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DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

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The Ohio State University
1967

Approved

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Dedication

To Sally Diane
ACKNOWLEDGMENT

The author is grateful to Dr. Leo A. Paquette for his guidance throughout the course of this investigation.
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PUBLICATIONS


"A Novel Rearrangement Attending the Addition of Sulfenes to 1,3-Bis(dimethylamino)-3-phenyl-1-propene." Tetrahedron Letters, No. 8, 703 (1967).

"The Reaction of Sulfenes with 1,3-Bis(dimethylamino)-l-alkenes. Mechanistic Dichotomy as a Function of Substitution." Journal of the American Chemical Society, 89, 4102 (1967).

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INTRODUCTION

The current search for highly strained and highly reactive molecules stimulated a study concerning the mechanistic aspects of the reaction of sulenes (1) with electron-rich olefins, especially as applied to the synthesis of unsaturated small ring compounds containing the sulfone group. This dissertation describes the approaches utilized in the synthesis of a methylene thiete dioxide molecule (2) and the interesting rearrangements encountered when sulenes are used in preparation of possible precursors of 2.

\[ \text{RR'C=SO}_2 \quad \text{H}_2\text{C}=\text{SO}_2 \]

\[ 1 \quad 2 \]

Fused aromatic thiete dioxides (3) and bicyclic systems containing a thietane dioxide (4) represent a further extension.

\[ 3 \quad 4 \]
in this area, and synthetic routes to these systems will be presented.

This dissertation consists of three parts:

Part I. The Reaction of Sulfenes with 1,3-Bis(dimethyl-amino)-1-alkenes. Mechanistic Dichotomy as a Function of Substitution.

Part II. Synthetic Approaches to, and Reactions of, the Methylene Thiete Dioxide System.

Part III. Preliminary Studies Concerning the Preparation of Bicyclic and Fused Aromatic Derivatives of Thiete Dioxide.
PART I

THE REACTION OF SULFENES WITH 1,3-BIS(DIMETHYLAMINO)-1-ALKENES. MECHANISTIC DICHOTOMY AS A FUNCTION OF SUBSTITUTION

Introduction

The nature of the bonding in sulfenes

In 1911, the action of tertiary amines on an aliphatic sulfonyl halide was said to lead to a species, $RR'C=SO_2$ (1), which was named a sulfene, by analogy with ketene which had been discovered only a short time before. Subsequent study has lent considerable support to the idea that sulfenes are intermediates in this and other transformations. Before discussing the above reactions, the type of bonding in sulfene will be described.

(1) E. Wedekind and D. Schenk, Ber., 44, 198 (1911).

A priori, five canonical forms for sulfene can be conceived. Structure 5b is based on the expected polarization in thiocarbonyl...
groups where the sulfur atom may even carry a partial positive charge.³


However, the presence of oxygens bonded to sulfur might influence the bonding in sulfene to be more carbonyl-like (5c) and, if the negative charge is concentrated about the oxygen atom, 5d becomes a possibility. Structure 5e, the cyclic anhydride of hydroxymethanesulfinic acid,
is derived from the cyclization of 5d; however, no evidence for this three-membered ring has been found. This text will depict sulfene in its cumulative form, but the relative significance of the canonical forms 5a-5e in sulfene cannot be assessed with certainty, though the reactions of sulfene discussed below have led to the suggestion that 5b is more important than the others. The fact that no sulfenes have yet been isolated demonstrates the instability imparted to the thiocarbonyl skeleton by further S-oxidation and any further discussion of their electronic structure would be pointless until their detection and isolation have been achieved.

Various reactions where sulfenes are generated

1. Elimination of hydrogen chloride from sulfonyl chlorides

The earliest reference to a sulfene is found in the studies concerning the decomposition of 3,5-dibromo-4-hydroxybenzenesulfonyl chloride (6) in the presence of sodium acetate.\(^4\) Initially, a yellow color is formed in this reaction, followed by the formation of a polymer. The authors attributed the transient yellow coloration to the formation of quinoid sulfene (7). The structure of the colorless product of this reaction has been assigned as a linear oligomer (8) (eq 1).\(^5\)
This reaction was reinvestigated with the intention of trapping \( \text{Z} \) with hydrogen fluoride and hydrogen bromide (eq 2).^6

However, neutralization of the basic solutions of \( \text{Z} \) with ethereal hydrogen bromide or hydrogen fluoride resulted in the regeneration of the starting phenol. The fact that only the starting phenol was produced indicated that the reaction was simply an acid-base interconversion and that the yellow species was the phenolate anion \((\text{Z}^-)^6\).

The synthesis of ketenes^7 and the discovery in 1911 that

---


(7) E. Wedekind and W. Weisswange, Ber., 39, 1631 (1906).
triethylamine removed the elements of hydrogen chloride from phenylmethylene sulfonyl chloride in cold benzene to give triethylamine hydrochloride, sulfur dioxide, and stilbene as products provided the stimulus for future search in the sulfene area.\(^1\) The proposed mechanism for this reaction involved initial abstraction of a proton to produce a benzylic carbanion, chloride-ion elimination to produce phenylsulfene (8), loss of sulfur dioxide to form phenylcarbene, and dimerization of the carbene to produce stilbene (eq 3).
This reaction has since been repeated and generalized and sulfenes are now recognized as intermediates. The transformation shows a dependence on solvent; several minor products have been isolated; and, mechanisms for the formation of all products have been postulated. In addition, these recent studies stress the fact that the isolated olefins probably do not arise via the dimerization of a carbene, since attempts to trap such a species have been fruitless.

The idea of an elimination-addition mechanism via sulfenes
has been rigorously proven by detailed labelling experiments.\(^{10,11}\)


Of particular relevance to this discussion is the conclusion that sulfenes, if actually formed as hypothesized, must react with water to form the corresponding sulfonic acid, with alcohols to yield the appropriate esters, and with ammonia or primary or secondary amines to give the sulfonamides. In essence, these studies showed that in the presence of base, the solvolysis of alkanesulfonyl chlorides is accompanied by exchange of one and only one hydrogen (see structure \(11\)); in the absence of base no such exchange occurs (eq 4).

\[
\text{RCH}_2\text{SO}_2\text{Cl} + \text{ROD} \xrightarrow{\text{base}} \text{RCH}_2\text{SO}_2\text{OR} + \text{RCHDSO}_2\text{OR}
\]

\(2\) \hspace{1cm} \(10\) \hspace{1cm} \(11\)  

\((4)\)

If the deuterium were incorporated at the sulfonyl chloride (\(2\)) or ester stages (\(10\)) by base-catalyzed deuterium exchange, then the other protons would have been replaced indiscriminately and scrambling would have been found. The fact that the esters produced were partially undeuterated (\(10\)), coupled with the observation that
exchange between alcohol and ammonium chloride does not occur under the reaction conditions, leads to the conclusion that competing sulfene and "nonsulfene" reactions are taking place. The effect of the leaving group, the solvent, and the structure of the sulfonyl chloride on the amount of deuterium incorporated are all in accord with competing elimination (E₂) and substitution reactions (S₅₂) between the sulfonyl chloride and triethylamine (eq 5).

\[
\begin{align*}
\text{RCH} = \text{SO}_2 + \text{Et}_3\text{NHCl} & \xrightarrow{\text{ROD}} \text{RCH}_2\text{SO}_2\text{Cl} + \text{Et}_3\text{N} \\
\text{RCH}_2\text{SO}_2\text{Cl} + \text{Et}_3\text{N} & \xrightarrow{\text{S}_2} \text{RCH}_2\text{SO}_2\text{Et}_3\text{Cl} \xrightarrow{\text{ROD}} \text{RCH} = \text{SO}_2 + \text{Et}_3\text{NHCl}
\end{align*}
\]

(eq 5)

