showed the presence of uncomplexed starting material, **1a**. No change was observed after several hours at −78°. When warmed (−15 to 25°), the solution turned yellow and an orange precipitate was formed; no uncomplexed starting material was evident in the solution by tlc analysis. The collected, dried precipitate, which appeared during 30 min at 25°, weighed 100 mg and accounted for approximately 25% of the combined weight of the thioketal **1a** and the silver perchlorate. The precipitate (fraction A), resuspended in tetrahydrofuran, and the filtrate (fraction B) were treated separately with hydrogen sulfide in ether and the resulting silver sulfide was removed. Water was added to each of the filtrates, followed by extraction with ether. The solvents were removed from the ether-soluble portions and the residues were separated by tlc (chloroform–acetone 95:5). From the original filtrate (fraction B) unreacted starting material **1a** was obtained; no **1a** was present in the precipitate (fraction A).

The components isolated from the precipitate (fraction A) were 3-thioindole,[4] 3-thioindolyl disulfide,[4] and 1-(2′-tetrahydropyranyl)-3-thioindolyl disulfide (**6a**): mp 136–140°; nmr δ 1.5–2.1 (m, 3′–5′-H), 3.68 (m, 6′-H), 4.0 (m, 6′-H), 5.39 (m, 2′-H), 6.9–7.6 (m, 2,4–7-H); mass spectrum *m/e* (rel intensity) 464 (3), 432 (4), 348 (4), 264 (19), 149 (100), 148 (20), 117 (20), 85 (60).

Reaction of Silver Complex 2a with Methyl Iodide. To a solution of silver complex **2a** (methyl iodide was unreactive toward **1a** in the absence of silver ion) prepared in tetrahydrofuran as described above was added an excess of methyl iodide. After several hours at room temperature (at lower temperatures, no reaction occurred) a yellow precipitate of silver iodide had formed. The mixture was filtered, water was added to the filtrate, and the solution was extracted with ether. By preparative chromatography the starting thioketal (**1a**). 3-methylthioindole[9] (**7**), 1-(2′-tetrahydropyranyl)-3-(2′-tetrahydropyranylthio)indole (**8a**), and 1-(2′-tetrahydropyranyl)-3-methylthioindole (**9a**) were isolated. 3-Methylthioindole[9] (**7**) had nmr δ 2.32 (s, SMe), 7.05–7.24 (m, 2,5–7-H), 7.68 (m, 4-H), 7.9 (br, NH). 1-(2′-Tetrahydropyranyl)-3-(2′-tetrahydropyranylthio)indole (**8a**) had nmr δ 1.5–2.1 (m, 3′–5′, 3″–5″-H), 3.4–3.8 (m, 6′,6″-H), 3.9–4.2 (m, 6′,6″-H), 4.80 (m, 2′-H), 5.38 (m, 2″-H), 6.9–7.7 (m, 2,4–7-H); mass spectrum *m/e* (rel intensity) 317 (11), 233 (43), 149 (100), 117 (6), 85 (63). 1-(2′-Tetrahydropyranyl)-3-methylthioindole (**9a**) had nmr δ 1.5–2.1 (m, 3′–5′-H), 2.29 (s, SMe), 3.60 (m, 6′-H), 4.0 (m, 6′-H), 5.32 (dd, J_1 = 8, J_2 = 4 Hz, 2′-H), 7.0–7.4 (m, 2,5–7-H), 7.62 (m, 4-H); mass spectrum *m/e* (rel intensity) 247 (51), 163 (100), 148 (32), 117 (6), 85 (50).

Reactions of Raney Nickel with 3-(2′-Tetrahydropyranylthio)indole (1a), 3-Methylthioindole[9] (7), and 1-(2′-Tetrahydropyranyl)-3-methylthioindole (9a). A few milligrams of **1a**, **7**, or **9a** in methanol was treated with a large excess (*ca.* tenfold by weight) of Raney nickel. After standing at room temperature for 0.5 hr, the suspension was filtered and the filtrate was evaporated. In the case of **1a** or **7**, the resulting product was identified as indole by tlc and comparison of spectra. In the case of **9a** the product was indistinguishable from 1-(2′-tetrahydropyranyl)indole (**4a**), prepared as described.

Acknowledgment. The authors wish to thank the National Institute of General Medical Science (Grant GM-18588) for support of this work and William R. Anderson, Jr., and Thomas E. Stone for providing spectra.

Registry No.—**1a**, 50639,97-9; **1b**, 50639-98-0; **4a**, 50639-99-1; **4b**, 50640-00-1; **5b**, 50640-01-2; **6a**, 50640-02-3; **7**, 40015-10-9; **8a**, 50640-03-4; **9a**, 50640-04-5; Ag^+, 14701-21-4; silver nitrate, 7761-88-8; silver perchlorate, 7783-93-9; 3-thioindole, 480-94-4; 2-chlorotetrahydropyran, 3136-02-5; 2-chlorotetrahydrofuran, 13369-70-5.

References and Notes

(1) For a general review see R. J. Suhadolnik, "Nucleoside Antibiotics," Wiley-Interscience, New York, N. Y., 1970.
(2) G. F. Holland and L. A. Cohen, *J. Amer. Chem. Soc.*, **80**, 3765 (1958).
(3) A reaction reminiscent of the Stevens rearrangement; see, for example, A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, p 304.
(4) R. L. N. Harris, *Tetrahedron Lett.*, 4465 (1969).
(5) G. F. Woods and H. Sanders, *J. Amer. Chem. Soc.*, **68**, 2111 (1946); S. Hattori, *Yuki Gosei Kagaku Kyokai Shi*, **19**, 522 (1961); *Chem. Abstr.*, **55**, 20928 (1961).
(6) A. Kankaanpera and K. Miikki, *Suom. Kemistilehti B*, **41**, 42 (1968).
(7) Similarly, acid-catalyzed hydrolyses of acetals of glucofuranosides are faster than hydrolyses of acetals of glucopyranosides, where the available data suggest that different mechanisms are involved: B. Capon and D. Thacker, *J. Chem. Soc. B*, 185 (1967); W. G. Overend, C. W. Rees, and J. S. Sequeira, *J. Chem. Soc.*, 3429 (1962).
(8) Indoles substituted at the β position with electron-releasing substituents have a marked propensity toward oxidative degradation (see ref 10, p 290). Mass spectrometry provided evidence that this polar material was at least partially dimeric with apparent molecular ions at *m/e* 302 and 372 (indole dimer with one and two tetrahydrofuranyl substituents, respectively).
(9) P. G. Gassman and T. J. Van Bergen, *J. Amer. Chem. Soc.*, **95**, 591 (1973).
(10) See, for example, R. J. Sundberg, "The Chemistry of Indoles," Academic Press, New York, N. Y., 1970, pp 77–83.
(11) A. H. Jackson and B. Naidoo, *J. Chem. Soc., Perkin Trans. 2*, 548 (1973).
(12) G. Casnati, A. Dossena, and A. Pochini, *Tetrahedron Lett.*, 5277 (1972).
(13) N. S. Bhacca, L. F. Johnson, and L. N. Shoolery, "High Resolution Nmr Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962.
(14) See also R. V. Jardine and R. K. Brown, *Can. J. Chem.*, **41**, 2067 (1963).
(15) L. B. Townsend and R. K. Robins, *J. Heterocycl. Chem.*, **6**, 459 (1969).
(16) M. G. Reinecke, J. F. Sebastian, H. W. Johnson, Jr., and C. Pyun, *J. Org. Chem.*, **36**, 3091 (1971); J. C. Powers, W. P. Meyer, and T. G. Parsons, *J. Amer. Chem. Soc.*, **89**, 5812 (1967).
(17) G. E. Booth and R. J. Ouellette, *J. Org. Chem.*, **31**, 544 (1966).
(18) R. A. Heacock and S. Kasparek, *Advan. Heterocycl. Chem.*, **10**, 43 (1969).
(19) M. G. Reinecke, J. F. Sebastian, H. W. Johnson, Jr., and C. Pyun, *J. Org. Chem.*, **37**, 3066 (1972).
(20) N. A. Ryabinin, I. P. Kolenko, B. N. Lundin, and N. A. Milov, *Tr. Inst. Khim., Akad. Nauk SSSR, Ural. Filial*, 75 (1968); *Chem. Abstr.*, **70**, 87408 (1969).
(21) A. I. Vogel, "Practical Organic Chemistry," Wiley, New York, N. Y., 1956, p 334.

Stereoselective Formation of Some Thietane 1,1-Dioxides

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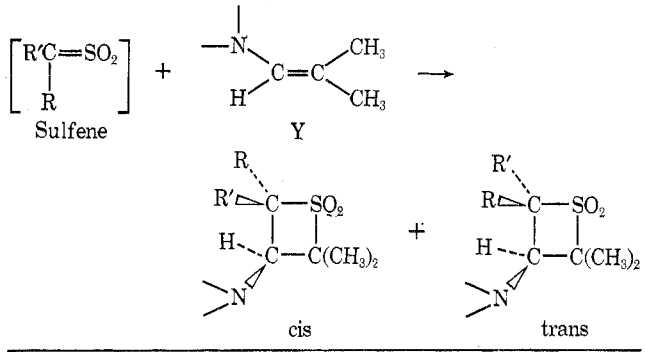
The reaction of substituted methanesulfonyl chlorides and ethanesulfonyl chlorides with triethylamine in the presence of 2-methyl-1-propenylamines is discussed. The observed stereoselectivity in the formation of products can be explained on the basis of a zwitterionic intermediate or a concerted $[_{\pi}2_s + _{\pi}2_s]$ process.

