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3*H*-1,2-Benzodithiole Oxides: Studies Directed toward the Generation of *o*-Thiobenzoquinone Methide and Benzo[*b*]thiete

Alfred G. Hortmann,* Alan J. Aron, and Ajit K. Bhattacharya

Department of Chemistry, Washington University, St. Louis, Missouri 63130

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o-Thiobenzoquinone methide (**1**) has been generated by photodesulfonylation of 3*H*-1,2-benzodithiole 2,2-dioxide (**3**) in benzene and was trapped with added *N*-phenylmaleimide as the [4 + 2] (or [8 + 2]) adduct (**4**). The 2,2-dioxide **3** was prepared in ~10% yield by either oxidation of 3*H*-1,2-benzodithiole (**5**) or oxidative cyclization of 2-mercaptomethylthiophenol (**7**) with *m*-chloroperoxybenzoic acid (MCPBA). Peroxyacetic acid oxidation of **7** also afforded **3** in low yield, along with the monoxides **3a** and **6a**; under somewhat more vigorous conditions **7** gave 3*H*-1,2-benzodithiol-3-one 1-oxide (**8**) in 29% yield. The 1-oxide **8** was also isolated (15% yield) along with a 65% yield of the corresponding 1,1-dioxide **9** from a direct oxidation of 3*H*-1,2-benzodithiol-3-one with MCPBA. Mild periodate oxidation of **5** at 24 °C cleanly afforded the monoxides **3a** and **6a** in a 1:1 ratio; brief treatment of this difficultly separable mixture with aqueous Na_2CO_3 led to complete disproportionation of **3a** to **3** and **5** under conditions which left **6a** unaffected and allowed its isolation and further oxidation with periodate (65 °C) to yield pure 3*H*-1,2-benzodithiole 1,1-dioxide (**6**). Alternatively, a 1:1 mixture of **3** and **6** could be obtained directly from **5** by vigorous periodate oxidation run at 70 °C and catalyzed by I_2. Irradiation of pure **6** under conditions used for the photolysis of **3**, as well as in the presence of benzophenone as a sensitizer, did not yield any of the desired benzo[*b*]thiete (**2**), nor was the formation of any adduct (**4**) of **1** (assuming that a conversion of **2** to **1** might occur) with added *N*-phenylmaleimide observed.

The original objectives of the research described in this report were the generation of *o*-thiobenzoquinone methide (**1**)[2] and a determination of whether or not **1** exists in equilibrium with its valence tautomer, benzothiete (**2**).[3] In pursuing these goals we reasoned that photochemically or thermally induced extrusion of SO_2 from 3*H*-1,2-benzodithiole 2,2-dioxide (**3**) might yield **1** and/or **2** directly[4] and that **1** would be sufficiently reactive toward dienophiles to undergo [4 + 2] (or [8 + 2]) cycloaddition reactions to yield stable adducts (e.g., **4** via condensation with *N*-phenylmaleimide[2]), thereby demonstrating its potential use in synthesis[5] as well as providing proof of its generation in solution. The 2,2-dioxide **3** might, in turn, be readily accessible by regioselective peroxyacid oxidation of the 2-sulfur atom (i.e., the presumably more electron-rich alkyl-substituted sulfur) of 3*H*-1,2-benzodithiole (**5**), an assumption that we initially felt was warranted by the results of a model study of the *m*-chloroperoxybenzoic acid oxidation of benzyl and ethyl phenyl disulfides.[6] In the event that nonregioselectivity proved to be the case in the oxidation of **5**,[7,8] obtention of **6** (and/or **6a**) would allow us, in addition, to test a direct and previously unexplored route to the parent benzothiete system (**2**) via extrusion of SO_2 from **6**.[9]

Results and Discussion

3*H*-1,2-Benzodithiole (**5**) was first prepared by slow addition of a 2% solution of 2-mercaptomethylthiophenol (**7**) to a 7.5% solution of ferric chloride in acetic acid–methanol at 10 °C as described by Lüttringhaus and Hägele.[10] Attempts to improve on their reported 40% yield of **5** led us to develop a modified procedure (see Experimental Section) whereby **5** was eventually obtainable in 81% yield (ca. 85% pure by ^1H NMR assay) by slow addition of a 1% alcoholic solution of **7** to a vigorously stirred 2% solution of cupric chloride dihydrate in either ethanol or methanol at 24 °C in the presence of air.[11] As had been observed previously,[10] **5** was found to deteriorate rapidly in the absence of solvent, and efforts to purify crude **5** by distillation in vacuo or by column chromatography (SiO_2; Al_2O_3) led to intractable decomposition products. Consequently, it was necessary to use **5** directly as obtained (after extraction) from the $CuCl_2$-catalyzed oxidation of **7** or to store **5** at −10 °C as a 2–3% solution in methylene chloride or diethyl ether until needed.

Preliminary studies on the oxidation of **5** with 2 mol equiv of *m*-chloroperoxybenzoic acid (MCPBA) in CH_2Cl_2 at 25 °C afforded small amounts (<10% yield) of a crystalline solid which analyzed correctly for $C_7H_6O_2S_2$. The product exhibited strong infrared bands at 1150 and 1335 cm^{-1} (–S–SO_2–) and ^1H NMR signals at δ 4.70 (s, 2) and 7.37 (broad s, 4). The data led to a tentative assignment of either **3** or **6** as possible structures for the new compound. A distinction in favor of structure **3** for the product was allowed by the observation that the ^{13}C NMR signal due to the $^{13}CH_2$ group in the new thiolsulfonate appears at 64.8 ppm downfield from Me_4Si, a typical value for ^{13}C in the $-SSO_2CH_2Ph$ moiety.[12]

Closer examination of the ^1H NMR spectrum of the crude product mixture derived from the oxidation of **5** with MCPBA indicated that two other products (which later proved to be **3a** and **6a**) were also formed in low yield. However, no improvement beyond the original optimum yield (ca. 10%) of isolable **3** could be effected despite considerable efforts in varying the reaction conditions.

