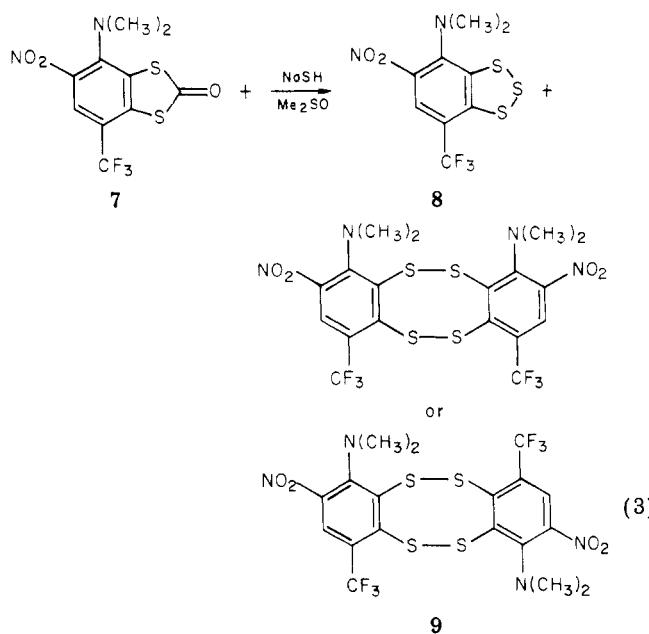


constitutes further evidence that dibenzotetrathiocins are intermediates in the formation of benzotrichioles **3a**, **3c**, and **3d**. The stereochemistry of **6** remains to be established.

Although the presence of a nitro group in the starting material appears to be a requirement for the 1,3-benzodithiol-2-one  $\rightarrow$  benzotrichiole conversion, the presence of other, even electron-donating, substituents results in the formation of the corresponding benzotrichiole. For example, **7**<sup>2</sup> was converted to benzotrichiole **8** (45%) and dibenzotetrathiocin **9** (13%) (eq 3).



The series of conversions described represent useful synthetic routes to the benzotrichiole and dibenzotetrathiocin ring systems. The isolation of benzotrichioles **3a**, **3c**, **3d**, and **8**, in particular, represents the first unequivocal synthesis of this ring system. The only other report known to us is that of Fehér and co-workers who obtained 5,6-dimethylbenzotrichiole from the reaction of dimercapto-*o*-xylene with sulfur dichloride.<sup>7</sup> The product isolated was reported to be impure and unstable and the structure of the product was deduced from its mass spectrum. Fields has reported the synthesis of a number of benzotrichioles by the reaction of halobenzenes with sulfur and sulfuric acid, based on mass spectra of product mixtures; pure compounds were not isolated.<sup>8</sup> The synthesis of the related 5-methylbenzotrichiole oxide from the reaction of 4-methyl-*o*-phenylenedithiole with thionyl chloride has

been described by Steinle and Schmidt.<sup>9</sup>

The synthesis and reactions of other benzotrichioles as well as the mechanism of these reactions are currently being investigated.

**4-Nitro-6-(trifluoromethyl)benzotrichiole (3a).** To a stirred and tap-water cooled solution of 28.1 g (0.1 mol) of 4-nitro-6-(trifluoromethyl)-1,3-benzodithiol-2-one (**2a**)<sup>12</sup> in Me<sub>2</sub>SO (200 mL) under nitrogen was added 44.5 g (0.5 mol) of NaSH as a powder. After the dark red mixture was allowed to stir (12 h) it was poured into water (600 mL) and acidified with 1 N HCl (hood, H<sub>2</sub>S evolution). The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3  $\times$  100 mL) and the organic extract washed with water (3  $\times$  500 mL) and dried (Na<sub>2</sub>SO<sub>4</sub>). The solvent was distilled to dryness in vacuo and the red crystalline residue was triturated with ethanol and suction filtered to yield 23 g (80.7%) of **3a**, mp 107–109 °C. Recrystallization of crude **3a** from ethanol gave analytically pure material as a brick red solid: mp 110–111 °C; NMR (CDCl<sub>3</sub>)  $\delta$  8.43 (m, 1 H), 8.03 (m, 1 H); mass spectrum, *m/e* 285. Anal. Calcd for C<sub>7</sub>H<sub>2</sub>F<sub>3</sub>NO<sub>2</sub>S<sub>3</sub>: C, 29.47; H, 0.70; N, 4.91; S, 33.68. Found: C, 29.40; H, 0.75; N, 4.72; S, 33.76.