2. Reaction of diazoalkanes with sulfur dioxide

A second method for the preparation of sulfenes \textit{in situ} was discovered during an attempt to prepare diphenylsulfene from diphenyldiazomethane and sulfur dioxide.\(^{12}\) However, the sulfene

\(^{12}\) (a) H. Staudinger and F. Pfenninger, \textit{Ber.}, \textbf{49}, 1941 (1916); (b) L. A. Paquette and L. S. Wittenbrock, \textit{J. Org. Chem.}, \textbf{31}, 1997 (1966) - see reference 3 in this article for a compilation of the references for this general reaction.
escaped direct detection because of rapid reaction with one of the starting materials (eq 6, p. 12). If an excess of sulfur dioxide is employed, a competing reaction which leads to the formation of benzophenone occurs. If, on the other hand, sulfur dioxide is passed into a solution of diphenyldiazomethane, the diazoalkane reacts with the sulfene and a three-membered ring sulfone is formed. This compound, when heated, affords tetraphenylethylene. When the reaction is performed in the presence of water, alcohols, ammonia, or primary or secondary amines, it gives products whose formation can be explained through the intermediacy of a sulfene.
Equation 6

\[ \text{[S}_2\text{O}_3\text{]} + (\text{C}_6\text{H}_5)_2\text{CO} \rightarrow (\text{C}_6\text{H}_5)_2\text{C}=\text{SO}_2 \]

\[ (\text{C}_6\text{H}_5)_2\text{CN}_2 + \text{SO}_2 \rightarrow (\text{C}_6\text{H}_5)_2\text{C}^-\text{N}_2 + (\text{C}_6\text{H}_5)_2\text{C}=\text{SO}_2 \]

\[ (\text{C}_6\text{H}_5)_2\text{CN}_2 \rightarrow (\text{C}_6\text{H}_5)_2\text{C}^-\text{N}_2 + (\text{C}_6\text{H}_5)_2\text{C}=\text{SO}_2 \]
3. Sulfene production by photochemical methods

Irradiation of cyclic sultones (12) in methanol or in an ether solution containing benzylamine gave either a methyl ester (13) or the corresponding sulfonamide (14) (eq 7).\(^\text{13}\)


Since these reactions do not take place in the dark, it is assumed that they proceed by photochemical ring cleavage to form the keto-vinylsulfenes (12a).

Recently, the attempt was made to prepare photochemically a simple sulfene under neutral aprotic conditions.\(^\text{14}\) These
workers postulated that a sulfene could be formed by the irradiation of a β-ketosulfone bearing a hydrogen atom attached to the γ-carbon with subsequent abstraction of this atom by the electron-deficient oxygen of the excited carbonyl group followed by a Norrish Type II cleavage (eq 8).

\[
\begin{align*}
\text{RCH=SO}_2^+ \quad \text{CH}_3\text{OH} & \rightarrow \quad \text{RCH=SO}_2^+ \quad \text{CH}_3\text{OH} \\
\hspace{2cm} \quad \text{HO-C=CH}_2 & \rightarrow \quad \text{RCH}_2\text{SO}_2\text{OCH}_3
\end{align*}
\]

However, only products formed by the cleavage of the carbon-sulfur bond beta to the carbonyl group were formed.

The irradiation of α-diazosulfones in methanol gives mainly aryl methoxymethyl sulfones. Part of the sulfonyl-carbene, however,
apparently rearranges to the sulfene to form on reaction with methanol the sulfonate ester (eq 9).\(^\text{15}\)

\[\text{X-SO}_2\text{CHN}_2 \xrightarrow{\text{hv}} \text{ArSO}_2\text{OH} \rightarrow \text{ArCH}==\text{SO}_2\]

\[\xrightarrow{\text{CH}_3\text{OH}} \xrightarrow{\text{ca. 10\%}} \text{ArSO}_2\text{CH}_2\text{OCH}_3 \quad \text{ArCH}_2\text{SO}_2\text{OCH}_3\]

(9)

The tendency of the aryl group to migrate from sulfur to the carbene carbon is low, as is evident from the product composition.\(^\text{15}\)

The important feature about this reaction is that it is the first example of sulfene formation by rearrangement.

**Cycloaddition reactions of enamines and sulfones**

Several extensive reviews concerning sulfenes and their reactions with reactive substrates have appeared\(^\text{9,16}\) and these


(16) (a) T. J. Wallace, *Quart. Rev.*, 20, 67 (1966);
can be consulted for a more comprehensive compilation of the chemical reactivity of this interesting family of intermediates.

When an alkanesulfonyl chloride is treated with triethylamine in the presence of electron-rich olefins (e.g. enamines, ketene O,N-acetals, ketene aminals, ketene acetals, dienamines, and vinyl ethers), cycloaddition usually occurs and thietane 1,1-dioxides are formed.  


(18) Sulfenes can also react with: (a) diazoalkanes - reference 12b (see reference 4 in this article for a compilation of the references for this reaction); (b) nitrones and nitrile oxides - F. Eloy and A. van Overstraeten, Bull. Soc. Chim. Belges, 76, 63 (1967) and references cited therein; (c) chloral - D. Borrmann and R. Wegler, Chem. Ber., 99, 1245 (1966) and (d) sulfonium ylides - H. Nozaki, M. Takaku, and Y. Hayasi, Tetrahedron Letters, 2303 (1967).

At the outset, the intention was to examine in some detail the mechanism by which enamines react with sulfenes. This reaction was first observed independently by Opitz and by Stork who noticed that enamines (16) did not undergo C-acylation when reacted with methanesulfonyl chloride and triethylamine but instead afforded thietane 1,1-dioxides (17) (eq 10).  


The intermediacy of sulfenes has been invoked in this process because the most plausible alternative mechanism for the formation of such four-membered heterocycles has been ruled out by the data of several groups of workers (eq 11).  

\[ \text{NR}_2 \text{CH} \quad + \quad \text{R}_2\text{CHSO}_2\text{Cl} \quad \xrightarrow{\text{Et}_3\text{N}} \quad \text{R}_2\text{N} \quad \text{SO}_2 \quad \text{R} \quad \text{R} \]

(10)

(21) (a) I. J. Borowitz, J. Am. Chem. Soc., 86, 1166 (1964);
(b) G. Opitz and K. Fischer, Z. Naturforsch., 18b, 775 (1963);
Equation 11
It is unknown whether the cycloaddition is concerted (a) or non-concerted (b) (eq 12).

Collapse of the zwitterion (18) in the non-concerted pathway can give either 17 or the enamino sulfone (19). The extent of neutralization of charge in 18 via path c depends on the degree of substitution in the enamines and sulfenes. The attempt was made to
establish the timing of this sulfene-enamine cyclization process.

In the beginning, the possibility of a two-step addition mechanism was considered since thermal 2+2 cycloadditions are not symmetry allowed. If this were operative, then replacement of a simple enamine by a 1,3-bis(dimethylamino)-1-alkene such as 20 should lead, after reaction with a sulfene, to the zwitterionic intermediate 21. This functionized intermediate (21) could collapse by two pathways, one (path A) gives the thietane dioxide, and the other (path B) affords cleavage (eq 13, page 21). Path B would be expected to be favored substantially in those instances where R and R' could assist in the stabilization of the respective fragments. Part I describes the results of such experiments.
Equation 13

\[ \text{RCH} = \text{N(CH}_3\text{)}_2 + (\text{CH}_3\text{)}_2 \text{NCH} = \text{CHSO}_2 \text{CHR}^\prime \]

\[ \xrightarrow{\text{H}^\oplus} (\text{CH}_3\text{)}_2 \text{NCH} = \text{CHSO}_2 \text{CH}_2 \text{R}^\prime \]
Results

N,N,N',N'-Tetramethylpropene-1,3-diamine (20a). Reaction of 20a with two equivalents each of methanesulfonyl chloride and triethylamine in cold (-15°) tetrahydrofuran gave a dark viscous oil which, when chromatographed on Florisil, yielded three characterizable products (22, 23 and 24) as outlined in Chart I. The Experimental Section summarizes the spectral data and elemental analyses of these and all other materials obtained in subsequent experiments described in this thesis. In all the reactions performed with 20a and 20b, maximum yields were observed when two equivalents of sulfene were employed. The reasons for this phenomenon will be considered in the Discussion. The structure of 23 was confirmed by hydrogenation to 1-dimethylamino-3-thiapentane 3,3-dioxide (25), which was prepared in unequivocal fashion by permanganate oxidation of the corresponding sulfide (26). Compounds 23 and 24 were interrelated by the Michael addition of dimethylamine to 23. In addition, 24 was hydrogenated to 27 which proved identical in all respects with an authentic sample.