A literature report[13] describing the peroxyacetic acid oxidation of the mercaptans RSH, where R = cyclopentyl and cyclohexyl, to yield the corresponding thiolsulfonates RSO_2SR in 34 and 61% yields led us to attempt a direct peroxyacid-mediated oxidative cyclization of 2-mercaptomethylthiophenol (**7**) to **3** and/or **6**. Indeed, upon treatment of **7** with 3 mol equiv of MCPBA in CH_2Cl_2 at 0 °C, an 11% yield of **3** was obtained. Similarly, treatment of **7** with excess commercial 40% peroxyacetic acid in $CHCl_3$ at 0–5 °C for 1 h afforded what later proved to be (by ^1H NMR assay) a 3:6:7 mixture of

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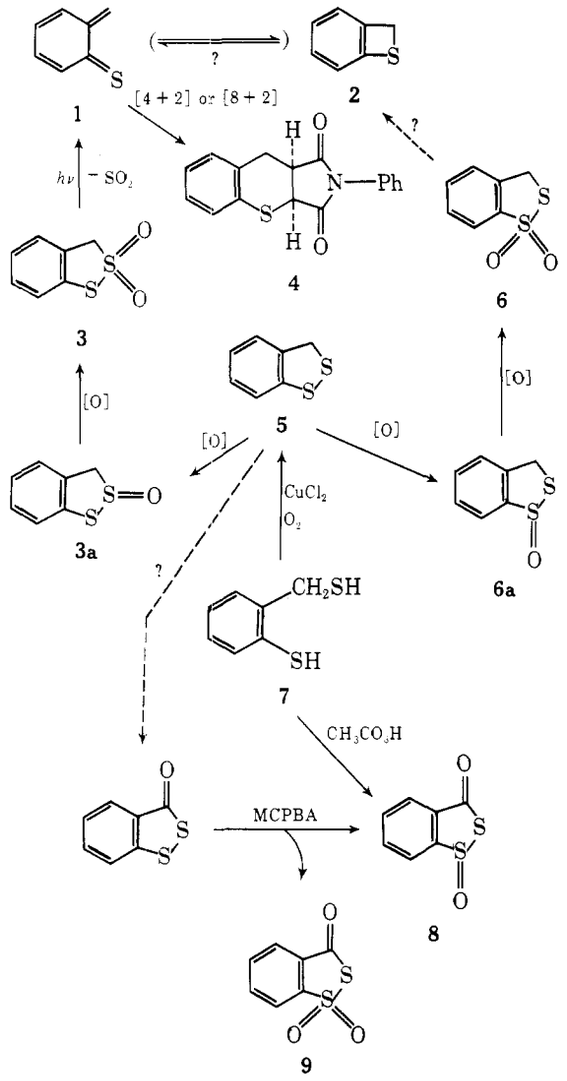
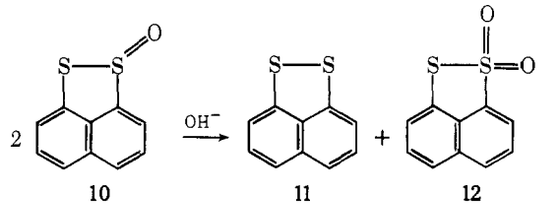


3, 3a, and 6a in about 40% yield. However, a somewhat more vigorous peroxyacetic acid oxidation of 7 (1 h at 0 °C followed by 3 h at 24 °C) afforded not 3, but instead a colorless crystalline substance which analyzed for $C_7H_4O_2S_2$ as the only readily isolable product. The structure of this product, which was obtained pure in 29% yield, was tentatively formulated as 8 on the basis of its infrared and ^1H NMR spectra (ν_{max} at 1705 and 1095 cm^{-1}; multiplet at δ 7.7–8.2).

The formation of 8 via oxidation of 7 was presumed to occur via hydride removal from the initially formed and reactive 3H-1,2-benzodithiole system (5) to yield 3H-1,2-benzodithiol-3-one,[14] followed by subsequent peroxyacid oxidation at the more electron-rich 1-sulfur. On this basis, a direct preparation of 8 was attempted. Treatment of 3H-1,2-benzodithiol-3-one[15] with 2 mol equiv of MCPBA at <−20 °C for ca. 1 h was followed by stirring for 24 h at 20 °C. Two products were obtained; the minor product, obtained pure in 15% yield, was 8, and the major product, obtained pure in 65% yield, analyzed for $C_7H_4O_3S_2$ and was tentatively formulated as 9 on the basis of its IR (ν_{max} 1710, 1335, 1168, and 1160 cm^{-1}) and ^1H NMR (multiplet at δ 7.7–8.3) spectra.[16]

A search for alternative oxidants which might convert 5 both cleanly and efficiently to, preferably, 3 and/or 6 led to a study of periodate oxidation[17] of the disulfide 5. In a preliminary experiment, oxidation of 5 with 1 mol equiv of sodium metaperiodate at 24 °C for ca. 1.5 h gave a 1:1 mixture of the two derivatives of 5, one having a 2 H singlet at δ 4.60 and the other exhibiting an AB pattern (J = 15 Hz) centered at δ 4.91. An attempt to separate the components of the product mixture by alumina chromatography led to a 40% recovery of material which consisted of a ca. 1:1 mixture of 5 and the unchanged oxidation product of 5 exhibiting the AB pattern centered at δ 4.91. The reappearance of the disulfide 5 and the loss of the periodate oxidation product of 5 having the 2 H singlet at δ 4.60 led us to believe that the latter, possibly a thiolsulfinate (3a or 6a), had undergone disproportionation on the column to the disulfide 5 and either 3 or 6. Subsequently, we also observed that when an aqueous acetonitrile solution of a similar 1:1 mixture of periodate oxidation products of 5 was shaken vigorously with an aqueous sodium carbonate solution for several minutes, and the solution was then extracted immediately with methylene chloride and assayed (^1H NMR), the final mixture was found to consist of 5, 3, and the (unchanged) periodate oxidation product of 5 exhibiting the AB pattern at δ 4.91 in a ratio of 1:1:2, respectively. The result clearly suggested that, at least in this experiment, a selective disproportionation of the periodate oxidation product having the 2 H singlet at δ 4.60 was indeed occurring, and the result was rationalized as being in apparent analogy with a similar disproportionation of the thiolsulfinate 10, which has been reported by Oae and co-workers[18] to occur upon attempted alkaline hydrolysis of 10 to yield the disulfide 11 and thiosulfonate 12. This explanation led to the conclusion

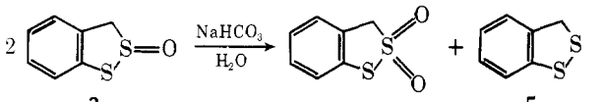


that *both* of the original periodate oxidation products derived from 5 must necessarily be thiolsulfinates (i.e., 3a and 6a) by virtue of the presence of magnetically nonequivalent geminal protons (AB pattern, J = 15 Hz, at δ 4.91) in the remaining unaffected periodate oxidation product. It remained then only to assign a precise structure, 3a or 6a, to each of the two thiolsulfinates since without a knowledge of the precise mechanism for the thiolsulfinate disproportionation the location of the sulfur-bound oxygen atoms in the final thiolsulfonate product (3) could not serve as an indicator for the location of the oxygen in the thiolsulfinate precursor of 3.

