would be more accessible to electrophilic attack by the peracid.

Experimental Section

Melting points are uncorrected. Infrared spectra were measured on a Perkin-Elmer Model 621 spectrometer. Nuclear magnetic resonance spectra were obtained on a Varian A-60A spectrometer. Microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Ind.

2-Methylthiolane was prepared in 60% yield by reaction of 1,4-dibromopentane with sodium sulfide nonahydrate in aqueous ethanol, bp 132° (lit.[15] 132°).

General Methods of Oxidation.—The procedures employed for the oxidations summarized in Table III are generally those previously reported for the oxidation of thianes.[4] Exceptions are noted below. In this work, where necessary, the sulfoxides were extracted from aqueous solutions with chloroform. The aqueous phase was then saturated with sodium chloride and the chloroform extraction repeated. The ratio of sulfoxide extracted by this procedure was identical with that present in water as shown by extracting known mixtures from water.

A. *m*-Chloroperbenzoic Acid (pH 12).[16]—The peracid (0.85 mmol) was added to 21 ml of a potassium chloride–sodium hydroxide buffer solution (pH 12) in water–dioxane (60:40). This solution was added over a 5-min period to 1 mmol of the sulfide in 10 ml water–dioxane cooled in an ice bath. The mixture was stirred at ice-bath temperature for 5 hr prior to work-up.

B. Iodobenzene Dichloride.[17]—A solution of iodobenzene dichloride (1 mmol) in anhydrous pyridine (3 ml) was added dropwise during 5 min to a stirred solution of the sulfide (1 mmol) in 3 ml of pyridine–water (20:80) and cooled in an ice bath. After 30 min at 0° the mixture was allowed to warm to 25°. The mixture was diluted with water prior to extraction.

C. *tert*-Butyl Hypochlorite.—To 1 mmol of the 1-methylthiolane in 10 ml of isopropyl alcohol at −78° was added 1 mmol of *tert*-butyl hypochlorite. After 30 min at that temperature 100 ml of 0.1 *N* aqueous sodium hydroxide was added and the mixture was shaken vigorously prior to extraction.

D. Isopropyl Hypochlorite.—A methylene chloride solution of isopropyl hypochlorite (1 equiv) was cooled to −78° and rapidly added to 1 equiv of the sulfide dissolved in methylene chloride and cooled to −78°. The reaction was worked up as described above for *tert*-butyl hypochlorite.

Analysis of Mixtures.—Percentage composition of mixtures were ascertained by planimetric integration of curves obtained from an F & M Model 720 chromatograph employing an 8 ft × 1/4 in. 20% Carbowax 20M on Chromosorb W column at 170°, a flow rate near 60 ml/min; retention times were 17 min for **2** and 21 min for **3**.

Separation of *cis*- and *trans*-1-Methylthiolane 1-Oxide.—Mixtures of sulfoxides were chromatographed on a 14 in. × 3/8 in. column of Fisher Scientific Co. alumina acid, activity I, employing ether, methylene chloride, and methanol as eluents. The fractions were monitored by vapor phase chromatography.

Registry No.—**1**, 1795-09-1; **2**, 25859-44-3; **3**, 25859-45-4; **4**, 1003-46-9.

(15) E. W. Whitehead, R. A. Dean, and F. A. Fidler, *J. Amer. Chem. Soc.*, **73**, 3632 (1951).

(16) For other examples of oxidations by peracids at high pH, see R. Curci, A. Giovini, and G. Modina, *Tetrahedron*, **4**, 1227 (1966).

(17) G. Barbieri, M. Cinquini, S. Colonna, and F. Montanari, *J. Chem. Soc. C*, 659 (1968).

3-Substituted Thietanes. Synthesis and Oxidation to Sulfoxides[1,2]

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Received March 13, 1970

A method is reported which appears to be general for the synthesis of 3-aryl and 3-alkylthietanes from the readily available aryl methyl and alkyl methyl ketones. The cycloaddition product of sulfene and the appropriate enamine is reduced to the desired 3-aryl- or 3-alkylthietane in three steps. Thietanes deuterated in the α position could be prepared by exchange under mild conditions at the sulfone stage. The oxidation of 3-alkylthietanes to the isomeric sulfoxides was examined with a variety of oxidants; the thietane system appears to be less sensitive to the nature of the oxidant than the previously examined thiane system. Isomeric cis and trans sulfoxides could be separated by chromatography on silica gel; the cis isomer was eluted prior to trans in each of six 3-substituted thietane systems examined.

With the increasing sophistication of the organic chemistry of sulfur has come the postulation of tetracovalent sulfur reaction intermediates of trigonal bipyramid geometry.[4] For intermediates of such geometry the ligands about sulfur must subtend an angle of either 90 or 120 degrees; thus the thietane ring system, in which the C-S-C angle is close to 90°, becomes an important model. Substituted thietane 1-oxides are also pertinent models for studying the intramolecular neighboring group effect of sulfinyl oxygen,[5] and for studying the competitive stereochemical requirements of sulfinyl oxygen and the nonbonded electron pair on trigonal sulfur.[6,7] It was our interest in the latter of these which established our need for a 3-substituted thietane system the isomeric sulfoxides of which could be identified stereochemically.

To simplify a study of the conformational preference of sulfinyl oxygen it was necessary to "anchor" the conformation of the thietane ring. The puckering of thietane rings is well documented.[8] By analogy to examples in cyclobutane chemistry, it is reasonable to hypothesize that a thietane molecule with a relatively bulky substituent at the 3 position would exist predominantly in a puckered conformation with the bulky substituent equatorial.[9] Thus, if the substituent at C_3 exerts a decided equatorial preference, a substituent

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(1) (a) Part XXIII in the series Chemistry of Sulfoxides and Related Compounds.

(2) We gratefully acknowledge support by the National Science Foundation (Grant No. GP-8648).

(3) National Aeronautics and Space Administration Trainee, 1966–1969.

(4) (a) S. Oae, M. Yokoyama, M. Kise, and N. Furukawa, *Tetrahedron Lett.*, 4131 (1968); (b) B. M. Trost, W. L. Schinski, and I. B. Mantz, *J. Amer. Chem. Soc.*, **91**, 4320 (1969); (c) R. Tang and K. Mislow, *ibid.*, **91**, 5644 (1969); (d) C. R. Johnson and J. J. Rigau, *ibid.*, 5398 (1969); (e) C. R. Johnson and D. McCants, Jr., *ibid.*, **87**, 5404 (1965).

(5) (a) S. M. Kotin, Ph.D. Dissertation, University of Pennsylvania, 1962; (b) J. J. Ubel, Ph.D. Dissertation, University of Illinois, 1964.

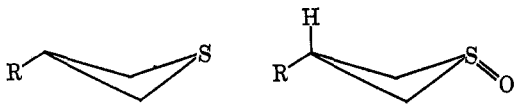
(6) C. R. Johnson and D. McCants, Jr., *J. Amer. Chem. Soc.*, **87**, 1109 (1965).

(7) (a) C. R. Johnson and W. O. Siegl, *ibid.*, **91**, 2796 (1969); (b) *Tetrahedron Lett.*, 1879 (1969).

