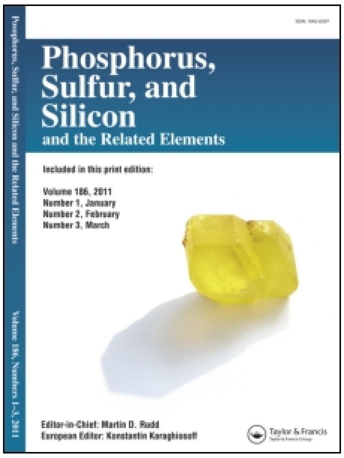

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REGIOSELECTIVITY OF METALATION OF 1,3-DITHIOLANES AND 1,3-DITHIOLANE 1-OXIDES

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REGIOSELECTIVITY OF METALATION OF 1,3-DITHIOLANES AND 1,3-DITHIOLANE 1-OXIDES

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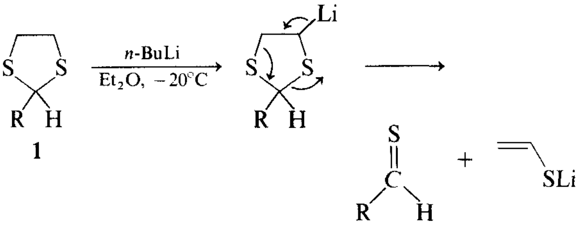
Deprotonation of 1,3-dithiolane 1-oxide (3) and trans-2-phenyl-1,3-dithiolane 1-oxide (5) leads to cleavage of the derived anions. Cleavage reactions do not occur with *trans*-hexahydro-1,3-benzodithiole (7), its 1-oxide, or its 1,1-dioxide all of which can be metalated and alkylated quantitatively at C-2. The preparation and reactions of the sulfoxides derived from 7 are not highly stereoselective.

INTRODUCTION

Anion reactions of 2-substituted-1,3-dithiolanes are sensitive to the nature of their substituents. Cleavage, through the intermediacy of the *4-lithio* derivative as depicted in Eq. 1, appears to be the dominant reaction which occurs on metalation of 2-alkyl-1,3-dithiolanes (**1**).[1,2] 2-Aryl-1,3-dithiolanes (**2**) are metalated at C-2, but these anions fragment also (Eq. 2).[3,4] When C-2 bears an efficient carbanion-stabilizing substituent as in 2-carboethoxy-1,3-dithiolane (**1**, R = CO_2Et), metalation at C-2 occurs readily to give an enolate which can be alkylated in a variety of synthetically useful operations.[5]



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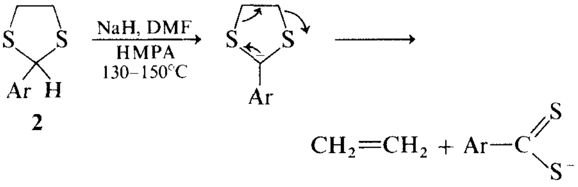

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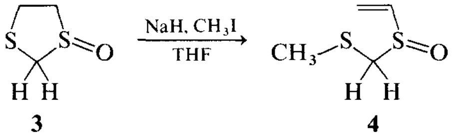
We have investigated the metalation of 1,3-dithiolanes in which regioselective proton abstraction at C-2 might be encouraged by the presence of appropriate substitution elsewhere in the molecule, thereby making C-2 available as a site for elaboration by reaction with alkylating agents.

RESULTS AND DISCUSSION

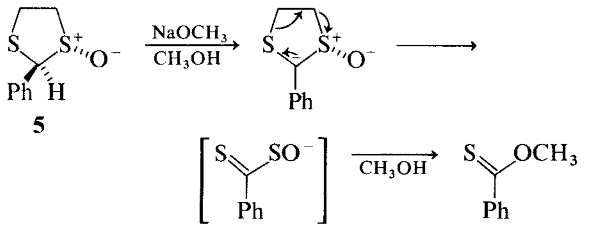
Our initial approach was to examine 1,3-dithiolane 1-oxide (**3**)[6] in order to determine if oxidation at sulfur affected either the regioselectivity of deprotonation or the stability of the resulting carbanion toward fragmentation.