Column chromatography (SiO_2) of the total product obtained from the disporportionation experiments described above led to isolation of 30% of pure 3 (based on the weight of the starting 1:1 mixture of 3a and 6a and the stoichiometry assumed for the disproportionation in the above discussion) and 48% of the pure unaffected periodate oxidation product. In agreement with its formulation as a thiolsulfinate (3a or 6a), the compound analyzed correctly for $C_7H_6OS_2$ and exhibited, in addition to the AB pattern at δ 4.91 (J = 15 Hz) in its ^1H NMR spectrum, an infrared ν_{max} at 1080 cm^{-1} (–S–S(O)–). The choice of 6a as the correct structure of this thiolsulfinate was made possible by the observation that further oxidation of the pure thiolsulfinate with potassium metaperiodate in aqueous acetonitrile at higher temperatures (65–68 °C) afforded a new compound ($C_7H_6O_2S_2$), *isomeric* with the thiolsulfonate 3, in nearly quantitative yield. In support of its structural assignment as the remaining thiolsulfonate (6), the product exhibited strong IR ν_{max} signals at 1315 and 1160 cm^{-1} (–S–SO_2–) and ^1H NMR signals at δ 4.78 (s, 2) and 7.4–7.9 (m, 4).

The quantitative formation of 6 by periodate oxidation of the thiolsulfinate having an AB pattern centered at δ 4.91 suggests that (in the simplest case) the latter is 6a and that the thiolsulfinate found earlier to readily disproportionate preferentially over 6a while in contact with aqueous sodium carbonate is 3a. Support for this scheme comes from the ob-

servation that in a periodate oxidation of **5** also run at 70 °C a 1:1 mixture of **3** and **6** was obtained, presumably via a straightforward and approximately quantitative oxidation of **3a** to **3** and **6a** to **6** in a reaction mixture in which the maximum amounts of **3a** and **6a** that ever form as intermediates are also in a ca. 1:1 ratio (the ratio expected based on the results of the separate $NaIO_4$ oxidation described earlier in which 1:1 formation of **3a** and **6a** occurred upon oxidation of **5** with $NaIO_4$ at 24 °C). Consequently, it was concluded that of the two thiolsulfinates, **3a** and **6a**, that were formed in a 1:1 ratio in the periodate oxidation of **5**, it was **3a** which, on brief treatment with aqueous sodium carbonate, disproportionated to **5** and **3** in a 1:1 ratio (under conditions which left **6a** unaf-



3a **3** **5**

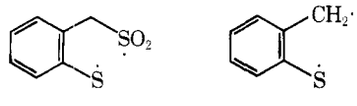
fected). These conclusions of course rely on the basic assumption that further periodate oxidation of **3a** yields **3** and of **6a** yields **6**.[19]

With pure samples of both **3** and **6** in hand, it remained only to test our assumptions regarding their suitability as precursors for the generation of *o*-thiobenzoquinone methide (**1**) and benzo[*b*]thiete (**2**).

Irradiation of solutions of **3** was carried out using a mercury lamp and a quartz apparatus. An insoluble solid, presumably polymeric, was obtained from photolysis of a methanolic solution of **3**. Subsequent photolyses of **3** were performed in chloroform, benzene, and THF and in presence of maleic anhydride or *N*-phenylmaleimide. Of these solvents, only benzene finally proved to be a satisfactory one. Generated by the photodesulfonylation of **3** in benzene, *o*-thiobenzoquinone methide (**1**) could be trapped with reasonable efficiency with *N*-phenylmaleimide to afford the adduct **4** in 43% yield. The reaction of **1** with maleic anhydride also afforded a similarly constituted adduct, but in low yield (^1H NMR assay). No adduct was formed in the presence of dimethyl acetylenedicarboxylate;[5] only an insoluble solid was obtained. In chloroform and THF solutions, dark-colored products were produced and purification of the desired adduct was more difficult. In the absence of a trapping agent (e.g., *N*-phenylmaleimide), polymeric amorphous solids which were insoluble in common organic solvents were generally formed.

Irradiation of **6** in either benzene or diethyl ether solution containing added *N*-phenylmaleimide under conditions similar to those used for the photolysis of **3** led to formation of an intractable amorphous product; none of the desired benzothiete **2** or the adduct of **1** (assuming that a conversion of **2** to **1** might occur) was observed. In an attempted sensitized photolysis of **6** in benzene solution containing benzophenone and *N*-phenylmaleimide using Pyrex-filtered ultraviolet light, only an insoluble amorphous solid was obtained.

Alternative explanations (also suggested by the referees) for the formation of the adduct **4** might invoke the stepwise addition to *N*-phenylmaleimide of either the diradical **13** (with loss of SO_2 at an intermediate step) or the triplet diradical **14**. Although we have no data which can definitively



13 **14**

rule out these possibilities, the absence (^1H NMR assay) of any trans-fused **4** in the crude product from which *cis*-**4** was isolated suggests that the product arose predominantly from a concerted [4 + 2] cycloaddition of **1** to *N*-phenylmaleimide.

Experimental Section[20]

3*H*-1,2-Benzodithiole-3-thione was prepared in 73% yield by treatment of 2,2′-dithiodibenzoic acid with P_4S_{10} in refluxing pyridine, as described by E. Klingsberg and A. M. Schreiber.[26]

3*H*-1,2-Benzodithiol-3-one was prepared in 48% yield by addition of thiolacetic acid to a solution of 2-thiolbenzoic acid in concentrated H_2SO_4, as described by McKibben and McClelland:[15] IR ($CHCl_3$) 1780 (w), 1670, and 895 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.2–7.7 (m, 3) and 7.8–8.1 (m, 1).