The chemistry of sulfenes has received considerable attention in the past decade and several reviews have appeared.[1] The reaction of sulfenes with enamines is probably the most extensively investigated reaction of these chemical intermediates, but data concerning the stereochemistry of the products derived from the reaction of substituted sulfenes with enamines is meager and inconclusive.[2] The present study deals with the stereochemistry of the products obtained in the reaction of a number of substituted methanesulfonyl and ethanesulfonyl chlorides with triethylamine in the presence of N,N-disubstituted 2-methyl-1-propenylamines.

Table I



Compd	R'	R	Y	% cis	% yield[a]
1	p-$C_6H_4CH_3$	H	I	82	50[b]
2	C_6H_5	H	I	74	94
3	C_6H_5	H	II	77	100
4	C_6H_5	H	III	73	100
5	p-C_6H_4Cl	H	I	62	75[b]
6	p-$C_6H_4NO_2$	H	I	0	69
7	Cl	H	I	65	34[b]
8	Cl	CH_3	I	72	77
9	Cl	CH_3	II	77	100
10	Cl	CH_3	III	85	98
11	Cl	CH_3	IV	72	100
12	Br	H	I	59	43[b]
13	Br	H	II	67	100
14	Br	H	III	73	100
15	I	H	I	63	82
16	CN	H	I	0	42
17	CN	CH_3	I	84	49[b]
18	CN	CH_3	II	83	83
19	CN	CH_3	III	74	81
20	CN	CH_3	IV	72	63
21	CH_3	H	I	42	24[c]
22	n-C_3H_7	H	I	39	32[c]
23	$CH_2C_6H_5$	H	I	45	98
24	O=CC_6H_5	H	I	0	*d*
25	O=CC_6H_5	H	II	0	64
26	O=CC_6H_5	H	III	0	88
27	O=COEt	CH_3	II	0	93
28	O=COEt	CH_3	III	27	89

[a] Crude yield. [b] Yield after recrystallization. [c] Yield after distillation; extensive decomposition occurred with the formation of polymeric tars. [d] Decomposed on standing.

Results

The reaction of mono- and disubstituted sulfenes with the following enamines, *N,N*-dimethyl-2-methyl-1-propenylamine (I), 2-methyl-1-propenylpyrrolidine (II), 4-(2-methyl-1-propenyl)morpholine (III), and *N,N*-diisopropyl-2-methyl-1-propenylamine (IV), led almost exclusively to a mixture of cis- and trans-substituted thietane 1,1-dioxides.[3] Surprisingly, in a large number of examples (see Table I, **1–5, 7–15, 17–20**), the preferred orientation in these cyclic sulfones was one in which the amino moiety and the sulfene substituent (other than alkyl) were in the less thermodynamically stable cis arrangement. A summary of the results of these experiments is presented in Table I.

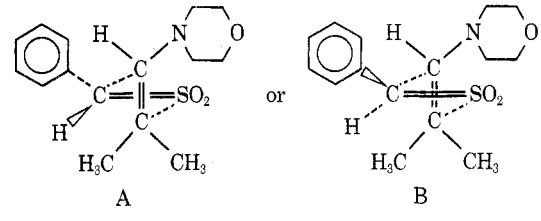
The cis percentages were determined by nmr analysis of crude reaction products obtained as explained in the Experimental Section. To avoid erroneous results due to possible differing solubilities of isomeric cycloadducts in the nmr solvent, samples for analysis were obtained by dissolving the entire crude residue in the solvent and analyzing an aliquot of this. In the experiments employing substituted methanesulfonyl chlorides, pure trans cycloadducts could be obtained quantitatively by equilibrating the isomeric mixtures with potassium *tert*-butoxide in *tert*-butyl alcohol for a period of from 1 day to 2 weeks. Further evidence for the stereochemical assignments to the products will be presented later.

Discussion

An investigation of the current literature on the addition of sulfenes to enamines suggests that this reaction may proceed *via* a two-step process.[4,5] Scheme I illustrates this stepwise process for the reaction of α-toluenesulfonyl chloride with triethylamine in the presence of *N,N*-dimethyl-2-methyl-1-propenylamine.

A rationale for the formation of the less stable cis isomer can be postulated based on the above reaction scheme in that electrostatic attractions between the positive and negative charges of the 1,4-dipolar intermediate, which can be delocalized by the amino and phenyl moieties, respectively, should favor cis geometry.[6] Even in those cases where the electronegative group stabilizing the carbanion moiety of the postulated intermediate is limited in its ability to delocalize the charge *via* resonance (*i.e.*, halides)[7] cis preference was still observed. The data in Table I, demonstrating that cis preference was not observed for substrates incapable of appreciable negative character β to the sulfonyl group in the zwitterionic intermediate, offers support for this theory (*e.g.*, Table I, **21–23**).

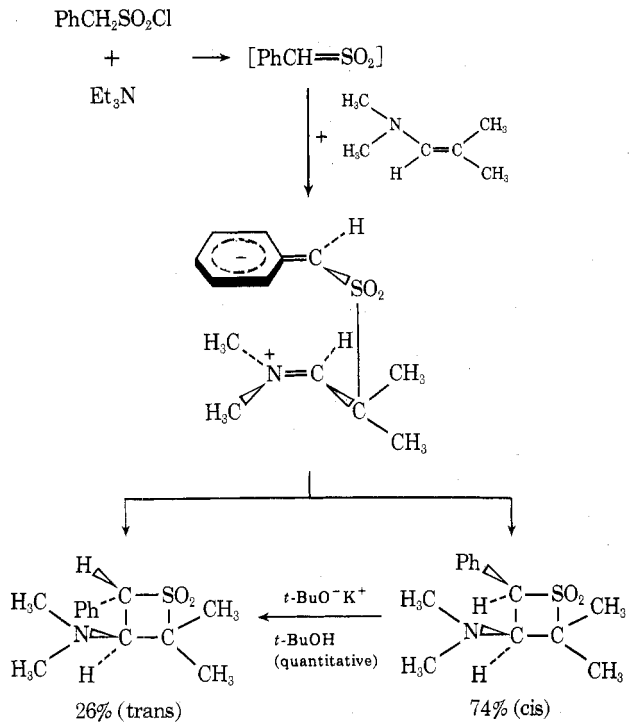
A concerted process [$_\pi2_s + {}_\pi2_a$] could conceivably account for cis preference in the geometry of these products if steric considerations are taken into account along with a secondary orbital interaction between the amine lone pair and the π framework of the sulfene. Current theory requires that for this concerted process one unsaturated system must approach the other with an orthogonal orientation.[8] A cursory analysis of these interactions gives the following orientations as the most probable in the transition state for the reaction of phenylsulfene and III.



Either frontal or rear attack by sulfene on this enamine should yield the cis cycloadduct. If the reaction, however, were indeed proceeding *via* this mechanistic scheme, cis preference should not be limited to those cases involving electronegative substituents. As already indicated, aliphatic sulfonyl chlorides react under these conditions to give predominantly trans cycloadducts (Table I, **21–23**). If only conventional steric factors are considered, the alternate geometry would be expected from a concerted [$_\pi2_s + {}_\pi2_a$] process.

A third alternative explanation which should not be overlooked is the concerted [$_\pi2_s + {}_\pi2_s$] process. Although this process is thermally disallowed by Woodward–Hoffmann rules, recent theoretical considerations indicate that this would be the favored mode of addition in the case of cycloaddends of substantially different electron-accepting and -donating abilities and has been invoked to explain the results of the cycloaddition reactions of ketenes.[9a] In the reaction of sulfenes, a concerted process of this type coupled with the secondary electronic effects possible between the electron-donating amine moiety and the electron-attracting substituents of the sulfene moiety would sufficiently explain the results obtained in the course of this investigation. In the absence of the electron-attracting substituents trans products would predominate.

Scheme I



Preliminary results of semiempirical SCF-MO calculations do not support the idea of a stereochemistry-maintaining cisoid dipolar intermediate and thus lends further support to the pericyclic $[\pi 2_s + \pi 2_s]$ process.[9b] It is of interest to note that the difference between the $[\pi 2_s + \pi 2_s]$ process and the cisoid dipolar intermediate may be merely one of semantics and that the $[\pi 2_s + \pi 2_s]$ complex and the so-called dipolar intermediate are in fact one and the same species.