Efforts to aklylate **3** at C-2 under a variety of conditions were unsuccessful. Complex mixtures were obtained on attempted metalation with either lithium diisopropylamide or *n*-butyllithium followed by treatment with methyl iodide. Reaction of **3** with sodium hydride and methyl iodide in tetrahydrofuran at room temperature cleanly afforded a single product identified as vinyl methylthiomethyl sulfoxide (**4**) in 96% yield. Thus, metalation of **3** leads to a cleavage reaction which is closely related to that of **1** in that it involves a β-elimination across C-4, C-5 as a critical feature.[7]



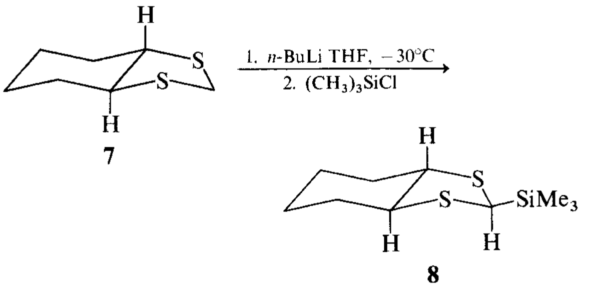
3 **4**

Similarly, aryl substitution at C-2 of the 1,3-dithiolane 1-oxide system led to anionic reactivity related to that expressed earlier for **2**. When *trans*-2-phenyl-1,3-dithiolane 1-oxide (**5**)[8] was refluxed with 0.1 M sodium methoxide in methanol for four hours, methyl thionbenzoate (**6**) was isolated as the only identifiable product in 35% yield. Its formation is suggested to occur by the process described in Eq. 3 and involves fragmentation of the anion at C-2.

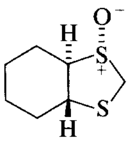


No alkylation of **5** could be effected on treatment with sodium hydride and methyl iodide in tetrahydrofuran. Apparently the anion at C-2 was generated under these conditions, however, since recovered starting material provided to be a 1 : 1 mixture of **5** and its C-2 epimer *cis*-2-phenyl-1,3-dithiolane 1-oxide.

Given the propensity of anions derived from 1,3-dithiolanes to undergo cleavage reactions, we next directed our attention to *trans*-hexahydro-1,3-benzodithiole (**7**)[9] in the expectation that the elimination pathways observed earlier would be suppressed in this compound. The gauche relationship in the H-C_4-C_5-S unit should lead to a slower rate of β-elimination across C_4-C_5 in **7** than in **1** and **3**. Concerted cycloelimination of dithioformate from the anion at C-2 would lead to *trans*-cyclohexene and should not take place. Indeed, it was found that metalation of **7** at C-2 occurred smoothly and that the resulting lithio derivative produced 2-trimethylsilyl-*trans*-hexahydro-1,3-benzodithiole **8** in 93% yield on reaction with chlorotrimethylsilane. In the same fashion, metalation of the trimethylsilyl derivative **8** followed by addition of methyl iodide gave 2-methyl-2-trimethylsilyl-*trans*-hexahydro-1,3-benzodithiole (**9**) in 95% yield. These results clearly demonstrate that metalation and alkylation at C-2 of 1,3-dithiolanes is not only feasible but can be highly efficient if the competing fragmentation reactions of the anion are suppressed.



