oil which crystallized from acetonitrile to provide 0.9 g (29%) of cyclic sulfamide **3** (R = $CH_3$): mp 199–201 °C; NMR ($CDCl_3$) δ 2.1 (s, 3 H, 2.20–2.65 (m, 2 H), 3.15 (s, 3 H), 3.65 (t, $J$ = 6 Hz, 2 H), 4.15 (broad s, 2 H).

Anal. Calcd for $C_9H_{13}N_3O_4S$: C, 41.69; H, 5.05; N, 16.21. Found: C, 41.69; H, 5.08; N, 16.23.

**Registry No.**—1 (R = *i*-Pr), 67210-12-2; **2** (R = $CH_3$), 67210-13-3; **3** (R = $CH_3$), 67210-14-4; **4**, 7318-00-5; **5**, 26118-67-2; **6**, 67210-15-5; **7**, 67210-16-6; **8**, 67210-17-7; **9a**, 1128-00-3; **9b**, 65277-17-0; **10a**, 67210-18-8; **10b**, 67210-19-9; **11**, 67210-20-2; **13** (R = $CH_3$), 4160-61-6; **14** (R = $CH_3$), 67210-21-3; **16** (R = $C_2H_5$) HCl, 4644-61-5; **17** (R = $C_2H_5$), 4451-85-8; **18** (R = $CH_3$), 67210-22-4; 2-carbethoxycyclohexanone, 1655-07-8; urethane, 51-79-6; *N*-methylsulfamoyl chloride, 10438-96-7.

## References and Notes


(1) Presented in part at the 175th National Meeting of the American Chemical Society, Anaheim, Calif., March, 1978.
(2) E. Cohen and B. Klarberg, *J. Am. Chem. Soc.*, **84**, 1994 (1962).
(3) (a) A. Zeidler, A. Fisher, and G. Weiss, U.S. Patent 3 708 277 (1973); (b) Netherlands Patent 7 412 249 (1974).
(4) E. F. Degering and J. E. Wilson, *J. Org. Chem.*, **17**, 339 (1952).
(5) J. A. Kloek and K. L. Leschinsky, *J. Org. Chem.*, **41**, 4028 (1976).
(6) For cases such as **9a**, synthesis is best accomplished by condensation with urethane followed by selective decarboxylation with methoxide; cf. T. Takaya, H. Yoshimoto, and E. Imoto, *Bull. Chem. Soc. Jpn.*, **41**, 2176 (1968). However, in cases such as **9b**, where ester interchange is a problem, efficient conversions are accomplished by a procedure developed in these laboratories: J. A. Kloek and K. L. Leschinsky, *J. Org. Chem.*, **43**, 1460 (1978).
(7) G. M. Atkins, Jr., and E. M. Burgess, *J. Am. Chem. Soc.*, **89**, 2502 (1967).
(8) G. M. Bennett and L. V. D. Scorah, *J. Chem. Soc.*, 194 (1927).
(9) Commercially available.


# Sulfoxides, Sulfilimines, Methoxysulfonium Salts, and Sulfoximines Derived from 3-Methyl-3-phenylthietane[1]

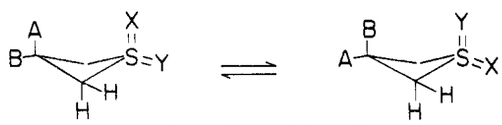

Maris Buza,[2] Kenneth K. Andersen,* and Michael D. Pazdon

*Department of Chemistry, University of New Hampshire, Durham, New Hampshire 03824*


*Received March 7, 1978*


3-Methyl-3-phenylthietane (**1**), 3-isopropyl-3-phenylthietane (**10**), 3-(*p*-bromophenyl)-3-methylthietane (**11**), 2-thiaspiro[3.5]nonane (**12**), 2-thiaspiro[3.5]non-6-ene (**13**), 3-methyl-3-nitrothietane (**14**), 5-methyl-2-thiaspiro[3.5]nonane (**15**), 6-methyl-2-thiaspiro[3.5]nonane (**16**), and 7-methyl-2-thiaspiro[3.5]nonane (**17**) were prepared by treating the corresponding 2,2-disubstituted 1,2-trimethylene bis(benzenesulfonates) with sodium sulfide in dimethyl sulfoxide. Oxidation of **1** by hydrogen peroxide or by sodium hypochlorite gave 3-methyl-*t*-3-phenylthietane *r*-1-oxide (**2**) and 3-methyl-*c*-3-phenylthietane *r*-1-oxide (**3**). Configurations were determined by NMR spectroscopy. Thermal interconversion of **2** and **3** proceeds at rates comparable to acyclic analogues and much slower than the rate reported for 3-*tert*-butylthietane 1-oxide. Relative rates of reaction of water and hydroxide ion at sulfur and methyl carbon in the hydrolysis of the diastereomeric methoxysulfonium salts derived from **2** and **3** were determined. Mass spectra of 2,2,4,4-tetradeuterated derivatives of **1**, **2**, **3**, and 3-methyl-3-phenylthietane 1,1-dioxide (**18**) were obtained. Sulfoxides **2** and **3** showed no differences in their mass spectra. An improved synthesis of *N*-*p*-toluenesulfilimines by the reaction of sulfides with anhydrous Chloramine-T–dimethylformamide solutions was used to synthesize 3-methyl-*c*-3-phenylthietane-*r*-*N*-(*p*-toluenesulfonyl)sulfilimine (**6**) and its diastereomer (**7**). Their rates of interconversion measured at 165 °C were somewhat slower than that for an acyclic arylalkyl analogue, but faster than that for an acyclic dialkyl *N*-acylsulfilimine. Silver ion formed complexes with sulfilimines with bonding at the N atom.


Thietanes and their S-substituted derivatives have been investigated extensively in recent years, but no 3-alkyl-3-arylthietanes or derivatives are included in these studies.[3–8] In fact, we found no mention of such compounds in the literature at all. We have synthesized 3-methyl-3-phenylthietane (**1**), converted it to diastereomeric sulfoxides **2** and **3**, methoxysulfonium salts **4** and **5**, sulfilimines **6** and **7**, and sulfoximines **8** and **9**, assigned configurations to these derivatives, determined the equilibrium between **2** and **3** and between **6** and **7**, and also studied some additional chemistry of these and related compounds. Our results and their relationship to previous investigations of various sulfoxides, sulfilimines, and sulfoximines, especially cyclic analogues, are described below.



| | A | B | X | Y |
|---|---|---|---|---|
| 1 | Ph | Me | – | – |
| 2 | Ph | Me | – | O |
| 3 | Me | Ph | – | O |
| 6 | Me | Ph | – | NTs |
| 7 | Ph | Me | – | NTs |
| 8 | Me | Ph | O | NTs |
| 9 | Ph | Me | O | NTs |
| 18 | Ph | Me | O | O |

## Results and Discussion

**3-Methyl-3-phenylthietane 1-Oxides (2 and 3).** Thietane 1-oxides are prepared by oxidation of thietanes which are obtained most often through ring closure of 1,3-dibromides or 1,3-disulfonate esters[3,10,11] by sulfide ion, through fusion of cyclic carbonate esters of 1,3-diols with thiocyanate ion,[4,9] or by reduction of thietane 1,1-dioxides obtained by the cycloaddition of enamines with sulfene ($CH_2$=$SO_2$).[12–17] But 3-alkyl-3-arylthietanes and their derivatives had not been synthesized prior to our work; in fact, an attempt to prepare 3-ethyl-3-phenylthietane via the cyclic carbonate had failed.[18] Our preparation of 3-methyl-3-phenylthietane (**1**) was achieved by treatment of 2-methyl-2-phenyltrimethylene bis(benzensulfonate) with sodium sulfide in dimethyl sulfoxide. This modification of a standard thietane synthesis was also successful in preparing 3-isopropyl-3-phenylthietane (**10**) as well as the other 3,3-disubstituted thietanes (**11–17**) listed in Table I. In the two cases where comparisons are possible,