In the reaction of para-substituted phenylsulfenes a noticeable decrease in cis preference is observed in going from electron-donating to electron-withdrawing substituents. Whether this is due largely to substituent effects in the postulated intermediates or to differing rates of postisomerization in the products is still unclear. The effect of electron-withdrawing substituents on the aromatic ring on the intermediate zwitterion would be twofold: first, the intermediate carbanion moiety would be stabilized to a greater extent and perhaps permit an increased production of the more thermodynamically stable trans product; and second, the substituent would disperse the negative charge to a greater degree and reduce the "effective" electrostatic attractions. However, once the product has been formed, it is itself capable of postisomerization *via* carbanion formation at the 4 position. During the early stages of the reaction, triethylamine is in excess and the cycloadducts themselves contain a tertiary amine, either of which should be capable of catalyzing the isomerization. This isomerization was demonstrated to occur in the presence of Et_3N for the product mixture from the reaction of phenylsulfene and I but only slowly (see Experimental Section). This indicated that the substituents do play a role in the stereochemical course of the reaction but in order to assess the relative contribution of postisomerization in products 1–6 the substituted α-phenylethanesulfonyl chlorides[10] would need to be employed. Attempts to prepare these compounds, however, were not successful.

Postisomerization in the case of the less acidic halocycloadducts does not appear to be a problem, since pure *cis*-2,2-dimethyl-3-(*N*,*N*-dimethylamino)-4-chlorothietane 1,1-dioxide remained unchanged when treated with an equimolar amount of triethylamine in anhydrous diethyl ether for 3 days or acetonitrile for 1 day. The apparent "anomalies" associated with the products derived from benzoyl and cyanosulfenes are easily understood on the basis of this postisomerization phenomena due to the enhanced acidity of the 4 hydrogen in these cycloadducts.[11]

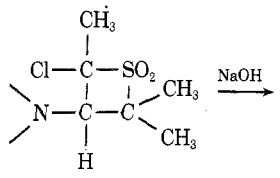
The results obtained with the substituted ethanesulfonyl chlorides are more significant on the basis that carbanion formation at the 4 position and subsequent isomerization is no longer possible. For the reactions of both α-cyanoethanesulfonyl chloride and α-chloroethanesulfonyl chloride, cis cycloaddition products predominated (Table I, **8–11** and **17–20**). With the former reaction, the results indicated that postisomerization was probably operative (Table I, **16**). The products derived from α-chloroethanesulfonyl chloride had a higher cis/trans ratio than was true for the chlorosulfene cycloadducts (see Table I, **7–11**), but this may simply reflect the decreased thermodynamic differences between the two isomers. Equilibration attempts, under reaction conditions, of pure *cis*-**7** afforded only cis isomer on work-up, demonstrating that postisomerization for this system was not occuring.

The results with α-carbethoxyethanesulfonyl chloride (Table I, **27** and **28**) were, however, puzzling at first in view of the postulated reaction scheme. This substrate was reported to react with triethylamine in the presence of 2-methyl-1-propenylpiperidine to give exclusively the trans cycloadduct in an 83% yield.[2b] The fact that ethyl chlorosulfonylacetate ($EtO_2CCH_2SO_2Cl$) gave only trans products was understandable owing to the ease of isomerization expected for this product, but, as in the case of the cyanosulfenes (Table I, **17–20**), a predominance of cis product was expected in the former reaction. Our own experiments confirmed the earlier report in that trans products predominated. A closer inspection of molecular framework models then revealed that for a zwitterionic intermediate of this type, with extensive delocalization of charges, electrostatic forces could effectively stabilize both cis and trans zwitterionic precursor forms. If this is the case, then the more thermodynamically stable product would be expected to predominate and steric factors would dictate product distribution. Several attempts were made to prepare and isolate the interesting α-benzoylethanesulfonyl chloride to further test this hypothesis, but they were unsuccessful.[12]

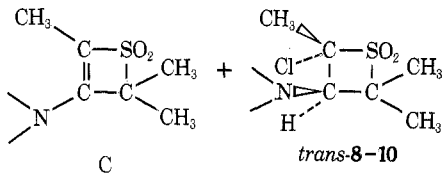
There has been some speculation in the literature[2a,b,13] that the Karplus correlation[14] is reliable for the thietane 1,1-dioxide ring system and hence applicable for assigning the cis–trans geometry of this ring system. The coupling constants observed in the cis and trans cycloadducts obtained during this investigation did not bear this out (see Experimental Section). A recent application of shift reagent, $Eu(fod)_3$, to this problem has allowed for an unambiguous designation of the stereochemistry of the products derived from bromosulfene and 1-(morpholino)cyclohexene.[2d] The results of this investigation confirmed earlier structural assignments based on equilibration data. An extension of these nmr data to the data obtained from the cycloadducts prepared in this investigation, coupled with the equilibration studies, allows their stereochemical assignments to be unambiguously made.

Another method, which has proved most helpful with products derived from disubstituted sulfenes, was reported recently for α-halothietane 1,1-dioxides.[2c] When a mixture of cis and trans isomers, *e.g.*, **9**, was subjected to treatment by aqueous alkali followed by acidic work-up, the keto sulfone 2,4,4-trimethylthietan-3-one 1,1-dioxide (D) and the pure trans cycloadduct (**10**) were obtained.

The absolute stereochemistry of these trans cycloadducts has been confirmed by X-ray diffraction data on pure *trans*-**10**.[15] A comparison of nmr chemical shift data

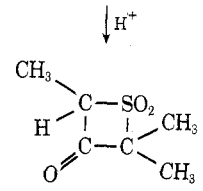


cis- and *trans*-**8–10**



trans-**8–10**

C



D

of these known systems with that of the similarly substituted cycloadducts (Table I, **17–20**) shows definite trends and similarities and allows for unambiguous stereochemical assignments.[28]

Conclusion

The question of whether or not sulfene reactions with enamines are concerted or stepwise processes is still not definitively resolved. Certainly these are limiting cases and perhaps the course of the reaction of sulfenes with enamines depends on the nature of the reactants. In those cases where electron-withdrawing groups are present to stabilize a zwitterionic intermediate, perhaps the reactions are more stepwise in character, whereas, when these groups are absent, such as with sulfene itself, there is a "substantial degree of concertedness"[5] to the cycloaddition. The nature of the reactive sulfenes and the instability of the cis enamines makes this problem even more difficult to resolve. The reaction could indeed be a concerted process and the stereochemical consequences dependent on the properties of the cycloaddends as suggested by Epiotis,[9] and not a consequence of a dipolar intermediate. The mechanism of this reaction thus remains obscure but the steroechemical outcome of these reactions is indeed interesting to note.

Experimental Section

All reactions were performed in a nitrogen atmosphere. The nmr spectra were recorded on a Varian A-60A instrument in $CDCl_3$ with trimethylsilane as the internal standard and the data for cis isomers were obtained from mixtures except where noted. The infrared (ir) spectra were recorded on a Beckman IR-33 or a Perkin-Elmer Infracord. All melting points and boiling points are uncorrected. Ethanesulfonyl, butanesulfonyl, and α-toluenesulfonyl chlorides were obtained from Eastman Organic Chemicals (White Label). The following sulfonyl chlorides were prepared according to the literature: haloalkanesulfonyl chlorides,[16-19] cyanoalkanesulfonyl chlorides,[20] α-carbethoxyethanesulfonyl chloride,[2b] β-phenylethanesulfonyl chloride,[10] benzoylmethanesulfonyl chloride,[21] and para-substituted α-toluenesulfonyl chlorides.[22] Triethylamine, obtained from Matheson Coleman and Bell, was distilled from α-naphthyl isocyanate (2%), bp 88–89°, and stored over sodium hydroxide prior to use.[23] The enamines were also prepared according to the literature, enamines I, II, and III by the reaction of isobutyraldehyde (flash distilled, Aldrich) with the appropriate freshly distilled amine in the presence of $TiCl_4$[24] and IV [bp 55–56° (17 mm), $n^{30}D$ 1.4310] by the reaction of the aldehyde with diisopropylamine (Matheson Coleman and Bell) in the presence of molecular sieves.[25] No attempt was made to maximize the isolated purified yields of the cycloadducts. Microanalyses were performed by Dr. C. S. Yeh and staff.

General Procedure for Preparing Thietane 1,1-Dioxide Derivatives from Monosubstituted Sulfonyl Chlorides. To an ethereal solution of 1.0 equiv of the enamine and 1.0 equiv of triethylamine at room temperature, an ethereal solution of 1.0 equiv of the sulfonyl chloride was added dropwise over a period of 10–30 min. After the addition was complete, the reaction was stirred for an additional 30 min. Triethylammonium chloride was then filtered and washed with several small portions of diethyl ether. The combined filtrate and washings were then evaporated *in vacuo*, affording a crude residue which after drying over P_2O_5 under reduced pressure for several hours was dissolved in $CDCl_3$. After an aliquot of this was analyzed *via* nmr the solvent was again removed *in vacuo* and the residue was recrystallized from a suitable solvent. Pure trans isomers were obtained by stirring isomeric mixtures (~2.0 g) with a catalytic amount of potassium *tert*-butoxide (~0.1 g) in *tert*-butyl alcohol for a period of from 1 day to 2 weeks. Recrystallization or sublimation gave analytically pure products.