In order to examine the metalation and alkylation of a 1,3-dithiolane 1-oxide not susceptible to cleavage, **7** was oxidized with *m*-chloroperoxybenzoic acid in dichloromethane. After chromatography a 68% yield of a mixture containing comparable amounts of both 1-oxides **10** and **11** was obtained, along with a small amount (6%) of a *trans*-1,3-dioxide (**12** or **13**) (see Experimental Section). One of the monosulfoxides **10** or **11** (mp 67–68°C) was obtained readily on recyrstallization from ether but it was not possible to deduce its stereochemistry on the basis of the available information. Lithiation of this diastereomer and reaction with methyl iodide gave a mixture of diastereomeric 2-methyl-*trans*-hexahydro-1,3-benzodithiole 1-oxides (**14** and **15**) in quantitative yield. The two products **14** and **15** were determined to be present in approximately equal amounts by NMR analysis of the crude reaction mixture. This experiment demonstrates that metalation of a 1,3-dithiolane 1-oxide and alkylation of the resulting anion are highly efficient, albeit non-stereoselective, processes when cleavage reactions are suppressed.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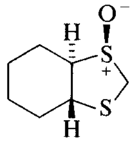
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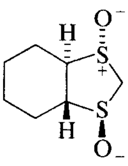
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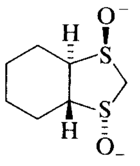
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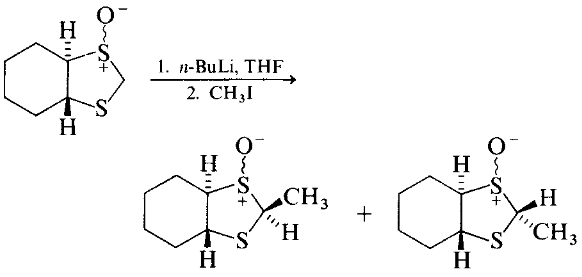
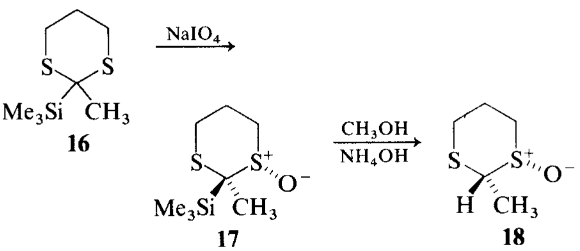
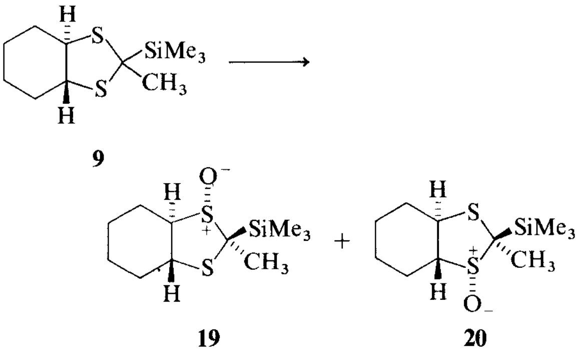


In an attempt at a stereoselective synthesis of **14** or **15** recourse was made to a strategy used with success in previous studies of 2-methyl-1,3-dithiane 1-oxides.[10] We found in our earlier work that 2-methyl-2-trimethylsilyl-1,3-dithiane **16** gave a single 1-oxide **17** on oxidation with sodium metaperiodate and that the trimethylsilyl group of **17** could be easily and stereospecifically cleaved (CH_3OH, NH_4OH, 25°C) with retention of configuration to give *cis*-2-methyl-1,3-dithiane 1-oxide (**18**).

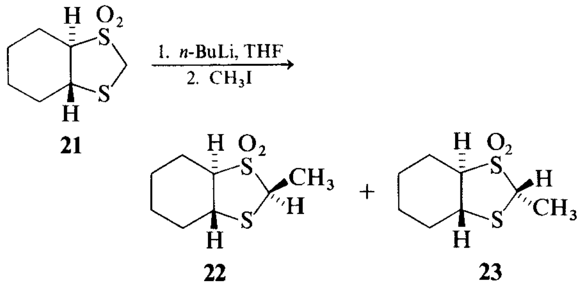


Application of this sequence to 2-methyl-2-trimethylsilyl-*trans*-hexahydro-1,3-benzodithiole **9** is slightly more complicated stereochemically since oxidation of **9**, even if it proceeds with the expected high stereoselectivity *trans* to the trimethylsilyl group,[11,12] can produce diastereomers **19** and **20**. Indeed, this proved to be the case.



Oxidation of **9** with sodium metaperiodate or with *m*-chloroperoxybenzoic acid appeared, from the NMR spectrum of the product, to give a *ca.* 65:35 mixture of two diastereomers. One of these could be obtained pure on recrystallization, however, and was subsequently treated with sodium methoxide in methanol. Cleavage of the trimethylsilyl group occurred smoothly but the product was a mixture of the same two diastereomeric 2-methyl-*trans*-hexahydro-1,3-benzodithioles **14** and **15** obtained earlier. Clearly, the trimethylsilyl group cleavage from C-2 in 1,3-dithiolane 1-oxides is not stereospecific while it is stereospecific in 1,3-dithiane 1-oxides.

