p*-Bromophenyl)thietane 1-oxide (0.46 g, 39%) was eluted next: mp 112–113 °C (from chloroform–petroleum ether); IR ν_{max} (chloroform) 1495, 1095, 1078, 1060 (br), 1011, 827 cm^{-1}; IR ν_{max} (Nujol) 1495, 1095, 1075, 1059 (br), 1010, 790 cm^{-1}; NMR δ 7.35 (2 H, d, J = 8.5 Hz), 6.98 (2 H, d, J = 8.5 Hz), 4.07–4.2 (1 H, m), 3.64 (4 H, d, J = 6 Hz); *m/e* 246, 244, 230, 228, 197, 195, 184, 182, 171, 169, 117, 116, 115, 103, 102, 91, 77. Anal. Found: C, 44.35; H, 3.8.

3-Methyl-3-phenylthietane 1,1-Dioxide. 2-Methyl-2-phenylpropane-1,3-diol was prepared by the Tollens condensation of 2-phenylpropionaldehyde (45.2 g) and 40% aqueous formaldehyde (105 g) in the presence of anhydrous potassium carbonate (33.7 g), ethanol (100 mL), and water (30 mL). The reactants were refluxed for 5 h, after which most of the volatile material was removed on a rotary evaporator and the residues were dissolved in dichloromethane.

The insoluble materials were removed by filtration and washed with dichloromethane, after which the organic solutions were combined and the solvent was removed to give a heavy viscous oil (21 g) which solidified on standing to give a white solid.

Some of this diol (18.5 g) was dissolved in dry pyridine (110 mL) and stirred at 0 °C. To this was added dropwise 2.2 equiv of benzenesulfonyl chloride while the temperature was kept below 12 °C with an ice bath. When the addition was complete, the mixture was allowed to warm to room temperature and stirred overnight. The product was isolated by pouring the resultant mixture into water (370 mL) while stirring vigorously. Filtration of the resultant precipitate yielded the crude dibenzenesulfonate ester as a pink solid, which was washed with water, 2 M hydrochloric acid, and water and air dried to give the ester, which was considered pure enough for direct use.

Toluene (100 mL) was added to the mixture of crushed sodium sulfide nonahydrate (24.5 g) and dimethyl sulfoxide (200 mL), and the mixture was heated under reflux with a Dean–Stark apparatus collecting the water which began to appear at 120 °C. When about 15 mL of water had been azeotroped from the system, the excess toluene was removed under slight vacuum. The resultant Me_2SO solution was slightly green with small gummy residues. The solution was cooled to 90 °C, and some of the previously prepared dibenzenesulfonate ester (30.4 g) was added to the stirred solution over 1 h. The mixture was stirred at 90 °C for 1.5 h more, after which it was cooled and poured into water (1 L). The aqueous solution was extracted with petroleum ether (5 × 100 mL), and the combined petroleum ether extracts were washed with water (2 × 100 mL). Drying and removal of the solvent gave a yellow oil (15 g), which on distillation afforded 3-phenyl-3-methylthietane (12 g) as a yellow oil: bp 140–160 °C (15 mm); NMR δ 6.82–7.48 (5 H, m), 3.79 (2 H, d, J = 9 Hz), 2.99 (2 H, d, J = 9 Hz), 1.78 (3 H, s).

Some of this material (2 g) was oxidized with peracetic acid (10 mL) to give 3-phenyl-3-methylthietane 1,1-dioxide as a white crystalline solid (2.1 g, 84%): mp 48–49 °C (chloroform–petroleum ether); NMR δ 7.12–7.71 (5 H, m), 4.39 (4 H, A'B' quartet), 1.82 (3 H, s); IR ν_{max} (dichloromethane) 1409, 1330, 1226, 1142, 1089 cm^{-1}; *m/e* 196, 132, 118, 117, 103, 91, 78, 77. Anal. Calcd for $C_{10}H_{12}SO_2$: C, 61.20; H, 6.16; S, 16.34. Found: C, 61.32; H, 6.36; S, 16.30.

***cis*- and *trans*-3-Phenyl-3-methylthietane 1-Oxide (10 and 11).** 3-Phenyl-3-methylthietane (1 g) was oxidized to the isomeric sulfoxide using *m*-chloroperoxybenzoic acid as described for the previous examples. Careful chromatography of this mixture on silica (50 g) using ether as the eluent gave the cis isomer as a clear oil (632 mg) followed by the trans isomer as a white crystalline solid (300 mg).