2-Mercaptomethylthiophenol (7). Method A. A solution of 46 g (0.25 mol) of 3*H*-1,2-benzodithiole-3-thione in 500 mL of anhydrous Et_2O–THF (1:1) was added dropwise during 1.25 h to a stirred suspension of 20 g of $LiAlH_4$ in 500 mL of Et_2O under N_2. The reaction mixture was stirred for 16 h at 25 °C. Unreacted $LiAlH_4$ was decomposed by the addition of 2-propanol (150 mL). The mixture was acidified with 450 mL of 10% H_2SO_4 solution, and the product was extracted into Et_2O. After washing with brine, the combined extracts were dried ($MgSO_4$) and concentrated. Distillation of the remaining 40 g of yellow liquid afforded 36 g (92%) of pure 2-mercaptomethylthiophenol as a pale yellow liquid: bp 64 °C (0.05 mm) [lit.[10] bp 125–126 °C (12 mm)]; ^1H NMR ($CDCl_3$) δ 1.83 (t, J = 7.5 Hz, 1), 3.63 (s, 1), 3.79 (d, J = 7.5 Hz, 2), and 7.0–7.6 (m, 4).

Method B. 3*H*-1,2-Benzodithiol-3-one (41 g) was reduced with $LiAlH_4$ essentially as described above for the corresponding 3-thione. The combined ethereal extracts were mixed with ice water and extracted with 1 L of 6% KOH solution. The aqueous alkali extracts were acidified with 10% H_2SO_4 and extracted with Et_2O. The combined Et_2O extracts were washed with H_2O, dried ($MgSO_4$), and concentrated in vacuo to yield 35 g of yellow oil. Distillation in the range of 77–90 °C (0.20–0.25 mm) afforded 24 g of a 3:1 mixture (^1H NMR assay) of 2-mercaptomethylthiophenol and 2-hydroxymethylthiophenol. The latter compound[21] (in $CDCl_3$) exhibited ^1H NMR signals at δ 2.1–2.8 (broad s, 1), 3.63 (s, 1), 4.67 (s, 2), and 7.0–7.6 (m, 4).

3*H*-1,2-Benzodithiole (5). A solution of 5.0 g of pure 2-mercaptomethylthiophenol in 420 mL of CH_3OH was added dropwise from a Hershberg addition funnel to a vigorously stirred solution of 10.0 g of $CuCl_2 \cdot 2H_2O$ in 500 mL of CH_3OH at 24 °C during 14 h. A slow stream of air was bubbled through the reaction mixture during the addition and while the mixture was stirred for an additional 3 h. The reaction mixture was decanted, diluted with ice water, and extracted with Et_2O. The combined extracts were washed with water. Partial removal of the Et_2O in vacuo afforded 200 mL of a dilute (ca. 2%) solution of **5**, which was dried ($MgSO_4$) and stored at ca. −10 °C. Complete removal of the solvent from an aliquot (15 mL) afforded 0.300 g (81%) of crude **5** (ca. 85% pure by ^1H NMR assay) as a deep yellow oil which evaporatively distilled at a bath temperature of 93–95 °C (3 mm) [lit.[10] bp 130–133 °C (12 mm)]: ^1H NMR ($CDCl_3$) δ 4.33 (s, 2) and 6.85–7.35 (m, 4).

Reaction of 3*H*-1,2-Benzodithiole (5) with *m*-Chloroperoxybenzoic Acid (MCPBA). A solution of 0.75 g (0.0040 mol) of purified MCPBA in 25 mL of CH_2Cl_2 was added dropwise during 7 min at 24 °C to a stirred CH_2Cl_2 solution (100 mL) containing 0.61 g (0.0040 mol) of 3*H*-1,2-benzodithiole (**5**), and the reaction mixture was stirred for an additional 3 min. Another 0.75 g (0.0040 mol) of MCPBA in 25 mL of CH_2Cl_2 were added during the next 7 min, and the mixture was stirred for 12 h at 25 °C. Removal of the solvent left a pale yellow solid which was mixed with anhydrous Et_2O and filtered to remove some insoluble viscous material. The ether filtrate was washed successively with dilute $NaHCO_3$ solution and brine and dried ($MgSO_4$). Removal of the solvent in vacuo afforded 0.41 g of a mixture of products which included **3**, **3a**, and **6a** in a ratio of 5:2:3, respectively, as determined by a ^1H NMR assay. The mixture was dissolved in CH_2Cl_2, washed with dilute $NaHCO_3$ solution, and dried ($MgSO_4$). Evaporation of the CH_2Cl_2 gave 0.180 g of a white solid. Recrystallization from anhydrous Et_2O afforded two kinds of visually distinct crystals (plates and needles) which were manually separated to yield 0.088 g of bis(*m*-chlorobenzoyl) peroxide, mp 124–125 °C dec (lit.[22] mp 125.0 °C dec), and 0.069 g (10%) of 3*H*-1,2-benzodithiole 2,2-dioxide (**3**) colorless needles: mp 117–118 °C; ^1H NMR ($CDCl_3$) δ 4.70 (s, 2) and 7.37 (m, 4); IR ($CHCl_3$) 1335 and 1150 cm^{-1}; mass spectrum (70 eV), *m/e* 186 (M^+); UV (EtOH) λ_{max} 205 nm (ϵ 26 380), 237 (9300), and 274 (570); ^{13}C NMR ($CDCl_3$) δ 64.8 ($^{13}CH_2$) and 125.0–129.6 ($^{13}C_6H_4$).

An analytically pure sample of **3** exhibited mp 118–119.5 °C. Anal. Calcd for $C_7H_6O_2S_2$: C, 45.14; H, 3.25; S, 34.43. Found: C, 45.34; H, 3.42; S, 34.23.

Reaction of 2-Mercaptomethylthiophenol with Commercial 40% Peroxyacetic Acid (CH_3CO_3H) under Controlled Conditions. Commercial 40% CH_3CO_3H[23] (0.9 mL) in 5 mL of $CHCl_3$ was added during 5 min to 40 mL of $CHCl_3$ containing 0.2 g of 2-mercap-

tomethylthiophenol at 0 °C. The reaction mixture was stirred for 1 h at 0–5 °C, washed with water, and dried ($MgSO_4$). Evaporation of the solvent in vacuo afforded 0.1 g of 3:6:7 mixture of **3** [^{1}H NMR ($CDCl_3$) δ 4.70 (s, 2) and 7.37 (m, 4)], **3a** [^{1}H NMR ($CDCl_3$) δ 4.60 (s, 2) and 7.1–7.6 (m, 4)], and **6a** [^{1}H NMR ($CDCl_3$) AB pattern centered at δ 4.93 (J = 15 Hz), 7.3–7.7 (m, 3), and 7.7–8.0 (m, 1)], respectively (^{1}H NMR assay).