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**Registry No.** **1a**, 59983-45-8; **1b**, 68151-94-0; **1c**, 68151-95-1; **1d**, 68200-48-6; **2a**, 62558-16-1; **2b**, 62558-22-9; **2c**, 63417-83-4; **2d**, 62558-20-7; **3a**, 70001-71-7; **3c**, 70001-71-7; **3d**, 70001-75-1; **4a**, 75083-33-9; **5**, 75101-74-5; **6**, 75101-70-1; **7**, 62558-23-0; **8**, 70001-74-0; **9**, 75083-34-0.

(9) K. Steinle and M. Schmidt, *Z. Naturforsch., B*, **28**, 686 (1973). See also L. Field and W. B. Lacefield, *J. Org. Chem.*, **31**, 3555 (1966).

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### Carbon-13 and Oxygen-17 Nuclear Magnetic Resonance Studies of Organosulfur Compounds: The Four-Membered-Ring Sulfone Effect

**Summary:** As revealed by carbon-13 and oxygen-17 NMR spectroscopy, thietane 1,1-dioxides and related four-membered-ring sulfonyl compounds show unusual  $\alpha$ -carbon and sulfonyl oxygen deshielding and  $\beta$ -carbon shielding when compared to other thiacycloalkane 1,1-dioxides and acyclic counterparts.

**Sir:** We report that 1,1-dioxides of thietanes, 1,2-dithietanes, and 1,3-dithietanes and a sulfoximide derived from a thietane display carbon-13 chemical shifts which are notably at variance with the bulk of the published chemical shift data on other organosulfur compounds and that this NMR effect is apparently uniquely associated with sulfur-containing four-membered rings. We also report the first oxygen-17 chemical shift data for sulfoxides (other than dimethyl sulfoxide)<sup>1</sup> and sulfones, note that the oxygen-17 shifts for a homologous series of thiacycloalkane 1-oxides and 1,1-dioxides also exhibit an anomaly for the four-membered rings, and point out that discrete oxy-

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Table I.  $^{13}\text{C}$  and  $^{17}\text{O}$  NMR Data (in ppm) for Thiacycloalkanes and Their S-Oxides in  $\text{CDCl}_3$  or Acetone<sup>a</sup>

	1	2	3	4	5	6	7
$^{13}\text{C}$ ( $\alpha$ , $\text{SO}_2$ )	81.6	65.6 <sup>d</sup>	51.1 <sup>b,f</sup>	52.6 <sup>c</sup>	55.6	53.6	52.8
$^{13}\text{C}$ ( $\alpha$ , $\text{SO}$ )	33.8	52.7	54.3 <sup>b</sup>	49.0 <sup>c</sup>	52.1	50.3	
$^{13}\text{C}$ ( $\alpha$ , S)	18.1	26.1	31.7 <sup>b</sup>	29.1 <sup>c</sup>	33.9	32.7	32.3
$^{13}\text{C}$ ( $\beta$ , $\text{SO}_2$ )		5.8 <sup>e</sup>	22.7 <sup>b,g</sup>	25.1 <sup>c</sup>	21.3		
$^{13}\text{C}$ ( $\beta$ , $\text{SO}$ )		10.4	25.4 <sup>b</sup>	19.3 <sup>c</sup>	19.1		
$^{13}\text{C}$ ( $\beta$ , S)		28.0	31.2 <sup>b</sup>	27.9 <sup>c</sup>	31.7		
$^{17}\text{O}$ ( $\text{SO}_2$ )	111 (111)	182 (182) <sup>h</sup>	165 (164) <sup>i</sup>	142 (149)	150 (154)	134 (137)	
$^{17}\text{O}$ ( $\text{SO}$ )	-71 (70)	61 (68)	15 (12)	-3 (-2)	11		

<sup>a</sup> Shifts in acetone are given in parentheses.  $^{17}\text{O}$  shifts are reported in parts per million downfield from natural-abundance  $^{17}\text{O}$  in  $\text{H}_2\text{O}$  ( $\pm 1$  ppm; in capillary tube) and were determined on a JEOL FX-90Q or FX-100 spectrometer. <sup>b</sup> Reference 6b.