Preparation of *exo*-8-Thiatetracyclo[2.2.1.1.0]octane 8-Oxide[10] (13). The addition product of sulfur dichloride and norbornadiene (20 g) was treated with hot aqueous sodium carbonate. The reaction was worked up after 30 min; there was no change. Treatment for 3 h, however, gave a small amount of the desired sulfoxide after workup (1.93 g, 13.4%): mp 72–78 °C [lit.[10] 76–77 °C]; NMR δ 4.31–4.55 (1 H, br m), 3.23–3.44 (2 H, m), 1.98–2.22 (1 H, m), 2.53–2.90 (4 H, m); IR ν_{max} (dichloromethane) 3050, 2939, 2862, 1125, 1049 cm^{-1}; MS *m/e* 140, 123, 91; ^{13}C NMR (ppm downfield of Me_4Si) 9.82, 21.18, 34.09, 45.13, 64.36.

Preparation of *endo*-8-Thiatetracyclo[2.2.1.1.0]octane 8-Oxide (12). Some of the previously prepared exo sulfoxide (1.2 g) was suspended–dissolved in dry ether (50 mL) with stirring at 0 °C. Lithium aluminum hydride (0.2 g) was slowly added to this mixture over 10 min with rapid stirring. The reaction was allowed to warm to room temperature and stirred for 4 h. Usual workup gave a bad-smelling colorless oil. The NMR spectrum still showed some traces of the starting material but there were other resonances at δ 3.53–3.72 (m), 2.89–3.08 (m), and 2.15–2.49 which could be reasonably assigned to the sulfide. TLC on silica eluting with ether showed two spots, one of them coincident with the starting material, R_f 0.052, and the other one R_f 0.84. This material was stirred in excess aqueous sodium metaperiodate (3 g unsaturated) for 2 days at room temperature, after which extraction with dichloromethane and normal workup gave a white solid (1.0 g). The NMR spectrum showed none of the exo sulfoxide. TLC (silica) eluting with ether showed two spots, R_f 0.032 and 0.26. Careful chromatography of some of this material (0.75 g) on silica (80 g) eluting with pure ether increasing to 2% methanol in ether gave two compounds as white crystalline solids. The first compound to be eluted (R_f 0.26) was 8-thiatetracyclo-[2.2.1.1.0]octane 8,8-dioxide (350 mg): mp 135 °C dec (lit.[10] 130 °C dec); NMR δ 3.90–4.10 (2 H, m), 2.70–2.95 (1 H, br m), 2.10–2.37 (1 H, m), 1.87–2.10 and 1.66–1.85 (4 H, m); IR ν_{max} (dichloromethane) 3060, 2950, 2815, 1300, 1175, 1097; MS *m/e* (no molecular ion) 92, 91, 65, 65; ^{13}C NMR (ppm) 13.23, 21.34, 31.17, 34.90, 76.78. The second compound, R_f 0.032 (101 mg), gave the following data: mp 113–115 °C; NMR δ 3.49–3.79 (2 H, m); IR ν_{max} (dichloromethane) 3051, 2942, 2875, 1138, 1080 cm^{-1}; *m/e* 140, 123, 91; ^{13}C NMR (ppm) 21.02, 27.35, 32.55, 36.36, 68.01. Anal. Calcd for C_7H_8OS: C, 59.99; H, 5.75; S, 22.84. Found: C, 60.06; H, 5.76; S, 22.54.

The remainder of the crude oxidation mixture (250 mg) was dissolved in peracetic acid (4 mL) and stirred for 4 days. Workup gave a white solid (200 mg) with the same NMR spectrum as that of the known sulfone.[10]

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Registry No. 1, 27832-55-9; 2, 25145-03-3; 3, 25145-02-2; 4, 25902-69-6; 5, 25902-66-3; 6, 26091-84-9; 7, 25902-67-4; 8, 55779-41-4; 9, 55779-40-3; 10, 66809-92-5; 11, 66810-23-9; 3-methylthiete 1,1-dioxide, 71887-62-2; 3-*tert*-butylthiete 1,1-dioxide, 25903-16-6; 3-phenylthiete 1,1-dioxide, 25903-17-7; 3-(*p*-bromophenyl)thiete 1,1-