Reaction of 2-Mercaptomethylthiophenol with Commercial 40% Peroxyacetic Acid: Formation of 3H-1,2-benzodithiol-3-one 1-Oxide (8). To a solution of 3.50 g of a 3:1 mixture of 2-mercaptomethylthiophenol and 2-hydroxymethylthiophenol in 50 mL of $CHCl_3$ at 0 °C was added 12 mL of commercial 40% peroxyacetic acid[23] during 10 min, and the mixture was stirred for 1 h at 0 °C and for 3 h at 24 °C. The reaction mixture was diluted with ice water and extracted with Et_2O. The organic extract was washed with water and dried ($MgSO_4$), and the solvent was evaporated in vacuo, yielding a brown viscous material which on precipitation from a cold chloroform–hexane solution (−25 °) gave 1.2 g of 3H-1,2-benzodithiol-3-one 1-oxide (**8**) as an off-white solid, mp 99–101 °C (39% yield based on starting 2-mercaptomethylthiophenol). Recrystallization of 0.20 g of the crude product from chloroform–hexane afforded 0.15 g (29%) of pure **8** as colorless needles: mp 101.5–103 °C; ^{1}H NMR ($CDCl_3$) δ 7.7–8.2 (m); IR ($CHCl_3$) 1780 (w), 1705, 1095, and 890 cm^{-1}; mass spectrum (70 eV), m/e 184 (M^+).

An analytically pure sample of **8** exhibited mp 101.5–103 °C. Anal. Calcd for $C_7H_4O_2S_2$: C, 45.64; H, 2.19; S, 34.81. Found: C, 45.61; H, 2.22; S, 34.92.

3H-1,2-Benzodithiol-3-one 1-Oxide (8) and 3H-1,2-Benzodithiol-3-one 1,1-Dioxide (9). A solution of 2.20 g of *m*-chloroperoxybenzoic acid (85%; 0.010 mol) in 35 mL of CH_2Cl_2 was added during 0.5 h to a stirred solution of 0.84 g (0.005 mol) of 3H-1,2-benzodithiol-3-one in 35 mL of CH_2Cl_2 at −20 to −23 °C. Stirring was continued below −30 °C for 45 min and at +20 °C for an additional 24 h. The reaction mixture was fractionally crystallized several times from CCl_4–Et_2O to yield 0.65 g (65%) of **9** as colorless crystals: mp 70–72 °C;[24] ^{1}H NMR ($CDCl_3$) δ 7.7–8.3 (m); IR ($CHCl_3$) 1785 (w), 1710, 1335, 1168, 1160, and 895 cm^{-1}; mass spectrum (70 eV), m/e 200 (M^+).

An analytical sample of **9**, later found to contain ca. 5% of **8** (IR), had mp 71–73 °C. Anal. Calcd for $C_7H_4O_3S_2$: C, 41.99; H, 2.01; S, 32.02. Found: C, 42.20; H, 2.17; S, 32.06. Pure **9** exhibited mp 98–99 °C.

The remaining isolable material (0.15 g, 15%) was **8**: mp 101–103 °C; ^{1}H NMR ($CDCl_3$) δ 7.7–8.2 (m); IR ($CHCl_3$) 1780 (w), 1705, 1095, and 890 cm^{-1}.[24]

Reaction of 3H-1,2-Benzodithiole (5) with Sodium Metaperiodate at 24 °C: Formation of a 1:1 Mixture of 3a and 6a. A solution of 0.87 g of **5** (ca. 85% pure) in 50 mL of acetonitrile was added dropwise during 10 min to a stirred aqueous solution (100 mL) containing 1.80 g (0.004 mol) of $NaIO_4$ at room temperature (24 °C) and stirred for an additional 1.25 h. The reaction mixture was washed successively with water and brine and dried ($MgSO_4$). The solvent was removed in vacuo to yield 0.88 g (92%) of a 1:1 mixture of **3a** and **6a** (which was of ca. 85% purity by a ^{1}H NMR assay) based on the relative integrated areas beneath a 2 H singlet at δ 4.60 (due to **3a**) and an AB pattern centered at δ 4.91 (i.e., consisting of 2 doublets (J = 15 Hz) centered at δ 4.58 and 5.25 (due to **6a**)).

The mixture of thiolsulfinates was quite stable under a variety of nonbasic conditions: e.g., the mixture was (i) stored for 6 days at 24 °C in the presence of diffuse light, (ii) heated in an NMR tube ($CDCl_3$ solution) for 13 h at 50 °C followed by 25 h at 58–60 °C, (iii) refluxed with 3% aqueous acetic acid containing acetonitrile for 13 h, and (iv) distilled at reduced pressure, bp 88–96 °C (0.16 mm), without any apparent change in every case.[25]

Reaction of a 1:1 Mixture of 3H-1,2-Benzodithiole 2-Oxide (3a) and 3H-1,2-Benzodithiole 1-Oxide (6a) on Alumina. A 1:1 mixture of 500 mg of **3a** and **6a** was chromatographed on 10 g of neutral alumina (Woelm activity grade III) using petroleum ether (bp 63–69 °C) followed by CH_2Cl_2 as eluents to yield 100 mg of crude **5**, purity ca. 75% (^{1}H NMR assay), and 90 mg of crude **6a**, purity ca. 90% (^{1}H NMR assay).

Reaction of a 1:1 Mixture of 3H-1,2-Benzodithiole 2-Oxide (3a) and 3H-1,2-Benzodithiole 1-Oxide (6a) with Aqueous Sodium Carbonate: Disproportionation of 3a to Form 3 and 5. A solution of 2.5 g of a 1:1 mixture of **3a** and **6a** in 150 mL of acetonitrile and 65 mL of water was mixed with 1.1 g of anhydrous Na_2CO_3 in 10 mL of water in a separatory funnel and shaken vigorously for 3 min. A deep yellow color immediately developed. The reaction mixture was mixed with ice, acidified with 5% H_2SO_4 solution 3 min later, and immediately extracted with CH_2Cl_2. The combined organic extracts were washed successively with brine and water and dried ($MgSO_4$). The solvent was removed in vacuo, yielding 1.6 g of a mixture of **3, 5,** and **6a** in a ratio of 1:1:2 (^{1}H NMR assay). The crude product was chromatographed on silica gel (34 g). Elution with 3% Et_2O in petroleum ether (bp 33–37 °C) gave 0.5 g of a viscous yellow residue containing **5,** which was discarded. Subsequent elution with a 2:1 mixture of Et_2O–CH_2Cl_2 afforded 0.50 g of a yellow solid which on crystallization from CCl_4–CH_2Cl_2 and recrystallization from absolute EtOH afforded 0.20 g (30%) of pure **3:** mp 116–118 °C; ^{1}H NMR ($CDCl_3$) δ 4.70 (s, 2) and 7.37 (m, 4).