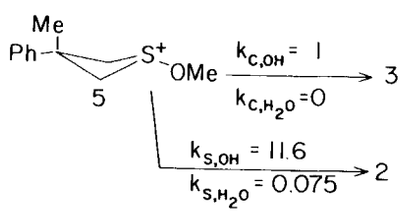
0022-3263/78/1943-3827$01.00/0 

**Table I. Thietanes Prepared from Benzenesulfonate Esters of 1,3-Diols**

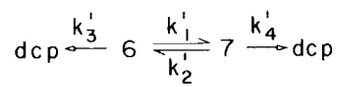
| compd | thietane | yield, % | reaction time, h | bp, °C (mm) | sulfone registry no. | sulfone mp,[k] °C | benzenesulfonate registry no. | benzenesulfonate mp, °C | NMR, δ 3,3 substituent | NMR, δ α protons |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 3-methyl-3-phenylthietane | 65 | 2 | 115–117 (12) | 66809-99-2 | 54–55 | 66810-41-1 | 133.5–134.5 | 1.77 (s, 3 H)[h] | 2.99 (d, 2 H, $J$ = 9 Hz) |
| | | | | | | | | | 7.21 (m, 5 H) | 3.78 (d, 2 H, $J$ = 9 Hz) |
| 10 | 3-isopropyl-3-phenylthietane | 22 (58)[a] | 1 | 142–154 (10) | 66810-33-1 | 89–90.5 | 66810-42-2 | 93.5–94.5 | 0.77 (d, 6 H, $J$ = 7 Hz)[h] | 3.27 (d, 2 H, $J$ = 9.5 Hz) |
| | | | | | | | | | 2.50 (sept, 1 H, $J$ = 7 Hz) | 3.62 (d, 2 H, $J$ = 9.5 Hz) |
| | | | | | | | | | 7.15 (m, 5 H) | |
| 11 | 3-(*p*-bromophenyl)-3-methylthietane | 66 | 3 | 56–57 (mp) | 66810-34-2 | 137–138.5 | 66810-08-0 | 133.5–134.5 | 1.74 (s, 3 H)[i] | 2.93 (d, 2 H, $J$ = 9 Hz) |
| | | | | | | | | | 7.19 (2d, 4 H) | 3.65 (d, 2 H, $J$ = 9 Hz) |
| 12 | 2-thiaspiro[3.5]nonane | 75 (26,[b] 42,[c] 57[d]) | 2 | 82–84 (7) | 66810-35-3 | 71.5–72.5 | 2658-61-9 | 101–102 | 1.20–1.87 (m, 10 H)[i] | 2.83 (s, 4 H) |
| | | | | 89–90 (13)[d] | | 72.5–73[b] | | 101–102[e] | | |
| 13 | 2-thiaspiro[3.5]non-6-ene | 67 (34)[f] | 7 | 111–115 (32) | 66810-36-4 | 110.5–111.5 | 66810-09-1 | 103–104 | 1.63–2.58 (m, 6 H)[h] | 2.63 (d, 2 H, $J$ = 8 Hz) |
| | | | | | | | | | 5.63 (m, 2 H) | 2.80 (d, 2 H, $J$ = 8 Hz) |
| 14 | 3-methyl-3-nitrothietane | 41 | 2 | 101–102 (27) | 66810-37-5 | 118–119 | 66810-10-4 | 112.5–114 | 1.98 (s, 3 H)[j] | 3.17 (d, 2 H, $J$ = 10 Hz) |
| | | | | | | | | 114[g] | | 4.03 (d, 2 H, $J$ = 10 Hz) |
| 15 | 5-methyl-2-thiaspiro[3.5]nonane | 48 | 42 | 93–95 (7) | 66810-38-6 | 44–45.5 | 66810-11-5 | 89–90 | 0.83–2.27 (m 12 H)[i] | 2.45–3.17 (m, 4 H) |
| 16 | 6-methyl-2-thiaspiro[3.5]nonane | 64 | 14 | 92–94 (7) | 66810-39-7 | 66–67 | 66810-12-6 | 76–78 | 0.68–2.40 (m, 12 H)[j] | 2.78 (s, 2 H) |
| | | | | | | | | | | 2.83 (s, 2 H) |
| 17 | 7-methyl-2-thiaspiro[3.5]nonane | 48 | 49 | 88–93 (7) | 66810-40-0 | 67–68 | 66810-13-7 | 100–101 | 0.66–2.37 (m, 12 H)[h] | 2.85 (s, 2 H) |
| | | | | | | | | | | 2.92 (s, 2 H) |

[a] Obtained using anhydrous conditions (see Experimental Section). [b] H. J. Backer and A. F. Tamsma, *Recl. Trav. Chim. Pays-Bas*, **57**, 1183 (1938); from diol via the dibromide. [c] Reference 18. [d] Reference 11. [e] L. Shotte, *Ark. Kemi*, **9**, 309 (1956). [f] Prepared using the cyclic carbonate method of ref. 18. [g] J. L. Riebsomer, *J. Org. Chem.*, **11**, 182 (1946). [h] $CDCl_3$. [i] $CCL_4$. [j] Neat. [k] Thietanes were coverted to sulfones, which analyzed for carbon and hydrogen within 0.3% of theory.

**Scheme I**




**Scheme II**



higher yields, based on the common 1,3-diol precursors, were obtained using this procedure, e.g., 2-thiaspiro[3.5]nonane (**12**) was obtained in 26% yield from the dibromide, 42% from the cyclic carbonate, and 56% from the bis(benzenesulfonate) in ethylene glycol; our modification using the latter in dimethyl sulfoxide gave 75%. In our hands, 2-thiaspiro[3.5]-6-nonene (**13**) was formed in 34% yield via the cyclic carbonate method, while the bis(benzenesulfonate) procedure gave 67%.

The various thietanes were prepared by stirring the corresponding 1,3-bis(benzenesulfonate) esters with sodium sulfide nonahydrate in dimethyl sulfoxide at temperatures below 100 °C. Some of the reactions proceeded exothermically, whereas others needed prolonged heating on the steam bath to complete the reaction (see Table I). Product isolation was usually accomplished by extraction of the nonpolar thietanes into pentane from the water-diluted reaction mixtures. Distillation of the concentrated pentane extracts gave the thietanes in a high state of purity. The use of $Me_2SO$ solutions of sodium sulfide from which most of the water had been removed by azeotropic distillation gave a dramatic increase in the yield of 3-phenyl-3-isopropylthietane (**10**) when compared to the untreated nonahydrate reaction yields, but it did not seem to affect the yield of 3-methyl-3-phenylthietane (**1**). Apparently, the yield of **10** was increased at the expense of the corresponding oxetane, formed in the reactions with the sodium sulfide nonahydrate.

Other compounds produced and identified by their spectral data were $\alpha$-methylstyrene and 3-methyl-3-phenyloxetane in the reaction to form **1** and $\alpha$-isopropylstyrene and 3-isopropyl-3-phenyloxetane in the reaction to form **10.** The other distilled thietanes (without an aromatic substituent), especially those whose production required long reaction times, showed up to 5% of an impurity by GLC analysis, which probably corresponded to the oxetane. Searles et al. also observed oxetane formation and fragmentation to olefins in the carbonate ester fusions.[18] Water- and pentane-insoluble gums, as well as nonvolatile but pentane-soluble products, were also present in our reactions.

Characterization of 3-methyl-3-phenylthietane (**1**) was accomplished by NMR spectroscopy and by oxidation to sulfone **18,** which gave an NMR spectrum and C,H analysis consistent with the proposed structure. Reduction of sulfone **18** by lithium aluminum hydride regenerated thietane **1.**

Diastereomeric 3-methyl-3-phenylthietane 1-oxides (**2** and **3**), obtained through oxidation of thietane **1** by hydrogen peroxide in acetic acid, were formed, without accompanying sulfone, in a ratio of 34:66 for **2/3,** isolated by distillation in 87% yield, and separated from one another by crystallization and column chromatography.

**Assignment of Configuration to 2 and 3.** Configurations as well as predominant conformations, were deduced mainly from the $^1H$ NMR spectra of **2** and **3,** in particular, from the resonances of the four thietane ring hydrogens which form an AA'BB' spin system. For sulfoxide **2** these $\alpha$-methylene hydrogens gave rise to two very sharp multiplets, each consisting of eight resolved peaks, symmetrically disposed about a mirror plane separating them. The other sulfoxide, **3,** also gave rise to two multiplets. Although the low-field multiplet was sharp and resembled very closely the half-spectrum of **2,** the high-field multiplet was broadened due to long range coupling, as verified by decoupling experiments, between axial $\alpha$- and 3-methyl protons, the latter appearing as a triplet.[7,19] One highly predominant conformation for **2** is consistent with the sharpness of its AA' and BB' multiplets, especially since thietane **1** and sulfone **18,** which are expected to be undergoing rapid ring inversion between two folded-ring conformations, both have one-half of their ring proton spectra broadened.

Microwave spectroscopy shows that thietane 1-oxide in the gas phase prefers the folded-ring conformation with the sulfinyl oxygen equatorial.[20] Both *cis*- and *trans*-3-(*p*-bromophenyl)thietane 1-oxides have similar conformations in the solid state,[21] as does a lanthanide complex of 3,3-dimethylthietane 1-oxide.[7] Solution conformations, while not as rigorously defined, also prefer equatorial rather than axial oxygen.[10b,22]

If the sulfinyl oxygen is equatorial, then **2** and **3** must have the configurations shown in the stereoformulas; this follows from the axial hydrogen axial methyl coupling predicted for and exhibited by **3** and not predicted for and absent in **2.**

Aromatic solvent induced shifts (ASIS), frequently used to assign configurations to cyclic sulfoxides,[13,24,25] are consistent with these stereochemical assignments. Benzene, thought to form a collision complex with the positive sulfur of the S–O dipole, shields the equatorial protons of **3** which must be closest to the complexed aromatic ring if the oxygen is equatorial and shifts their signals upfield relative to their signals in chloroform solution. The broadened, methyl-coupled, axial proton signals of **3** were shifted only 0.29 ppm compared to 0.72 ppm for the equatorial proton signals. In **2,** the axial protons should resonate upfield since they are anti to the sulfur lone pair of the equatorial sulfinyl group. Consistent with this, they undergo only a 0.44 ppm ASIS compared to 0.60 ppm for their equatorial counterparts. Had the sulfinyl oxygen been axial, the ASIS differences between protons should have been less pronounced.