2,2-Dimethyl-3-(*N,N*-dimethylamino)-4-*p*-tolylthietane 1,1-Dioxide (1). The cis–trans mixture was prepared on a 0.1-molar scale according to the general procedure. The isomeric mixture would not crystallize: nmr ($CDCl_3$) cis δ 1.58 and 1.72 (s, 3 H each, *gem*-dimethyl groups), 2.03 [s, 6 H, $N(CH_3)_2$] 2.29 (s, 3 H, $PhCH_3$), 3.13 (d, J = 10 Hz, 1 H, NCH), 5.25 (d, J = 10 Hz, 1 H, $CHSO_2$), 7.13 and 7.53 (m, 2 H each, ortho and meta aromatic H). An analytical sample of the trans isomer was obtained after isomerization of the crude material for 1 day as described above, recrystallization from methanol, and sublimation at 100° (0.4 mm): mp 134°; ir (KBr) (SO_2) 1305, 1285, 1160, 1110, and 1045 cm^{-1}; nmr ($CDCl_3$) δ 1.61 and 1.67 (s, 3 H each, *gem*-dimethyl groups), 2.06 [s, 6 H, $N(CH_3)_2$], 2.33 (s, 3 H, $PhCH_3$), 2.92 (d, J = 10 Hz, 1 H, CHN), 5.06 (d, J = 10 Hz, 1 H, $CHSO_2$), and 7.27 (m, 4 H, aromatic H).

Anal. Calcd for $C_{14}H_{21}NO_2S$: C, 62.88; H, 7.92; N, 5.24; S, 11.99. Found: C, 62.87; H, 8.07; N, 5.02; S, 12.20.

2,2-Dimethyl-3-(*N,N*-dimethylamino)-4-phenylthietane 1,1-Dioxide (2). A cis–trans mixture was obtained on a 0.1-molar scale in an 82% yield after recrystallization from 95% ethanol: nmr ($CDCl_3$) cis δ 1.63 and 1.75 (s, 3 H each, *gem*-dimethyl groups), 2.08 [s, 6 H, $N(CH_3)_2$], 3.18 (d, J = 10 Hz, 1 H, CHN), 5.29 (d, J = 10 Hz, 1 H, $CHSO_2$), and 7.25–7.80 (m, 5 H, aromatic H). Equilibration of a 2.0-g sample of the isomeric mixture with 0.1 g of potassium *tert*-butoxide in 50 ml of *tert*-butyl alcohol for 3 days followed by solvent removal afforded 2.0 g of the isomerically pure trans cycloadduct. Recrystallization from 95% ethanol afforded an analytically pure sample: mp 164° (lit.[26] mp 165–166); ir (KBr) (SO_2) 1290, 1115, and 1050 cm^{-1}; nmr ($CDCl_3$) δ 1.63 and 1.67 (s, 3 H each, *gem*-dimethyl groups), 2.05 [s, 6 H, $N(CH_3)_2$], 2.95 (d, J = 10 Hz, 1 H, CHN), 5.09 (d, J = 10 Hz, 1 H, $CHSO_2$), and 7.39 (s, 5 H, aromatic H).

Anal. Calcd for $C_{13}H_{19}NO_2S$: C, 61.63; H, 7.56; N, 5.53; S, 12.65. Found: C, 61.80; H, 7.29; N, 5.50; S, 12.77.

2,2-Dimethyl-3-(*N*-pyrrolidino)-4-phenylthietane 1,1 Dioxide (3). This material was isolated on a 0.01-molar scale as the trans cycloadduct after stirring the initial crude reaction products with 0.2 g of potassium *tert*-butoxide in 50 ml of *tert*-butyl alcohol for 40 hr and recrystallization from 95% ethanol: nmr ($CDCl_3$) cis δ 1.60 and 1.70 (s, 3 H each, *gem*-dimethyl groups), 1.42 and 2.20 (m, 8 H, pyrrolidino H), 3.28 (d, J = 10 Hz, 1 H, CHN), 5.28 (d, J = 10 Hz, 1 H, $CHSO_2$), 7.23–7.82 (m, 5 H, aromatic H). Pure trans cycloadduct had mp 136–137.5° [lit.[27] mp 161° (ligroin)]; ir (KBr) (SO_2) 1310, 1300, and 1105 cm^{-1}; nmr ($CDCl_3$) δ 1.65 (s, 6 H, *gem*-dimethyl groups), 1.42 and 2.10 (m, 8 H, pyrrolidino H), 3.05 (d, J = 10 Hz, 1 H, CHN), 5.08 (d, J = 10 Hz, 1 H, $CHSO_2$), and 7.40 (s, 5 H, aromatic H).

2,2-Dimethyl-3-(*N*-morpholino)-4-phenylthietane 1,1-Dioxide (4). This reaction was carried out on a 0.01-molar scale to give a quantitative yield of an isomeric mixture of products: nmr ($CDCl_3$) cis δ 1.62 and 1.73 (s, 3 H each, *gem*-dimethyl groups), 2.26 [m, 4 H, $(CH_2)_2N$], 3.30 (d, J = 10 Hz, 1 H, CHN), 3.55 [m, 4 H, $(CH_2)_2O$], 5.33 (d, J = 10 Hz, 1 H, $CHSO_2$), and 7.25–7.78 (m, 5 H, aromatic H). The crude material was dissolved in 75 ml of *tert*-butyl alcohol and 0.2 g of potassium *tert*-butoxide was added. After stirring at room temperature for 2 days, work-up and recrystallization from 95% ethanol afforded a 73% overall yield of pure trans cycloadduct: mp 181–182.5°; ir (KBr) (SO_2) 1310 and 1110 cm^{-1}; nmr ($CDCl_3$) δ 1.60 and 1.63 (s, 3 H each, *gem*-dimethyl groups), 2.23 [m, 4 H, $(CH_2)_2N$], 3.08 (d, J = 10 Hz, 1 H, CHN), 3.55 [m, 4 H, $(CH_2)_2O$], 5.10 (d, J = 10 Hz, 1 H, $CHSO_2$), and 7.37 (s, 5 H, aromatic H).

4-*p*-Chlorophenyl-2,2-dimethyl-3-(*N,N*-dimethylamino)thie-

tane 1,1-Dioxide (5). A mixture of cis and trans cycloadducts was obtained in a 75% yield on a 0.05-molar scale according to the general procedure: nmr ($CDCl_3$) cis δ 1.63 and 1.73 (s, 3 H each, *gem*-dimethyl groups), 2.10 [s, 6 H, $N(CH_3)_2$], 3.15 (d, J = 10 Hz, 1 H, CHN), 5.25 (d, J = 10 Hz, 1 H, $CHSO_2$), and 7.22–7.72 (m, 5 H, aromatic H). Recrystallization of the mixture from methanol afforded a 45% yield of trans cycloadduct which was purified further by sublimation at 121° (0.4 mm): mp 138°; ir (KBr) (SO_2) 1310, 1118, and 1050 cm^{-1}; nmr ($CDCl_3$) δ 1.64 and 1.68 (s, 3 H each, *gem*-dimethyl groups), 2.08 [s, 6 H, $N(CH_3)_2$], 2.88 (d, J = 10 Hz, 1 H, CHN), 5.08 (d, J = 10 Hz, 1 H, $CHSO_2$), and 7.42 (s, 5 H, aromatic H).

Anal. Calcd for $C_{13}H_{18}ClNO_2S$: C, 54.25; H, 6.30; Cl, 12.32; N, 4.87; S, 11.14. Found: C, 54.50; H, 6.46; Cl, 12.54; N, 4.76; S, 11.18.

2,2-Dimethyl-3-(*N,N*-dimethylamino)-4-*p*-nitrophenylthietane 1,1-Dioxide (6). The starting sulfonyl chloride (*p*-nitro-α-toluenesulfonyl chloride) is only slightly soluble in Et_2O; so 0.05 mol was suspended in 250 ml of Et_2O and a solution containing the enamine I (0.05 mol) and triethyamine (0.05 mol) was slowly added to it. In this fashion only trans cycloadduct was obtained. According to the general procedure, employing a large volume of Et_2O (800 ml) to dissolve the acid chloride, only trans isomer was again obtained. Products **1**, **2**, and **5** were also prepared by this inverse addition route but no differences were observed in the cis/trans ratios. The product **6** was also only moderately soluble in Et_2O but an nmr analysis of the solid filtered off indicated only trans isomer along with triethylammonium chloride. An analytical sample was obtained by sublimation at 110° (0.1 mm): mp 154–155°; ir (KBr) (SO_2) 1300, 1118, 1050 and (NO_2) 1520 and 1345 cm^{-1}; nmr ($CDCl_3$) δ 1.67 and 1.70 (s, 3 H each, *gem*-dimethyl groups), 2.08 [s, 6 H, $N(CH_3)_2$], 2.98 (d, J = 10 Hz, 1 H, CHN), 5.21 (d, J = 10 Hz, 1 H, $CHSO_2$), and 7.63 and 8.27 (m, 2 H each, ortho and meta aromatic H).

Anal. Calcd for $C_{13}H_{18}N_2O_4S$: C, 52.33; H, 6.08; N, 9.39; S, 10.75. Found: C, 52.49; H, 6.24; N, 9.16; S, 10.88.