(8) (a) B. Z. Zrbuzov, O. N. Nuretdinova, and A. N. Vereshchagin, *Dokl. Akad. Nauk SSSR*, **172**, 591 (1967); (b) W. D. Keller, T. R. Lusebrink, and C. H. Sederholm, *J. Chem. Phys.*, **44**, 782 (1966); (c) S. Allenmark, *Ark. Kemi*, **26**, 73 (1966); (d) D. O. Harris, H. W. Harrington, A. C. Luntz, and W. D. Gwinn, *J. Chem. Phys.*, **44**, 3467 (1966).

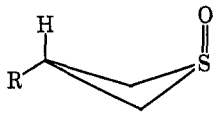
(9) J. Lillien and R. A. Doughty, *J. Amer. Chem. Soc.*, **89**, 155 (1967).

introduced at sulfur (*e.g.*, oxygen) is required to be either axial (trans isomer) or equatorial (cis somer) in a conformational fixed system. The *p*-chlorophenyl group was chosen because its dipole would allow assignment of cis and trans stereochemistry to the isomeric sulfoxides **2a** and **3a** from dipole moment determinations.[6] The *tert*-butyl substituent was also desired for its ability to anchor a ring conformation and for its lack of a significant dipole contribution which might influence geometry and chemistry.

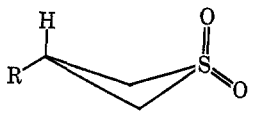


1

2 (cis)



3 (trans)



4

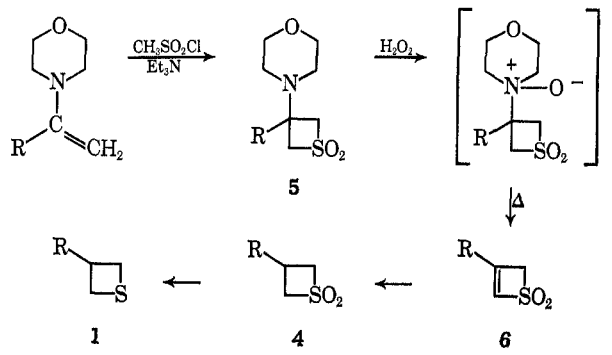
a, R = *p*-ClC$_6$H$_4$
b, R = *t*-C$_4$H$_9$
c, R = C$_6$H$_5$
d, R = Cl
e, R = OCOCH$_3$
f, R = CH$_3$

Only one synthesis of a 3-arylthietane (unsubstituted at C_2 and C_4) appears in the literature, the preparation of 3-hydroxy-3-phenylthietane by the treatment of 3-thietanone with phenylmagnesium bromide.[10] Syntheses[11] of 3-alkylthietanes have been limited to the methyl and ethyl cases. The cycloaddition of enamines with sulfene (CH_2=SO_2) provides a convenient entry to substituted thietane 1,1-dioxide systems but the sulfoxides can only be obtained by reduction of the sulfone to the sulfide stage and selective back oxidation to the sulfoxide. Conceptually, the cycloaddition of sulfine (CH_2=SO) to an enamine would eliminate these last two steps, but to date no one has successfully carried out this reaction.[12,13]

We report here an application of the enamine–sulfene cycloaddition for the synthesis of 3-substituted thietanes (Scheme I). The method appears general for 3-aryl- and certain 3-alkylthietanes. Stereochemistry was assigned to **2a** and **3a** from the dipole moments and to other 3-substituted thietane 1-oxides from spectral data as reported in our preliminary communications.[7] Continuing our interest in the stereochemical course of the oxidation of sulfides to sulfoxides, data are presented for the oxidation of 3-*tert*-butylthietane and 3-methylthietane to their sulfoxides.

Synthesis.—Scheme I was first attempted on the enamine of morpholine and acetophenone,[14] to yield the crystalline 1:1 cycloaddition product (**5c**) (46% yield

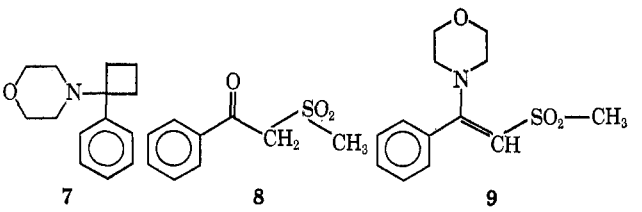
SCHEME I



5

1 **4** **6**

from acetophenone). The nmr spectrum of **5c** contained a four proton singlet for the ring methylene hydrogens of which there are clearly two nonequivalent pairs. Even in benzene, which often accentuates the nonequivalence of protons, the thietane ring hydrogens appear as a singlet. The sulfone **5c** was reduced with lithium aluminum hydride to 3-morpholino-3-phenylthietane (**7**) in which the thietane ring hydrogens appear as the expected AB quartet.



7 **8** **9**

The adduct **5c** could be converted to 3-phenylthiete 1,1-dioxide (**6c**) in almost quantitative yield by oxidation with hydrogen peroxide in acetic acid–acetic anhydride and subsequent pyrolysis of the amine oxide. The olefinic double bond of **6c** was considerably less reactive than reported for the unsubstituted thiete 1,1-dioxide.[15] Although **6c** would add bromine[16] and undergo the expected hydrolysis in aqueous base,[15,17] it failed to add secondary amines. The hydrolysis of **6c** to benzoic acid and dimethyl sulfone probably occurs *via* the *β*-keto sulfone **8** which is subsequently cleaved by hydroxide. If the amino sulfone **5c** is subjected to similar conditions, the enamine **9** is obtained. When the reaction is acidified before extraction, **8** is isolated.

The conversion of **6c** to 3-phenylthietane 1,1-dioxide (**4c**) could be accomplished by treatment with sodium borohydride in isopropyl alcohol at 60° (65% yield) or in dimethylformamide at 60–70° (37% yield). Catalytic hydrogenation of the olefinic double bond of **6c** with palladium on carbon or platinum oxide proceeded only in very low yield.

The sulfone **4c** was reduced to the volatile sulfide **1c** with lithium aluminum hydride. Attempts to reduce **6c** directly to 3-phenylthietane (**1c**) with lithium aluminum hydride were unsuccessful, yielding only what was believed to be 2-phenylpropanethiol from the spectral data.

Scheme I was repeated with the enamine from morpholine and *p*-chloroacetophenone as the starting material; experimental conditions were kept the same. The yield of 3-*p*-chlorophenyl-3-morpholinothietane 1,1-

(10) A. Luettringhaus, S. Kabuss, H. Prinzbach, and F. Langenbucher, *Ann Chem.*, **653**, 195 (1962).

(11) The synthesis of thietanes has been reviewed: M. Sanger, *Chem. Rev.*, **66**, 341 (1966); Y. Etienne, R. Soulas, and H. Lumbroso in "Heterocyclic Compounds with Three- and Four-Membered Rings," Part Two, A. Weissberger, Ed., Interscience, New York, N. Y., 1964, Chapter 5; L. L. Muller and J. Hamer, "1,2-Cycloaddition Reactions," Interscience, New York, N. Y., 1967.

(12) W. E. Truce and J. R. Norell, *J. Amer. Chem. Soc.*, **85**, 3231 (1963); W. A. Sheppard and J. Diekmann, *ibid.*, **86**, 1891 (1964); A. M. Hamid and S. Trippett, *J. Chem. Soc. C*, 1612 (1968).

(13) A sulfine has recently been trapped in a 1,4 cycloaddition reaction: B. Zwanenburg, L. Thijs, and J. Strating, *Tetrahedron Lett.*, 4461 (1969).

(14) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963).