In addition, the protons of the presumed axial 3-methyl group of **3** appear upfield ($\delta$ 1.47) compared to the equatorial methyl protons in **2** ($\delta$ 1.65). Since the sulfinyl bond shields groups which lie directly behind it along the S–O axis,[10b] this relative order of shifts agrees with the configurational assignments made to **2** and **3** with both molecules existing with the sulfinyl group predominantly equatorial.

Finally, an analysis of the NMR spectra of **2** and **3** measured in the presence of lanthanide chemical shift reagents supports the above assignments and not the reverse.[22]

**Equilibration of 2 and 3.** Sulfoxides **2** and **3** were equilibrated in chloroform and in dioxane by adding small amounts of hydrochloric acid to the solutions.[26,27] In chloroform the equilibrium ratio of **2** to **3** was 26:74; in dioxane the ratio was 29:71.

Thermal equilibration of **2** and **3** proceeded very slowly at 183 °C; e.g., after 1.4 h **3** did not form any detectable amount of **2.** Decomposition prevented measurements at higher temperature. These results contrast sharply with those obtained by Johnson[25] for the isomeric 3-*tert*-butylthietane 1-oxides which equilbrated in 15 min at 170–175 °C to a 85:15 cis/trans mixture;[27] the hydrochloric acid equilibration at 25 °C also gave this ratio. The integrated rate equation for the interconversion of **2** and **3** is shown by eq 1, where $k_1$ and $k_2$ are the rate constants for the forward and reverse reactions, $K$ is the equilibrium constant, and the quantities in brackets are the concentrations of **2** and **3** at times 0 and $t$. Using a value of $K$ based on the HCl-induced equilibrations and the concentrations of **2** and **3** after short periods of heating and before decomposition was judged serious, values of $k_1 + k_2 = 0.35 \times 10^{-5}$ s$^{-1}$ at 164 °C and $1.8 \times 10^{-4}$ s$^{-1}$ at 201 °C were obtained. Extrapolation of the 164 °C value to 200 °C, using a fivefold rate increase per 20 °C as found by Mislow and coworkers[28] for acyclic sulfoxides, gave $8 \times 10^{-5}$ s$^{-1}$. Mislow obtained constants of a similar magnitude: e.g., $1.4 \times 10^{-5}$ s$^{-1}$ for the racemization of phenyl *p*-tolyl sulfoxide at 200 °C and $1.2 \times 10^{-5}$ s$^{-1}$ for 1-adamantyl methyl sulfoxide at 210 °C. Our approximate approach to $k_1 + k_2$ suggests that sulfoxides **2** and **3** are similar to the various acyclic sulfoxides with respect to the rates of thermally induced pyramidal inversion at sulfur. The facile isomerization of 3-*tert*-butylthietane 1-oxide is puzzling and resembles the benzylic and allylic sulfoxide cases, where processes other than pyramidal inversion are

believed to be the cause of racemization.[29,30]

$$\ln \frac{[2]K - [3]}{[2^0]K - [3^0]} = -(k_1 + k_2)t \quad (1)$$

**Oxidation of 1 to 2 and 3.** Johnson and co-workers have studied the stereochemistry of the oxidation of various cyclic sulfides, including 3-substituted thietanes.[15,23] We used hydrogen peroxide and sodium hypochlorite as oxidants to prepare sulfoxides **2** and **3** from thietane **1**. Hydrogen peroxide yielded 66% of the thermodynamically most stable isomer, **3**, compared to 34% of **2**, but sodium hypochlorite gave 39% of **3** and 48% of **2** together with 13% of sulfone **18**. If thietane **1** exists principally in the folded conformation with the methyl axial, an assumption based on the smaller $\Delta G$ value for a methyl compared to a phenyl in cyclohexane systems[31] and on the broadening of the axial methyl proton NMR signal, then the peroxide appears to approach the sulfur atom preferentially along the least sterically hindered equatorial direction (steric approach control[15]). A more hindered axial approach involving the less likely conformation of **1** would also yield **3**, but if this argument is correct such a path should be of minor importance. To be self consistent, this description of the oxidation process then requires formation of **2** from the less stable conformer of **1** also by equatorial approach of the oxidant.

An explanation accounting for the greater amount of **2** compared to **3** formed when sodium hypochlorite is the oxidant follows similar lines.[15,23] A chlorosulfonium ion, $R_2SCl^+$, could be formed by equatorial attack of positive halogen on the preferred conformation of **1**. Sulfoxide **2** would result when chloride ion is displaced by an oxygen nucleophile such as water with inversion of configuration.[5] Since the reaction mechanism is not known with certainty, other speculative explanations are possible. The description just given has the virtue of being consistent with our interpretation of the peroxide oxidation results.

Johnson and co-workers found that hydrogen peroxide oxidation of 3-substituted thietanes gave predominantly the trans sulfoxides (axial oxygen and equatorial 3 substituent) rather than the thermodynamically more stable cis isomers (both substituents equatorial).[15] Apparently the 3-methyl substituent in **1** reverses the ease of approach to the diastereotopic faces of the sulfur atom relative to the 3-H in Johnson's thietanes.

**Synthesis and Hydrolysis of Methoxysulfonium Salts 4 and 5.** O-Methylation of sulfoxides **2** and **3** using trimethyloxonium tetrafluoroborate gave analytically pure samples of methoxysulfonium salts of retained configuration: **2** gave **4**, and **3** gave **5**. Alkaline hydrolysis of each salt produced sulfoxide with predominant inversion of configuration; some retention was always observed. Johnson has proposed that retention occurs by a competing $S_N2$ displacement on the alkoxy carbon with consequent C–O bond cleavage.[32] This proposal is supported by $^{18}O$ labeling studies.[33] Pseudorotation at sulfur, which might lead to overall retention of configuration, is thought not to occur.[34]

Solutions of the pure salts, either **4** or **5**, in tetramethylene sulfone (about 2 mL) were injected into a large volume (50–100 mL) of vigorously stirred, standardized sodium hydroxide solution which contained, whenever possible, a large stoichiometric excess of base. The amount of sulfoxide with retained configuration at sulfur increased monotonically with increasing base concentration to reach about 8% content at the highest base concentration used (4.6 N). Hydrolysis of the salts in pure water gave only the sulfoxide with inverted configuration. These results suggest that the sulfoxides with retained configurations arise from an attack of hydroxide ion on the *O*-methyl carbon atom. Pseudorotation of the tetracoordinate intermediate to give some sulfoxide with retained configuration would not be expected to show a dependence on the base concentration.

An analysis is shown for **5** in Scheme I; an analogous analysis is applicable for salt **4**. The rate expressions for this system, assumed to be those for typical second-order rate processes with a first-order dependence upon the salt concentration, the hydroxide ion concentration, and the water concentration, could be solved under the assumptions that the hydroxide ion concentration remained approximately constant during reaction (this was not strictly true for the second point, equivalent to a 0.0419 N NaOH solution, where the hydroxide ion concentration dropped about 35% in value) and that the rate constant for the attack of water on the *O*-methyl carbon was small enough to be neglected, that is, set equal to 0 inasmuch as no retention of configuration was observed in pure water. Solution of these equations showed that a plot of [sulfoxide, inverted]/[sulfoxide, retained] vs. $[H_2O]/[OH^-]$ should yield a straight line with a slope equal to $k_{S,H_2O}/k_{C,OH}$ and an intercept equal to $k_{S,OH}/k_{C,OH}$, where the $k$'s are the second-order rate constants as shown in Scheme I. Good least-squares regression lines were obtained for both methoxysulfonium salts. The relative rate constants for **5** are summarized in Scheme I with $k_{C,OH} = 1$. The values obtained for **4** are $k_{C,H_2O} = 0$, $k_{C,OH} = 1$, $k_{S,H_2O} = 0.116$, and $k_{S,OH} = 10.4$.

**Mass Spectra of 1, 2, 3, and 18.** Fragmentation patterns elucidating the mass spectra of **1, 2, 3,** and **18** were proposed and corroborated by a comparison with the spectra of 2,2,4,4-tetradeuterated derivatives (**1**-*d*, **2**-*d*, **3**-*d*, and **18**-*d*).

Thietane **1** gave a molecular ion at *m/e* 164 (*m/e* 168 for **1**-*d*), a base peak at *m/e* 118 by loss of $CH_2S$ (*m/e* 120 by loss of $CD_2S$ for **1**-*d*), and a peak at *m/e* 103 by further loss of $CH_3$ (*m/e* 105 for **1**-*d*).

Sulfone **18** exhibited a fragmentation pattern similar to that of thietane **1**, except that the parent ion at *m/e* 196 lost $CH_2SO_2$ and $CH_3SO_2$ fragments ($CD_2SO_2$ and $CD_3SO_2$ for **18**-*d*) to give ions at *m/e* 118 and 117 (*m/e* 120 and 118 for **18**-*d*). Furthermore, loss of $HSO_2$ from **18** ocurred to give an ion at *m/e* 131 (*m/e* 135 for **18**-*d*); presumably the proton was abstracted from the 3-methyl group.