4-Chloro-2,2-dimethyl-3-(*N,N*-dimethylamino)thietane 1,1-Dioxide (7). Fractional recrystallization of the crude reaction product obtained from 0.1 mol of reactants according to the general procedure afforded 13.5% pure cis cycloadduct: mp 102–103°; ir (KBr) (SO_2) 1330, 1310, 1180, and 1060 cm^{-1}; nmr ($CDCl_3$) δ 1.56 and 1.75 (s, 3 H each, *gem*-dimethyl groups), 2.30 [s, 6 H, $N(CH_3)_2$], 2.94 (d, J = 7 Hz, 1 H, CHN), 5.33 (d, J = 7 Hz, 1 H, $CHSO_2$).

Anal. Calcd for $C_7H_{14}ClNO_2S$: C, 39.71; H, 6.64; Cl, 16.76; N, 6.61; S, 15.15. Found: C, 40.00; H, 6.76; Cl, 16.85; N, 6.59; S, 15.42.

Further crystallizations afforded only cis-trans mixtures (20.5%), which were then equilibrated (as described previously) for 4 days to yield pure trans product: mp 82–83°; ir (KBr) (SO_2) 1320, 1170, 1120, and 1060 cm^{-1}; nmr ($CDCl_3$) δ 1.56 and 1.58 (s, 3 H each, *gem*-dimethyl groups), 2.27 [s, 6 H, $N(CH_3)_2$], 2.63 (d, J = 8 Hz, 1 H, CHN), 5.27 (d, J = 8 Hz, 1 H, $CHSO_2$).

4-Bromo-2,2-dimethyl-3-(*N,N*-dimethylamino)thietane 1,1-Dioxide (12). A cis-trans mixture was obtained in a 43% yield on a 0.1-molar scale after recrystallization from 95% ethanol: nmr ($CDCl_3$) cis δ 1.54 and 1.78 (s, 3 H each, *gem*-dimethyl groups), 2.30 [s, 6 H, $N(CH_3)_2$], 2.83 (d, J = 7 Hz, 1 H, CHN), 5.48 (d, J = 7 Hz, 1 H, $CHSO_2$). Equilibration as before for 3 days afforded pure trans cycloadduct, which was purified by sublimation at 58° (0.3 mm): mp 83–84°; ir (KBr) (SO_2) 1315, 1160, 1110, and 1050 cm^{-1}; nmr ($CDCl_3$) δ 1.56 and 1.58 (s, 3 H each, *gem*-dimethyl groups), 2.28 [s, 6 H, $N(CH_3)_2$], 2.77 (d, J = 8 Hz, 1 H, CHN), 5.35 (d, J = 8 Hz, 1 H, $CHSO_2$).

Anal. Calcd for $C_7H_{14}BrNO_2S$: C, 32.81; H, 5.47; Br, 31.22; N, 5.47; S, 12.53. Found: C, 33.10; H, 5.64; Br, 31.00; N, 5.20; S, 12.70.

4-Bromo-2,2-dimethyl-3-(*N*-pyrrolidino)thietane 1,1-Dioxide (13). The cis-trans mixture was obtained in a crude quantitative yield on a 0.01-molar scale: nmr ($CDCl_3$) cis δ 1.56 and 1.77 (s, 3 H each, *gem*-dimethyl groups), 1.57 and 2.40 (broad m, 8 H, pyrrolidino H), 2.88 (d, J = 6.5 Hz, 1 H, CHN), 5.47 (d, J = 6.5 Hz, 1 H, $CHSO_2$). Equilibration of the crude material for 6 days and recrystallization from 95% ethanol gave a 64% yield of the trans isomer: mp 81–82°; ir (KBr) (SO_2) 1320, 1310, 1175, and 1110 cm^{-1}; nmr ($CDCl_3$) δ 1.57 and 1.62 (s, 3 H each, *gem*-dimethyl groups), 1.56 and 2.43 (broad m, 8 H, pyrrolidino H), 2.90 (d, J = 8 Hz, 1 H, CHN), 5.33 (d, J = 8 Hz, 1 H, $CHSO_2$).

4-Bromo-2,2-dimethyl-3-(*N*-morpholino)thietane 1,1-Dioxide (14). The crude cis-trans mixture was obtained in a quantitative yield on a 0.01-molar scale according to the general procedure: nmr ($CDCl_3$) cis δ 1.57 and 1.78 (s, 3 H each, *gem*-dimethyl groups), 2.52 [m, 4 H, $(CH_2)_2N$], 2.96 (d, J = 7 Hz, 1 H, CHN), 3.77 [m, 4 H, $(CH_2)_2O$], 5.52 (d, J = 7 Hz, 1 H, $CHSO_2$). After equilibration, as before, for 4 days the pure trans isomer was obtained in a 50% yield recrystallized from 95% ethanol: mp 141–143°; ir (KBr) (SO_2) 1310, 1110, and 880 cm^{-1}; nmr ($CDCl_3$) δ 1.57 and 1.78 (s, 3 H each, *gem*-dimethyl groups), 2.50 [m, 4 H, $(CH_2)_2N$], 2.90 (d, J = 8.5 Hz, 1 H, CHN), 3.72 [m, 4 H, $(CH_2)_2O$], 5.39 (d, J = 8.5 Hz, 1 H, $CHSO_2$).

2,2-Dimethyl-3-(*N,N*-dimethylamino)-4-iodothietane 1,1-Dioxide (15). The crude mixture of cis and trans cycloadducts was obtained in an 83% yield on a 0.01-molar scale: nmr ($CDCl_3$) cis δ 1.51 and 1.83 (s, 3 H each, *gem*-dimethyl groups), 2.31 [s, 6 H, $N(CH_3)_2$], 2.24 (d, J = 7.5 Hz, 1 H, CHN), 5.73 (d, J = 7.5 Hz, 1 H, $CHSO_2$). Pure trans isomer was obtained only after equilibration, as before, for 2 weeks. The cycloadduct was very hygroscopic: ir ($CHCl_3$) (SO_2) 1330, 1170, and 1055 cm^{-1}. It was, therefore, converted to the picrate for analysis: mp 152–156°; ir (KBr) (NO_2) 1645, 1630, and 1340, (SO_2) 1328 cm^{-1}.

Anal. Calcd for $C_{13}H_{17}IN_4O_9S$: C, 29.55; H, 3.21; I, 23.80. Found: C, 29.65; H 3.49; I, 23.98.

4-Cyano-2,2-dimethyl-3-(*N,N*-dimethylamino)thietane 1,1-Dioxide (16). The crude reaction material was obtained in a 42% yield according to the general procedure on a 0.02-molar scale. The crude material, mp 95–108°, was sublimed at 65° (2 mm) to yield a product, mp 98–108°. Equilibration for 3 days had no effect on the nmr and an attempt to prepare the picrate was unsuccessful: ir (KBr) (CN) 2270, (SO_2) 1335, 1170, 1125, and 1065 cm^{-1}; nmr ($CDCl_3$) δ 1.60 and 1.63 (s, 3 H each, *gem*-dimethyl groups), 2.30 [s, 6 H, $N(CH_3)_2$], 2.91 (d, J = 9 Hz, 1 H, $CHSO_2$).

3-(*N,N*-Dimethylamino)-2,2,4-trimethylthietane 1,1-Dioxide (21). A cis-trans mixture of this material was obtained according to the general procedure after distillation of the crude material: bp 118–120° (2.5 mm); nmr ($CDCl_3$) cis δ 1.44 (d, J = 7 Hz, 3 H, $CHCH_3$), 1.48 and 1.58 (s, 3 H each, *gem*-dimethyl groups), 2.20 [s, 6 H, $N(CH_3)_2$], 2.72 (d, J = 8.5 Hz, 1 H, CHN), 4.03 (m, 1 H, $CHSO_2$). Equilibration for 1 day under the usual conditions afforded pure trans cycloadduct: bp 89° (0.3 mm); ir (salt plates) (SO_2) 1300, 1285, 1110, and 1040 cm^{-1}; nmr ($CDCl_3$) δ 1.43 (d, J = 7 Hz, 3 H, $CHCH_3$), 1.49 and 1.52 (s, 3 H each, *gem*-dimethyl groups), 2.18 (d, J = 9 Hz, 1 H, CHN), 2.20 [s, 6 H, $N(CH_3)_2$], 4.03 (octet, J = 9 and 7 Hz, 1 H, $CHSO_2$).

Anal. Calcd for $C_8H_{17}NO_2S$: C, 50.23; H, 8.96; N, 7.32; S, 16.76. Found: C, 50.00; H, 8.94; N, 7.29; S, 16.56.