Finally, metalation of the monosulfone *trans*-hexahydro-1,3-benzodithiole 1,1-dioxide (**21**) was examined. Oxidation of the mixture of monosulfoxides **10** and **11** with potassium permanganate[13] gave **12** in 75% yield. Methylation of the anion of **21** produced, in 98% yield, a mixture of two diastereomeric 2-methyl derivatives **22** and **23**.



In summary, we find that anions at C-2 of 1,3-dithiolanes are not inherently unstable. They can be prepared readily by metalation and alkylated cleanly when competing reactions are precluded. The presence of oxygen substituents on one of the sulfur atoms does not exert a pronounced effect on the stereoselectivity of alklyation at C-2.

EXPERIMENTAL SECTION

Infrared spectra were obtained on a Perkin-Elmer 337 grating spectrometer as KBr disks or thin films. Melting points and boiling points are uncorrected. Microanalyses were performed by Atlantic Microlab, Inc., Atlanta, Georgia. Proton NMR spectra were obtained at 60 MHz on a Hitachi Perkin-Elmer R-20 spectrometer. Carbon-13 NMR spectra were recorded using a JEOL-PS 100 P/EC-100 Fourier transform spectrometer. The operating conditions are described in reference 14.

Reaction of 1,3-dithiolane 1-oxide (3) with sodium hydride and methyl iodide

A solution of 1.52 g (12.4 mmol) of 1,3-dithiolane 1-oxide (**3**)[6] in 10 mL of tetrahydrofuran was added dropwise to a stirred mixture of 864 mg (18 mmol) of a 50% mineral oil dispersion of sodium hydride in 20 mL of tetrahydrofuran containing 2.50 mL (40.0 mmol) of methyl iodide. The mixture was stirred at room temperature for 5.5 hr, 20 mL of water was added, and the tetrahydrofuran removed by evaporation. The residue was extracted with three 40-mL portions of chloroform, the extracts dried (Na_2SO_4) and evaporated to leave 1.62 g (96%) of crude product which was purified by distillation through a short path column giving 1.05 g (62%) of vinyl methylthiomethyl sulfoxide (**4**) as a light yellow liquid: bp. 77–81° (0.55 torr); ir (neat) 3100, 3040, 3015, 2980, 2930, 1420, 1360, 1320, 1180, 1050 (vs, S = 0), 960 (s), 815, 755, 700, and 680 cm^{-1}; NMR ($CDCl_3$) δ 2.32

(s, 3, SCH_3), 3.71 (s, 2, SCH_2), 5.99 (d, 1, $J = 10$ Hz, cis vinyl H), 6.09 (d, 1, $J = 16$ Hz, trans vinyl H), and 6.84 ppm (*d* of *d*, 1, $J_{trans} = 16$ Hz, $J_{cis} = 10$ Hz, $CH_2 = CH$); mass spectrum *m/e* (rel intensity) 136 (3), 120 (8), 76 (26), 61 (100).

The analytical sample was obtained by preparative thin layer chromatography (silica gel; 15% 2-propanol in carbon tetrachloride).

Anal. Calcd for $C_4H_8OS_2$: C, 35.26; H, 5.92; S, 47.07. Found: C, 35.08; H, 5.96; S, 46.83.

Attempted reaction of trans-2-phenyl-1,3-dithiolane 1-oxide (5) *with sodium hydride and methyl iodide*

To a suspension containing 96 mg (2.0 mmol) of a 50% sodium hydride dispersion in mineral oil and 0.50 mL (8.0 mmol) of methyl iodide in 16 mL of tetrahydrofuran was added a solution of 297 mg (1.50 mmol) of *trans*-2-phenyl-1,3-dithiolane 1-oxide (**5**)[8] in 5 mL of terahydrofuran. After 1 hr at room temperature, water (15 mL) was added and the tetrahydrofuran was evaporated. The residue was extracted with three portions of chloroform totaling 100 mL and the combined chloroform extracts dried over Na_2SO_4. After evaporation, 280 mg of a liquid remained which was identified as a 1 : 1 mixture of **5** and its *cis*-2-phenyl epimer[8] (94% recovery).