The fragmentation patterns of sulfoxides **2** and **3** were not distinguishable from one another. Apparently the molecular ions are equivalent. The patterns do differ somewhat from those observed for **1** and **18**. Loss of HSO gave a base peak at *m/e* 131 (*m/e* 134 for **2**-*d* and **3**-*d*) in contrast to the base peak at *m/e* 118 common to both **1** and **18** due to the loss of $CH_2S$ and $CH_2SO_2$, respectively, but ions at *m/e* 118, 117, 115, 103, and 91 were found in common with **1** and **18**, although with different intensities. Neither **2** nor **3** appeared to abstract a proton from the 3-methyl as did sulfone **18**.

***N*-Tosyl-3-methyl-3-phenylthietane Sulfilimines 6 and 7.** Sulfilimines **6** and **7**, prepared from Chloramine-T in the usual way, were contaminated by the corresponding sulfoxides.[35] This is not uncommon, but results from water present in the solvent or in the usual commercial Chloramine-T which is a trihydrate. To avoid this diversion of the starting thietane, the water was removed from a dimethylformamide (DMF) solution of Chloramine-T by adding chlorobenzene followed by distillation under vacuum until DMF was the only component in the distillate. The residual bright greenish-yellow solution of the haloamide salt, judged to be an essentially anhydrous solution of Chloramine-T in DMF, had to be used within a few days of its preparation since it lost strength rather rapidly on storage. However, the slight amount of precipitate (assumed to be sodium chloride) that formed during its preparation implied that its formation was not accompanied by extensive decomposition.

The reaction of this solution with sulfides gave a dramatic

**Table II. *N*-Tosylsulfilimines**

| compd | registry no. | sulfide precursor[l] | yield,[a] % | mp, °C | % isomer distribution[b] |
|---|---|---|---|---|---|
| **20** | 53799-67-0 | butyl methyl sulfide (**19**) | 78,[c] 38,[d] 0[e] | 89–90<br>89–90.5[f] | |
| **22** | 10330-18-4 | ethyl phenyl sulfide (**21**) | 92,[c] 98,[d] 60[e] | 98–99<br>97–98[g] | |
| **6** | 66810-14-8 | 3-methyl-3-phenythietane (**1**) | 95,[c] 74[d] | 154–155 | 54.5 ± 2.5[h] |
| **7** | 66810-15-9 | | | 114–115 | 45.5 ± 2.5[i] |
| **23** | 66810-16-0 | 3-methyl-3-(*p*-bromophenyl)thietane (**11**) | 98[c] | 155.5–156.5 | 52.6 ± 0.5[h] |
| **24** | 66810-17-1 | | | 159.5–160.5 | 47.4 ± 0.5[i] |
| **25** | 66810-18-2 | 3-isopropyl-3-phenylthietane (**10**) | 100[c] | | 42.7 ± 1.2 |
| **26** | 66810-19-3 | | | | 57.3 ± 1.2 |
| **27** | 66810-20-6 | 3-methyl-3-nitrothietane (**14**) | 93[c] | | 64.5 ± 1.2[j] |
| **28** | 66810-21-7 | | | | 34.6 ± 1.2[k] |

[a] Isolated, base-washed product. [b] Determined by NMR. [c] Anhydrous Chloramine-T in DMF. [d] Chloramine-T trihydrate in DMF. [e] Chloramine-T trihydrate in pyridine. [f] M. A. McCall, D. S. Tarbell, and M. A. Harill, *J. Am. Chem. Soc.*, **73**, 4476 (1951). [g] K. Tsujihara, N. Furakwa, and S. Oae, *Bull. Chem. Soc. Jpn.*, **43**, 2153 (1970). [h] Aryl group and nitrogen are cis. [i] Aryl group and nitrogen are trans. [j] Nitro group and nitrogen are cis. [k] Nitro group and nitrogen are trans. [l] Registry no.: **19**, 628-95-5; **21**, 622-38-8.

increase in the yields of the crude isolated sulfilimines, formed practically quantitatively in many cases. The results are summarized in Table II. Even methyl butyl sulfide gave a 78% yield compared to 38% for its reaction with the Chloramine-T trihydrate in DMf. The data of Table II reveal the potential synthetic utility of the "anhydrous" reagent for the preparation of *N*-tosylsulfilimines from sulfides.[36,37]

*N*-Tosylsulfilimine pairs **6** and **7** and **23** and **24** were separated by tedious column chromatography on silica gel and then characterized by spectral and elemental analyses. Stereochemical assignments to **6** and **7** were made in the same way as for sulfoxides **2** and **3**. That is, **6** gave one methyl-coupled, broadened half-spectrum, the lower half in contrast to the sulfoxides, for the ring hydrogen absorptions, but **7** in benzene gave two sharp symmetrical halves. Thus, **6** and **7** have the configurations shown by the stereoformulas. Similar considerations permitted configurational assignments to be made to sulfilimines **23** and **24**, the *p*-bromophenyl group and nitrogen are cis in **23** and trans in **24**. Sulfilimines **6** and **23**, as well as sulfoxide **3**, all of the same configuration, migrated more rapidly over silica gel than did their corresponding isomers. Sulfilimines prepared from **10** and from **14** were not separated, although their NMR spectra (as mixed isomers) were entirely consistent with their proposed composition. NMR-based structural assignments to isomers **27** and **28** were accomplished by noting that the methyl signal of one of the isomers in the mixture was about twice as broad as the other methyl signal assigned to the other isomer. Therefore, the predominant isomer with the broadened methyl signal has the nitro group and nitrogen cis.

Sulfilimines **6** and **7** were oxidized to the corresponding sulfoximines with sodium permanganate, a reaction known to proceed with retention of configuration at the sulfur atom.[38,39]

**Silver Complexes of Sulfilimines.** The separation of the sulfilimines **6** and **7** was greatly facilitated by the discovery that **6** formed a slightly soluble molecular complex with silver nitrate while **7** remained in the supernatant solution. When a solution of sulfilimines **6** and **7** in a chloroform–benzene mixture was stirred with solid silver nitrate, a fine precipitate was deposited. Examination of the supernatant solution by NMR spectroscopy showed that it now contained isomer **7** in greater than 93% purity. Isomer **7** could be regenerated readily from the filtered solution by treatment with aqueous sodium chloride. A similar treatment of the insoluble precipitate gave **6**. Recrystallization of the recovered sulfilimines gave the pure isomers. However, isomer **6**, even after several recrystallizations, was unsuitable as the starting material for the thermal equilibrations described below because it decomposed on heating at a rate considerably faster than material which had not been treated with silver nitrate. Traces of silver nitrate in the sulfilimine probably caused this acceleration. Sufficient quantities of isomer **6** could be obtained free of **7** by crystallization without using the silver nitrate treatment. Isomer **7** did not show any difference in behavior dependent on whether the substance was obtained as above or by chromotography.

Attempts to crystallize **6**·$AgNO_3$ from methanol–toluene mixtures deposited crystals which at times were free of silver. This might be expected in relatively weak complexes. An infrared spectrum of **6**·$AgNO_3$, mechanically separated from the coarse silver nitrate crystals, was similar to the spectrum of the free sulfilimine **6**, but the strong S=N absorption[40] present at 970 $cm^{-1}$ in **6** now appeared at 933 $cm^{-1}$. The material melted at 153–154 °C with strong darkening and evolution of brown fumes; the mp of **6** is 154–155 °C.

In order to circumvent these difficulties and still obtain additional data, *S*-ethyl-*S*-phenyl-*N*-(*p*-toluenesulfonyl)-sulfilimine (**22**) was chosen to serve as a model for the sulfilimine–silver nitrate adducts. The adduct of **22** and silver nitrate (**22**·$AgNO_3$) was somewhat more soluble than **6**·$AgNO_3$, and the formation of the complex was apparently much faster than its rate of crystallization, a fact which permitted separation of unchanged silver nitrate prior to the isolation of the adduct. Analysis (C,H,N) gave values agreeing very closely with a 1:1 ratio of **22** to silver nitrate. The melting point of **22**·$AgNO_3$ (130–131 °C) was quite different from the melting point of **22** (98–99 °C) or of silver nitrate (212 °C). The infrared spectrum of **22**·$AgNO_3$ showed that the S=N band was displaced from 972 $cm^{-1}$ in **22** to 906 $cm^{-1}$ in the adduct, although the rest of the spectrum remained similar to that of the free sulfilimine. The NMR spectrum of the complex showed striking differences from that of the free sulfilimine. Thus, the absorptions of **22**·$AgNO_3$ were shifted downfield with respect to the absorptions of **22**; the greatest effect was observed for the aromatic protons [$\delta$(**22**·$AgNO_3$) − $\delta$(**22**) = 0.27] and for the methylene group adjacent to the sulfur atom [$\delta$(**22**·$AgNO_3$) − $\delta$(**22**) = 0.38]. In addition, the methylene quartet of **22** now appeared as a multiplet, an indication that the accidental magnetic equivalence of the two diastereotopic protons had been removed. This latter effect could be greatly enhanced by the successive addition of benzene to the sample; the multiplet was finally separated into two distinct overlapping octets at $\delta$ 2.99 and at 3.17. Kucsman and co-workers[41] noted that benzene alone did not remove the accidental degeneracy of the diastereotopic methylene protons of **22**, an

observation consistent with our own observations.