2,2-Dimethyl-3-(*N,N*-dimethylamino)-4-*n*-propylthietane 1,1-Doxide (22). A cis-trans mixture was obtained from the crude reaction material on a 0.1-molar scale after distillation: bp 113° (0.05 mm); nmr ($CDCl_3$) cis δ 0.97 (t, J = 6.5 Hz, 3 H, CH_2CH_3), 1.2–2.45 (m, 4 H, CH_2's), 1.51 and 1.62 (s, 3 H each, *gem*-dimethyl groups), 2.20 [s, 6 H, $N(CH_3)_2$], 2.74 (d, J = 9 Hz, 1 H, CHN), 3.91 (m, 1 H, $CHSO_2$). Equilibration for 1 day afforded pure trans cycloadduct: bp 95–100° (0.4 mm); ir (salt plates) (SO_2) 1300, 1115, and 1050 cm^{-1}; nmr ($CDCl_3$) δ 0.97 (t, J = 6.5 Hz, 3 H, CH_2CH_3), 1.2–2.3 (m, 4 H, CH_2's), 1.50 and 1.53 (s, 3 H each, *gem*-dimethyl groups), 2.20 [s, 6 H, $N(CH_3)_2$], 2.19 (d, J = 9 Hz, 1 H, CHN), 3.88 (m, J = 9 Hz, 1 H, $CHSO_2$).

Anal. Calcd for $C_{10}H_{21}NO_2S$: C, 54.78; H, 9.61; N, 6.39; S, 14.63. Found: C, 54.54; H, 9.52; N, 6.21; S, 14.43.

4-Benzyl-2,2-dimethyl-3-(*N,N*-dimethylamino)thietane 1,1-Dioxide (23). The crude cis-trans mixture of the cycloadduct, prepared on a 0.1-molar scale, defied crystallization: nmr ($CDCl_3$) cis δ 1.47 and 1.62 (s, 3 H each, *gem*-dimethyl groups), 2.15 [s, 6 H, $N(CH_3)_2$], 2.74 (d, J = 9 Hz, 1 H, CHN), 2.95–3.45 (m, 2 H, $PhCH_2$), 3.9–4.35 (m, 1 H, $CHSO_2$), 7.23 (s, 5 H, aromatic H). The crude material was therefore equilibrated for 1 week and the resulting residue was recrystallized from methanol to give a 57% yield of the trans isomer: mp 97–98°; ir (KBr) (SO_2) 1300, 1290, and 1115 cm^{-1}; nmr ($CDCl_3$) δ 1.53 (s, 6 H, *gem*-dimethyl groups), 2.23 [s, 6 H, $N(CH_3)_2$], 2.36 (d, J = 8.5 Hz, 1 H, CHN) 2.77–3.72 (nine-peak ABC pattern, 2 H, $PhCH_2$), 4.21 (octet, 1 H, $CHSO_2$), and 7.28 (s, 5 H, aromatic H). An analytical sample was obtained by sublimation at 80° (0.3 mm).

Anal. Calcd for $C_{14}H_{21}NO_2S$: C, 62.88; H, 7.92; N, 5.24; S, 11.99. Found: C, 62.67; H, 7.98; N, 5.20; S, 12.20.

4-Benzoyl-2,2-dimethyl-3-(*N,N*-dimethylamino)thietane 1,1-Dioxide (24). This material was prepared on a 0.1-molar scale by the inverse addition method owing to the low solubility of benzoylmethanesulfonyl chloride in Et_2O. The product was identified by the nmr of the crude reaction material but was too unstable to give a satisfactory melting point or analysis. Equilibration had no effect on the nmr: ir (KBr) (SO_2) 1310 (C=O), 1680 cm^{-1}; nmr δ

1.60 and 1.69 (s, 3 H each, *gem*-dimethyl groups), 2.18 [s, 6 H, $N(CH_3)_2$], 3.44 (d, J = 9.2 Hz, 1 H, $CHSO_2$), 7.47–7.68 (m, 3 H, meta and para aromatic H), and 8.0–8.2 (m, 2 H, ortho aromatic H).

4-Benzoyl-2,2-dimethyl-3-(*N*-pyrrolidino)thietane 1,1-Dioxide (25). Only the trans isomer of this material was obtained in a 64% yield on a 4.6-millimolar scale. Recrystallization from 95% ethanol gave the pure trans isomer: mp 112–115°; ir (KBr) (SO_2) 1315 (C=O), 1690 cm^{-1}; nmr ($CDCl_3$) δ 1.60 and 1.67 (s, 3 H each, *gem*-dimethyl groups), 1.47 and 2.27 (broad m, 8 H, pyrrolidino H), 3.48 (d, J = 9.5 Hz, 1 H, CHN), 5.58 (d, J = 9.5 Hz, 1 H, $CHSO_2$), 7.50 (m, 3 H, meta and para aromatic H), and 8.08 (m, 2 H, ortho aromatic H).

4-Benzoyl-2,2-dimethyl-3-(*N*-pyrrolidino)thietane 1,1-Dioxide (26). The crude reaction material obtained in this reaction according to the general procedure on a 4.6-millimolar scale contained only trans isomer. Recrystallization from 95% ethanol afforded an analytically pure material: mp 168–171°; ir (KBr) (SO_2) 1315 and 1120, (C=O) 1688 cm^{-1}; nmr ($CDCl_3$) δ 1.58 and 1.67 (s, 3 H each, *gem*-dimethyl groups), 2.35 [m, 4 H, $(CH_2)_2N$], 3.54 (d, J = 9 Hz, 1 H, CHN), 3.63 [m, 4 H, $(CH_2)_2O$], 5.58 (d, J = 9 Hz, 1 H, $CHSO_2$), 7.53 (m, 3 H, meta and para aromatic H), and 8.08 (m, 2 H, ortho aromatic H).

Anal. Calcd for $C_{16}H_{21}NO_4S$: C, 59.42; H, 6.55; N, 4.33; S, 9.92. Found: C, 59.24; H, 6.49; N, 4.36; S, 9.92.

Postequilibration Experiment on 2. A sample of **2** (2.6 g, 0.01 mol) containing 74% cis isomer was dissolved in acetonitrile and stirred with an equimolar amount of triethylamine for 16 hr. Removal of the solvent and triethylamine *in vacuo* afforded a quantitative recovery of cycloadducts which now contained only 64% cis cycloadduct, demonstrating a slow postisomerization under these conditions.

General Procedure for Preparing Thietane 1,1-Dioxide Derivatives from α,α-Disubstituted Sulfonyl Chlorides. These thietane 1,1-dioxide derivatives were prepared as described for the monosubstituted sulfene reactions with the exception that the reactions were carried out in an ice–salt bath maintained between 0 and 5°.

2-Chloro-3-(*N,N*-dimethylamino)-2,4,4-trimethylthietane 1,1-Dioxide (8). A cis–trans mixture of this material was prepared on a 0.05-molar scale according to the general procedure: mp 88–94°; nmr ($CDCl_3$) cis δ 1.57 and 1.75 (s, 3 H each, *gem*-dimethyl groups), 1.97 [s, 3 H, $C(Cl)CH_3$], 2.32 [s, 6 H, $N(CH_3)_2$], and 2.58 (s, 1 H, CHN). Refluxing a 2.0-g (8.8 mmol) sample of this mixture with a threefold excess of sodium hydroxide in 50% aqueous ethanol for 6 hr followed by removal of the organic phase *in vacuo* afforded 1.5 g of a mixture of cycloadducts and the enamine C as indicated by ir absorption for this double bond at 1620 cm^{-1}. Subsequent treatment of this mixture with 8 ml of 30% H_2SO_4 in 8 ml of absolute ethanol and removal of the organic solvent afforded 0.7 g (49%) of 2,4,4-trimethylthietan-3-one 1,1-dioxide: mp 105–106 (lit.[26] mp 104–105°; nmr ($CDCl_3$) δ 1.56 (d, J = 7 Hz, 3 H, $CHCH_3$), 1.57 and 1.70 (s, 3 H each, *gem*-dimethyl groups), and 5.12 (q, J = 7 Hz, 1 H, $CHCH_3$). Neutralization of the aqueous phase with 10% sodium hydroxide then afforded predominantly trans cycloadduct (~18% cis): mp 69–70°; ir (KBr) (SO_2) 1320, 1120, and 1060 cm^{-1}; nmr ($CDCl_3$) δ 1.60 and 1.64 (s, 3 H each, *gem*-dimethyl groups), 2.07 [s, 3 H, $C(Cl)CH_3$], 2.29 [s, 6 H, $N(CH_3)_2$], and 2.84 (s, 1 H, CHN).

2-Chloro-3-(*N*-pyrrolidino)-2,4,4-trimethylthietane 1,1-Dioxide (9). This material was prepared as a cis–trans mixture on a 0.05-molar scale and after recrystallization from 95% ethanol a 71% yield of isomeric cycloadducts was realized: mp 78–83°; nmr ($CDCl_3$) cis δ 1.55 and 1.72 (s, 3 H each, *gem*-dimethyl groups), 1.95 [s, 3 H, $C(Cl)CH_3$], 1.57 and 2.42 (broad m, 8 H, pyrrolidino H), and 2.67 (s, 1 H, CHN). Treatment of a 5.1-g (0.02 mol) sample of this mixture as described for 8 yielded a product that was predominantly trans (18% cis): mp 86–92°; ir (KBr) (SO_2) 1320 and 1110 cm^{-1}; nmr ($CDCl_3$) δ 1.58 and 1.62 (s, 3 H each, *gem*-dimethyl groups), 2.02 [s, 3 H, $C(Cl)CH_3$], 1.59 and 2.40 (broad m, 8 H, pyrrolidino H), and 2.92 (s, 1 H, CHN).