Reaction of 5 *with sodium methoxide in refluxing methanol. Isolation of methyl thionbenzoate.*

A solution of 854 mg (4.30 mmol) of **5** in 25 mL of methanol containing 4.35 mmol of sodium methoxide was refluxed for 4 hr. After cooling, the solvent was removed in vacuo. The red residue was acidified with 4 mL of 1 *N* HCl and partitioned between 50 ml of brine and 60 mL of chloroform. The aqueous phase was extracted twice with 40 mL portions of chloroform, and the combined organic extracts were dried over sodium sulfate. Removal of solvent gave 870 mg of red oil, which was chromatographed on a column containing 20 g of silica gel. Elution of the least polar component with 135 mL of carbon tetrachloride provided 228 mg (35%) of methyl thionbenzoate as a brownish-yellow liquid. Identification was based upon its NMR and mass spectra and was confirmed by comparison of its NMR spectrum and retention time (GC) with those of authentic material.[15]

trans-Hexahydro-1,3-benzodithiole (7).[9]

Cyclohexene trithiocarbonate was prepared in 88% yield in accordance with the literature procedure.[16] Reduction of this material with lithium aluminium hydride[17] produced cyclohexane-*trans*-1,2-dithiol in 97% yield: bp 50°C (0.24 Torr), n^{24}D 1.5513 lit.[18] bp 104–106°C (18-19 Torr), n^{20}D 1.5515. The usual method[19] was used to prepare **7** in 94% yield (with the modification that the reaction mixture was refluxed an additional 1 hr after addition of the chloroform solution of dithiol and methylal).

2-Trimethylsilyl-trans-hexahydro-1,3-benzodithiole (8)

n-Butyllithium (9.30 mL of 2.2 *M* solution) was added to a solution of 3.276 g (20.4 mmol) of *trans*-hexahydro-1,3-benzodithiole (7) in 40 mL of THF at −45 to −30°C. The pale yellow solution was stirred at −45°C for 1 hr, and 2.72 mL (21.4 mmol) of trimethylchlorosilane was added. The yellow color dissipated after 2.5 hr of stirring, during which the temperature rose from −45 to −10°C. The mixture warmed to room temperature over an additional 1-hr period. Ten milliliters of water was added, and the THF was evaporated. The residue was partitioned between 75 mL of water and 76 mL of *n*-pentane. The layers were separated, and the aqueous phase was extracted with *n*-pentane (2 × 50 mL). The combined organic extracts were washed with 100 mL portions of water, 10% potassium hydroxide, and water and dried over potassium carbonate. Removal of solvent yielded 4.435 g (93%) of crude product, mp 42–47°C, which was recrystallized from methanol to give 3.43 g of **8**: mp 50–51°C; ir (KBr) 1240, 841, and 753 cm^{-1} ($-SiMe_3$); NMR ($CDCl_3$) δ 0.16 (s, 9, $SiMe_3$), 1.0–3.1 (m, 10, cyclohexane ring H), and 3.61 ppm (s, 1, C-2 H); mass spectrum *m/e* (rel intensity) 232 (26), 151 (65), 136 (55), 74 (100).

Anal. Calcd. for $C_{10}H_{20}S_2Si$: C, 51.66; H, 8.67; S, 27.59. Found: C, 51.83; H, 8.70; S, 27.71.

2-Methyl-2-trimethylsilyl-trans-hexahydro-1,3-benzodithiole (9)

n-Butyllithium (5.1 mmol, 2.3 ml of 2.2 *M* solution) was added to a solution of 1.16 g (5.00 mmol) of **8** in 20 mL of THF at −45 to −35°C. The resulting pale yellow solution was stirred at −40°C for 50 min, after which 0.62 mL (10 mmol) of methyl iodide was added. Within two minutes, the yellow coloration was gone. The solution was stirred at −45 to −30°C for 50 min, then warmed to room temperature. The isolation procedure for **8** was followed, and **9** was obtained as 1.175 g (95%) of pale yellow oil. Crystallization from methanol at −25°C afforded the analytical sample: mp 24.5–25°C; NMR ($CDCl_3$) δ 0.16 (s, 9, $SIMe_3$), 1.0–2.3 (m, 8, CH_3), 1.65 (s 3, Me), and 2.8–3.2 ppm (m, 2, trans H's); mass spectrum *m/e* (rel intensity) 246 (13), 230 (2), 189 (2), 173 (13), 164 (5), 149 (21), 73 (48), 59 (100), 45 (72).