Treatment of 20a with equimolar amounts of phenylmethanesulfonyl chloride and triethylamine led to the different set of products depicted in Chart II. The structure of 29 was deduced from its nmr spectrum. Structure 31 was formulated on the basis of spectral characteristics and by its hydrogenation to the known 2-(benzylsulfonyl)-N,N-dimethylethylamine (32). When the reaction of
CHART I

\[
\begin{align*}
\text{H-C} & \quad \xrightarrow{2 \text{CH}_3\text{SO}_2\text{Cl}} \quad \xrightarrow{2\text{Et}_3\text{N}, \text{THF}} \quad -15^\circ \quad \text{CH}_3\text{SO}_2\text{N(CH}_3)_2 + \\
\text{CH}_2\text{N(CH}_3)_2 & \end{align*}
\]

\[
\begin{align*}
\text{(CH}_3)_2\text{N} & \quad \xrightarrow{23} \quad \xrightarrow{24} \\
\text{C} & \quad \xrightarrow{25} \quad \xrightarrow{26} & \quad \xrightarrow{27} \\
\text{C} & \quad \xrightarrow{20a} \\
\text{H}\text{SO}_2 & \\
\text{H} & \quad \text{N(CH}_3)_2 & \quad \text{N(CH}_3)_2 \\
\text{CH}_2\text{N(CH}_3)_2 & \quad \text{CH}_2\text{CH}_2\text{N(CH}_3)_2 & \quad \text{CH}_2\text{CH}_2\text{N(CH}_3)_2 \\
\text{H}_2, \quad \text{Pd-C} & \quad \text{H}_2, \quad \text{Pd-C} &
\end{align*}
\]
CHART II

\[ \text{N(CH}_3\text{)}_2\text{C}^\equiv\text{C} \xrightarrow{\text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{Cl}} \text{H} \xrightarrow{\text{Et}_3\text{N}, \text{THF}} -15^\circ \]

\[ \text{C}_6\text{H}_5\text{CH}_2\text{N(CH}_3\text{)}_2 \]

\[ \text{C}_6\text{H}_5\text{C}^\equiv\text{C} \xrightarrow{\text{H}_2, \text{Pd-C}} \text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{CH}_2\text{CH}_2\text{N(CH}_3\text{)}_2 \]

\[ \text{28} \]

\[ \text{29} \]

\[ \text{30} \]

\[ \text{31} \]

\[ \text{32} \]
20a was repeated with two equivalents of phenylsulfene, the yields of the various products were seen to change dramatically. The results of these two experiments are documented in Table 1. The increased yield of trans-stilbene (28) is to be expected when

**TABLE 1**

Variation in Product Yields Observed in the Addition of Phenylmethanesulfonyl Chloride and Triethylamine to 20a

<table>
<thead>
<tr>
<th>Relative molar proportions,</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{Cl}\text{-Et}_3\text{N}/20a )</td>
<td>28</td>
</tr>
<tr>
<td>1.0</td>
<td>trace</td>
</tr>
<tr>
<td>2.0</td>
<td>30.3</td>
</tr>
</tbody>
</table>

larger quantities of phenylsulfene are generated because of the established rapid conversion of this intermediate to trans-stilbene and sulfur dioxide. However, the observation that the excess phenylsulfene destroys the initially formed thietane dioxide 29 in a process which does not give characterizable products apart from a small increase in the yield of 30 is more important. This conclusion has been verified by treating pure 29 with phenylsulfene under the original reaction conditions. Chromatographic workup of the resulting gum afforded only 28 and a small amount of 30. It has, however, been established that 29 does react with sulfene to produce characterizable products (see Discussion).
N,N,N',N'-Tetramethyl-1-butene-1,3-diamine (20b). The reaction of two equivalents of sulfene and 20b in cold (-15°C) tetrahydrofuran led to a different spectrum of products (Chart III). Confirmation of structure 33 was obtained by a combination of nmr spectroscopy and catalytic hydrogenation to 36, which was prepared unequivocally by the method outlined in sequence 14.

\[
\begin{align*}
\text{(CH}_3\text{)}_2\text{N} & \quad \text{S} & \quad \text{C} & \quad \text{H} & \quad \text{C} & \quad \text{CH}_3 \\
\text{H} & \quad \text{H} & \quad \text{C} & \quad \text{H} & \quad \text{C} & \quad \text{CH}_3 \\
\text{S}_2 & \quad \text{O}_2 & \quad \text{N} & \quad \text{N} & \quad \text{C} & \quad \text{H} & \quad \text{C} & \quad \text{H} & \quad \text{C} & \quad \text{H} & \quad \text{C} & \quad \text{CH}_3 \\
\text{H}_2 & \quad \text{Pd-C} & \quad \text{H}_2 & \quad \text{K}_2\text{MnO}_4 & \quad \text{HOAc}
\end{align*}
\]

The structures of 34 and 35 were derived from their nmr spectra whereby 34 was shown to be a substituted 3-dimethylaminothietane dioxide and not an open-chain compound and whereby the disulfone 35 possessed a lone upfield, multiply-coupled proton. It should be noted that the nmr spectra of the various bithietane tetroxides
CHART III

\[
\begin{align*}
\text{H} & \text{C} \quad \text{H}
\end{align*}
\]

\[
\begin{align*}
\text{CH} & \quad \text{CH}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \quad \text{N(CH}_3)_2
\end{align*}
\]

\[
\begin{align*}
\text{N(CH}_3)_2
\end{align*}
\]

\[
\begin{align*}
\text{H}_-\text{C} & \quad \text{H}
\end{align*}
\]

\[
\begin{align*}
\text{Et}^N, \text{THF}
\end{align*}
\]

\[
\begin{align*}
\text{2CH}_3\text{SO}_2\text{Cl}
\end{align*}
\]

\[
\begin{align*}
\text{2Et}_3\text{N}, \text{THF}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{SO}_2\text{N(CH}_3)_2
\end{align*}
\]

\[
\begin{align*}
\text{+}
\end{align*}
\]

\[
\begin{align*}
\text{22}
\end{align*}
\]

\[
\begin{align*}
\text{20b}
\end{align*}
\]

\[
\begin{align*}
\text{23}
\end{align*}
\]

\[
\begin{align*}
\text{33}
\end{align*}
\]

\[
\begin{align*}
\text{34}
\end{align*}
\]

\[
\begin{align*}
\text{35}
\end{align*}
\]
such as 35 described in this section were generally of inferior quality because of the very limited solubility of these substances in organic solvents. Further support for structure 35 follows from its partial degradation as outlined in sequence 15. Thus, Hofmann elimination of its methiodide gave rise to the α,β-un saturated sulfone 38 which in addition to the one upfield proton possessed a vinyl hydrogen in its nmr spectrum. Hydrogenation of 38 gave 39 which possessed three upfield protons in its nmr, consistent with the 2,3'-bithietane tetroxide structure.