(15) D. C. Dittmer and M. E. Christy, *ibid.*, **84**, 399 (1962).

(16) C. R. Johnson and G. A. Dutra, unpublished results.

(17) J. N. Wells and F. S. Abbott, *J. Med. Chem.*, **9**, 489 (1966).

dioxide (**5a**), from the cycloaddition of sulfene and the morpholine enamine of *p*-chloroacetophenone, was higher (52 *vs.* 37%) when benzene replaced ether as the solvent. The conversion of **5a** to 3-*p*-chlorophenylthiete 1,1-dioxide (**6a**) was almost quantitative. The double bond of **6a** resembled that of **6c** in its lack of reactivity and it was necessary to employ the reaction conditions mentioned above to effect the desired reduction. Base hydrolysis of **6a** produced *p*-chlorobenzoic acid and dimethyl sulfone.

With some slight modification Scheme I was employed for the synthesis of 3-*tert*-butylthietane (**1b**). Because of the sterically hindered carbonyl function of pinacolone, its dimethylamine enamine was prepared by the procedure of White and Weingarten.[18] The sulfene–enamine adduct, 3-dimethylamino-3-*tert*-butylthietane 1,1-dioxide,[19] was prepared and converted to 3-*tert*-butylthiete 1,1-dioxide (**6b**) by experimental procedures analogous to those described above. The olefinic double bond of **6b** was more reactive than that of **6a** or **6c**; it underwent catalytic hydrogenation and reacted with sodium borohydride in 2-propanol at 25° to yield 3-*tert*-butylthietane 1,1-dioxide (**4b**). The sulfone **4b** was reduced to the volatile 3-*tert*-butylthietane (**1b**) with lithium aluminum hydride.

When attempting to extend the stereochemical assignments from **2a** and **3a** to the sulfoxides of **1b** and **1c** it became necessary to prepare the α-tetradeuterated sulfoxides in order that the chemical shift values of the β-ring hydrogens be more accurately assigned. This was accomplished by treating the sulfones **4a** and **4b** with sodium deuterioxide in deuterium oxide–dioxane at 50°. Complete exchange of the sulfone α-methylene hydrogens could be effected under these conditions, whereas the corresponding sulfoxides were inert. The deuterated sulfones were converted to the α-tetradeuterated sulfides with lithium aluminum hydride and were subsequently oxidized to the tetradeuterated sulfoxides.

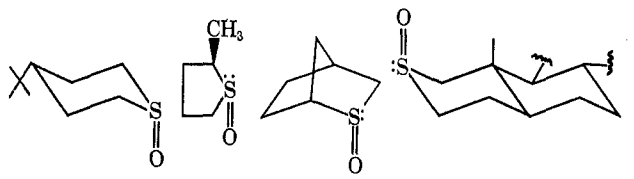
Sulfoxides. Separation and Assignment of Configuration.—To draw conclusions about the nature of cis and trans sulfoxides resulting from the oxidation (see below) of 3-substituted thietanes it was first necessary to separate the sulfoxide isomers, to ascertain their isomer purity, and to assign stereochemistry. Although Backer and Keuning in 1933 reported[20] the first separation of two isomers of a thietane 1-oxide (isomerism due to configuration at sulfur), by fractional crystallization of diastereomeric platinum complexes of the optical isomers of **10**, no other reports were published in the years between their work and the start of our studies.

10

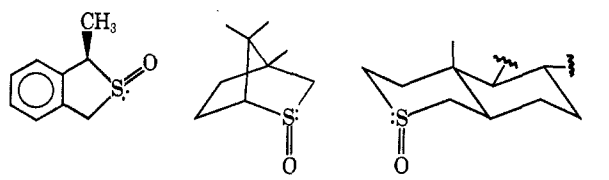
Preparative column chromatography over silica gel offered an effective method for separating the cis and trans isomers with little noticeable isomerization. Isomer purity for the sulfoxides of **1b** and **1f** was determined by vapor phase chromatography, the isomers eluting in the same order as from silica gel. For the sulfoxides of **1a**, **1c**, **1d**, and **1e** purity was determined from the nmr signals of the α-methylene hydrogens.[7b]

Dipole moment values of 3.22 ± 0.09 and 2.80 ± 0.03 D obtained for the sulfoxides of **1a** in their order of elution from silica gel were in fair agreement with values of 2.99 and 2.47 calculated from models of a puckered (37°) thietane 1-oxide, for **2a** and **3a**.[7a] From such models it is apparent that the β-ring hydrogen has a cis-diaxial relationship to the S=O bond in the trans isomer and thus should appear at significantly lower field in the nmr spectrum than the β hydrogen in the cis sulfoxide.[21] Experimentally, the β hydrogen signal for the isomer eluted first, assigned structure **2a**, appears at higher field than its counterpart in the isomer of longer retention time. Assignments for the sulfoxides of systems **1b–f** were made on this basis.[7b] For the sulfoxides assigned cis stereochemistry (**2a–f**) on the basis of the β hydrogen chemical shift, each has an α-methylene proton signal which is considerably broader than the signal for the trans isomer.[22] These assignments are supported by the recent configuration assignment made to **3d** from a dipole moment study.[8a]

The property of chromatographic retention times have been employed for the assignment of configuration to cyclic sulfoxides.[6,23–26] Elution rates from silica gel in particular have been employed, but to our knowledge the order or elution from silica gel for isomeric sulfoxides usually agrees with the order of elution from vpc columns. It is certainly noteworthy that for the six 3-substituted thietane 1-oxide systems examined the cis isomer was in each case eluted prior to the trans. The cyclic sulfoxides **11**,[6] **12**,[26] **13**,[24] **14**,[23a] and **15**[23b] are reported in the literature to have shorter retention times than their diastereomers. Retention times were also employed to distinguish **16** and **17** from their isomers; although not stated explicitly by the authors,[23b,25] it is assumed that the isomers shown here were eluted first. The apparent stereochemical feature which



11 **12** **13** **14**



16 **17** **15**

(18) W. A. White and H. Weingarten, *J. Org. Chem.*, **32**, 213 (1967).

(19) The thietane ring hydrogens of this material (as with **5a** and **5c**) appears as a singlet in the nmr spectrum. Thus offsetting proximity effects of the proton cis to the α-nitrogen atom and of the proton cis to the phenyl group of **7** are not a satisfacoty explanation.

(20) H. Backer and K. Keuning, *Recl. Trav. Chim. Pays-Bas*, **53**, 808 (1934).

(21) A. B. Foster, T. D. Inch, M. H. Qadir, and J. M. Webber, *Chem. Commun.*, 1086 (1968), and previous papers.

(22) The significance of these nmr spectra will be discussed in more detail in a subsequent paper.

(23) (a) P. B. Sollman, R. Nagarajan, and R. M. Dodson, *Chem. Commun.*, 552 (1967); (b) R. Nagarajan, B. H. Chollar, and R. M. Dodson, *ibid.*, 550 (1967).

(24) C. R. Johnson, H. Diefenbach, J. E. Keiser, and J. C. Sharp, *Tetrahedron*, **25**, 5649 (1969).

(25) F. A. L. Anet, L. M. Sweeting, T. A. Whitney, and D. J. Cram, *Tetrahedron Lett.*, 2617 (1968).

(26) J. J. Rigau, C. C. Bacon, and C. R. Johnson, *J. Org. Chem.*, **35**, 3655 (1970).