Further elution with methylene chloride afforded 0.60 g (48%) of pure **6a** as a bright yellow oil: bp 140 °C (0.06 mm); ^{1}H NMR ($CDCl_3$) AB pattern centered at δ 4.91 (J = 15 Hz), 7.3–7.7 (m, 3), and 7.7–8.0 (m, 1); IR (CH_2Cl_2) 1080 and 1055 cm^{-1}; mass spectrum (70 eV), m/e 170 (M^+). Anal. Calcd for $C_7H_6OS_2$: C, 49.38; H, 3.55; S, 37.67. Found: C, 49.18; H, 3.48; S, 37.77.

3H-1,2-Benzodithiole 1,1-Dioxide (6). A mixture containing a small crystal of iodine (10 mg), 0.30 g (0.0017 mol) of the pure 1-oxide **6a,** and 0.45 g (0.0019 mol) of KIO_4 in 42 mL of water–acetonitrile (5:2) was heated to 65 °C during 15 min and maintained at 65–68 °C under N_2 for 1.25 h. The reaction mixture was cooled, diluted with water, and extracted with diethyl ether. The combined ether extracts were washed successively with a minimum amount of dilute $NaHSO_3$ solution (to remove iodine) and brine and dried ($MgSO_4$). Removal of the solvent in vacuo gave 0.30 g of crude **6** as an off-white grayish solid, mp 118–121 °C. Recrystallization from CH_2Cl_2 afforded 0.26 g (79%) of pure **6** as colorless crystals: mp 121–122.5 °C; ^{1}H NMR ($CDCl_3$) δ 4.78 (s, 2) and 7.4–7.9 (m, 4); IR (CH_2Cl_2) 1315, 1160, and 1125 cm^{-1}; mass spectrum (70 eV), m/e 186 (M^+); UV (EtOH) λ_{max} 213 nm (ϵ 5810), 260 (570), 266 (720), and 273 (620).

An analytical sample of **6** had mp 121–122.5 °C. Anal. Calcd for $C_7H_6O_2S_2$: C, 45.14; H, 3.25; S, 34.43. Found: C, 45.39; H, 3.33; S, 34.64.

Reaction of 3H-1,2-Benzodithiole (5) with Potassium Metaperiodate for a Prolonged Period. A solution of 0.78 g of **5** (ca 85% pure) in 55 mL of 10:1 acetonitrile–diethyl ether was added dropwise during 25 min and at 20 °C to a stirred aqueous solution (300 mL) containing 2.20 g (ca. 0.01 mol) of KIO_4, and the reaction mixture was stirred for an additional 50 h under N_2. The reaction mixture was extracted with Et_2O, and the combined extracts were dried ($MgSO_4$). Evaporation of the solvent in vacuo yielded 0.63 g of crude product which included **3, 3a,** and **6a** in a ratio of 2:3:3, respectively (^{1}H NMR assay).

Reaction of 3H-1,2-Benzodithiole (5) with Potassium Metaperiodate at Elevated Temperature. A solution of 250 mg of **5** (ca. 85% pure) in 12 mL of acetonitrile was added dropwise at room temperature to a stirred aqueous solution (70 mL) containing 700 mg (3.0 mmol) of KIO_4, and the reaction mixture was stirred for an additional 0.5 h. One small crystal of iodine (10 mg) was added, and the mixture was heated under N_2 at 70 °C for 1 h. The reaction mixture was cooled and extracted with Et_2O. The combined Et_2O extracts were washed with a minimum amount of dilute $NaHSO_3$ solution (to remove iodine) and water and dried ($MgSO_4$). Removal of the solvent in vacuo left 100 mg of a solid residue. Recrystallization from ethanol afforded 52 mg of a ca. 1:1 mixture (mp 88–105 °C) of **3** [^{1}H NMR ($CDCl_3$) δ 4.70 (s, 2) and 7.37 (m, 4)] and **6** [^{1}H NMR ($CDCl_3$) δ 4.78 (s, 2) and 7.4–7.9 (m, 4)].

Generation and Trapping of *o*-Thiobenzoquinone Methide (1): Photolysis of 3H-1,2-Benzodithiole 2,2-Dioxide (3) in the Presence of *N*-Phenylmaleimide. A solution of 80 mg of pure **3** and 120 mg of *N*-phenylmaleimide in 25 mL of anhydrous benzene was irradiated in a standard photolysis apparatus for 5 h using a 450-W high-pressure Hanovia Hg lamp and a quartz lamp well. The solution was maintained near room temperature by cooling the outer jacket of the irradiation vessel in a water bath (20–30 °C). Prior to and during the irradiation, argon was slowly bubbled through the solution to aid in deoxygenating and to provide agitation. Removal of the solvent in vacuo left a solid material which was partially dissolved in a small amount of $CHCl_3$–CCl_4, and the suspension was filtered to remove colored impurities. The filtrate was concentrated in vacuo to give a crude solid material which was chromatographed on silica gel using a 1:1 mixture of anhydrous benzene–diethyl ether as eluent to afford a yellow solid containing unreacted *N*-phenylmaleimide and the adduct **4** (^{1}H NMR assay). The solid was partially dissolved in a small amount of petroleum ether (bp 63–69 °C)–diethyl ether, and the suspension was filtered to yield 80 mg (ca. 63%) of crude **4** as the remaining insoluble yellow-brown solid, mp 159–164 °C. Recrystallization from CH_2Cl_2–hexane yielded 55 mg (43%) of pure **4** as tan-colored crystals: mp 166–168 °C (lit.[2] mp 167–168 °C); mass spectrum (70 eV), m/e 295 (M^+). The ^{1}H NMR spectrum of **4** in $CDCl_3$ was identical with that already reported.[2]

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Registry No.—**1**, 59130-11-9; **2**, 63559-01-3; **3**, 66303-96-6; **3a**, 66324-14-9; **4**, 66303-97-7; **5**, 272-21-9; **6**; 66303-98-8; **6a**, 66303-99-9; **7**, 66324-13-8; **8**, 66304-00-5; **9**, 66304-01-6; 3*H*-1,2-benzodithiole-3-thione, 3354-42-5; 3*H*-1,2-benzodithiol-3-one, 1677-27-6; MCPBA, 937-14-4; bis(*m*-chlorobenzoyl) peroxide, 845-30-7; 2-hydroxymethylthiophenol, 4521-31-7.