<sup>c</sup> Reference 4b. <sup>d</sup> In  $\text{D}_2\text{O}$  68.3 ppm, in the solid state (magic angle spinning) 68.5 ppm. <sup>e</sup> In  $\text{D}_2\text{O}$  8.6 ppm, in the solid state ca. 8 to 9 ppm. <sup>f</sup> In  $\text{D}_2\text{O}$  54.0 ppm. <sup>g</sup> In  $\text{D}_2\text{O}$  25.3 ppm. <sup>h</sup> In  $\text{D}_2\text{O}$  176 ppm. <sup>i</sup> In  $\text{D}_2\text{O}$  172 ppm.

gen-17 resonances may be observed for nonequivalent sulfone oxygens.

Carbon-13 NMR spectroscopy has recently found wide application in organosulfur chemistry.<sup>2-7</sup> Several trends have emerged in the extensive chemical shift data that have thus far been collected for organosulfur compounds: (1) oxidation of a sulfide to a sulfone results in a 20–25-ppm  $\alpha$ -carbon downfield shift and a somewhat smaller (e.g., 4–9 ppm) upfield  $\beta$ -carbon shift;<sup>2,4,5</sup> (2) surprisingly there is very little difference in the  $\alpha$ -carbon shifts of sulfoxides and sulfones (on occasion the latter may even appear slightly upfield of the former) despite the difference in inductive effects of these groups<sup>2,6,7</sup> and the difference

generally seen in proton chemical shifts of related sulfones and sulfones (see below).

While a wide range of five- and six-membered-ring sulfur compounds have been examined by carbon-13 NMR, there is limited information available on cyclic sulfur compounds of other ring sizes.<sup>2,6,7</sup> Table I presents comparative NMR data on three- to eleven-membered-ring thiacycloalkanes and their 1-oxides and 1,1-dioxides.<sup>8</sup> Of greatest interest are the unusual 40-ppm  $\alpha$ -carbon downfield shift observed on oxidation of thietane (**2a**) to thietane 1,1-dioxide (**2c**), the 13-ppm difference in the  $\alpha$ -carbon shift of thietane 1-oxide (**2b**) and **2c**, and the 22-ppm  $\beta$ -shielding experienced by **2c** in comparison with **2a**. The unusual carbon-13 chemical shift effects for **2c** seem to be mirrored by somewhat smaller effects in the proton chemical shifts.<sup>9</sup> The remaining carbon-13 chemical shift data in Table I are unremarkable, generally following the trends noted above in points 1 and 2. The order of  $\alpha$ -proton shifts for a particular ring size is sulfenyl < sulfinyl (average) < sulfonyl, in accord with the inductive effects for these groups.<sup>11</sup> Shielding in the three-membered series (thiiranes, **1**) is probably dominated by bond and group anisotropies that distinguish it from the other ring sizes. Consequently, the thiirane resonances are more highly shielded than those of the larger rings. The three-membered sulfoxide and sulfone nonetheless have similar resonance positions. Thus the anomalous relative frequency of the sulfone is found only in the four-membered ring.

We have also determined the oxygen-17 chemical shifts for the series of cyclic sulfoxides and sulfones in Table I and find a dramatic variation in these shifts with ring size. The four-membered-ring sulfone again is considerably deshielded with respect to the five-, six-, and three-mem-

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(4) (a) J. R. Wiseman, H. O. Krabbenhoft, and B. R. Anderson, *J. Org. Chem.*, **41**, 1518 (1976); (b) J. B. Lambert, D. A. Netzel, H. Sun, and K. K. Lilianstrom, *J. Am. Chem. Soc.*, **98**, 3778 (1976).