TABLE I

OXIDATION OF 3-METHYLTHIETANE AND 3-*tert*-BUTYLTHIETANE

Reagent	Conditions solvent (°C)	3-Methylthietane 1-oxides, cis/trans	3-*tert*-Butylthietane 1-oxides, cis/trans
Dinitrogen tetroxide	(0)	75/25	82/18
Sodium metaperiodate	H_2O–MeOH (0)	59/41	51/49
tert-Butyl hypochlorite	MeOH (0)	55/45	59/41
Chromic acid	C_5H_5N (25)	54/46	70/30
Hydrogen peroxide (30%)	HOAc (0)	46/54	43/57
Hydrogen peroxide (30%)	CH_3COCH_3 (0)	46/54	43/57
m-Chloroperbenzoic acid	CH_2Cl_2 (0)	45/55	45/55
Ozone	CH_2Cl_2 (25)	41/59	
N-Chlorotriazole	MeOH (−78)	33/67	
Nitric acid	Ac_2O (0)	Sulfone	Sulfone

these isomers hold in common is a more sterically hindered sulfinyl oxygen. That is, the negative end of their S–O dipole is less accessible for association with the absorbant. Thus the axial oxygen of trans 3-substituted thietane 1-oxides must be more accessible for interaction with the absorbant than the equatorial oxygen of the cis isomer. This is apparently a result of the bulk effect of the substituent.

Although the 1200–1000 cm^{-1} region of the infrared spectra of the cis and trans 3-substituted thietane 1-oxides differ significantly in each case, the differences do not appear to follow a simple pattern which might be useful in determining stereochemistry.

Stereochemistry of Oxidation.—Our study of the stereochemical course of oxidation to sulfoxides was limited to the oxidations of the **1b** and **1f** systems for which the cis/trans ratios of products could be determined rapidly and quantitatively by vpc analysis. Our results for a variety of oxidants are presented in Table I.

The oxidation with dinitrogen tetroxide, known to occur *via* thermodynamic product control,[6] gave a predominance of the cis isomer from 3-methylthietane. This supports our earlier report that sulfinyl oxygen in a 3-substituted thietane 1-oxide has an equatorial preference.[7a] Attempts to equilibrate a mixture of **2f** and **3f** with hydrogen chloride led to decomposition.

Oxidations with peroxy reagents usually involve steric approach control,[6] yielding the isomer in which oxygen is bonded to the least hindered side of the sulfur. The less stable isomer predominates in the oxidation of both **1b** and **1f** with peroxy reagents. Thus, approach to the sulfur atom of a puckered 3-alkylthietane must be less hindered from the side trans to the substituent at C_3. If the degree of ring puckering changes little upon oxidation, the axial oxygen of the trans isomer would be least hindered for association with a chromatography absorbant, in agreement with the greater retention time observed for the trans isomer.

In general, the 3-alkylthietane systems appear to be less sensitive to the nature of the oxidant than the 4-alkylthiane system.[6]

Experimental Section

Melting points were determined with a Thomas–Hoover capillary melting point apparatus and are uncorrected. The microanalyses were performed by Midwest Microlabs Inc., Indianapolis, Ind. The ir spectra were recorded on Perkin-Elmer infrared spectrophotometers, Models 137B and 621. The nmr spectra were taken on a Varian A-60A spectrometer. Vapor phase chromatography (vpc) was performed on an F and M Model 5750 (thermal conductivity) chromatograph with 0.25 in. columns. The mass spectral data was obtained on either an Atlas CH4 or an AEI MS9 mass spectrometer.

α-Morpholinostyrene.—A solution of 60 g (0.5 mol) of acetophenone, 65 g (0.75 mol) of redistilled morpholine, 45 mg of *p*-toluenesulfonic acid, and 150 ml of benzene was refluxed over a water separator until no further separation of water was observed (10–14 days). After concentration of the solution to a yellow oil vpc analysis indicated a mixture (~1/3) of acetophenone and a material of higher retention time. Reduced pressure distillation of the oil afforded 16.0 g of pure enamine, bp 85° (0.08 mm) [lit.[27a] bp 86–89° (0.1 mm)], ir (film) strong absorption at 1540 and 1590 cm^{-1}.

3-Phenyl-3-morpholinothietane 1,1-Dioxide (5c).—This reaction was run under nitrogen using either the pure enamine or a crude enamine–acetophenone mixture. Morpholinostyrene (0.5 mol), 51.0 g (0.5 mol) of triethylamine, and 200 ml of solvent (ether or benzene) were cooled to 0° in a 1-l. three-necked flask. Methanesulfonyl chloride (57.2 g, 0.5 mol) was added dropwise with stirring over a 45-min period. The ice bath was removed and the stirring was continued for 12 hr at room temperature. The yellow slurry was filtered and the residue washed with solvent. The residue was swirled with 400 ml of water (to remove triethylamine hydrochloride), filtered, and recrystallized from ethanol to yield white crystals: mp 193.5–194°; ir ($CHCl_3$) 1120 and 1320 cm^{-1} (sulfone); nmr ($CDCl_3$) δ 2.25 (m, 4), 3.70 (m, 4), 4.45 (s, 4), and 7.27 (m).

Anal. Calcd for $C_{13}H_{17}O_3NS$: C, 58.40; H, 6.41. Found: C, 58.33; H, 6.57.

The combined filtrate and organic washes from above were concentrated *in vacuo*; 50 ml of ethanol was added and on cooling white crystals, mp 86–89°, were obtained. Recrystallization from ethanol yielded *N*-methanesulfonylmorpholine as white plates: mp 91–93.5° (lit.[27b] mp 90–91°); ir ($CHCl_3$) 960, 1075, 1110, 1158, and 1345 cm^{-1}; nmr ($CDCl_3$) δ 2.78 (s, 3), 3.17 (m, 4), and 3.90 (m, 4).

The yield of **5c** from the reaction with pure enamine in benzene was 74% and from crude enamine in benzene or ether it was 33 or 46%, respectively.

When pure enamine was employed in this reaction α-methylsulfonylacetophenone was obtained in low yield as a by-product, crystallizing from solution after the cycloaddition product. After two recrystallizations from ethanol white crystals were obtained: mp 106.5–107° (lit.[28] mp 106–107°); ir ($CHCl_3$) 1675, 1324, 1277, 1151, and 1122 cm^{-1}; nmr ($CDCl_3$) δ 3.12 (s, 3), 4.61 (s, 2), and 7.5–8.1 (m, 5).

3-Phenylthiete 1,1-Dioxide (6c).—To a solution of 0.02 mol of **5c** in 10 ml of glacial acetic acid and 10 ml of acetic anhydride at ice bath temperature, was added dropwise with stirring 4.6 g (an excess) of 30% hydrogen peroxide solution. The reaction mixture was stirred over night at room temperature and then cooled again to ice bath temperature and neutralized with a concentrated solution of sodium hydroxide. Pyrolysis of the amine oxide was effected by heating the reaction mixture *in vacuo* on a rotary evaporator at ~65° for 2 hr or until dry. The residue was washed thoroughly with 60 ml of water, filtered, and recrystallized from ethanol to yield white crystals: mp 145–147°;

(27) (a) S. Huenig, K. Hiebner, and E. Benzing, *Chem. Ber.*, **95**, 926 (1962); (b) A. G. Kostsova, E. I. Kozachenko, O. M. Osina, V. P. Volokhova, and L. D. Maslova, *Zh. Org. Khim.*, **1**, 728 (1965).