References and Notes

(1) Abstracted in part from the Ph.D. Dissertation of Ajit Kumar Bhattacharya, Washington University, St. Louis, Mo., 1975.

(2) The generation of vinyl-substituted *o*-thiobenzoquinone methides (allides) had been invoked earlier by R. S. Becker and J. Kolc [*J. Phys. Chem.*, **72**, 997 (1968)] to explain the photochromic behavior of 2*H*-thiochromene and 2,2-diphenyl-2*H*-thiochromene upon irradiation in 3-methylpentane at 77 K. During the course of our work a report appeared on the generation of *o*-thiobenzoquinone methide (**1**) by photodecarbonylation of 1-thia-2-indanone: G. Jacqmin, J. Nasielski, G. Billy, and M. Remy, *Tetrahedron. Lett.*, 3655 (1973). The formation of **1** was established by its reaction in the presence of added *N*-phenylmaleimide as a trapping agent to give the [4 + 2] (or [8 + 2]) adduct **4**.

(3) The heretofore elusive parent benzothiete system (**2**) has only recently been prepared for the first time: W. J. M. van Tilborg and R. Plomp, *J. Chem. Soc., Chem. Commun.*, 130 (1977). See also E. Voigt and H. Meier, *Angew. Chem., Int. Ed. Engl.*, **15**, 117 (1976). Benzothiete (**2**) was reported to be stable for several days at room temperature; at temperatures >100 °C it dimerizes to 6*H*,12*H*-dibenzo[*b*,*f*][1,5]dithiocin, apparently via **1**.

(4) For example, extrusion of SO_2 during irradiation of the sultone derived from *o*-hydroxytoluene-α-sulfonic acid has been reported to yield *o*-quinone methide by O. L. Chapman and C. L. McIntosh, *J. Chem. Soc., Chem. Commun.*, 383 (1971).

(5) The potential synthetic utility of the reaction of **1** and substituted analogues of **1** with acetylenes was also of interest to us as a possible route to the relatively inaccessible 1-thio-2-chromenes, which might serve as precursors of 1-thianaphthalenes; see A. G. Hortmann, R. L. Harris, and J. A. Miles, *J. Am. Chem. Soc.*, **96**, 6119 (1974).

(6) A. K. Bhattacharya and A. G. Hortmann, *J. Org. Chem.*, **43**, 2728 (1978).

(7) It should be noted that 1,2-dithioles are generally more reactive toward chemical oxidants than either cyclic disulfides with larger rings or open-chain disulfides (B. Lindberg and G. Bergson, *Ark. Kemi*, **23**, 319 (1965), and references cited therein), presumably as a consequence of significant differences in electronic interactions between the nonbonding electrons on the sulfurs in the 1,2-dithiole rings (which are constrained with regard to rotation about the S–S bond, resulting in a dihedral angle [ϕ] of ca. 25 ° between the C–S bonds) vs. similar interactions in acyclic disulfides ([ϕ] ~ 90 °). Hence, it seems probable that in unsymmetrically substituted disulfides the relative reactivity of one sulfur vs. the other toward a particular reagent will also vary markedly where comparisons are being made between acyclic disulfides vs. 1,2-dithioles. Consequently, considering the present state-of-the-art in predicting the outcome of, e.g., peroxyacid oxidations of unsymmetrical acyclic disulfides (see ref 6), predictions regarding the relative reactivities of the sulfurs of unsymmetrical 1,2-dithioles in similar reactions would seem to be, at best, tenuous.

(8) Cf. R. M. Wilson, D. N. Buchanan, and J. E. Davis, *Tetrahedron. Lett.*, 3919 (1971); L. Field in "The Organic Chemistry of Sulfur", S. Oae, Ed., Plenum Press, New York, N.Y., 1977, Chapter 7.

(9) An elegant example of photochemically induced extrusion of SO_2 from a dithiole 1,1-dioxide to afford a thietane derivative appears in the efficient synthesis of the single-atom (sulfur) peri-bridged naphthalene derivative naphtho[1,8-*bc*]thiete by UV irradiation of naphtho[1,8-*cd*]-1,2-dithiole 1,1-dioxide (**12**): J. Meinwald and S. Knapp, *J. Am. Chem. Soc.*, **96**, 6532 (1974); see also J. Meinwald, S. Knapp, S. K. Obendorf, and R. E. Hughes, *ibid.*, **98**, 6643 (1976). A thermally induced extrusion of SO_2 from a 1,2-dithiolane 1,1-dioxide to yield a thietane in 55% yield has also been reported: A. Padwa and R. Gruber, *J. Org. Chem.*, **35**, 1781 (1970).

(10) A. Lüttringhaus and K. Hägele, *Angew. Chem.*, **67**, 304 (1955).

(11) Cf. the oxidation of a series of alkyl- and arylthiols in aqueous alkaline solution in the presence of various metal ions and oxygen: J. D. Hopton, C. J. Swan, and D. L. Trimm, *Adv. Chem. Ser.*, No. **75**, 216 (1968).

(12) The ^{13}C NMR chemical shifts for $-^{13}CH_2-$ in the following compounds were used for comparison (see ref 6): $PhSS\mathbf{C}H_2Ph$, δ 43.3; $PhSSO_2\mathbf{C}H_2Ph$, δ 65.9; and $PhSO_2S\mathbf{C}H_2Ph$, δ 40.2. In contrast to the situation regarding such differences for ^{13}C chemical shifts, it should be noted that similar comparisons of differences in chemical shifts of protons of the type $-CH_2SS(O)_2-$ vs. $-CH_2S(O)_2S-$ or $-CH_2SS(O)-$ vs. $-CH_2S(O)S-$ are generally of little value in distinguishing between pairs of structurally related compounds bearing these structural moieties since the differences in the proton shifts are generally <~0.3 ppm (see, e.g., the chemical shifts for the CH_2 protons in **3** vs. **6** and in **3a** vs. **6a** (vide infra) and for the CH_2 protons in the pairs of thiolsulfonates reported in ref 6). Such insignificant differences in proton chemical shifts are also commonplace within the same compound; e.g., in dibenzyl thiolsulfonate the two $-CH_2-$ singlets appear at δ 4.02 and 4.19, and in the corresponding thiolsulfinate they appear at δ 4.23 and 4.27 (P. Allen, Jr., P. J. Berner, and E. R. Malinowski, *Chem. Ind. (London)*, 208 (1963).