2-Chloro-3-(*N*-morpholino)-2,4,4-trimethylthietane 1,1-Dioxide (10). The cis–trans mixture was obtained in a 60% yield after recrystallization from 95% ethanol on a 0.05-molar scale: mp 138–145°; nmr ($CDCl_3$) cis δ 1.53 and 1.70 (s, 3 H each, *gem*-dimethyl groups), 1.93 [s, 3 H, $C(Cl)CH_3$], 2.48 [m, 4 H, $(CH_2)_2N$], 2.70 (s, 1 H, CHN), and 3.73 [m, 4 H, $(CH_2)_2O$]. Treatment of a 6.1-g sample (0.023 mol) of this mixture as described above for 8 yielded the keto sulfone D as well as pure *trans*-**10**: mp 184–185° (lit.[26] mp 186°); ir (KBr) (SO_2) 1320 and 1120 cm^{-1}; nmr δ 1.60 and 1.63 (s, 3 H each, *gem*-dimethyl groups), 2.03 [s, 3 H, $C(Cl)CH_3$], 2.50 [m, 4 H, $(CH_2)_2N$], 3.00 (s, 1 H, CHN), and 3.77 [m, 4 H, $(CH_2)_2O$].

2-Chloro-3-(*N,N*-diisopropylamino)-2,4,4-trimethylthietane 1,1-Dioxide (11). This material was obtained as a cis–trans mixture in an 83% yield after recrystallization from 95% ethanol on a 0.02-molar scale, mp 96–122°. Attempts to isolate pure trans adduct as for **8–10** were unsuccessful and repeated recrystallizations only afforded a product containing 86% cis and a product containing 46% cis isomer: ir (KBr) (SO_2) 1310, 1160, and 1105 cm^{-1}; nmr ($CDCl_3$) (*cis*-**11**) δ 1.06 and 1.12 (d, J = 6.5 Hz, 6 H each, isopropyl *gem*-dimethyl groups), 1.50 and 1.80 (s, 3 H each, ring *gem*-dimethyl group), 1.92 [s, 3 H, $C(Cl)CH_3$], 3.58 [septet, J = 6.5 Hz, 2 H, $CH(CH_3)_2$], and 3.60 (s, 1 H, CHN); (*trans*-**11**) δ 1.06 and 1.15 (d, J = 6.5 Hz, 6 H each, isopropyl *gem*-dimethyl groups), 1.62 and 1.65 (s, 3 H each, ring *gem*-dimethyl groups), 2.05 [s, 3 H, $C(Cl)CH_3$], 3.46 [d, J = 6.5 Hz, 2 H, $CH(CH_3)_2$], and 3.80 (s, 1 H, CHN).

2-Cyano-3-(*N,N*-dimethylamino)-2,4,4-trimethylthietane 1,1-Dioxide (17). The cis–trans mixture was prepared on a 0.01-molar scale according to the general procedure in a 63% yield. Recrystallization from 95% ethanol gave a cis–trans mixture in a 49% yield: mp 106–109°; ir (KBr) (CN) 2260 (SO_2) 1327 and 1115 cm^{-1}; nmr ($CDCl_3$) (*cis*-**17**) δ 1.59 and 1.82 (s, 3 H each, *gem*-dimethyl groups), 1.85 [s, 3 H, $C(CN)CH_3$], 2.33 [s, 6 H, $N(CH_3)_2$], and 2.46 (s, 1 H, CHN); (*trans*-**17**) δ 1.63 and 1.69 (s, 3 H, each, *gem*-dimethyl groups), 1.93 [s, 3 H, $C(CN)CH_3$], 2.30 [s, 6 H, $N(CH_3)_2$], and 2.70 [s, 1 H, CHN]. An analytical sample was obtained by sublimation at 87° (0.3 mm).

Anal. Calcd for $C_9H_{16}N_2O_2S$: C, 49.98; H, 7.46; N, 12.95; S, 14.83. Found: C, 50.23; H, 7.56; N, 12.74; S, 14.74.

2-Cyano-3-(*N*-pyrrolidino)-2,4,4-trimethylthietane 1,1-Dioxide (18). This material was prepared on a 0.01-molar scale and isolated as a cis–trans mixture in a 56% yield after recrystallizing the crude reaction products from 95% ethanol: mp 140–143° (83% cis); ir (KBr) (CN) 2260, (SO_2) 1330, 1175, and 1030 cm^{-1}; nmr ($CDCl_3$) (*cis*-**18**) δ 1.58 and 1.78 (s, 3 H each, *gem*-dimethyl groups), 1.83 [s, 3 H, $C(CN)CH_3$], 1.60 and 2.38 (broad m, 8 H, pyrrolidino H), and 2.57 (s, 1 H, CHN); (*trans*-**18**) δ 1.62 and 1.65 (s, 3 H each, *gem*-dimethyl groups), 1.88 [s, 3 H, $C(CN)CH_3$], 1.60 and 2.38 (broad m, 8 H, pyrrolidino H), and 3.07 (s, 1 H, CHN).

2-Cyano-3-(*N*-morpholino)-2,4,4-trimethylthietane 1,1-Dioxide (19). The material was prepared on a 0.01-molar scale according to the general procedure as a cis–trans mixture. Recrystallization from 95% ethanol afforded the pure cis isomer in a 50% yield: mp 134–135°; ir (KBr) (CN) 2260 (SO_2) 1327 and 1115 cm^{-1}; nmr ($CDCl_3$) δ 1.60 and 1.78 (s, 3 H each, *gem*-dimethyl groups), 1.83 [s, 3 H, $C(CN)CH_3$], 2.52 [m, 4 H, $CH_2)_2N$], 2.65 (s, 1 H, CHN), and 3.80 [m, 4 H, $CH_2)_2O$]; nmr ($CDCl_3$) (*trans*-**19**) δ 1.63 and 1.67 (s, 3 H each, *gem*-dimethyl groups), 1.88 [s, 3 H, $C(CN)CH_3$], 2.40 [m, 4 H, $CH_2)_2N$], 3.12 (s, 1 H, CHN), and 3.73 [m, 4 H, $(CH_2)_2O$].

2-Cyano-3-(*N,N*-diisopropylamino)-2,4,4-trimethylthietane 1,1-Dioxide (20). This material was obtained as a cis–trans mixture on a 0.01-molar scale. Recrystallization from pentane afforded almost pure cis isomer: mp 92–99°; ir (KBr) (CN) 2255 (SO_2) 1325, 1170, 1120, and 1100 cm^{-1}; nmr ($CDCl_3$) δ 1.08 and 1.10 (d, J = 6.5 Hz, 6 H each, isopropyl *gem*-dimethyl groups), 1.49 (s, 3 H, ring *gem*-dimethyl group trans to CN), 1.81 and 1.83 [two s, 3 H each, $C(CN)CH_3$ and ring *gem*-dimethyl group cis to CN], 3.47 (s, 1 H, CHN), and 3.58 [q, 2 H, J = 6.5 Hz, $CH(CH_3)_2$].

2-Carbethoxy-3-(*N*-pyrrolidino)-2,4,4-trimethylthietane 1,1-Dioxide (27). This material was obtained as the trans isomer according to the general procedure on a 3-millimolar scale. Recrystallization from hexane afforded the pure material in a 23% yield: mp 77–79°; ir (KBr) (C=O) 1748 (SO_2) 1315, 1260, and 1110 cm^{-1}; nmr ($CDCl_3$) δ 1.32 (t, J = 7 Hz, 3 H, CH_2CH_3), 1.57 and 1.63 (s, 3 H each, *gem*-dimethyl groups), 1.82 [s, 3 H, $C(SO_2)CH_3$], 1.55 and 2.30 (broad m, 8 H, pyrrolidino H), 3.38 (s, 1 H, CHN), and 4.28 (q, J = 7 Hz, 2 H, CH_2CH_3).

2-Carbethoxy-3-(*N*-morpholino)-2,4,4-trimethylthietane 1,1-Dioxide (28). This material was obtained as a cis–trans mixture according to the general procedure on a 7.5-millimolar scale. Recrystallization from 95% ethanol afforded the pure trans isomer in a 35% yield: mp 109–111°; ir (KBr) (C=O) 1750 (SO_2) 1310 and 1260 cm^{-1}; nmr ($CDCl_3$) δ 1.32 (t, J = 7 Hz, 3 H, CH_2CH_3), 1.57 and 1.65 (s, 3 H each, *gem*-dimethyl groups), 1.82 [s, 3 H, $C(SO_2)CH_3$], 3.40 (s, 1 H, CHN), 3.70 [m, 4 H, $(CH_2)_2N$], 4.07 [m, 4 H, $(CH_2)_2O$], and 4.28 (q, J = 7 Hz, 2 H, CH_2CH_3).