(5) This applies only to  $\text{sp}^3$ -hybridized carbon atoms; there are occasional exceptions in complex systems [e.g., see C. R. Harrison and P. Hodge, *J. Chem. Soc., Perkin Trans. 1*, 1722 (1976)].

(6) (a) G. W. Buchanan, C. Reyes-Zamora, and D. E. Clarke, *Can. J. Chem.*, **52**, 3895 (1974); (b) G. Barbarella, P. Dembech, A. Garbesi, and A. Fava, *Org. Magn. Reson.*, **8**, 108 (1976).

(7) (a) G. C. Levy and D. C. Dittmer, *Org. Magn. Reson.*, **4**, 107 (1972); (b) E. Jongejan, T. S. V. Buys, H. Steinberg, and T. J. de Boer, *Recl. Trav. Chim. Pays-Bas*, **97**, 214 (1978); (c) J. Jokisaari, J. Juonanoja, and A.-M. Hakkinen, *Z. Naturforsch. A*, **33A**, 7 (1978); (d) D. C. Dittmer in "New Trends in Heterocyclic Chemistry", R. B. Mitra, N. R. Agyavgar, V. N. Gogte, R. M. Acheson, and N. Cromwell, Eds., Elsevier, New York, 1979.

(8) (a) Synthesis of thiacycloalkanes: L. Mandolini and T. Vontor, *Synth. Commun.*, **9**, 857 (1979). (b) At  $-93^\circ\text{C}$ , thiane 1-oxide (**4**,  $n = 1$ ) shows two sets of carbon-13 signals corresponding to the conformers with an axial oxygen ( $\text{C}_\alpha$ , 45.1 ppm;  $\text{C}_\beta$ , 15.5 ppm) and an equatorial oxygen ( $\text{C}_\alpha$ , 52.1 ppm;  $\text{C}_\beta$ , 23.3 ppm).<sup>4b</sup> The temperature dependence of the oxygen-17 spectra of **4** ( $n = 1$ ) and the other conformationally mobile sulfoxides is currently under investigation and will be reported separately.

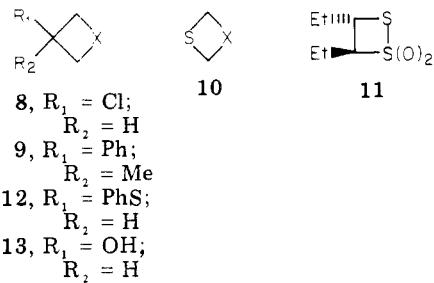
(9) (a) The  $\alpha$  protons of **2a** and **2c** appear at  $\delta$  3.21 and 4.09, respectively, while the  $\beta$  protons appear at  $\delta$  2.94 and 2.14, respectively;<sup>10</sup> in thioline (**3**,  $n = 0$ ) and thiolane 1,1-dioxide (**3**,  $n = 2$ ) the  $\alpha$  protons appear at  $\delta$  2.82 and 3.01, respectively, while the  $\beta$ -protons appear at  $\delta$  1.93 and 2.21, respectively.

(10) C. Cistaro, G. Fronza, R. Mondelli, S. Bradamante, and G. A. Pagani, *J. Magn. Reson.*, **15**, 257 (1974).

(11) W. O. Siegel and C. R. Johnson, *Tetrahedron*, **27**, 341 (1971).

bered rings. For oxygen-17 shifts, the sulfoxides also follow this trend; the oxygen-17 shift of thirane *S*-oxide (-71 ppm) is the most highly shielded oxygen thus far reported.<sup>1</sup> It should be noted that carbon-13 shifts in cycloalkanes,<sup>12</sup> phosphacycloalkanes,<sup>13</sup> and in this work thiacycloalkanes and nitrogen-15 shifts in azacycloalkanes<sup>14</sup> do not show an anomaly at the four-membered ring (the shifts move up-field monotonically as the ring size decreases) while small downfield carbon-13 shifts are observed for the  $\alpha$ -carbons of oxetane and cyclobutanone as compared to those of homologues of other ring sizes.<sup>15,16</sup>