(13) L. N. Aristarkhova and B. G. Boldyrev, *Zh. Org. Khim.*, **8**, 2071 (1972); *Chem. Abstr.*, **78**, 57832n (1973). See, however, W. G. Filby, K. Günther, and R. D. Penzhorn, *J. Org. Chem.*, **38**, 4070 (1973).

(14) Cf. the formation of 1,2-dithiolium cations via oxidation of 1,2-dithiole derivatives: H. Prinzbach and E. Futterer, *Adv. Heterocycl. Chem.*, **7**, 39 (1966). Collapse of a peroxyester formed by C–O bond formation between the peroxyacid and the 3*H*-1,2-benzodithiolium cation might reasonably lead to the intermediate 3*H*-1,2-benzodithiol-3-one.

(15) M. McKibben and E. W. McClelland, *J. Chem. Soc.*, 170 (1923). See also A. T. Fanning, Jr., G. R. Bickford, and T. D. Roberts, *J. Am. Chem. Soc.*, **94**, 8505 (1972).

(16) The observation that all of the ^1H NMR signals due to aromatic protons in **8** and **9** appear downfield from δ 7.6 lends further support to these structural assignments as opposed to alternate structures having no oxygen substitution at the 1-sulfur since the latter types of compounds generally show ^1H NMR signals upfield from δ 7.6 associated with proton(s) ortho to nonoxygenated sulfur substituents on phenyl rings; see, e.g., the ^1H NMR spectra of aromatic protons in **7**, **5**, **3**, and **3a** vs. **6** and **6a** and the spectra of the phenyl-substituted disulfides and thiolsulfonates reported in ref 6 above.

(17) For a review, see A. J. Fatiadi, *Synthesis*, 229 (1974). For examples of periodate oxidation of disulfides to thiolsulfinates and thiolsulfonates, see J. E. McCormick and R. S. McElhinney, *J. Chem. Soc., Perkin Trans 1*, 2795 (1972); P. K. Srivastava and L. Field, *J. Org. Chem.*, **37**, 4196 (1972); and H. Yanagawa, T. Kato, H. Sagami, and Y. Kitahara, *Synthesis*, 607 (1973). See also A. Padwa and R. Gruber, cited in ref 6 above, and Oae et al., (ref 18).

(18) S. Tamagaki, H. Hirota, and S. Oae, *Bull. Chem. Soc. Jpn.*, **46**, 1247 (1973). Disproportionations of thiolsulfinates in alkaline media to give thiolsulfonates and disulfides might involve initial attack of hydroxide ion at either the sulfenyl sulfur (–S–) or the sulfinyl sulfur (–S(O)–); see J. L. Kice and T. E. Rogers, *J. Am. Chem. Soc.*, **96**, 8009 (1974).

(19) An alternative to the above explanation in which the structures of **3a** and **6a** are switched would require the periodate oxidation of **3a** to yield **6**, possibly by way of disproportionation of an intermediate α-disulfoxide (see footnote 4 in ref 6), to explain the concommitant transposition of the oxygen on S-2 in **3a** to S-1 in **6**. To explain, however, the apparently also exclusive formation of **3** from **6a** in this context would require *exclusive formation of the stereoisomer of the above α-disulfoxide* in order to avoid the obvious problem of a common intermediate in the two reactions, a rationalization which, although conceivable, appears improbable.

(20) Melting points were determined in unsealed capillary tubes using a Unimelt apparatus (Arthur H. Thomas Co.) and are uncorrected. Boiling points are uncorrected. Proton magnetic resonance (^1H NMR) spectra were obtained using a Varian Associates A-60A instrument; tetramethylsilane (Me_4Si) was used as an internal standard (δ = 0.00 ppm). Infrared spectra (IR) were recorded on a Perkin-Elmer Model 457 grating spectrophotometer. Ultraviolet (UV) spectra were obtained on a Cary Model 14 instrument. Mass spectra were run on a Varian Model M-66 spectrometer. ^{13}C nuclear magnetic resonance (^{13}C NMR) spectra were recorded using a Bruker 90-MHz spectrometer operating in the pulsed Fourier transform mode; ^{13}C NMR chemical shifts are reported in δ (ppm downfield from Me_4Si) based on $\delta_{Me_4Si} = \delta_{CDCl_3} - 77.0 = 0.00$ ppm. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

(21) G. W. Stacy, F. W. Villaescusa, and T. E. Wollner, *J. Org. Chem.*, **30**, 4074 (1965).

(22) G. Tsuchihashi, S. Miyajima, T. Otsu, and O. Simamura, *Tetrahedron*, **21**, 1039 (1965).

(23) See L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. I, Wiley, New York, N.Y., 1967, p 785.

(24) In later preparations of larger quantities of pure **8** and **9** for photochemical studies, B. H. Lee of this laboratory has found that treatment of 3*H*-1,2-benzodithiol-3-one with 3 mol equiv of MCPBA under similar conditions (−30 °C for 30 min and then 25 °C for 35 h) afforded **9** essentially uncontaminated with **8**. Alternatively, oxidation using an equimolar amount of MCPBA (−30 °C for 20 min and then 25 °C for 1.5 h) afforded essentially pure **8** in 78% yield.

(25) The above results are surprising in view of the fact that acyclic thiolsulfinates, in general, are unstable compounds which readily undergo thermally induced disproportionation to yield the corresponding disulfides and thiolsulfonates. For example, methyl methanethiolsulfinate (MeSS(O)Me), upon standing for a few days at room temperature, gives a mixture of dimethyl disulfide and methyl methanethiolsulfonate; see E. Block and J. O'Connor, *J. Am. Chem. Soc.*, **96**, 3921 (1974).

(26) E. Klingsberg and A. M. Schreiber, *J. Am. Chem. Soc*, **84**, 2941 (1962).