Anal. Calcd for $C_{11}H_{22}S_2Si$: C, 53.59; H, 9.00; S, 26.02; Si, 11.39. Found: C, 53.64; H, 8.88; S, 25.88; Si, 11.31.

Oxidation of trans-hexahydro-1,3-benzodithiole (7)

A solution of 2.40 g (15.0 mmol) of **7** in 50 mL of dichloromethane was cooled to −15°C and a solution of 3.05 g (15.0 mmol) of *m*-chloroperoxybenzoic acid in 75 mL of dichloromethane added slowly over the course of 1 hr. The solution was allowed to stand at −25°C overnight, then washed with 100 mL of 10% sodium carbonate solution and 100 mL of brine. After drying (Na_2SO_4) and evaporation, 2.46 g of an orange oil was obtained which was chromatographed on 79 g of silica gel. Elution with 400 mL of carbon tetrachloride and 625 mL of 2% 2-propanol/carbon tetrachloride gave a pale yellow liquid (202 mg) which was discarded. Further elution with 625 mL of 2% 2-propanol/carbon tetrachloride and 250 mL of 4% 2-propanol/carbon tetrachloride afforded 1.793 g (68%) of a mixture of diastereomeric 1-oxides **10** and **11**. This material was recrystallized from ether at −25°C to give 349 mg of a single diastereomer, mp 63–65°C. Recrystallization from 10% benzene/cyclohexane gave the analytical sample: mp 67–68°C; ir (KBr) 1030 cm^{-1} (S = 0); NMR ($CDCl_3$) δ 1.0–2.7 (m, 9, cyclohexane ring H), 3.3–4.0 (m, 1, cyclohexane ring H α to S = 0), 3.61 (d, 1, C-2 H), and 4.11 ppm (d, 1, C-2 H); ^{13}C NMR ($CDCl_3$) 23.8 (C-6), 24.5 (C-7, C-8), 30.0 (C-9), 48,8 (C-4), 52.8 (C-2), and 71.6 ppm (C-5); mass spectrum *m/e* (rel intensity) 176 (29), 81 (100).

Anal. Calcd. for $C_7H_{12}OS_2$: C, 47.69; H, 6.86; S, 36 38. Found: C, 47.77; H, 6.87; S, 36.26.

Continued elution of the column with 8% 2-propanol/carbon tetrachloride afforded a negligible quantity of additional monosulfoxide. Elution with methanol gave 415 mg of orange-white solid, mp 127–140°C which was recrystallized from acetone to afford 171 mg (6%) of *trans*-hexahydro-1,3-benzodithiole *trans*-1,3-dioxide (**12** or **13**), mp 149.5–151.5°C. The *trans* relationship of the sulfoxide groups follows from its ^{1}H NMR spectrum in which the protons at C-2 are isochronous and its ^{13}C NMR spectrum in which C-4 and C-5 are isochronous. A *cis*-1,3-dioxide would possess diastereotopic protons at C-2 and diastereotopic carbons at C-4 and C-5. The analytical sample was obtained by recrystallization from cyclohexane: mp 512 – 153°C ir (KBr) 1010 cm^{-1} (S = 0); ^{1}H NMR ($CDCl_3$) δ 1.0–2.6 (m, 8, CH_2), 3.29 (m, 2, trans H's), and 4.18 ppm (s, 2, C-2 H); mass spectrum *m/e* (rel intensity) 192 (42), 130 (77), 81 (100); ^{13}C NMR ($CDCl_3$) δ 23.0 (C-7, C-8), 23.4 (C-6, C-9), 62.1 (C-4, C-5), and 75.0 ppm (C-2).

Anal. Calcd for $C_7H_{12}O_2S_2$: C, 43.72; H, 6.29; S, 33.35. Found: C, 43.63; H, 6.31; S, 33.31.