We have examined a variety of other sulfur-containing four-membered rings including a thietane sulfoximide and several dithietanes and find that the effect seen with **2c** appears to be general for a sulfonyl or sulfoximido group in a saturated four-membered ring. Thus for **8** the  $\alpha$ -carbon-13 shifts (in parts per million) are 38.9 ( $X = S$ ), 63.3 ( $X = SO$ , *cis*), 60.4 ( $X = SO$ , *trans*), and 75.4 ( $X = SO_2$ ), for **9**<sup>17a</sup> are 38.2 ( $X = S$ ), 63.2 ( $X = SO$  *cis* to Ph), 62.9 ( $X = SO$  *trans* to Ph), 75.6 ( $X = SO_2$ ), 61.8 ( $X = SNTs$  *cis* to Ph), and 75.6 ( $X = S(O)NTs$ , *NTs cis* to Ph), for **10**<sup>17b</sup> are 18.6 ( $X = S$ ), 53.1 ( $X = SO$ ), and 68.4 ( $X = SO_2$ ), and for **11**<sup>17c</sup> are 39.2 ( $\alpha$ -sulfenyl C) and 97.9 ( $\alpha$ -sulfonyl C). We have determined the carbon-13 shift of **2c** in the solid state and in aqueous solution and find little change (see Table I, footnote *d*). We find that decreasing the C-S-C angle in thiolane 1,1-dioxides does *not* bring about an effect similar to that seen with **2c** (e.g., the bridgehead carbon in 7-thiabicyclo[2.2.1]heptane 7,7-dioxide,<sup>18a</sup> which should have a C-S-C angle very similar to that in **2c**,<sup>18b,c</sup> appears at 51.3 ppm compared to a shift of 53.2 ppm for 9-thiabicyclo[3.3.1]nonane 9,9-dioxide<sup>4a</sup>).



For **11** the oxygen-17 chemical shifts are 210 and 243 ppm (in chloroform), for **12** ( $X = SO_2$ ), 182 and 198 ppm

(in acetone), and for **13** ( $X = SO_2$ ; sulfone oxygens), 184 and 187 ppm (in acetone). These results demonstrate that discrete oxygen-17 chemical shifts may be observed for nonequivalent sulfone oxygens, at least in four-membered rings, and that substantial remote substituent effects on these shifts are possible. We have obtained oxygen-17 chemical shift data for a limited number of sulfones of other types and find that substituent effects are generally, but not always, smaller than those seen on varying the ring size and that the influence of solvent and concentration is generally minor.<sup>19</sup> Thus the oxygen-17 chemical shifts in parts per million downfield from  $H_2^{17}O$  in chloroform (or acetone) appear for dimethyl sulfone at  $\delta$  163 (165), for bis(chloromethyl)sulfone at 150, for di-*n*-butyl sulfone at 145 (145), for diphenyl sulfone at 139 (137), for 1,3-dithiane 1,1-dioxide at 143 (143), and for 3,3-dimethylthietane 1,1-dioxide at 181 (180). Neat dimethyl sulfoxide appears at  $\delta$  20.

What is the physical basis for the unusual NMR effects seen in thietane 1,1-dioxide (**2c**) and related systems? The strong electric field at carbon 3 in **2c** ( $\beta$  shielding) and also in **2b** may possibly be associated with particularly effective multiple-pathway  $\gamma$ -effects by the sulfone (and sulfoxide) oxygens, although the conformation of the  $C_\beta C_\alpha SO$  group is far from being antiperiplanar.<sup>2e,20,21</sup> The cause of the unusual  $\alpha$ -deshielding seen in four-membered-ring sulfonyl and sulfoximido derivatives would not seem to be directly related to the  $\beta$ -shielding effect since thietane 1-oxides (such as **2b**) show pronounced  $\beta$  shielding yet show "normal"  $\alpha$ -carbon shifts. The  $\alpha$ -deshielding effect does not seem to be directly attributable to interactions involving the  $\alpha$ -hydrogens, since replacing these hydrogens with methyl groups does not eliminate the effect (the quaternary carbons of 2,2,4,4-tetramethylthietane and 2,2,4,4-tetramethylthietane 1,1-dioxide appear at  $\delta_C$  37.1 and 75.46, respectively). It would appear that the factor(s) responsible for the negation or even reversal of the "expected" sulfinyl and sulfonyl inductive effects on  $\alpha$ -carbon shifts in the majority of organosulfur compounds studied is apparently cancelled out in the case of four-membered-ring sulfonyl compounds, perhaps by unusual nonbonded interactions. In conclusion we suggest that a solution to the riddle of the "four-membered-ring sulfone effect" may provide valuable insight into the mechanism of carbon-13 shielding.