(28) H. D. Becker and G. A. Russell, *J. Org. Chem.*, **28**, 1897 (1963).

yields 90–97.5%; ir ($CHCl_3$) 1125, 1310, 1563 (w), 1600 cm^{-1}; nmr ($CDCl_3$) δ 4.47 (s, 2), 7.00 (s, 1), 7.45 (s, 5).

Anal. Calcd for $C_9H_8O_2S$: C, 59.98; H, 4.47. Found: C, 60.18; H, 4.66.

3-Phenylthietane 1,1-Dioxide (4c). Procedure A.—A solution of 3.0 g (17.3 mmol) of **6c** and 0.70 g (~35 mmol) of sodium borohydride in 10 ml of dimethylformamide was heated with stirring for 1 hr at 60–70°. Stirring was continued at room temperature for an additional 8 hr. The solution was cooled in an ice bath and acidified with 1 *N* sulfuric acid. A white precipitate was collected and recrystallized from methanol to yield 1.12 g (37%) of white crystals: mp 101–102°; ir ($CHCl_3$) 1130, 1324, and 1600 cm^{-1}; nmr ($CDCl_3$) δ 3.93–4.75 (m, 5), and 7.38 (s, 5).

Anal. Calcd for $C_9H_{10}O_2S$: C, 59.32; H, 5.53. Found: C, 59.39; H, 5.74.

Procedure B.—To 1.2 g (an excess) of sodium borohydride in 50 ml of isopropyl alcohol at 60° was added 1.0 g of sulfone **6c** in small amounts over a 2-hr period. Stirring was continued at 60° for 4 days; an additional 100 mg of sodium borohydride was added the first day and again after the second. The reaction mixture was cooled, made slighlty acidic by dropwise addition of dilute sulfuric acid, and evaporated *in vacuo* to dryness. The residue was extracted with hot ethyl acetate. The extract was concentrated *in vacuo* to an oil which was placed on a short column of silica gel. Elution with ethyl acetate yielded 0.65 g (65%) of pure **4c**.

3-Phenylthietane (1c).—To 400 mg (~10 mmol) of lithium aluminum hydride in 30 ml of anhydrous ether at ice bath temperature was added dropwise with stirring a solution of 600 mg (3.42 mmol) of **4c** in 100 ml of ether. After stirring for 1 hr at ice bath temperature, saturated sodium sulfate solution was added dropwise until the reaction mixture turned white. The ether layer was decanted and the residue was washed with methylene chloride. The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo* to yield 389 mg of colorless oil. Chromatography over silica gel with methylene chloride as eluent yielded 150 mg (31%) of a colorless oil which produced only one peak on vpc analysis; ir, no sulfone bands; nmr ($CDCl_3$) δ 3.15–3.75 (m, 4), 4.3–4.9 (m, 1), and 7.3 (s, 5).

The mercuric chloride adduct was a white solid, mp 147–149°.

Anal. Calcd for $C_9H_{10}Cl_2HgS$: C, 25.63; H, 2.39. Found: C, 25.53; H, 2.42.

***cis*- and *trans*-3-Phenylthietane 1-Oxides (2c and 3c).**—To 330 mg of crude sulfide **1c** in 12 ml of reagent acetone at ice bath temperature added 160 mg (1.4 mmol) of 30% hydrogen peroxide. The solution was stirred at room temperature for 11 hr. The reaction mixture was concentrated *in vacuo* to a yellow oil. Chromatography of the oil over silica gel (elution by hexane, methylene chloride, and 1:1 (v/v) methylene chloride and chloroform) yielded 106 mg of the cis sulfoxide (**2c**) as white crystals, mp 91–91.5°, and 150 mg of the trans sulfoxide (**3c**) as a colorless oil. The cis isomer was eluted prior to the trans. The ir spectra of the two isomers differed in the 1250–950 cm^{-1} region. From the nmr spectra stereochemical assignments could be made and the isomer purity could be determined.[7b]

Anal. Calcd for $C_9H_{10}OS$ (cis isomer, **2c**): C, 65.02; H, 6.06. Found: C, 64.78; H, 6.09.

A mercuric chloride adduct (3:2) of the trans sulfoxide (**3c**) was prepared, white solid, mp 119–120°.

Anal. Calcd for $C_{18}H_{20}Cl_6Hg_3O_2S_2$: C, 18.85; H, 1.76. Found: C, 19.23; H, 1.90.

3-Morpholino-3-*p*-chlorophenylthietane 1,1-Dioxide (5a).—Crude *p*-chloro-α-morpholinostyrene was treated with triethylamine and methanesulfonyl chloride under conditions identical with those described for the preparation of **5c**. Higher yields were obtained (52% based on starting ketone) when benzene (*vs.* ether) was employed as the solvent. Recrystallization of the crude product from ethanol yielded white crystals: mp 193–194°; ir ($CHCl_3$) 1120, 1325, 1600 cm^{-1}; nmr ($CDCl_3$) δ 2.27 (m, 4), 3.70 (m, 4), 4.41 (s, 4), and 7.27 (q, 4).

Anal. Calcd for $C_{13}H_{16}ClNO_3S$: C, 51.74; H, 5.34. Found: C, 51.59; H, 5.63.

3-*p*-Chlorophenylthiete 1,1-Dioxide (6a).—The oxidation and amine oxide pyrolysis were conducted as described for the preparation of 3-phenylthiete 1,1-dioxide. The crude product was recrystallized from ethanol to yield white needles: mp 244.5–246°; yields were 90% or better; ir ($CHCl_3$) 1095, 1130, 1310, and 1600 cm^{-1}.

Anal. Calcd for $C_9H_7ClO_2S$: C, 50.36; H, 3.29. Found: C, 50.52; H, 3.49.

3-*p*-Chlorophenylthietane 1,1-Dioxide (4a). Procedure A.—A solution of 5.0 g (23.2 mmol) of unsaturated sulfone **6a** and 5.0 g (132 mmol) of sodium borohydride in 25 ml of dimethylformamide was heated with stirring at 60–65° for 3 to 4 hr. The solvent was removed under reduced pressure with gentle heating. To the residue was added 15 ml of water and the mixture was quickly acidified (dilute sulfuric acid) and filtered. The white residue was washed with water and recrystallized from methanol to yield 2.27 g (45%) of white plates: mp 116.5–118°; ir ($CHCl_3$) 1015, 1095, 1135, 1320, 1395, and 1490 cm^{-1}.

Anal. Calcd for $C_9H_9ClO_2S$: C, 49.89; H, 4.19. Found: C, 49.72; H, 4.33.

Procedure B.—The reduction of **6a** to **4a** could also be effected with sodium borohydride in isopropyl alcohol as described above for synthesis of **4c**; the yield of **4a** was 65% by this method.

3-*p*-Chlorophenylthietane (1a).—The saturated sulfone (**4a**) was reduced with lithium aluminum hydride in ether by a procedure analogous to that employed in the synthesis of **1c**. After chromatography of the crude product over silica gel (eluting with benzene) a yield (33%) of colorless oil was obtained which exhibited only one peak on vpc analysis; ir ($CHCl_3$) 1009, 1090, and 1489 cm^{-1} (no SO_2 bands).