It was quite surprising to realize that *N*-tosylsulfilimines formed adducts with silver nitrate because at the time there were no published reports of any metal–sulfilimine complexes. Examination of the NMR spectra of solutions of *N*-tosylsulfilimines and a lanthanide shift reagent led Nielsen and Kjaer[42] to conclude that no specific association existed between the nitrogen atom of the *N*-tosylsulfilimine and the lanthanide. However, complexes of palladium(II) and platinum(II) with *S,S*-dimethyl-*N*-benzoylsulfilimine (**29**) have been reported recently.[43] These authors concluded that the metal atom was coordinated to the nitrogen atom because the infrared frequency of the C=O bond was shifted to higher frequencies upon complexation with the metal. Unfortunately, these authors did not include a consideration of the S=N bond frequencies in their reports.

The infrared spectra of the adducts of *N*-tosylsulfilimines with silver(I) suggested that the metal atom in these compounds was also associated with the nitrogen atom. The shift of the S=N frequency to lower values in these adducts was analogous to the shifts observed in the sulfoxide–metal complexes bonded through the sulfinyl oxygen.[44,45] The NMR absorptions of **22**·$AgNO_3$ and the observed benzene-induced shifts in this compound also support this bonding situation in which the sulfur atom becomes more positive because of the complexation of the metal through the nitrogen atom.

Signals from both complexed and uncomplexed species of **29** were observed in the NMR spectra of the palladium complex.[43] This was not observed in the case of **22**·$AgNO_3$. These *N*-tosylsulfilimine complexes with the silver ion may probably best be regarded as the acid–base adducts of the "soft" Ag(I) acid with the substrate.[46]

**Equilibration of Sulfilimines 6 and 7.** Sulfilimines **6** and **7** could be thermally equilibrated. Samples of either isomer which had been heated longer than 45 min at 165 °C gave similar isomer distributions which were approximately independent of longer heating times. A competing decomposition, the extent of which varied between different runs, was a complicating factor. This decomposition introduced considerable scatter in the amount of sulfilimines not decomposed after each run and also affected the observed distributions of **6** and **7** in the samples. A consideration of the isomerization–decomposition process suggested that the sulfilimines isomerizations could be formally represented by Scheme II, which is mathematically equivalent to the two simultaneous first-order differential equations 2 and 3. The solution of this system of equations to give the rate constants $k_1'$ and $k_2'$ together with the equilibrium constant $K_{eq}' = k_1'/k_2'$ was obtained. The rate constants were $k_1' = (3.2 \pm 0.3) \times 10^{-4}$ s$^{-1}$ and $k_2' = (4.8 \pm 0.2) \times 10^{-4}$ s$^{-1}$ for the thermal isomerization of sulfilimines **6** and **7** at 165 °C. These values give $K_{eq}' = k_1'/k_2' = 0.667$; the equilibrium distribution of **6/7** at 165 °C is 60%: 40% with $\Delta G°_{165} = -0.353$ kcal/mol. The relative distributions of **6** and **7** (normalized to 100%) observed after equilibration times greater than 45 min were close to the equilibrium distributions of the isomers predicted by the kinetic data.

$$d[6]/dt = -(k_1' + k_3')[6] + k_2'[7] \quad (2)$$

$$d[7]/dt = k_1'[6] - (k_2' + k_4')[7] \quad (3)$$

Sulfilimine isomer **6** is configurationally analogous to the sulfoxide isomer **3**, and the equilibrium distributions of the sulfoxide and the sulfilimine isomers are consistent with a lower interaction between the 3 substituents of the thietane ring and the *N*-tosylimino group than between the same 3 substituents and the sulfinyl oxygen of the sulfoxides **2** and **3**. Experimental data on the conformational energies between the sulfinyl oxygen and the *N*-tosylimino group in the thiane system support this interpretation.[47]

The kinetics of the thermal isomerization of some optically active *N*-tosylsulfilimines[48] and *N*-acylsulfilimines[49] have been studied by other workers, who have proposed a pyramidal inversion mechanism for this process. The kinetic data obtained around 100 °C for *S*-methyl-*S*-(*p*-chlorophenyl)-*N*-(*p*-toluenesulfonyl)sulfilimine (**30**) gave a racemization rate constant of $2.2 \times 10^{-2}$ s$^{-1}$ at 165 °C from a plot of ln $k$ vs. $1/T$.[48] Comparison of this value with the analogous isomerization rates of **6** and **7**, equivalent to $k_1' + k_2' = 8.0 \times 10^{-4}$ s$^{-1}$, showed that the racemization of **30** was about 30 times faster. This difference may result from the aromatic *S*-(*p*-chlorophenyl) substituent of **30** absent in the thietane derivatives rather than CSC bond angle strain in the thietanes since the racemization rate of an *S,S*-dialkyl-*N*-acylsulfilimine was found to be much lower than the rates for **6, 7,** and **30**.[49]

## Experimental Section

**General.** Melting points were determined on a Hoover Uni-Melt capillary melting point apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 337 grating spectrometer. Nuclear magnetic resonance spectra were determined on a Varian A-60 or a Jeolco HM-100 spectrometer with an internal tetramethylsilane standard. Coupling constants are in hertz and are apparent rather than true calculated values. Mass spectra were determined on a Hitachi Perkin-Elmer Model RMU-6E spectrometer. Microanalyses were carried out on an F and M Model 185 C,H,N analyzer or by Schwarzkopf Laboratories, Woodside, N.Y.[50] Thin-layer chromatography was performed on Brinkmann Polygram Sil S-HR/$UV_{254}$ silica gel plates. Column chromatography was performed using Baker 60–200 mesh silical gel.

**Thietanes.** The preparation of **1** is given as representative of the other thietane syntheses, and the oxidation of **1** is given as representative of the sulfone preparations. However, hydrogen peroxide was used as the oxidant in the preparation of the sulfone derived from **13**. Water was removed in several cases from a $Me_2SO$–sodium sulfide nonahydrate solution by the addition of toluene followed by distillation of a toluene–water azeotrope from the mixture. All thietanes exhibited a characteristic infrared absorption band[18] at ca. 1175 cm$^{-1}$.

**3-Methyl-3-phenylthietane (1).** Freshly ground sodium sulfide nonahydrate (40.0 g, 0.17 mol) was added in one portion to crude 2-methyl-2-phenyltrimethylene bis(benzenesulfonate)[51] (205 g, 0.46 mol) in $Me_2SO$ (400 mL). The mixture was stirred at ca. 90 °C for 2 h. Occasionally, 0.3-mL aliquots were removed and diluted with water. The absence of a crystalline precipitate after 2 h was taken to mean completion of the reaction. The cooled reaction mixture was poured into water and extracted with pentane, and the combined organic layers were washed with water, dried ($MgSO_4$), filtered, concentrated in vacuo, and distilled through a 15 cm Vigreux column to give **1**, 37.2 g. GLC indicated it to be 98% pure. Similar preparations gave yields from 49 to 64%.

**Bis(benzenesulfonate) esters** of propane-1,3-diols were prepared by the addition of benzenesulfonyl chloride (2.2–2.4 mol) to the diols (1.0 mol) dissolved in pyridine at 15 °C or lower. The mixtures were allowed to stand overnight at room temperature, and then they were poured into an ice–water mixture. The crude esters were removed by filtration and were converted directly to the thietane or else purified by recrystallization from a solvent such as carbon tetrachloride.

**Propane-1,3-diols** used to prepare thietanes **10, 11,** and **16** were new compounds. 2-(*p*-Bromophenyl)-2-methylpropane-1,3-diol was prepared via the Tollens condensation[52] from *p*-bromohydratropaldehyde, formalin, and sodium hydroxide in aqueous ethanol in 77% yield: mp 86–87 °C; NMR ($CDCl_3$) $\delta$ 1.17 (s, 3 H, $CH_3$), 3.23 (s, 2 H, HO), 3.69 (q, 4 H, $J$ = 11.0 Hz, $CH_2$), 7.3 (m, 4 H, $C_6H_4$). 2-Phenyl-2-isopropylpropane-1,3-diol was prepared by the lithium aluminum hydride reduction of the mixed ethyl and isopropyl esters of 2-isopropyl-2-phenylmalonic acid prepared by the treatment of diethyl phenylmalonate with 2-bromopropane and sodium in 2-propanol: overall yield, 21%, mp 56–57 °C; NMR ($CCl_4$) $\delta$ 0.70 (d, 6 H, $J$ = 7.0 Hz, $CH_3$), 1.85 (heptet, 1 H, $J$ = 7.0 Hz, CH), 3.83 (q, 4 H, $J$ = 11.0 Hz, $CH_2$), 3.9 (s, 2 H, HO), 7.20 (s, 5 H, $C_6H_5$). 3-Methylcyclohexane-1,1-dimethanol was prepared via the Tollens condensation of 3-methycyclohexane-1-carboxaldehyde and formaldehyde in 25% yield: mp 72–73 °C; NMR ($CDCl_3$) $\delta$ 0.25–1.95 (m, 12 H, $C_6H_9CH_3$), 3.44 (s, 2 H, $CH_2O$), 3.73 (s, 2 H, $CH_2O$), 3.91 (s, 2 H, HO). The aldehyde was prepared via the Darzens glycidic ester condensation of 3-methycylohexanone and isoproypl chloroacetate and used without characterization.[52]