Methylation of trans-hexahydro-1,3-benzodithiole 1-oxide (**10** *or* **11**)

To a solution of the crystalline 1-oxide prepared in the previous experiment (155.5 mg, 0.882 mmol) in 20 mL of THF was added 0.41 mL (0.90 mmol) of 2.2 *M* *n*-butyllithium at −75 to −70°C. The mixture was stirred at −75 to −70°C for 1 hr. Following the addition of 0.11 mL (1.8 mmol) of methyl iodide, the mixture was stirred at −75 to −40°C for 4 hr, then allowed to warm to room temperature. The usual workup was employed, yielding 167.7 mg (100%) of crude product. The NMR spectrum of the material indicated that it consisted of two diastereomers, characterized by methyl peaks centered at 1.55 and 1.59 ppm, the former being slightly in excess. The mixture was recrystallized from ether at −25°C to give 43.4 mg of one essentially pure isomer: mp 102–102.5°C; ir (KBr) 1030 cm^{-1} (S = 0); NMR ($CDCl_3$) δ 1.59 (d, 3, J = 7 Hz, CH_3), 1.0–2.9 (m, 9, cyclohexane ring H), 3.5–4.4 (m, 1, cyclohexane ring H α to S = 0), and 4.23 ppm (q, 1, J = 7 Hz, C-2 H); mass spectrum *m/e* (rel intensity) 190 (18), 114 (25), 108 (17), 87 (100).

Anal. Calcd for $C_8H_{14}OS_2$: C, 50.48; H, 7.41; S, 33.70. Found: C, 50.38; H, 7.44; S, 33.66.

Oxidation of 2 - methyl - 2 - trimethylsilyl - trans - hexahydro - benzo - 1,3 - dithiole (**9**)

A) *With m-chloroperoxybenzoic acid.* A solution of 2.00 mmol of MCPBA in 10 mL of dichloromethane was added to a stirred solution of 493 (2.00 mmol) of **9** in 7 mL of dichloromethane at −25 to −15°C. The mixture was stirred for one hour, then stored at −25°C overnight. Following the usual workup, 522 mg of soft white solid was isolated. This material was chromatographed on silica gel using 6% 2-propanol/carbon tetrachloride as developing solvent. Extraction of the diffuse lower band in 25% ethanol/chloroform gave 319 mg (61%) of **19** and **20** mp 55–71°C. The NMR spectrum showed 66% of one isomer (methyl peak at δ 1.59 and trimethylsilyl peak at δ 0.18) and 34% of the other (methyl peak at δ 1.52 and trimethylsilyl peak at δ 0.22). Recrystallization from ether at −25°C gave the analytical sample: mp 85–89°C; NMR ($CDCl_3$) δ 0.18 and 0.22 (s, 9, SiMe_3), 1.52 and 1.59 (s, 3, Me), and 1.0–3.0 ppm (m, 10, cyclohexane ring H); mass spectrum *m/e* (rel intensity) 262 (19), 247 (30), 173 (100), 132 (65), 91 (90), 90 (57), 81 (97), 75 (81), 73 (100), 60 (88).

Anal. Calcd for $C_{11}H_{22}OS_2Si$: C, 50.33; H, 8.45; S, 24.43. Found: C, 50.22; H, 8.42; S, 24.33.

B) *With sodium metaperiodate.* Sodium metaperiodate (1.56 mmol) in 3 mL of water was added to a stirred solution of **9** (366.5 mg, 1.49 mmol) in 15 mL of methanol at −10 to 0°C. The mixture was stirred at −10°C for 1.5 hr, then stored at 0°C for 5 hr. The precipitate was removed by filtration, and methanol was removed in vacuo. The residue was partitioned between 30 mL of brine and 30 mL of dichloromethane. Layers were separated, and the aqueous layer was extracted with an additional 30 mL of dichloromethane. The organic extracts were dried (Na_2SO_4), and solvent was evaporated, leaving 359 mg of white solid. The NMR spectrum of this material indicated *ca.* 68% of one isomer (methyl peak at δ 1.58 and trimethylsilyl peak at δ 0.17) and 32% of the other. Preparative TLC of the crude product as before afforded 244 mg (62.5%) of a mixture of **19** and **20**. Recrystallization from ether gave 56.5 mg of one isomer, mp 81–88.5°C (NMR: methyl peak at δ 1.59, trimethylsilyl peak at δ 0.19).