Anal. Calcd for C_9H_9ClS: C, 58.53; H, 4.91. Found: C, 58.73; H, 5.06.

***cis*- and *trans*-3-*p*-Chlorophenylthietane 1-Oxides (2a and 3a).**—To 680 mg (3.64 mmol) of sulfide **1a** in 40 ml of reagent methylene chloride at 0° was added dropwise with stirring 700 mg (~3.6 mmol) of *m*-chloroperbenzoic acid in 20 ml of methylene chloride. After stirring at 0° for 12 hr the reaction mixture was filtered and the residue washed with methylene chloride. The filtrate was washed with saturated sodium hydrogen carbonate solution, dried, dried ($MgSO_4$), and concentrated *in vacuo* to an oil which crystallized on standing. The mixture could be resolved by chromatography over silica gel [eluting with hexane, methylene chloride, and a 1:1 (v/v) mixture of methylene chloride and chloroform]. The cis sulfoxide was eluted first as white crystals, mp 89–89.5°, the trans isomer as white crystals, mp 87–88.5°. The ir spectra differ significantly in the 1250–950 cm^{-1} region. Stereochemical assignments were based on dipole moments and were substantiated by the nmr spectra.

Anal. Calcd for C_9H_9ClOS (a mixture of the two isomers): C, 53.86; H, 4.52. Found: C, 53.91; H, 4.64.

Dipole Moments of *cis*- and *trans*-3-*p*-Chlorophenylthietane 1-Oxide (2a and 3a).—The dipole moments were measured with a Dipolemeter DM01 manufactured by Wissenschaftlich-Technische Werkstatlen using the measurement of the dielectric constant by the Heterodyne Beat Method according to the procedure of Allinger and Allinger.[29] The dipole moments were measured in benzene solution at 25 ± 0.01°. The dipole moment data for **3a** are α = 11.4557, β = 0.8331, e_1 = 2.27485, P_2 = 211.35, d_1 = 0.873011, R_D = 50.81, giving a dipole moment of 2.80 ± 0.03 D; for **2a** the data are α = 15.2567, β = 0.9656, e_1 = 2.27430, P_2 = 263.20, d_1 = 0.872929, R_D = 50.81, giving a dipole moment of 3.22 ± 0.09 D.

3-*tert*-Butyl-3-dimethylaminothietane 1,1-Dioxide.—This reaction was run in benzene using crude 2-dimethylamino-3,3-dimethylbutene[18] and employing the procedure described earlier for the synthesis of **5c**. The reaction mixture was filtered and the residue washed with benzene. The combined filtrate and washes were concentrated *in vacuo* to a brown oil. The oil was dissolved in 10% hydrochloric acid and the insolubles were discarded. Neutralization of the acid solution precipitated the crude product. After several recrystallizations from hexane a 31% yield of white needles, mp 104–104.5°, was obtained: ir ($CHCl_3$) 1135 and 1300 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 1.05 (s, 9), 2.60 (s, 6), and 4.10 (s, 4).

Anal. Calcd for $C_9H_{19}NO_2S$: C, 52.59; H, 9.34. Found: C, 52.61; H, 9.31.

3-*tert*-Butylthiete 1,1-Dioxide (6b).—The oxidation and amine oxide pyrolysis were carried out as described in the preparation of **6c**. Recrystallization of the crude product from hexane gave an 80% yield of white crystals: mp 65–65.5°; ir ($CHCl_3$) 1150, 1305, (SO_2), 1590 cm^{-1} (C=C); nmr (CCl_4) δ 1.20 (s, 9), 4.25 (s, 2), and 6.25 (s, 1).

Anal. Calcd for $C_7H_{12}O_2S$: C, 52.46; H, 7.56. Found: C, 52.40; H, 7.39.

(29) N. L. Allinger and J. Allinger, *J. Org. Chem.*, **24**, 1613 (1959).

3-*tert*-Butylthietane 1,1-Dioxide (4b).—To a solution of 8.0 g (0.05 mol) of 3-*tert*-butylthiete 1,1-dioxide in 70 ml of absolute ethanol was added 500 mg of 5% palladium on carbon. The mixture was placed on a Parr hydrogenation apparatus with hydrogen pressure of 40 psi for 2.5 days. The hydrogenation mixture was then filtered and concentrated *in vacuo* to a yellow oil. Vpc analysis showed only one component, which had a retention time shorter than that of starting material. Recrystallization from hexane gave 7.1 g (88%) of hydroscopic yellow-white crystals: mp 37–39°; ir (CCl_4) 1140, 1320 cm^{-1} (SO_2); nmr (CCl_4) δ 0.95 (s, 9), 2.50 (m, 1), and 3.92 (d, 4).

Anal. Calcd for $C_7H_{14}O_2S$: C, 51.81; H, 8.71. Found: C, 51.74; H, 8.73.

3-*tert*-Butylthietane (1b).—To 1.85 g (47 mmol) of lithium aluminum hydride in 70 ml of anhydrous ether at ice bath temperature was added dropwise with stirring a solution of 1.85 g (11.4 mmol) of sulfone (**4b**) in 100 ml of ether. Stirring was continued at ice bath temperature for 1 hr. An additional 100 ml of ether was added and the normal work-up procedure with saturated sodium sulfate solution was followed to yield 1.26 g of colorless oil. Chromatography over silica gel (eluting with hexane) yielded 842 mg (56%) of a colorless volatile oil for which vpc analysis showed only one peak. The infrared spectrum was void of sulfone absorption bands: nmr (CCl_4) δ 0.87 (s, 9), and 3.03 (m, 5).

The mercuric chloride adduct was obtained as a white solid, mp 177.5–178.5°.

Anal. Calcd for $C_7H_{14}Cl_2HgS$: C, 20.93; H, 3.51. Found: C, 21.08; H, 3.57.

***cis*- and *trans*-3-*tert*-Butylthietane 1-Oxides (2b and 3b).**—To 775 mg (3.7 mmol) of sodium metaperiodate in 8 ml of water at ice bath temperature was added 470 mg (3.7 mmol) of crude sulfide in 6 ml of methanol. The mixture was stirred at ice bath temperature for 12 hr. The reaction mixture was filtered and the filtrate extracted with chloroform. The dried (Na_2SO_4) extract was concentrated *in vacuo* to a yellow oil. Vpc analysis indicated approximately equivalent amounts of the two sulfoxides and a small amount of sulfone. The sulfoxide mixture could be resolved by elution chromatography over silica gel, eluting first with methylene chloride followed by 1:1 (v/v) methylene chloride and chloroform. The cis sulfoxide was eluted first (both sulfoxides are oils). Stereochemical assignments were based on the nmr spectra.[7b] The isomer purity was determined by vpc analysis on a 5-ft FFAP (on Chromosorb W) column at 145°. The ir spectra of the two sulfoxides differed in the region of 1200–1000 cm^{-1}. Oxidation of the sulfoxides yielded the sulfone **4b**. Mass spectra for **2b** (70 eV): *m/e* (relative intensities for *m/e* above 40) 41 (62), 43 (10), 55 (34), 57 (100), 69 (27), 83 (11), 97 (11), and 146 (30); for **3b**, 41 (65), 43 (15), 55 (34), 57 (100), 69 (26), 83 (12), 97 (10, and 146 (25). The calculated molecular weight is 146.

3-Chlorothietane (1d).—This oil was prepared from 3-thietanol[30] according to the procedure of Kotin.[5a] A yield of 33% was obtained.