**3-Methyl-3-phenylthietane 1,1-Dioxide (18).** A 10% aqueous solution of sodium permanganate was added in small portions to a vigorously stirred mixture of thietane **1** (1.5 g, 9.1 mmol), acetic acid (1 mL), and water (5 mL). When the purple color persisted for at least 15 min, the reaction mixture was diluted with water and the excess permanganate and manganese dioxide were discharged with sodium bisulfite. The solids were collected by filtration and extracted with chloroform. The extract was dried over magnesium sulfate, filtered, and concentrated in vacuo to give **18**, which was recrystallized from benzene–cyclohexane: 61% yield; mp 54–55 °C; NMR ($CDCl_3$) $\delta$ 1.78 (s, 3 H, C–$CH_3$), 4.09 (d, 2 H, $J$ = 12.5 Hz, S–CH), 4.48 (d, 2 H, $J$ = 12.5 Hz, S–CH), 7.26 (m, 5 H, $C_6H_5$).

**Reduction of 18 to 1.** Lithium aluminum hydride (1.70 g, 0.0712 mol) in ether (50 mL) was added with stirring over 1 h to sulfone **18** (10.80 g, 0.0550 mol) in ether (100 mL)–benzene (25 mL). After 2 h, water (3 mL), 15% sodium hydroxide (3 mL), and water (9 mL) were added in that order. The solids were filtered and washed with ether. Concentration of the filtrate and ether washings gave an oil which upon distillation yielded thietane **1** (6.44 g, 71% yield), bp 120–122 °C (12 mm).

**3-Methyl-3-phenylthietane 1-Oxides 2 and 3.** Hydrogen peroxide (30%; 9.5 mL, 0.105 mol) in acetic acid (40 mL) was added to a stirred ice-cold solution of thietane **1** in acetic acid (60 mL). After 0.5 h at 0 °C and 2 h at room temperature, the mixture was concentrated in vacuo to give **2** and **3**. Integration of the two NMR methyl signals at $\delta$ 1.61 (34.0%) and 1.46 (66.0%) gave the ratio of **2/3**. Distillation gave a mixture of **2** and **3** unchanged in isomer ratio: 15.6 g (87% yield); bp 125–132 °C (0.2 mm). A carbon tetrachloride solution of this mixture was treated with heptane to yield crude **2**, which was recrystallized from cyclohexane to give 3.3 g: mp 88–89 °C; IR (KBr) 1058 $cm^{-1}$ (SO); NMR ($CDCl_3$) $\delta$ 1.65 (s, 3 H, C–$CH_3$), 3.33 (d of t, 2 H, $J$ = 12.5 Hz, S–$CH_a$), 4.08 (d ot t, 2 H, $J$ = 12.5 Hz, S–$CH_e$), 7.07–7.62 (m, 5H, $C_6H_5$).

The residue (12.3 g) was chromatographed on 250 g of alumina to give crude **3**, which was furhter purified by vacuum distillation to yield 5.4 g: bp 117–120 °C (0.2 mm); IR (neat) 1071 $cm^{-1}$ (SO); NMR ($CDCl_3$) $\delta$ 1.47 (s, 3 H, C–$CH_3$), 3.43 (broad d, 2 H, $J$ = 11.0 Hz, S–$CH_a$), 3.86 (sharp d of t, 2 H, $J$ = 11.0 Hz, S–$CH_e$), 7.00–7.62 (m, 5 H, $C_6H_5$) Irradiation at $\delta$ 1.47 caused the peak at $\delta$ 3.43 to sharpen and resemble the $\delta$ 3.86 resonance.

**Reaction of 1 with Sodium Hypochlorite.** Thietane **1** (2.46 g, 15.0 mmol) was added to an aqueous solution[53] of sodium hypochlorite (33.0 mL, 16.7 mmol) at ice-bath temperature. After 1 h, the mixture was extracted with methylene chloride several times to give an oil (2.65 g) consisting of **2** (47.8%), **3** (38.7%), and **18** (13.6%) as determined by NMR spectroscopy.

**Thermal Equilibration of Sulfoxides 2 and 3.** Individual samples of **2** and **3** in NMR tubes under nitrogen were heated in the vapors of boiling mesitylene (164 °C), *p*-bromotoluene (183 °C), acetophenone (201 °C), and *p*-methylacetophenone (223 °C). Sulfoxide **2** gave 7% of **3** after 8.0 h at 164 °C, 10% of **3** after 0.5 h at 201 °C (slight decomposition), and extensive decomposition after 0.25 h at 223 °C. Sulfoxide **3** gave no appreciable **2** after 1.4 h at 183 °C, 7% of **2** after 0.5 h at 201 °C (negligible decomposition), and complete decomposition after 0.5 h at 223 °C.

**Chemical Equilibration of Sulfoxides 2 and 3.** Four samples each of **2** and **3** (0.2–0.3 g) in a mixture of $CDCl_3$ (0.5 mL) and 37% hydrochloric acid (5 $\mu$L) were allowed to stand for 48 h. The isomer distribution was measured by NMR spectroscopy: **2**, 24.9 ± 0.5%; **3**, 75.1 ± 0.5%. Analysis of the combined equilibrated mixtures by TLC ($Et_2O$) gave spots for **2** and **3** only.

Two samples of **2** and **3** were also equilibrated in dioxane containing hydrochloric acid. The resulting equilibrium mixtures were analyzed by NMR spectroscopy and TLC: **2**, 28.9 ± 0.7%; **3**, 71.2 ± 1.0%. The validity of NMR analysis by integration of the methyl protons was checked using known mixtures of **2** and **3**.

**1-Methoxy-3-methyl-3-phenylthietanium tetrafluoroborates 4 and 5** were prepared by treating sulfoxides **2** and **3** separately with a slight excess of trimethyloxonium tetrafluoroborate in methylene chloride. The mixtures were filtered, and ether was added to precipitate **4** and **5**, which then were recrystallized from chloroform or chloroform–carbon tetrachloride. Compound **4**: mp 113–115 °C; NMR ($CDCl_3$) $\delta$ 1.81 (s, 3 H, C–$CH_3$), 4.19 (s, O–$CH_3$), 4.19 and 4.78 (broad d of d, 4 H, $J$ = 14.0 Hz, $CH_2S$), 7.31 (m, 5 H, $C_6H_5$). Compound **5**: mp 80–82 °C; NMR ($CDCl_3$) $\delta$ 1.74 (s, 3 H, C–$CH_3$), 4.23 (s, O–$CH_3$), 4.38 and 4.80 (broad d of d, 4 H, $J$ = 13.4 Hz, $CH_2S$), 7.34 (m, 5 H, $C_6H_5$).

**Reaction of 4 and 5 with Sodium Hydroxide.** Aliquots (2.0 mL) of a solution (15.0 mL) of **4** (3.100 g, 10.99 mmol) in tetramethylene sulfone (sulfolane) were added in one portion to vigorously stirred aqueous solutions of sodium hydroxide of known normality. Five solutions of 50 mL each varying in normality from 0.307 to 4.58 N, one 100-mL solution of 0.0419 N, and pure water (100 mL) were used. After 1 h, the mixtures were extracted with methylene chloride to yield sulfoxides **2** and **3**. NMR analysis by integration of the 3-methyl signals gave the ratio of **2/3**. A least-squares regression analysis of [**3**]/[**12**] vs. $[H_2O]/[OH^-]$ gave a straight line with a slope of 0.16 ± 0.008, an intercept of 10.4 ± 1.1, and a multiple correlation coefficient of 0.993. In the same way, a regression line was obtained for isomer **5** with a slope of 0.075 ± 0.008, an intercept of 11.6 ± 1.1, and a multiple correlation coefficient of 0.982.

**2,2,4,4-Tetradeuterio-3-methyl-3-phenylthietane 1,1-Dioxide (18-*d*).** Sulfone **18** (12 g, 0.06 mol) and a solution prepared from sodium (0.23 g, 0.01 g-atom) in deuterium oxide (5 mL, 0.28 mol) were mixed and heated with stirring on a steam bath for 6 h. The mixture was concentrated in vacuo, a fresh portion of deuterium oxide (5 mL) was added, and the mixture was heated as before. This exchange process was repeated six times. Finally, the residue was extracted with carbon tetrachloride to yield, after recrystallization from benzene–cyclohexane, **18-*d*** (8.0 g).

A sublimed portion (65 °C, 0.1 mm) gave no depression in melting point with **18**. NMR ($CDCl_3$) $\delta$ 1.78 (s, 3 H, $CH_3$) and 7.29 (m 5 H, $C_6H_5$). Mass spectrometry indicated **18-*d*** to be 94.7% $d_4$ and 5.3% $d_3$.