Cleavage of 2 - methyl - 2 - trimethylsilyl - trans - hexahydro - 1,3 - benzodithiole 1 - oxide (**19** *or* **20**)

A solution of 52.7 mg (0.20 mmol) of the diastereomer isolated above in 3 mL of methanol was treated with eight drops of concentrated ammonium hydroxide. The solution was allowed to stand for 18.5 hr. Removal of solvent furnished 37.2 mg (97%) of white solid. The NMR spectrum indicated that the product consisted of the same two diastereomers **14** and **15** that were obtained upon direct methylation of **10** or **11** (methyl peaks at 1.55 and 1.59 ppm). Purification of the crude product by preparative TLC gave material of mp 82–96°C.

Anal. Calcd for $C_8H_{14}OS_2$: C, 50.48; H, 7.41; S, 33.70. Found C, 50.27; H, 7.41; S, 33.56.

trans-Hexahydro-1,3-benzodithiole 1,1-dioxide (**21**)

A solution of 538.7 mg (3.41 mmol) of potassium permanganate in 35 mL of water added dropwise to a solution containing 902 mg (5.11 mmol) of a mixture of **10** and **11** in 50 mL of water and 1.7 g of magnesium sulfate. After addition was complete, the mixture was stirred for 5 hr and the precipitated MnO_2 was dissolved by the addition of 2.0 g $Na_2S_2O_5$. A clear, colorless solution containing some white precipitate resulted which was extracted with 100 mL and 50 mL portions of chloroform. The combined $CHCl_3$ extracts were dried (Na_2SO_4) and evaporated to leave 947 mg of orange oil, which was chromatographed on a column containing 18 g of silica gel. Elution with 150 mL of benzene gave 153 mg of **21** along with higher R_f impurities. Elution with 50 mL of 25% ethyl acetate/benzene yielded 685 mg of crude **21**, which was recrystallized from ether to give 555 mg of **21**, mp 58–63°C. The material isolated from the mother liquor and the first fraction from the column were combined and chromatographed on two silica gel plates with 15% 2-propanol/carbon tetrachloride. Extraction of the lower band furnished an additional 184 mg of **21**, mp 59–62°C (total yield: 739 mg; 75%). Recrystallization from ethanol gave the analytical sample: mp 63.4–65°C; ir (KBr) 1300 and 1220 cm^{-1} (sulfone); ^{1}H NMR ($CDCl_3$) δ 1.0–3.6 (m, 10, cyclohexane ring H) and 3.89 ppm (AB q, J = 11 Hz, 2, C-2H); ^{13}C NMR ($CDCl_3$) 23.0, 23.6, 24.7, 31.1 (C-6, 7, 8, 9), 43.9 (C-4), 48.1 (C-2), and 66.1 ppm (C-5); mass spectrum *m/e* (rel intensity) 192 (5), 128 (10), 104 (13), 82 (65), 81 (75), 67 (100), 54 (61), 41 (55), 39 (59).

Anal. Calcd for $C_7H_{12}O_2S_2$: C, 43.72; H, 6.29; S, 33.35. Found: C, 43.83; H, 6.30; S, 33.24.

Methylation of trans-hexahydro-1,3-benzodithiole 1,1-dioxide (**21**)

Methylation of sulfone **21** was carried out under the conditions used for the monosulfoxide and gave, from 250 mg (1.3 mmol) of **21** , 262 mg (98% of white solid, mp 72–80°C. The NMR spectrum revealed that both possible diastereomers (**22** and **23**) characterized by methyl peaks at δ 1.57 and 1.61 (major), had formed. Attempts to separate the two isomers by TLC were not fruitful. Recrystallization from ether at −25°C gave the analytical samples as a mixture of diastereomers: mp 78–95°C; ir (KBr) 1300 and 1130 cm^{-1} (sulfone); NMR ($CDCl_3$) δ 1.0–3.6 (m, 10, cyclohexane ring H), 1.57, 1.61 (2 overlapping d, 3, CH_3), and 3.97, 4.17 ppm (2 overlapping q, 1, C-2 H); mass spectrum *m/e* (rel intensity) 206 (< 1), 133 (13), 110 (14), 83 (100), 69 (96).

Anal. Calcd for $C_8H_{14}O_2S_2$: C, 46.57; H, 6.84; S, 31.08. Found: C, 46.39; H, 6.83; S, 31.19.

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