***cis*- and *trans*-3-Chlorothietane 1-Oxides (2d and 3d).**—To 1.09 g (10 mmol) of sulfide **1d** in 29 ml of methylene chloride stirring at ice bath temperature was added 2.0 g (10 mmol) of *m*-chloroperbenzoic acid in 35 ml of methylene chloride. After stirring for 8 hr at ice bath temperature the mixture was filtered. The filtrate was diluted with chloroform and washed with saturated sodium hydrogen carbonate solution. The dried (Na_2SO_4) filtrate was concentrated *in vacuo* to 1.07 g of yellow oil. The two sulfoxides could be separated by chromatography over silica gel (eluting with 1:2 chloroform and methylene chloride). The cis isomer was eluted first, white crystals with mp 92–94° (lit.[5a] mp 91–93°). The trans isomer, white crystals, had mp 74–76° (lit. mp 70–72°[5a] or 74–75°[8a]). A stereochemical assignment is reported in the literature[8a] and is substantiated by the nmr spectra.[7b]

3-Acetoxythietane (1e).—The procedure of Adams, *et al.*,[31] was employed to convert 3-thietanol to the acetate **1e**: nmr (CCl_4) δ 1.97 (s, 3), 3.33 (m, 4), and 5.53 (m, 1).

***cis*- and *trans*-3-Acetoxythietane 1-Oxide (2e and 3e).**—To 2.43 g (11.4 mmol) of sodium metaperiodate in 30 ml of water at ice bath temperature was added with stirring 1.50 g (11.4 mmol) of sulfide **1e** in 3 ml of methanol. The mixture was stirred at ice bath temperature overnight and then filtered. The filtrate was extracted with chloroform and methylene chloride and the combined extracts were dried (Na_2SO_4) and concentrated *in vacuo* to 1.85 g of light yellow oil. Elution chromatography over silica gel with 1:1 (v/v) chloroform–methylene chloride followed by pure chloroform separated the two sulfoxides. The cis isomer was eluted prior to the trans. The ir spectra differed in the 1250–950 cm^{-1} region but isomer purity was best determined from the nmr spectra.[7b] Stereochemistry was assigned from the nmr spectra also.[7b] The cis isomer **2e** was a colorless oil: mass spectrum (70 eV) *m/e* (relative intensities for *m/e* above 40) 43 (54) 46 (13), 57 (25), 60 (13), 63 (32), 88 (100), 106 (12), 147 (0.9), and 148 (0.5). The calculated mol wt is 148. The **trans isomer (3e)** was recrystallized from ether to yield white crystals, mp 50–52.5°.

Anal. Calcd for $C_5H_8O_3S$: C, 40.53; H, 5.44. Found: C, 40.61; H, 5.45.

3-Acetoxythietane 1,1-Dioxide (4e).—Treatment of the sulfide **1e** with excess 30% hydrogen peroxide in acetone yielded the corresponding sulfone, a white crystalline solid, mp 117–117.5°.

Anal. Calcd for $C_5H_8O_4S$: C, 36.58; H, 4.91. Found: C, 36.49; H, 4.80.

3-Methylthietane (1f).—This volatile sulfide was prepared from 2-methyl-3-chloropropene according to the method of Bordwell and Hewett.[32]

***cis*- and *trans*-3-Methylthietane 1-Oxide (2f and 3f).**—These sulfoxides were recently reported by Tang and Mislow.[4c] Our samples were likewise prepared by the oxidation of 3-methylthietane and subsequent chromatography of the sulfoxide mixture over silica gel. The cis isomer was eluted prior to the trans; the stereochemical assignments have been reported.[4c] Cis/trans ratios could be determined by vpc on a 17 ft × 0.25 in. column of 7.5% Versamid on Diaport S at 126° with a helium flow of 1.5 ml/sec.

3-Methylthietane 1,1-Dioxide (4f).—Oxidation of **1f** with an excess of hydrogen peroxide yielded the corresponding sulfone **4f**, a colorless oil: ir (film) 2950, 1395, 1310, 1220, 1195 (sh), and 1160 cm^{-1}; nmr ($CDCl_3$) δ 1.35 (d, 3), 2.65 (m, 1), 3.95 (m, 4).

Anal. Calcd for $C_4H_8O_2S$: C, 39.98; H, 6.71. Found: C, 39.79; H, 6.83.

3-Morpholino-3-phenylthietane (7).—To 7.00 g (26.2 mmol) of sulfone **5c** and 3.8 g (100 mmol) of lithium alumuminum hydride was added dropwise 200 ml of anhydrous ether, keeping the reaaction flask in an ice bath. Stirring was continued at 0° for 10 hr after which time the excess lithium aluminum hydride was decomposed by dropwise addition of ethanol. The reaction mixture was made slightly acidic with 20% hydrochloric acid and the ether layer was decanted. The aqueous residue was extracted with ether and the combined ether extracts were dried ($MgSO_4$) and concentrated *in vacuo* to 4.4 g of an oil which crystallized in ethanol–hexane. Recrystallization from ethanol yielded 2.35 g (38%) of white crystals: mp 104–105°; ir ($CHCl_3$) no sulfone bands; nmr ($CDCl_3$) δ 2.25 (m, 4), 3.3–3.8 (m, 8), 7.35 (s, 5).

Anal. Calcd for $C_{13}H_{17}NOS$: C, 66.35; H, 7.28; N, 5.95. Found: C, 66.22; H, 7.29; N, 5.79.

Base Hydrolysis of 5c.—A mixture of amino sulfone **5c** (0.5 g), sodium hydroxide (3.0 g), water (30 ml), and methanol (30 ml) was heated on a steam bath for 2 hr and the methanol was allowed to evaporate. On cooling 0.25 g of unreacted starting material was collected by filtration. The aqueous filtrate was extracted with methylene chloride and the dried ($MgSO_4$) extract was concentrated *in vacuo* to 0.15 g of white solid. Recrystallization from ether–petroleum ether yielded 0.06 g of white crystals identified as the enamine **9**: ir ($CHCl_3$) 1552, 1320, 1145, and 1118 cm^{-1}; nmr ($CDCl_3$) δ 3.0 (s, 3), 3.0–3.15 (m, 4), 3.6–3.8 (m, 4), 5.45 (s, 1), and 7.5 (m, 5). A second crop of crystals, 0.02 g, was identified as dimethyl sulfone, a mixture melting point showed no depression.

If the aqueous filtrate above was acidified before extraction with methylene chloride, the β keto sulfone **8**, identified earlier, was isolated; a mixture melting point showed no depression.

Base Hydrolysis of 3-Phenylthiete 1,1-Dioxide (6c).—A mixture of sulfone **6c** (0.5 g), sodium hydroxide (3.0 g), water (30 ml), and methanol (30 ml) was heated on the steam bath for 2 hr. After cooling and acidification with dilute sulfuric acid a white solid precipitated. The white solid, 0.18 g, was collected

(30) D. C. Dittmer and M. E. Christy, *J. Org. Chem.*, **26**, 1324 (1961).

(31) E. P. Adams, K. N. Ayad, E. P. Doyle, D. O. Holland, W. H. Hunter, J. H. C. Nyler, and A. Queen, *J. Chem. Soc.*, 2665 (1960).