**2,2,3,4-Tetradeuterio-3-methyl-3-phenylthietane (1-*d*)** was prepared by the reduction of **18-*d*** using lithium aluminum hydride as **18** was reduced to **1**: NMR ($CDCl_3$) $\delta$ 1.72 (s, 3 H, $CH_3$), 7.18 (m, 5 H, $C_6H_5$). Mass spectrometry indicated **1-*d*** to be 94.37% $d_4$ and 5.7% $d_3$.

**2,2,4,4-Tetradeuterio-3-methyl-3-phenylthietane 1-oxides 2-*d* and 3-*d*** were prepared by oxidation of **1-*d*** using hydrogen peroxide as **1** was oxidized to a mixture of **2** and **3**. A mixture melting point of **2** with **2-*d*** and of **3** with **3-*d*** gave no depression. **2-*d***: NMR ($CDCl_3$) $\delta$ 1.64 (s, 3 H, $CH_3$), 7.30 (m, 5 H, $C_6H_5$). **3-*d***: NMR ($CDCl_3$) $\delta$ 1.43 (s, 3 H, $CH_3$), 7.19 (m, 5H, $C_6H_5$). Sulfoxide **2-*d*** contained at most 4.4% of **3-*d***; **3-*d*** contained at most 2.5% of **2-*d***.

**3-Methyl-3-phenylthietane-*N*-(*p*-toluenesulfonyl)sulfilimines 6 and 7.** Thietane **1** (8.20 g, 0.0499 mol) was added in one portion to an anhydrous solution of Chloramine-T in DMF (140 mL; 0.0553 mol of $Cl^+$[53]) kept at 5 °C in an ice bath. After 30 min, the mixture was poured into water (700 mL). The solids were collected and washed with water, 10% sodium hydroxide, and water again to give **6** and **7** (15.85 g, 95% yield). NMR analysis by integration of the 3-methyl signals ($CDCl_3$–$C_6H_5$) gave 54.5 ± 2.5% of **6** and 45.5 ± 2.5% of **7**. Isomer **6** crystallized from a benzene–ether solution of the mixture: IR (KBr) 970 $cm^{-1}$ (S=N); NMR ($CDCl_3$) $\delta$ 7.34–7.94 (m, 9 H, ArH), 4.20 (broad, 2 H, $J$ = 11.0 Hz, $SCH_aH_e$), 3.81 (d, $J$ = 11.0 Hz, $SCH_aH_e$), 2.48 (s, 3 H, $ArCH_3$), 1.72 (s, 3 H, $CH_3$). Irradiation at $\delta$ 1.72 caused the $\delta$ 4.20 broad doublet to become sharp.

Isomer **7** was obtained from the residue by recrystallization from 2-propanol: IR (KBr) 990 $cm^{-1}$ (S=N); NMR ($CDCl_3$) $\delta$ 7.33–7.89 (m, 9 H, ArH), 4.14 (s, 4 H, $CH_2S$), 2.38 (s, 3 H, $ArCH_3$), 1.67 (s, 3 H, $CH_3$). In benzene the $\delta$ 4.14 singlet separated into a doublet of doublets with additional fine structure.

An anhydrous DMF solution of Chloramine T was prepared by distilling a mixture of Chloramine-T trihydrate (100 g, 0.355 mol), DMF (500 mL), and chlorobenzene (150 mL) at 12 mm. The bright green-yellow solution which remained after 350 mL of distillate (bp 45–64 °C) had been collected lost its titer slowly, so it was used within several days of preparation.[53] *The solution was considered potentially explosive and was treated as such.*

**Control Reactions for 6/7 Product Ratio.** Thietane **1** (0.669 g, 4.07 mmol) in the presence of sulfilimine **6** (0.924 g, 2.77 mmol) was converted to a mixture of **6** and **7** (2.215 g, 97% yield) by reaction with anhydrous Chloramine-T–DMF (14.5 mL, 4.73 mmol) as described above. NMR analysis gave 71.4 ± 1% of **6** and 28.6 ± 1% of **7**, compared to the values of 74% of **6** and 26% of **7** calculated on the basis of a 55:45 **6/7** product ratio.

Similar treatment of **1** (0.686 g, 4.18 mmol) and **7** (0.920 g, 2.76 mmol) with Chloramine-T–DMF (4.73 mmol) gave a mixture of **6** and **7** (2.220 g, 96% yield) consisting of 32.7 ± 1% of **6** and 67.3 ± 1% of **7**; the calculated values were 32% of **6** and 68% of **7**.

Sulfilimines **6** and **7** treated separately with an equimolar amount of anhydrous Chloramine-T–DMF were recovered without change.

**3-(*p*-Bromophenyl)-3-methylthietane-*N*-(*p*-toluenesulfonyl)sulfilimines 23 and 24** were prepared from thietane **11** in the manner described for **6** and **7** and were isolated by chromatography ($SiO_2$; $CHCl_3$–$Et_2O$). Sulfilimine **23** was recrystallized from benzene: IR (mull) 971 $cm^{-1}$ (S=N); NMR ($CDCl_3$) $\delta$ 7.11–7.92 (m, 8 H, ArH), 4.33 (broad with fine structure, 2 H, $J$ = 11.0 Hz, $SCH_aH_e$), 3.93 (sh

d with fine structure, 2 H, $J$ = 11.0 Hz, $SCH_aH_e$), 2.40 (s, 3 H, $C_6H_4CH_3$), 1.62 (broad s, 3 H, 3-$CH_3$); NMR [2:1 (v/v) $C_6H_6$–$CDCl_3$] $\delta$ 4.09 (broad d, 1 H, $J$ = 11.0 Hz, $SCH_aH_e$), 3.17 (d, $J$ = 11.0 Hz, 1 H, $SCH_aH_e$), 2.12 (s, 3 H, $C_6H_4CH_3$), 1.03 (broad s, 3 H, 3-$CH_3$). Irradiation at $\delta$ 1.62 caused the broad doublet at $\delta$ 4.33 to become sharp.

The more highly retained isomer, **24**, was recrystallized from 2-propanol–water: Ir (mull) 985 $cm^{-1}$ (S=N); NMR ($CDCl_3$) $\delta$ 7.24–7.93 (m, 8 H, ArH), 4.19 (s, 4 H, $CH_2S$), 2.40 (s, 3 H, $C_6H_4CH_3$), 1.68 (s, 3 H, 3-$CH_3$); NMR [2:1 (v/v) $C_6H_6$–$CDCl_3$] $\delta$ 3.90 (d, $J$ = 11.0 Hz, $SCH_aH_e$) 3.48 (d, $J$ = 11.0 Hz, $SCH_aH_e$), 2.12 (s, 3 H, $C_6H_4CH_3$), 1.21 (s, 3 H, 3-$CH_3$).

**3-Isopropyl-3-phenylthietane-*N*-(*p*-toluenesulfonyl)sulfilimines 25 and 26 and 3-methyl-3-nitrothietane-*N*-(*p*-toluenesulfonyl)sulfilimines 27 and 28** were prepared as descripted above using anhydrous Chloramine-T. NMR analysis of the **27–28** mixture by integration of the 3-methyl protons at $\delta$ 1.99 (width at half-height, 0.8 Hz) assigned to **28** and at $\delta$ 1.82 (width at half-height, 1.6 Hz) assigned to **27** gave the isomer distributions listed in Table II. Integration of the unassigned isopropyl methyl group signals at $\delta$ 0.82 and 0.68 ($J$ = 7 Hz) gave the isomer distribution of **25** and **26**.

**3-Methyl-3-phenylthietane-*N*-(*p*-toluenesulfonyl)sulfoximines 8 and 9,** were prepared by oxidizing sulfilimines **6** and **7**, respectively, with sodium permanqanate in aqueous acetone. Oxidation of **6** gave **8** (81% yield from benzene), mp 165–166 °C, followed by resolidification: mp 174–175 °C; NMR ($CDCl_3$) $\delta$ 1.83 (s, 3 H, 3-$CH_3$), 2.40 (s, 3H, $C_6H_4CH_3$), 4.28 and 4.98 (d of d, 4 H, $J$ = 14 Hz, $CH_2S$), 7.08–7.92 (m 9 H, ArH). Oxidation of **7** gave **9** (67% yield from aqueous MeOH): mp 190–191 °C; NMR ($CDCl_3$) $\delta$ 1.93 (s, 3 H, 3-$CH_3$), 2.43 (s, 3 H, $C_6H_4CH_3$), 4.70 (d of d, 4 H, $CH_2S$), 7.05–8.02 (m, 9 H, ArH).

***S*-Ethyl-*S*-phenyl-*N*-(*p*-toluenesulfonyl)sulfilimine–Silver Nitrate Complex (22·$AgNO_3$).** This was prepared by adding silver nitrate (6.80 g, 0.0400 mol) to *S*-ethyl-*S*-phenyl-*N*-(*p*-toluenesulfonyl)sulfilimine (6.15 g, 0.0200 mol) in benzene (30 mL)–chloroform (30 mL). The excess silver nitrate was filtered off, and the filtrate was treated with pentane to give the 22·$AgNO_3$ complex (2.00 g, 21% yield): mp 130–131 °C; IR (mull) 906 $cm^{-1}$ (S=N); NMR ($CDCl_3$) $\delta$ 1.13 (t, 3H, $J$ = 7.5 Hz, $CH_2CH_3$), 2.31 (s, 3 H, $C_6H_6CH_3$), 3.08 (m, 2 H, $CH_2S$), 6.97–7.95 (m, 9 H, ArH).