Further experimentation involving 20b and sulfene showed that the yields of 22, 33, 34, and 35 were also dependent upon the quantity of sulfene utilized and on the duration and temperature of reaction (Table 2). Of particular importance is the fact that significant amounts of the thietane dioxide 34 can be isolated after short reaction periods. However, prolonged exposure of the material to the reaction conditions resulted in its disappearance.
TABLE 2
Product Composition in the Condensation of 20b with Varying Quantities of Methanesulfonyl Chloride and Triethylamine

<table>
<thead>
<tr>
<th>Relative molar proportions, CH₂SO₂Cl-Et₃N/20b</th>
<th>Yields</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>22</td>
</tr>
<tr>
<td>1.0</td>
<td>35.9</td>
</tr>
<tr>
<td>2.0</td>
<td>33.0</td>
</tr>
<tr>
<td>3.0</td>
<td>34.7</td>
</tr>
<tr>
<td>2.0ᵇ</td>
<td>c</td>
</tr>
</tbody>
</table>

ᵃ Not observed.ᵇ In this run, the workup was commenced 1 hr after completion of the sulfonyl chloride addition instead of after the customary reaction period of 12 hr. ᶜ Not examined.

Indeed, when a pure sample of 3₄ is resubmitted to the original reaction conditions, 2₂ and 2₃ were produced (see Experimental Section).

Exposure of a cold tetrahydrofuran solution of 20b to two equivalents of phenylsulfene afforded after chromatographic workup two new products in addition to three compounds which have been previously described (2₈, 2₀, and 3₁) (Chart IV). The thiete dioxide 4₀ was assigned the cycloaddition structure on the basis of its strong ultraviolet absorption in ethanol at 256 μμ (ε 17,800) and its appropriate nmr spectrum. The bithietane tetroxide 4₁ possessed spectral properties similar to those of 3₅.

1,3-Bis(dimethylamino)-3-phenyl-l-propane (2₀c). This enamine was prepared by treating an ethereal solution of cinnamaldehyde containing powdered potassium carbonate with dimethylamine under
**CHART IV**

\[ \text{N(CH}_3\text{)}_2 \text{CH} = \text{C} \text{CH}_3 + \text{N(CH}_3\text{)}_2 \text{CH} = \text{C} \text{H}_5 \text{C}_6 \]

\[
\begin{align*}
\text{N(CH}_3\text{)}_2 & \quad \text{C}_6 \text{H}_5 \\
\text{H} & \quad \text{H} \\
\text{CH}_3 & \quad \text{C}_6 \text{H}_5 \\
\text{N(CH}_3\text{)}_2 & 
\end{align*}
\]

28

\[
\begin{align*}
\text{C}_6 \text{H}_5 \text{CH}_2 \text{SO}_2 \text{N(CH}_3\text{)}_2 & \quad \text{C}_6 \text{H}_5 \\
\text{H} & \quad \text{H} \\
\text{C}_6 \text{H}_5 \text{CH}_2 \text{SO}_2 & \quad \text{N(CH}_3\text{)}_2 \\
\text{H} & 
\end{align*}
\]

30

\[
\begin{align*}
\text{C}_6 \text{H}_5 \text{CH}_2 \text{SO}_2 \text{N(CH}_3\text{)}_2 & + \text{C}_6 \text{H}_5 \\
\text{H} & \quad \text{N(CH}_3\text{)}_2 \\
\text{C}_6 \text{H}_5 \text{CH}_2 \text{SO}_2 & + \text{N(CH}_3\text{)}_2 \\
\text{H} & 
\end{align*}
\]

31

\[
\begin{align*}
\text{CH}_3 \text{SO}_2 & \quad \text{CH}_3 \\
\text{N(CH}_3\text{)}_2 & \quad \text{N(CH}_3\text{)}_2 \\
\text{C}_6 \text{H}_5 & \quad \text{C}_6 \text{H}_5 \\
\text{SO}_2 & \\
\text{O}_2 \text{S} & \quad \text{CH}_3 \\
\text{N(CH}_3\text{)}_2 & \quad \text{O}_2 \text{S} \\
\text{C}_6 \text{H}_5 & \\
\text{C}_6 \text{H}_5 & \\
\text{O}_2 \text{S} & \\
\text{O}_2 \text{S} & \\
\text{C}_6 \text{H}_5 & \\
\text{C}_6 \text{H}_5 & \\
\text{O}_2 \text{S} & \\
\text{O}_2 \text{S} & \\
\text{C}_6 \text{H}_5 & \\
\text{C}_6 \text{H}_5 & \\
\text{O}_2 \text{S} & \\
\text{O}_2 \text{S} & \\
\text{C}_6 \text{H}_5 & \\
\text{C}_6 \text{H}_5 & \\
\text{O}_2 \text{S} & \\
\text{O}_2 \text{S} & \\
\text{C}_6 \text{H}_5 & \\
\text{C}_6 \text{H}_5 & \\
\text{O}_2 \text{S} & \\
\text{O}_2 \text{S} & \\
\text{C}_6 \text{H}_5 & \\
\text{C}_6 \text{H}_5 & \\
\text{O}_2 \text{S} & \\
\text{O}_2 \text{S} & \\
\text{C}_6 \text{H}_5 & \\
\text{C}_6 \text{H}_5 & \\
\text{O}_2 \text{S} & \\
\text{O}_2 \text{S} & \\
\text{C}_6 \text{H}_5 & \\
\text{C}_6 \text{H}_5 & \\
\text{O}_2 \text{S} & \\
\text{O}_2 \text{S} & \\
\text{C}_6 \text{H}_5 & \\
\text{C}_6 \text{H}_5 & \\
\text{O}_2 \text{S} & \\
\text{O}_2 \text{S} & \\
\text{C}_6 \text{H}_5 & \\
\text{C}_6 \text{H}_5 & \\
\text{O}_2 \text{S} & \\
\text{O}_2 \text{S} & \\
\text{C}_6 \text{H}_5 & \\
\text{C}_6 \text{H}_5 & \\
\text{O}_2 \text{S} & \\
\text{O}_2 \text{S} & \\
\text{C}_6 \text{H}_5 & \\
\text{C}_6 \text{H}_5 & \\
\text{O}_2 \text{S} & \\
\text{O}_2 \text{S} & \\
\text{C}_6 \text{H}_5 & \\
\text{C}_6 \text{H}_5 & \\
\text{O}_2 \text{S} & \\
nitrogen at ambient temperature. Sulfene addition to 20c in cold
tetrahydrofuran afforded by direct crystallization a 51.0% yield
of the highly crystalline 42 (Chart V). Chromatography of the
remaining noncrystalline residue on neutral alumina gave two addi­
tional compounds, 43 (2-3%) and 44 (3-4%). Initially, the molecular
frameworks of 42 and 43 were observed to be similar. Chromatog­
raphy of 42 on neutral alumina gave 43; hence, 43 appears to be
an artifact of the sulfene reaction and arises because small quan­
tities of 42 which remain in the noncrystalline residue undergo
\( \beta \)-elimination of dimethylamine on chromatographic workup.

The spectral properties of 42 demonstrate the presence of
sulfonamide and styryl groups. The identification of a 1-phenyl-
butadienyl chromophore in 43 was made on the basis of its strong
ultraviolet absorption in ethanol at 301 \( \mu \) (\( \epsilon \) 38,700); by com­
parison, trans,trans-1,4-diphenyl-1,3-butadiene\(^{24,25}\) and 1-phenyl-

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\( (24) \) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of
1951, Spectrum No. 129.