(32) F. G. Bordwell and W. A. Hewett, *J. Org. Chem.*, **27**, 292 (1962).

by filtration, dried, and compared with an authentic sample of benzoic acid. The ir spectra were superimposable and a mixture melting point showed no depression. The aqueous layer was extracted with methylene chloride and the dried extract was concentrated *in vacuo* to ~0.3 g of white solid. After recrystallization this solid was identified as dimethyl sulfone by ir and a mixture melting point. Under the conditions described above 3-*p*-chlorophenylthiete 1,1-dioxide was converted to *p*-chlorobenzoic acid and dimethyl sulfone.

Reduction of 3-Phenylthiete 1,1-Dioxide (6c) with Lithium Aluminum Hydride.—A solution of lithium aluminum hydride (1.0 g) in 50 ml of freshly distilled THF was refluxed for 30 min. To this was added dropwise with stirring 1.0 g of sulfone (**6c**) in 50 ml of THF; addition time was 45 min. Stirring was continued at room temperature for 12 hr after which the excess hydride was decomposed with a 20% ammonium chloride solution. The organic layer was filtered and the residue was washed with ether. The dried ($MgSO_4$) organic solution was concentrated *in vacuo* to a foul smelling oil which was analyzed as predominantly a single component on vpc. This major component, a colorless oil, was collected from vpc and tentatively identified as 2-phenylpropanethiol: ir (film) 3000–2850, 1600, 1490, 1440, 1365 (w), 1060 (w), 1010 (w), 905 (w), 755, and 690 cm^{-1}; nmr (CCl_4) δ 1.0 (t, 1), 1.35 (d, 3), 2.5–2.9 (m, 3), and 7.17 (s, 5). On shaking the nmr sample with D_2O the triplet at δ 1.0 disappeared and the multiplet at δ 2.5–2.9 became less complex.

H–D Exchange of α-Methylene Protons of Thietane 1,1-Dioxide.—Sodium (60 mg, 2.5 mg-atoms) was added to 2.60 g (130 mmol) of deuterium oxide; to that solution was added 2.75 mmol of sulfone **4a** or **4b** in 6 ml of dioxane. The mixture was heated with stirring at 40–50° for 24 hr; stirring was continued at room temperature for an additional 24 hr. Concentrated hydrochloric acid (2.5 ml) was added with stirring. The reaction mixture was evaporated *in vacuo* to dryness and the residue was extracted with ethyl acetate. The extract was concentrated and the residue was recrystallized from methanol to yield 88% of the α-tetradeuterated sulfone. The melting point and ir spectrum remained very similar to that of starting material. In the nmr spectrum the signal for the α-methylene protons had disappeared and the multiplet for the methine proton collapsed to a broad singlet.

The α-tetradeuterated thietane derivatives were reacted under the same conditions as their hydrogen analogs.

Oxidation of Thietanes.—The general methods of oxidation employed for the oxidation study were reported earlier.[6] The use of *N*-chlorotriazole as an oxidant for sulfides has been reported in a more recent communication from this laboratory.[33] Special care was observed to avoid over oxidation to sulfone, less than 1 equiv of oxidant per mole of sulfide was employed. The ratios given in Table I were obtained from planimetric integration of the vpc graphs.

Registry No.—**1a**, 25903-01-9; **1b**, 25903-02-0; mercuric chloride adduct of **1b**, 25903-03-1; mercuric chloride adduct of **1c**, 25957-63-5; **1f**, 22438-40-0; **2a**, 25902-65-2; **2b**, 25902-66-3; **2c**, 25902-67-4; **3a**, 25902-68-5; **3b**, 25902-69-6; mercuric chloride adduct of **3c**, 25902-70-9; **3e**, 25902-71-0; **4a**, 25903-04-2; **4b**, 25903-05-3; **4c**, 25636-64-0; **4e**, 25903-14-4; **4f**, 25903-07-5; **5a**, 25903-08-6; **5c**, 25957-61-3; **6a**, 25903-15-5; **6b**, 25903-16-6; **6c**, 25903-17-7; **7**, 25903-18-8; 3-*tert*-butyl-3-dimethylaminothietane 1,1-dioxide, 25957-62-4.

Acknowledgment.—We gratefully acknowledge the very able technical assistance of Mr. A. Geertsema with the synthesis of 3-*tert*-butylthietane and of Mr. H. Levin with the oxidation study of 3-methylthietane. We are also grateful to Mr. J. Sprague for the dipole moment determinations.

(33) W. D. Kingsbury and C. R. Johnson, *Chem. Commun.*, 365 (1969).

The Stevens Rearrangements of *N,N,N*-Trimethylneopentylammonium Iodide[1]

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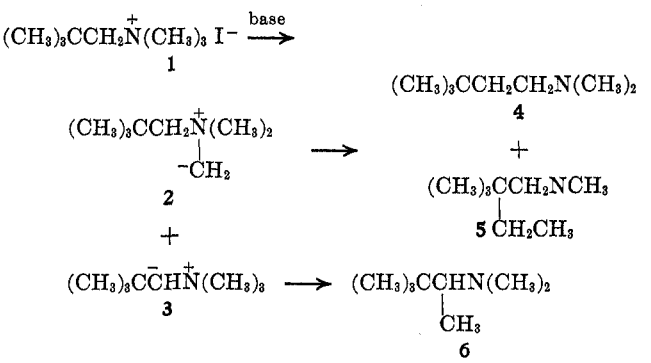
Received April 8, 1970

The Stevens rearrangements of *N,N,N*-trimethylneopentylammonium iodide (**1**) have been investigated using a series of base–solvent systems. In all cases 3,3,*N,N*-tetramethyl-1-butylamine (**4**) is the major rearrangement product, with *N*-ethyl-*N*-methylneopentylamine (**5**) and 3,3,*N,N*-tetramethyl-2-butylamine (**6**) being formed in low yields. In addition, *N,N*-dimethylneopentylamine (**7**) from a displacement reaction becomes the major product in more acidic solvents. Thermal decomposition (294°) leads to **7** and methyl iodide. An ion-pair rearrangement pathway is proposed consistent with the minor side products, *N,N*-dimethylbenzylamine (**10**), from phenyllithium, *N,N*-dimethyl-1-pentylamine (**11**) from *n*-butyllithium, and neopentane (**9**).

Although the Stevens rearrangement[2] of quaternary ammonium salts has been the subject of many studies since its discovery in 1932,[3] very little work has been reported using simple alkylammonium systems.[4] As a continuation of our interest in this area, we have studied the Stevens rearrangements of *N,N,N*-trimethylneopentylammonium iodide (**1**) with a series of base–solvent systems. The quaternary ammonium salt **1** has the characteristic of being the potential precursor for three different Stevens rearrangement products, **4**, **5**, and **6**, through ylides of similar carbanion stability,[5] **2** and **3**,



but differing steric requirements. In the following we report the results of this study and their relevance to the mechanism of the Stevens rearrangement.

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(1) The authors thank the National Science Foundation and the donors of the Petroleum Research Fund for partial support of this work.

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(3) For leading references, see S. H. Pine, *Org. React.*, **18**, 403 (1970).

(4) (a) H. Daniel and J. Paetsch, *Chem. Ber.*, **101**, 1445 (1968); (b) W. K. Musker, *J. Org. Chem.*, **32**, 3189 (1967); (c) G. Wittig and D. Krauss, *Justus Liebigs Ann. Chem.*, **679**, 34 (1964).

(5) D. J. Cram in "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 21.