**Thermal Equilibration of Sulfilimines 6 and 7.** This was carried out at 165 °C in the same way as described for sulfoxides **2** and **3**.

**Acknowledgment.** Support by the National Science Foundation, GP 23637, is gratefully acknowledged.

**Registry No.**—**1**, 66810-25-1; **1**-*d*, 66810-22-8; **2**, 66810-23-9; **2**-*d*, 66180-24-0; **3**, 66809-92-5; **3**-*d*, 66841-99-4; **4**, 66809-94-7; **5**, 66809-96-9; **8**, 66809-97-9; **9**, 66809-98-1; **10**, 66810-26-2; **11**, 66810-27-3; **12**, 185-11-5; **13**, 66810-28-4; **14**, 66810-29-5; **15**, 66810-30-8; **16**, 66810-31-9; **17**, 66810-32-0; **18**, 66809-99-2; **18**-*d*, 66810-00-2; **22**·$AgNO_3$, 66810-58-0; 2-(*p*-bromophenyl)-2-methylpropane-1,3-diol, 66810-01-3; *p*-bromohydratropaldehyde, 40460-91-1; formalin, 50-00-0; 2-phenyl-2-isopropylpropane-1,3-diol, 66810-02-4; diethyl 2-isopropyl-2-phenylmalonate, 66810-03-5; diisopropyl 2-isopropyl-2-phenylmalonate, 66810-05-7; ethyl isopropyl 2-isopropyl-2-phenylmalonate, 66810-04-6; 3-methylcyclohexane-1,1-dimethanol, 66810-06-8; 3-methylcyclohexane-1-carboxaldehyde, 13076-16-9; 2-methyl-2-phenylpropane-1,3-diol, 24765-53-5; cyclohexande-1,1-dimethanol, 2658-60-8; 3-cyclohexene-1,1-dimethanol, 2160-94-3; 2-methyl-2-nitropropane-1,3-diol, 77-49-6; 2-methylcyclohexane-1,1-dimethanol, 66810-07-9; 4-methylcyclohexane-1,1-dimethanol, 65172-49-8; trimethyloxonium tetrafluoroborate, 420-37-1.

## References and Notes

(1) Most of this work is from the Ph.D. Thesis of M. Buza, University of New Hampshire, 1975. The mass spectral data is in part from the M.S. Thesis of M. Pazdon, University of New Hampshire, 1977.
(2) Deceased Jan. 1, 1978.
(3) M. Sander, *Chem. Rev.*, **66**, 341 (1966).
(4) N. Kharasch, *Int. J. Sulfur Chem.*, **8**, 649 (1976).
(5) L. Van Acker and M. J. O. Anteunis, *Bull. Soc. Chim. Belg.*, **86**, 299 (1977).
(6) W. O. Siegl and C. R. Johnson, *Tetrahedron*, **27**, 341 (1971).
(7) R. M. Wing, J. J. Uebel, and K. K. Andersen, *J. Am. Chem. Soc.*, **95**, 6046 (1973).
(8) C. Guimon, D. Liotard, and G. Pfister-Guillouzo, *Can. J. Chem.*, **53**, 1224 (1975).
(9) L. A. Paquette and J. P. Freeman, *J. Org. Chem.*, **35**, 2249 (1970).
(10) (a) M. S. Newman, J. R. LeBlanc, H. A. Karnes, and G. Axelrad, *J. Am. Chem. Soc.*, **86**, 868 (1964); (b) R. M. Dodson, E. H. Jancis, and G. Klose, *J. Org. Chem.*, **35**, 2520 (1970).
(11) A. Biezais and G. Bergson, *Acta Chem. Scand.*, **18**, 815 (1964).
(12) G. Optiz, H. Schempp, and H. Adolph, *Justus Liebigs Ann. Chem.*, **684**, 92 (1965).
(13) W. E. Truce and P. N. Son, *J. Org. Chem.*, **30**, 71 (1965).
(14) L. A. Paquette and M. Rosen, *J. Org. Chem.*, **33**, 3027 (1968).
(15) W. O. Siegl and C. R. Johnson, *J. Org. Chem.*, **35**, 3657 (1970).
(16) I. J. Borowitz, *J. Am. Chem. Soc.*, **86**, 1146 (1964).
(17) D. C. Dittmer and F. A. Davis, *J. Am. Chem. Soc.*, **87**, 2064 (1965).
(18) S. Searles, Jr., H. R. Hays, and E. F. Lutz, *J. Org. Chem.*, **27**, 2828 (1962).
(19) (a) W. Wucherpfenning, *Tetrahedron Lett.*, 765 (1970). (b) The terms axial and equatorial are often called pseudoaxial and pseudoequatorial in the thietane ring system.
(20) J. W. Bevan, A. C. Legon, and D. J. Millen, *J. Chem. Soc., Chem. Commun.*, 659 (1974).
(21) J. H. Barlow, C. R. Hall, D. R. Russell, and D. J. H. Smith, *J. Chem. Soc., Chem. Commun.*, 133 (1975).
(22) J. J. Uebel and D. J. H. Smith, private communication.
(23) J. J. Rigau, C. C. Bacon, and C. R. Johnson, *J. Org. Chem.*, **35**, 3655 (1970).
(24) K. K. Andersen, R. L. Caret, and I. Karup-Nielsen, *J. Am. Chem. Soc.*, **96**, 8026 (1974).
(25) C. R. Johnson and W. O. Siegl, *J. Am. Chem. Soc.*, **91**, 2796 (1969).
(26) K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **86**, 1452 (1964).
(27) S. A. Khan, T. McAllister, and H. Mackle, *J. Chem. Soc., Chem. Commun.*, 121 (1973).
(28) D. R. Rayner, A. J. Gordon, and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4854 (1968).
(29) E. G. Miller, D. R. Rayner, H. T. Thomas, and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4861 (1968).
(30) P. Bichart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4869 (1968).
(31) J. A. Hirsch, *Top. Sterochem.* **1**, Chapter 4 (1967).
(32) C. R. Johnson and D. McCants, Jr., *J. Am. Chem. Soc.*, **87**, 5404 (1965).
(33) M. Kishi and T. Komeno, *Int. J. Sulfur Chem., Part A*, **2**, 1 (1972).
(34) R. Tang and K. Mislow, *J. Am. Chem. Soc.*, **91**, 5644 (1969).
(35) F. G. Mann and W. J. Pope, *J. Chem. Soc.*, **121**, 1052 (1922).
(36) K. Tsujihara, N. Furukawa, K. Oae, and S. Oae, *Bull. Chem. Soc. Jpn.*, **42**, 2631 (1969).
(37) F. Ruff and A. Kucsman, *Acta Chim. Acad. Sci. Hung.*, **65**, 107 (1970.
(38) M. A. Sabol and K. K. Andersen, *J. Am. Chem. Soc.*, **91**, 3603 (1969).
(39) D. J. Cram, J. Day, D. R. Rayner, D. M. Von Schriltz, D. J. Duchamp, and D. C. Garwood, *J. Am. Chem. Soc.*, **92**, 7369 (1970).
(40) I. Kapovits, F. Ruff, J. Gulyas, and A. Kucsman, *Tetrahedron*, **32**, 1811 (1976).
(41) F. Ruff, A. Kucsman, I. Schuster, and I. Kapovits, *Acta Chim. Acad. Sci. Hung.*, **58**, 85 (1968).
(42) I. Karup-Nielsen and A. Kjaer, *Acta Chem. Scand.* **26**, 852 (1972).
(43) G. Matsubayashi, M. Toriuchi, and T. Tanaka, *Bull. Chem. Soc. Jpn.*, **47**, 765 (1974).
(44) D. W. Meek, W. E. Hatfield, R. S. Drago, and T. S. Piper, *Inorg. Chem.*, **3**, 1637 (1964).
(45) R. Francis and F. A. Cotton, *J. Chem. Soc.*, 2078 (1961).
(46) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).
(47) J. B. Lambert, C. E. Mixan, and D. S. Bailey, *J. Am. Chem. Soc.*, **94**, 208 (1972).
(48) N. Furukawa, K. Harada, and S. Oae, *Tetrahedron Lett.*, 1377 (1972).
(49) B. C. Menon and D. Darwish, *Tetrahedron Lett.*, 4119 (1973).
(50) All new compounds analyzed for carbon and hydrogen within 0.3% of theory.
(51) P. Mastagli, P. Lambert, and G. Francois, *Bull. Soc. Chim. Fr.*, 764 (1957).
(52) H. Krauch and W. Kunz, "Namenrektionen der Organischen Chemie", 2nd ed., Dr. Alfred Huthig Verlag GmbH., Heidelberg, 1972, pp 112, 463.
(53) Titration with potassium iodide–sodium thiosulfate (starch indicator) in dilute sulfuric acid was used to assay the reagent for positive chlorine.