1,3-butadiene\(^{25}\) are reported to absorb in ethanol at 328 \( \mu \)
(\( \epsilon 41,000 \)) and 280 \( \mu \) (\( \epsilon 28,000 \)), respectively. The structures
proposed for 42 and 43 were considered secured when catalytic
hydrogenation of 43 was shown to give N,N-dimethyl-4-phenyl-1-
butanesulfonamide (45), which was identical in all respects to the
CHART IV

\[
\begin{align*}
\text{N(CH}_3\text{)}_2 \\
\text{C}_6\text{H}_5 - \text{CH} = \text{CHCHCH}_2\text{SO}_2\text{N(CH}_3\text{)}_2 \\
\text{C}_6\text{H}_5 - \text{CH} = \text{CH} - \text{CH} = \text{CHSO}_2\text{N(CH}_3\text{)}_2 \\
\text{C}_6\text{H}_5 \text{C} = \text{C} - \text{C} = \text{C} - \text{SO}_2\text{N(CH}_3\text{)}_2
\end{align*}
\]
sulfonamide prepared from the known 4-phenyl-1-butanesulfonyl chloride and dimethylamine (seq 16).

\[
\begin{align*}
\text{C}_6\text{H}_5\text{CH} &= \text{CH} - \text{CH} - \text{CHSO}_2\text{N(CH}_3\text{)}_2 & \text{C}_6\text{H}_5\text{(CH}_2\text{)}_4\text{SO}_2\text{Cl} \\
\begin{array}{c}
\text{C}_6\text{H}_5\text{(CH}_2\text{)}_4\text{SO}_2\text{N(CH}_3\text{)}_2 \\
\text{H}_2 \\
Pd-C
\end{array}
\end{align*}
\]

Compound 44 was identified as a styryl enamino sulfone on the basis of its spectral parameters and by virtue of its catalytic hydrogenation to 45, which was prepared unequivocally by the manner shown in sequence 17.
In like fashion, the interaction of 20c and phenylsulfene afforded 47 (48%) as its principal product, and, to a lesser extent, compounds 30 (22%) and 31 (3%) (Chart VI). The structure of 47 was derived by elemental and spectral analysis and by additional chemical transformations similar to those employed in the case of 42. These reactions are outlined in the Experimental Section.
CHART VI

\[
\begin{align*}
&\text{N(CH}_3\text{)}_2 \\
&\text{C}_6\text{H}_5 \\
&\text{CH} \\
&\text{C} \quad \text{C}_g\text{H}_5\text{CH}_2\text{SO}_2\text{Cl} \\
&\text{Et}_3\text{N}, \text{THF} \\
&\text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{N(CH}_3\text{)}_2 \\
&\text{20c}
\end{align*}
\]

\[
\begin{align*}
&\text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{N(CH}_3\text{)}_2 \\
&\text{30}
\end{align*}
\]

\[
\begin{align*}
&\text{C}_6\text{H}_5\text{CH}_2\text{SO}_2 \\
&\text{N(CH}_3\text{)}_2 \\
&\text{H} \\
&\text{31}
\end{align*}
\]

\[
\begin{align*}
&\text{N(CH}_3\text{)}_2 \\
&\text{C}_6\text{H}_5\text{CH} = \text{CH}\text{CHCHSO}_2\text{N(CH}_3\text{)}_2 \\
&\text{C}_6\text{H}_5 \\
&\text{47}
\end{align*}
\]
Discussion

The above results would tend to suggest that the reaction of sulfenes with 1,3-bis(dimethylamino)-1-alkenes such as 20 is dependent on the nature of the substituent at C3. However, closer examination of the results will show that this conclusion is not completely valid and that there are a number of additional factors which play significant roles.

Cleavage of the thietane dioxide ring system

The reaction of 20a and 20b with sulfene affords two common products, the sulfonamide 22 and the vinyl enamino sulfones 23 and 33 (see Charts I and III). Isolation of 22, the reaction product of sulfene or methanesulfonyl chloride and dimethylamine, demonstrates that the latter is eliminated at some stage in the reaction. The proposed pathway of these transformations is outlined in Chart VII.

In both cases, the reaction proceeds to a cycloadduct such as 48 which serves as a key intermediate. Thietane dioxides such as 48 have been depicted as puckered four-membered rings because of overwhelming experimental evidence favoring this conformational representation. The amount of puckering in a ring can be considered to arise from two opposing forces. One is ring strain which tends to keep the ring planar, since puckering the ring further decreases the ring angles, and the other is the force arising from the preferred staggered
CHART VII

20a or 20b

\[ CH_2 = SO_2 \]

48

\[ \text{O=S} \]

50

\[ \text{O=S} \]

51

52

\[ (\text{CH}_3)_2\text{NH} \]

23, R = H

33, R = CH₃

24
positions of the substituents on the adjacent ring carbon atoms.

Spectroscopic investigations of thietane and several of its derivatives\(^{26}\) have shown that this heterocyclic system possesses an angle


between the planes of approximately 30° while oxetane was found to be planar.\(^{27}\) The normal C-S bond angles (usually 4° or more smaller


than C-O bond angles in similar compounds), coupled with the increased length of C-S bonds, are believed responsible for the preferred puckered conformation in the thietane molecule. Cyclobutane is known to be puckered by about 30°,\(^{28}\) thereby leading to pseudo-axial


and pseudo-equatorial designations for its substituents. In thietane, the ring sulfur atom decreases the ring strain and thus allows for more ring puckering, but the loss of one methylene group (as compared with cyclobutane) decreases the tendency toward the staggered representation apparently the former factor has the
most influence. In the 1,1-dioxide derivatives, the introduction of two oxygens on the sulfur atom can be expected to result in the generation of severe nonbonded interactions and a strong preference for the puckered conformation. The conformational preference of the thietane 1,1-dioxide ring is evident from the report that trans-2,4-diphenylthietane dioxide (53) is less stable than its cis isomer 54 under epimerization conditions.  

\begin{equation}
\text{(29) R. M. Dodson and G. Klose, Chem. Ind. (London), 450 (1963).}
\end{equation}

The initially-formed thietane dioxide can have two different configurations about the side-chain carbon atom, 48 or 49, wherein the orientation of the two substituents are quasi-equatorial.
The quasi-equatorial position of these groups is expected regardless of whether four-membered ring formation is concerted or non-concerted. Reversible protonation of 48 or 49 at the less hindered tertiary nitrogen atom generates an electron-deficient center which can be ejected by a flow of electrons from the 3-dimethylamino substituent with concomitant ring rupture, as illustrated. A sufficient source of protons is generated in the medium by the elimination of the elements of hydrogen chloride from the sulfonyl chloride, and a significant quantity of liberated acid is precipitated from solution as the triethylamine salt. In order to account for the formation of 24 the involvement of protons in this step must occur to a significant extent (E⁺=H⁺, loss of dimethylamine) but it is realized that any available electrophile (i.e., sulfene or methanesulfonyl chloride) could initiate the ring opening process.

The driving force in this transformation is perhaps the relief of strain achieved by the rupture of the ring. However, there is another important consideration concerning the geometrical relationship between the electron pair of the 3-dimethylamine group and the departing ammonium ion. Extensive studies by Grob and co-workers on the solvolytic ionization of various γ-amino alkyl

---


Halides (or esters) have demonstrated that the amino function may assist ionization of the alkyl halide when certain geometrical requirements are met. Ions $\text{50}$ and $\text{51}$ have this $\text{trans,trans}$ configurational requirement. Inspection of these ions suggests that $\text{51}$ should possess somewhat higher ground-state energy than $\text{50}$; therefore, when $R=H$, $\text{50}$ can be expected to predominate. However, when $R=\text{CH}_3$, both possible configurational isomers ($\text{50}$ and $\text{51}$) are likely to be present. In fact, the interaction between the tetravalent nitrogen and the sulfone group in $\text{51}$ might favor the population of another rotamer. Significantly, in the reaction of $\text{20a}$ with sulfene no thietane dioxide could be isolated even under conditions of rapid workup, whereas in the case of $\text{20b}$, the reaction readily gives such a compound ($\text{34}$).