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Registry No.—I, 6906-32-7; II, 2403-57-8; III, 2403-55-6; IV, 23297-04-3; *cis*-**1**, 50640-23-8; *trans*-**1**, 50640-24-9; *cis*-**2**, 50640-25-0; *trans*-**2**, 50640-26-1; *cis*-**3**, 50640-27-2; *trans*-**3**, 50640-28-3; *cis*-**4**, 50640-29-4; *trans*-**4**, 50640-30-7; *cis*-**5**, 50640-31-8; *trans*-**5**, 50640-32-9; *trans*-**6**, 50640-33-0; *cis*-**7**, 41959-68-6; *trans*-**7**, 41959-69-7; *cis*-**8**, 50640-34-1; *trans*-**8**, 50640-35-2; *cis*-**9**, 50640-36-3; *trans*-**9**, 50640-37-4; *cis*-**10**, 50640-38-5; *trans*-**10**, 31752-27-9; *cis*-**11**, 50640-39-6; *trans*-**11**, 50640-40-9; *cis*-**12**, 50640-41-0; *trans*-**12**, 50640-42-1; *cis*-**13**, 50640-43-2; *trans*-**13**, 50640-44-3; *cis*-**14**, 50640-45-4; *trans*-**14**, 50640-46-5; *cis*-**15**, 50640-47-6; *trans*-**15** picrate, 50640-49-8; *trans*-**16**, 50640-50-1; *cis*-**17**, 50640-51-2; *trans*-**17**, 50640-52-3; *cis*-**18**, 50640-53-4; *trans*-**18**, 50640-54-5; *cis*-**19**, 50640-55-6; *trans*-**19**, 50640-56-7; *cis*-**20**, 50640-57-8; *trans*-**20**, 50640-58-9; *cis*-**21**, 50640-59-0; *trans*-**21**, 50640-60-3; *cis*-**22**, 50640-61-4; *trans*-**22**, 50640-62-5; *cis*-**23**, 50640-63-6; *trans*-**23**, 50640-64-7; *trans*-**24**, 50640-65-8; *trans*-**25**, 50640-66-9; *trans*-**26**, 50640-67-0; *trans*-**27**, 50640-68-1; *cis*-**28**, 50640-69-2; *trans*-**28**, 50640-70-5; 2,4,4-trimethylthietan-3-one 1,1-dioxide, 31686-74-5.

References and Notes

(1) (a) T. J. Wallace, *Quart. Rev., Chem. Soc.*, **20**, 67 (1966); (b) G. Opitz, *Angew. Chem., Int. Ed. Engl.*, **6**, 107 (1967); (c) W. E. Truce and L. K. Liu, *Mech. React. Sulfur Compounds*, **4**, 145 (1969); (d) T. Nagai and N. Tokura, *Int. J. Sulfur Chem. B*, **7**, 207 (1972).

(2) (a) L. A. Paquette, *J. Org. Chem.*, **29**, 2854 (1964); (b) L. A. Paquette, J. P. Freeman, and R. W. Houser, *ibid.*, **34**, 2901 (1969); (c) G. Pagani and S. Maiorana, *Chim. Ind. (Milan)*, **53**, 261 (1971); (d) C. T. Goralski, *J. Org. Chem.*, **37**, 2080 (1972).

(3) In a few reactions with I small amounts (6% or less) of *N,N*-dimethylsulfonamides were obtained.

(4) (a) Opitz, *et al.*, *Justus Liebigs Ann. Chem.*, **684**, 98 (1965); (b) L. A. Paquette and M. Rosen, *J. Amer. Chem. Soc.*, **89**, 4102 (1967); (c) A. M. Hamid and S. Trippett, *J. Chem. Soc. C*, 1612 (1968); (d) L. A. Paquette, *J. Org. Chem.*, **34**, 2896 (1969); (e) K. Nagarajan and S. R. Mehta, *ibid.*, **35**, 4248 (1970); (f) O. Tsuge, S. Iwanami, and S. Hagio, *Bull. Chem. Soc. Jap.*, **45**, 237 (1972).

(5) A concerted process has been proposed to account for the asymmetric synthesis obtained in the reaction of sulfene with optically active enamines: L. A. Paquette, J. P. Freeman, and S. Maiorana, *Tetrahedron*, **27**, 2599 (1971).

(6) R. Gompper, *Angew. Chem., Int. Ed. Engl.*, **8**, 312 (1969).

(7) For a discussion on carbanion stabilization by halogen atoms see K. J. Klabunde and D. J. Burton, *J. Amer. Chem. Soc.*, **94**, 5985 (1972), and references cited therein.

(8) R. B. Woodman and R. Hoffman, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 68–69.

(9) (a) N. D. Epiotis, *J. Amer. Chem. Soc.*, **94**, 1924 (1972); (b) N. D. Epiotis, private communication.

(10) B. Evans, *et al.*, *J. Chem. Soc.*, 1159 (1927), report the synthesis of this compound but later work by M. S. Kharash, *J. Org. Chem.*, **3**, 180 (1938), indicated that the earlier report was erroneous and all attempts by Kharash to prepare this compound were unsuccessful.

(11) W. E. Truce and C.-I. M. Lin, *J. Amer. Chem. Soc.*, **95**, 4426 (1973).

(12) This compound has been obtained in solution contaminated with the corresponding acid, and isolated as an anilide: W. E. Truce and J. Woodman, unpublished results.

(13) L. A. Paquette, M. Rosen, and H. Stucki, *J. Org. Chem.*, **33**, 3020 (1968).

(14) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

(15) G. D. Andreetti, L. Cavalco, and P. Sgarabotto, *Gazz. Chim. Ital.*, **101**, 440 (1971).

(16) V. Z. El-Hewehi, *J. Prakt. Chem.*, **23**, 38 (1964).

(17) Pyong Nae Son, Ph.D. Thesis, Purdue University, 1966.

(18) A. Lanson and R. B. Tinkler, *J. Chem. Soc. C*, 654 (1969).

(19) V. Z. El-Hewehi and D. Hempel, *J. Prakt. Chem.*, **21**, 286 (1963).

(20) M. P. Sammes, C. M. Wylie, and J. G. Hoggert, *J. Chem. Soc. C*, 2151 (1971).

(21) Prepared by J. Woodman according to the method of W. E. Truce and C. W. Vriesen, *J. Amer. Chem. Soc.*, **75**, 2525 (1953).

(22) J. R. Norell, Ph.D. Thesis, Purdue University, 1963.

(23) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. I, Wiley, New York, N. Y., 1967, p 1198.

(24) W. A White and H. Weingarten, *J. Org. Chem.*, **32**, 213 (1966).

(25) D. P. Roelofsen and H. Van Bekkum, *Recl. Trav. Chim. Pays-Bas*, **91**, 605 (1972).

(26) T. Klingler, Ph.D. Thesis, Purdue University.

(27) G. Opitz, H. Schempp, and H. Adolph, *Justus Liebigs Ann. Chem.*, **684**, 92 (1965).

(28) Note added in Proof. P. D. Buttero and S. Maiorana, *J. Chem. Soc., Perkin Trans.*, **1**, 2540 (1973).

Preparation of 3,4-Dimethylenepyrrolidine and 1-Alkyl-3,4-dimethylenepyrrolidines by the Thermal Elimination of Sulfur Dioxide

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The reaction of 3,4-bis(bromomethyl)-2,5-dihydrothiophene 1,1-dioxide with primary alkylamines gives 5-alkyl-1,3,4,6-tetrahydrothieno[3,4-*c*]pyrrole 2,2-dioxides as well as 1,4-HBr elimination products. These bicyclic thienopyrroles were thermally decomposed, eliminating sulfur dioxide, to give 3,4-dimethylenepyrrolidine and the corresponding *N*-alkyl-3,4-dimethylenepyrrolidines, which have been characterized spectrally and analytically.

The preparation of 1-substituted 3,4-dimethylenepyrrolidines and their sulfone precursors has recently been of considerable interest.[1-5] These compounds have specific utility as reactants in the Diels–Alder reaction,[6] as monomers in polymerization reactions, and for their medicinal applications. The synthetic utilization of sulfur dioxide as a protecting agent for the synthesis of 1-aryl-3,4-dimethylenepyrrolidines has been demonstrated.[2,4] This report describes the extension of this method to the preparation of the novel secondary amine, 3,4-dimethylenepyrrolidine as well as 1-alkyl-3,4-dimethylenepyrrolidines.

In the nucleophilic reaction of primary amines with 3,4-bis(bromomethyl)-2,5-dihydrothiophene 1,1-dioxide, it has been proposed[2,4] that a competing reaction was a 1,4-HBr elimination due to the acidic character of the sulfolene protons. We found no evidence for this type of elimination in our earlier study[2] of this reaction with monosubstituted anilines. However, this elimination appears to be more facile with primary alkylamines, and subsequently we were able to isolate for the first time the 1,4-HBr elimination product for a series of such amines from this reaction.

Results and Discussion

The reaction of alkylamines with **1** was carried out as previously described[1] and the bicyclic compounds (**2**) were isolated in moderate yields (21–40%) (Scheme I). The 1,4-HBr elimination products (**3**) were observed in the reaction mixtures for all cases by nmr. We were not able to isolate these compounds (**3**)[7] directly from the reaction