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(14) G. C. Levy and R. L. Lichter, "Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy", Wiley, New York, 1979.

(15) It is recognized that, except in the case of the phosphacycloalkane 1-oxides,<sup>18</sup> heteroatoms are present in these series of compounds only as *ring members* rather than also as *ring substituents* as in the case of thiacycloalkane 1-oxides and 1,1-dioxides.

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(19) Note, however, the sizeable solvent effect of water (Table I, footnotes *h* and *i*).

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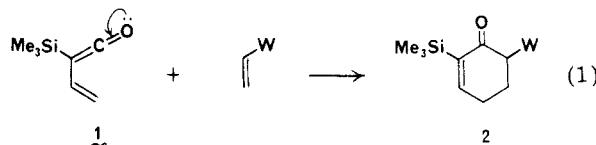
### (Trimethylsilyl)vinylketene: A Stable Vinylketene and Reactive Enophile in [4 + 2] Cycloadditions

**Summary:** (Trimethylsilyl)vinylketene has been prepared by dehydrohalogenation of (*Z*)-2-(trimethylsilyl)-2-butenyl chloride and shown to be a relatively stable compound which participates in Diels–Alder reactions as a reactive diene.

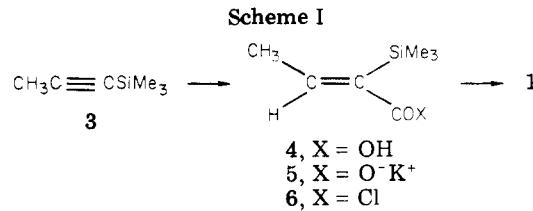
**Sir:** The recent extension of the Diels–Alder reaction to include highly functionalized dienes has greatly expanded the utility of this important synthetic method.<sup>1</sup> An objective of continuing interest in this area has been the development of vinylketene equivalents capable of participating as diene components in Diels–Alder reactions.<sup>2</sup> The tendency of vinylketenes to form only [2 + 2] cyclo-

adducts with olefins<sup>3</sup> and the intrinsic instability of these substances<sup>4</sup> precludes their direct use as [4 + 2] enophiles. The availability of a generally effective synthon of this type would greatly facilitate the synthesis of cyclohexenone derivatives and phenolic compounds and could provide a new approach to the synthesis of anthracyclinone antitumor agents.

In this communication we describe a particularly simple enophilic vinylketene equivalent, (trimethylsilyl)vinylketene (1).<sup>5</sup> Our investigation of this compound was founded on the hypothesis that it would be a *relatively stable substance, inert to [2 + 2] cycloadditions*,<sup>6</sup> and *would participate in Diels–Alder reactions as a reactive diene*. It was further anticipated that the directing effect of the carbonyl group would dominate in controlling the regiochemical course of cycloadditions involving this diene (eq 1, where W is an electron-withdrawing group).<sup>7</sup>



(Trimethylsilyl)vinylketene (1) was conveniently prepared as outlined in Scheme I. Treatment of 1-(trimethylsilyl)propane (3)<sup>8</sup> with 1.1 equiv of diisobutylaluminum hydride (25 °C, 21 h) and 1.1 equiv of methylolithium (0 °C, 0.5 h) in ether–hexane,<sup>9</sup> followed by reaction of the resulting vinyl alanate with anhydrous



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