The $\text{trans}$ configuration about the vinylsulfonyl group in $\text{33}$ most probably results in the elimination step during fragmentation of the ring, whereas the $\text{trans}$ nature of the enamino sulfone substituent is established later in the mechanistic sequence. However, the isolation of $\text{trans}$-enamino sulfones is of no mechanistic significance since $\text{cis}$-enamino sulfones are known to be readily transformed to their more stable $\text{trans}$ isomers at room temperature. $\text{31}$

The entire mechanistic picture offered in Chart VII gains significance from the observation that when pure 34 (48 or 49 when \( R=\text{CH}_3 \)) was resubmitted to the original reaction conditions it could be recovered only to the extent of 30% and the sulfonamide 22 and the enamino sulfone 33 were obtained. This fact also emphasizes that fragmentation via ion 51 is also feasible.

The possibility that vinyl sulfones such as 23 could have resulted by a retro-Michael process of an initially formed \( \beta \)-dimethylaminoethyl precursor such as 24 was considered but disproved when it was found that 25 could be recovered quantitatively after treatment with excess sulfene. Compound 24 most probably arises by Michael addition of the elements of dimethylamine to 23 shortly after its elimination and prior to the time of its competitive reaction with sulfene. Compounds 23 and 24 have been interrelated by the independent addition of dimethylamine to the former (see Chart I). Traces of a material similar to 24 have been observed, but not fully characterized, in the reaction of sulfene with 20b (eq 18). The lack of significant in situ Michael addition of dimethylamine to 33 (relative to 23) might be caused by the added steric interference of the methyl group.
Possible sources for the bithietane tetroxides

The origin of the bithietane tetroxide $35$ was next considered. Before the result of the reaction of $34$ with sulfene was known, the possibility that $35$ could result from $34$ was considered (eq 19, p. 44). A good model compound for the testing of this hypothesis was phenyl propeny1 sulfone ($\text{CH}_3\text{CH}=$\text{CH-SO}_2\text{C}_6\text{H}_5$).$^{32}$ This substance on treatment with sulfene was recovered in high yield. No other products were formed. The apparent lack of loss of a proton from the allylic position in this compound (triethylamine as base) and

\[ \begin{align*}
\text{CH}_2=\text{SO}_2 & \rightarrow \text{CH}_3\text{C}=\text{C-H} & \text{CH}_3\text{C}=\text{C-N}(&\text{CH}_3)_2 \\
\text{O}_2 & + \text{other} & \text{products} \\
\downarrow \quad \downarrow & \quad \quad \downarrow \quad \downarrow & \quad \quad \downarrow \quad \downarrow \\
(\text{CH}_3)_2\text{NCH-CH}_2\text{SO}_2\text{CH=CHN}(&\text{CH}_3)_2 & \quad \quad \text{(not isolated pure)}
\end{align*} \]

(18)

absence of the subsequent reaction of the anion with sulfene eliminated the idea that 35 could result from 34.

It is known that 1-dialkylamino-1,3-butadienes generally are prone to undergo 1,4-addition to reactive olefins.\(^{33}\) The

possibility that bithietane tetroxide \( \text{35} \) could arise by virtue of initial elimination of dimethylamine from \( \text{20b} \) to give 1-dimethylamino-1,3-butadiene (56) followed by a double addition of sulfene was shown to be a feasible pathway by independently submitting 56 to the same reaction conditions. This experiment afforded the bithietane tetroxide \( \text{35} \) in 50\% yield (eq 20). Opitz has also reported

\[
\begin{align*}
\text{N(CH}_3\text{)}_2 & \quad \text{2CH}_2\text{=SO}_2 \\
\text{56} & \rightarrow \\
\text{35}
\end{align*}
\]

(20)

similar observations in his study of the reaction of sulfene with 1-dialkylaminobutadienes.\(^{34}\) On this basis, the formation of 56 from


\( \text{20b} \) can be derived mechanistically by invoking initial attack of the sulfene at the nonenamine tertiary nitrogen atom to afford zwitterion 55. Passage of 55 into 56 can occur either \textit{via} an intramolecular six-centered transition state with accompanying loss of sulfonamide 22 (path A), or by a process which involves
preliminary expulsion of the anion of 22 by the enamine system followed by neutralization of charge (cleavage-recombination process (eq 21, p. 47). Since no differentiation between these two possibilities has been achieved, any further discussion at this time would be pointless.

A mechanistic explanation of the double addition of sulfene to 56 necessitates that the initial sulfene molecule attack in an electrophilic sense the terminus of the diene system followed by ring closure at the adjacent carbon atom to produce intermediate 57 rather than the alternative possibility 58. This requirement is demanded by the fact that sulfenes undergo cycloaddition only to electron-rich olefin centers (see Introduction) such as is present in 57 but not in 58. The good yield of 35 that is obtained from 56 suggests that the terminus of this diene system is nucleophilic. The lone example of the
condensation of a similar dienamine with ketene suggests that cycloaddition to the $\alpha$- and $\beta$-carbon atoms predominated.\textsuperscript{33a} Yet, this mode of behavior is in direct contrast to 1-alkoxybutadienes which react with ketenes to afford cyclobutanones by cycloaddition to the $\gamma$- and $\delta$-carbons, and remains to be explained.\textsuperscript{35}


**Reaction of phenylsulfene with N,N,N',N'-tetramethylpropene-1,3-diamine (20a) and N,N,N',N'-tetramethyl-1-butene-1,3-diamine (20b)**

Examination of the results of the addition of phenylsulfene to 20a and 20b posed several questions. First, why does phenylsulfene addition prefer to lead to 2-dimethylamino-1-phenylmethanesulfonylethylene (31) in all cases (even with 20c) while the not too dissimilar sulfene leads to vinyl enamino sulfone formation (23 and 33). A first consideration suggests that the initially formed phenyl substituted thietane dioxide does not cleave in the manner described in Chart VII. Although such a thietane dioxide (29) has been obtained (Chart II), it gives no characterizable products on further treatment with excess phenylsulfene. In contrast, however, the action of sulfene on 29 afforded vinyl enamino sulfone 59 (eq 22). The structure for 59 has been confirmed by analytical and spectral analyses and by its catalytic hydrogenation as described in the Experimental Section.
Therefore, it does not seem likely that 31 arises from a four-membered ring precursor even though its formation in a mechanistic sense can occur from the ring opening of 29 (eq 23, p 50). The second and most probable explanation of the origin of 31 is that the addition of phenylsulfene to 20a and 20b (and even 20c; see below) is nonconcerted. One objective of this research was to obtain evidence for the presence of a zwitterion resulting from the postulated stepwise addition of sulfenes
with 1,3-bis(dimethylamino)-1-alkenes (20). This zwitterion (21) shown in equation 13 can partition itself between two possible subsequent reactions, one (path A) leading to thietane dioxide formation and a second (path B) leading to cleavage. The formation of 31 strongly suggests the occurrence of path B and it is apparent that when R' is a phenyl group this mode of fragmentation is extensive.
Also, the degree to which this mechanism is followed does not appear to depend on substitution at R (see Charts II, IV, and VI).

A mechanistic alternative other than mere cycloaddition is therefore available to the sulfene-enamine system, at least in those cases where phenylsulfene is used.

A number of examples have been reported where acyclic sulfones result in certain additions of sulfenes to enamines. In all cases except one, the origin of the sulfones was interpreted
on the basis of initial thietane dioxide formation, followed by a mechanistically unprecedented (using triethylamine as base) ring-opening of the heterocyclic system. As an alternative explanation, the acyclic products can perhaps arise by the initial formation of a zwitterion via a nonconcerted pathway, followed by a prototropic shift.