dioxide, 71887-63-3; 3,3-dimethylthietane 1,1-dioxide, 27832-56-0; 3-methylthietane 1,1-dioxide, 25903-07-5; 3-*tert*-butylthietane 1,1-dioxide, 25903-05-3; 3-phenylthietane 1,1-dioxide, 25636-64-0; 3-(*p*-bromophenyl)thietane 1,1-dioxide, 71887-64-4; 3-methyl-3-phenylthietane 1,1-dioxide, 66809-99-2; 3,3-dimethylthietane, 13188-85-7; 3-methylthietane, 22438-40-0; 3-*tert*-butylthietane, 25903-02-0; 3-phenylthietane, 25636-63-9; 3-(*p*-bromophenyl)thietane, 55779-42-5; 3-methyl-3-phenylthietane, 66810-25-1; *p*-bromoacetophenone, 99-90-1; morpholine, 110-91-8; *p*-bromo-α-morpholinostyrene, 55779-43-6; 2-methyl-2-phenylpropane-1,3-diol, 24765-53-5; 2-phenylpropionaldehyde, 93-53-8; 2-methyl-2-phenylpropane-1,3-diol dibenzenesulfonate ester, 66810-41-1; norbornadiene, 121-46-0; 8-thiatetracyclo[2.2.1.1.0]octane 8,8-dioxide, 22061-75-2; **12**, 71927-86-1; **13**, 22061-74-1.

Correlation of Structure and Transannular Interactions in a Series of Cage Compounds

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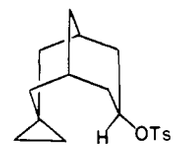
A series of cage systems with general structure **7** were synthesized. By variation of bridge C, the distance between functional groups A and B could be changed systematically and the chemical consequences of these changes investigated. Thus, Diels–Alder reactions between benzoquinone and cyclic dienes ranging from cyclobutadiene to cycloheptadiene, and including cyclooctatetraene, yielded endo dienes which were subsequently converted to cage structures photochemically. This transformation results in compounds **8**, **10**, **15**, **16**, and **17** with two transannular carbonyl groups positioned at varying distances. Under ketalization conditions some of these compounds—the ones with larger bridges C which brought the keto groups closer together—gave cyclized products rather than simple ketals. In the other cases, monoketals formed which were reduced to endo alcohols and studied further. Molecular mechanics calculations on hydrocarbon models for these systems provided a more quantitative basis for interpretation of the experimental results. The distance between A and B in **7** varied with the size of bridge C. The calculated energies of simulated ring-closure reactions (**40** → **39** and **41** → **39**) became more favorable as the number of atoms in bridge C was increased. These results parallel the experimental trends.

Rigid cage molecules are valuable substrates for the study of organic chemical transformations.[2] Compounds of this type have marked advantages over conformationally mobile molecules. Reaction centers in rigid molecules are fixed with respect to the remainder of the molecular skeleton; hence, perturbations due to conformational changes are effectively diminished or removed. This greatly simplifies the understanding of many chemical transformations and permits analysis of structure–reactivity relationships.

Not only mechanistic studies but also organic synthesis has taken advantage of the potential interaction between two reactive centers in conformationally restricted molecules. Polycyclic compounds of great rigidity and often of high symmetry, the so-called cage molecules, can result from transannular ring closure. For example, adamantanes and closely related compounds have been prepared from semirigid precursors. Thus, acetolysis of the spirocyclic tosylate **1** gives the homoadamantyl acetate **2**,[3] and 7-methylenebicyclo[3.3.1]nonan-3-one **3** provides the noradamantane **4** by reductive cyclization.[4] Transannular cyclizations of compounds such as **5** to produce the bridged structure **6**[5] are germane to the present work.

We wished to study the variations of chemical interactions in a series of closely related rigid molecules in which the transannular distance between functional groups could be altered systematically. The generalized pentacyclic system **7** fulfills these requirements. Compounds of this kind are readily available by sequences of Diels–Alder reactions and photochemical ring closures. The bridge C (in structure **7**) can be modified in order to alter the transannular relationship of functional groups A and B. Possibilities for such modifications and their consequences have been recognized previously.[6] Empirical force field



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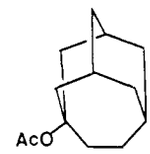

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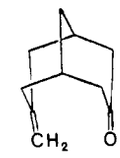

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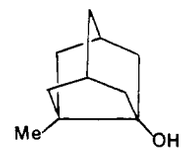

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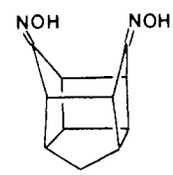

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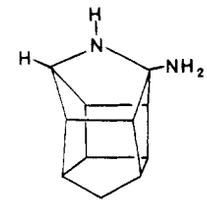

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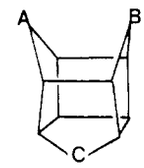

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