A second point of difference between phenylsulfene and sulfene in their reactions with 20a and 20b resides in the isolation of 29 in the case of 20a with phenylsulfene (Chart II) but no analogous product with 20b (Chart IV), a result completely opposite to the observations recorded earlier with sulfene (Charts I and III). However, no significance can be placed on this observation since the results cited in Chart IV are derived from the reaction of 20b with two equivalents of phenylsulfene. This addition was repeated with one equivalent of phenylsulfene under "fast conditions" (see Experimental Section) and the heterocycle corresponding to 29 was observed by infrared but the substance could not be isolated in pure form. In addition, the occurrence of thiete dioxide 40, (see Chart IV) demonstrated that its dimethylamino precursor was initially present (eq 24).
A third area of difference lies in the source of $N,N$-dimethylphenylmethanesulfonamide ($20b$). This substance finds its origin, at least in the case of $20b$, predominantly in the protonation of the carbanionic moiety formed in the fragmentation of an intermediate analogous to $55$ (see eq 21). This mechanistic pathway also represents the way in which bithetane tetroxide $41$ is formed, as discussed earlier for $35$. In addition, there exists a variety of other molecular routes by which $30$ could be formed in less significant amounts.

Reaction of sulfene and phenylsulfene with 1,3-bis(dimethylamino)-3-phenyl-1-propene ($20c$)

Examination of Charts V and VI shows that the addition of sulfene and phenylsulfene to $20c$ results in rearrangement of the carbon framework. The origin of $42$ and $47$ can be mechanistically derived by invoking initial attack of the sulfenes predominantly
at the benzylic nitrogen atom. This pathway was also used in explanation of the formation of \( \textit{56} \) from \( \textit{55} \) in the process leading to the bithietane tetroxides (see eq 21). The competition between the tertiary benzylic nitrogen and the \( \beta \)-carbon atom of the enamine system for sulfene is a reflection of their relative basicities. In fact, recent studies\(^{36} \) have shown that \( 1-N \)-morpholino-, \( 1-N \)-piperidino-, and \( 1-N \)-pyrrolidine-1-isobutene are all weaker than the corresponding saturated amines. The general question of the relative basicities of enamines versus their saturated counterparts has been reviewed by Hinman\(^{37} \) and shown to be dependent on the degree of substitution in the enamine. Since the instability of most enamines precludes their basicity measurements,\(^{37} \) the question is still unresolved; but the assumption that both centers can readily compete for the sulfene is valid on the basis of the products observed.

The conversion of the dipolar species (60) to the rearrangement products can result either by the intramolecular attack of the nucleophilic \( \alpha \)-sulfonyl carbanion at the \( \alpha \)-position of the enamine system with subsequent double-bond migration and cleavage of the bond to positively charged nitrogen (i.e., six-centered transition
state 60(a) or by a cleavage-recombination process as in 60(b) 
(eq 25, p. 56). A favorable driving force for this reaction is the 
formation of a conjugated styrene system. The point at issue in 
deciding between these two alternate pathways is the timing of the 
attack of the α-sulfonyl carbanion at the C_1 position. The answer 
to this question is not known at this time.\(^{38}\) However, the 

\[^{38}\text{An excellent model compound to test this mechanism would be CH}_2\text{=CH-CH-N(CH}_3^2\text{)}_2\text{, but at present this substance is unknown.}\]

The formation of \(\text{44}\) from the treatment of \(\text{20c}\) with sulfene can be attributed to a small amount of cycloaddition leading to a 
substituted 3-aminothietane dioxide which suffers ring-opening in 
a manner described earlier. The enamino sulfone \(\text{31}\) arises from the 
fact that the addition of phenylsulfene to \(\text{20c}\) is nonconcerted.
Equation 25

\[
RCH=SO_2 \rightarrow \begin{array}{c}
\text{N(CH}_3\text{)}_2 \\
\text{C}_6\text{H}_5 \\
\text{N(CH}_3\text{)}_2 \\
\text{C}_6\text{H}_5 \\
\text{N(CH}_3\text{)}_2 \\
\text{C}_6\text{H}_5 \\
\text{N(CH}_3\text{)}_2 \\
\text{C}_6\text{H}_5 \\
\text{N(CH}_3\text{)}_2 \\
\text{C}_6\text{H}_5 \\
\text{N(CH}_3\text{)}_2 \\
\text{C}_6\text{H}_5 \\
\text{N(CH}_3\text{)}_2 \\
\text{C}_6\text{H}_5 \\
\text{N(CH}_3\text{)}_2 \\
\text{C}_6\text{H}_5 \\
\end{array}
\]

42, \ R = H
47, \ R = C_6H_5

20c

RCH = SO_2

60a

60b
The reaction of sulfene with 1-dimethylamino-3-methoxy-1-butene (61)

To test further the effect of electronegative substituents disposed at C_3 of the enamine system (20) on the cycloaddition tendency with sulfenes the chemical behavior of 1-dimethylamino-3-methoxy-1-butene (61) with sulfene was examined. When 61 was exposed to sulfene under the conditions employed earlier, the cycloadduct 62 was obtained in high yield as the sole product of this reaction (Chart VIII). The further conversion of 62 to 63 and the spectral parameters of each served to establish the structural assignment (Chart VIII).

\[ \text{CH}_3 \quad \text{OCH}_3 \quad \overset{\text{N} \text{(CH}_3\text{)}_2}{\text{CH}_2 \equiv \text{SO}_2} \quad \overset{\text{CH}_3 \text{OCH}_3}{\text{CH}_3 \quad \text{OCH}_3} \quad \overset{1) \text{CH}_3\text{I}}{\text{SO}_2} \quad \overset{2) \text{IRA-400 (basic)}}{\text{CH}_3 \quad \text{OCH}_3} \]

**CHART VIII**

In conclusion, the unusual transformations observed with the 1,3-bis(dimethylamino)-1-alkenes (20a-c) are caused by the high degree of nucleophilicity and basicity of the 3-amino group as well as by the usual mobility associated with the unbonded
nitrogen electron pair. The next part of this dissertation will deal with further reactions of the foregoing thietane dioxides and, in addition, the synthetic utility of enamine reactions with sulfones will be examined further.
PART II

SYNTHETIC APPROACHES TO, AND REACTIONS OF,
THE METHYLENE THIETE DIOXIDE SYSTEM

Introduction

Exomethylene derivatives of small carbocyclic system.

Simple molecular-orbital calculations (LCAO)\(^{39}\) indicate

\(\text{(39) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, J. Am. Chem. Soc., 74, 4579 (1952).}\)

the substantial delocalization energy of 1.59\(\beta\) for the cyclobuta-dienylcarbinyl radical, cation, and anion. These intermediates conceivably could be obtained from methylenecyclobutene (64) by removal of a proton, hydrogen atom, or hydride-ion, respectively, from the 4-position. This prediction of the favorable delocalization energy for 64 provided the stimulus for its preparation and subsequent testing of the validity of the above calculations.

\[ \text{H}_2\text{C} \]

\[ 64 \]

\[ 59 \]
The synthesis of $\textit{64}$ has been achieved by the Hofmann reaction of either 2-methylene- or 3-methylene cyclobutyltrimethylammonium halides ($\textit{65}^{40}$ and $\textit{66}^{41}$, respectively, seq 26).

(40) D. R. Howton and E. R. Buchman, ibid., 78, 4011 (1956).

(41) D. E. Applequist and J. D. Roberts, ibid., 78, 4012 (1956).

The approach employed in the preparation of $\textit{66}$ represents a very useful method by which a methylene group can be protected while the remainder of the molecule is chemically modified (seq 27, p. 61).
Sequence 27

\[
\text{Cyclic compound} + \text{Acylating agent} \rightarrow \underbrace{\text{Product}}_{\Delta}
\]

\[\text{Cyclic compound} \rightarrow \text{Product} \quad \Delta\]

1) Curtius degradation
2) Exhaustive methylation

+ anthracene
In order to determine whether the properties of methylene-cyclobutene (64) are markedly dependent upon the presence of the hydrogen at the 4-position, the 4,4-dimethyl substituted compound (67) was prepared by the scheme outlined in sequence 28 and found to be unstable.  

A third method for the preparation of these materials was the condensation of allene with phenylacetylene, whereupon the 1-phenyl derivative (68) of 64 was obtained in approximately 1% yield (eq 29).
All three of these methylenecyclobutenes polymerized readily and spontaneously at room temperature.

Retro Diels-Alder reactions of anthracene adducts have been extended to the preparation of 3-methylenetrimethylene oxide (eq 30). However, ring strain appears to influence markedly the ease with which such reactions occur. Thus, the following adduct was found to be stable to 450°C.
The synthesis of 1,3-dimethylenecyclobutane (70) was undertaken to provide evidence, if any, for cross-ring \( n \)-type electronic interaction. Roberts and co-workers have prepared 70 by the extensive degradation of 3-methylenecyclobutanecarbonitrile (71) prepared from allene and acrylonitrile (eq 31), but could not discern

\[ \text{71} \xrightarrow{\text{heat}} \text{72} \]

\[ \text{72} \xrightarrow{\text{OH}^-} \text{70} \]

\[ \text{70} \xrightarrow{450^\circ} \text{CH}_2=\bigtriangleup \]

---

evidence for interaction from its ultraviolet spectrum. Electron diffraction data for 70 and its isomer 72 showed them to be planar (15°) with nearly square four-membered rings. Compound 70 reacted with only one mole of bromine and gave no rearrangement products, a fact in direct contrast to methylenecyclobutane 43 which gave extensive rearrangements under these conditions. This may be because of stabilization of the intermediate bromonium ion by cross-ring interaction.

\[ \text{CH}_2 \xrightarrow{\text{Br}_2} \text{Br} \]

(43) For leading reference see: (a) E. F. Kiefer and J. D. Roberts, ibid., 84, 784 (1962); (b) D. E. Applequist and J. D. Roberts, ibid., 78, 874 (1956).

In this regard, the synthesis and properties of cyclobutenyl cations have been extensively studied. 44 The possibility that either 70 or 72 might rearrange and react with metals to form cyclobutadiene-metal compounds similar to ferrocene or dibenzenechromium was

\[ \text{CH}_2 \text{Br} \]

(44) (a) T. J. Katz and E. H. Gold, ibid., 86, 1600 (1964); (b) M. Hanaack and K. Riedlinger, Chem. Ber., 100, 2107 (1967).
tested with ferrous iron and nickel carbonyl as reagents, but no metal-organic products were isolated.42

The observation that 1,3-dimethylenecyclobutanes readily undergo normal Diels-Alder reactions at room temperature to form cyclobutene derivatives45 suggested that the addition of dienophiles to suitable derivatives of dimethylenecyclobutene might yield cyclobutadienes.46 For this purpose, the triene 73 was prepared


(46) (a) A. T. Blomquist and Y. C. Meinwald, ibid., 81, 667 (1959); (b) G. W. Griffin and L. I. Peterson, ibid., 85, 2268 (1963).

and in the course of its preparation the interesting diene 74 was also obtained.

Both of these materials exhibited moderate stability. However, the triene 73 deteriorated rapidly at room temperature. Unlike the related hydrocarbon, 1,2-dimethylenecyclobutane, the triene was unreactive toward most dienophiles except for

\[ \begin{align*}
\text{73} & \quad \text{C}_6\text{H}_5 \quad \text{CH}_2 \\
& \quad \text{CH}_2
\end{align*} \]

\[ \begin{align*}
\text{74} & \quad \text{C}_6\text{H}_5 \quad \text{CH}_3 \\
& \quad \text{CH}_2
\end{align*} \]
tetracyanoethylene whereupon it gave the spiran 75. In like fashion, the diene 74 gave the spiro adduct (76).

\[
\begin{array}{c}
\text{CH}_2 \\
\text{C}_6\text{H}_5 \\
\text{C}_6\text{H}_5 \\
\text{(CN)}_2 \\
\end{array}
\text{75}
\quad
\begin{array}{c}
\text{CH}_3 \\
\text{C}_6\text{H}_5 \\
\text{C}_6\text{H}_5 \\
\text{(CN)}_2 \\
\end{array}
\text{76}
\]

Trienes 77 and 78 have been obtained by the Hofmann degradation of appropriate precursors; however, 78 undergoes rapid dimerization to the cyclooctadiene derivative 79. Although 78 is too reactive to be isolated and characterized by chemical methods, spectroscopic evidence for its existence was obtained at -80\(^\circ\).\(^{47}\)


\[
\begin{array}{c}
\text{CH}_2 \\
\text{CH}_3 \quad \text{H}_2\text{C} \\
\text{CH}_2 \quad \text{H}_2\text{C} \\
\end{array}
\text{77}
\quad
\begin{array}{c}
\text{CH}_2 \\
\text{H}_2\text{C} \\
\text{H}_2\text{C} \\
\end{array}
\text{78}
\quad
\begin{array}{c}
\text{CH}_2 \\
\text{R.T.} \\
\text{79} \\
\text{(or other isomer)}
\end{array}
\]
The synthesis of tetramethylenecyclobutane (80) completed the series.\textsuperscript{46b} This compound possesses four sp\textsuperscript{2}-hybridized ring carbon atoms (reminiscent of the situation in cyclobutadiene) and is indefinitely stable in dilute solution at -78°; however, on warming to room temperature, it undergoes dimerization to the unstable 1,5-cyclooctadiene 81. The hydrocarbon also affords with excess tetracyanoethylene the monoadduct 82 which is a stable triene (eq 32).

Recently, it was found that 1,5-alkadiynes undergo intramolecular rearrangement at elevated temperatures to give dimethylene-cyclobutenes. Thus, at 335° in a flow system, 1,5-hexadiyne rearranges rapidly to the known 3,4-dimethylenecyclobutene (83) (eq 33).\textsuperscript{48}
Unsaturated small ring heterocyclic systems

The three- and four-membered ring heterocyclic systems have been extensively reviewed. This discussion will be limited to representatives of the sulfur containing unsaturated four-membered rings (thiirene dioxide are discussed in reference 49c). Several molecules that fit this description follow.


The stimulus for the preparation of thiete (84) stems from the realization that its anion would be isoelectronic with cyclopentadiene.\textsuperscript{50} But, numerous attempts at the synthesis of 84 have been unsuccessful (seq 34).\textsuperscript{51}


\textsuperscript{51} D. C. Dittmer and M. C. Christy, \textit{J. Am. Chem. Soc.}, \textbf{84}, 399 (1962). However, the synthesis of 84 has very recently been reported - D. C. Dittmer, K. Takahashi, and F. A. Davis, \textit{Tetrahedron Letters}, 4061 (1967).

In the first instance (a) the quaternary hydroxide was prepared from the methosulfate and was pyrolyzed at 300°. Gas chromatography of the distillate indicated the presence of seven components, none of which have been identified. In the second
(34)

attempt (b), the Diels-Alder adduct of thiete was prepared but its pyrolysis at 300° (the adduct was stable at lower temperatures) gave anthracene and a non-volatile oil which was a mixture of at least six components. In both cases, the conditions for the introduction of the double bond were probably too severe for the isolation of 84.51

Several fused aromatic derivatives of 84 and 85 have been prepared,52 however, a detailed discussion of these will be deferred
to part III of this dissertation. Also, an aliphatic derivative of thiete (84) has been obtained. Nonetheless, the most im-

important fact to note considering structures 84-89 is that only thiete dioxide (85)\textsuperscript{54} and its dimethyl (90)\textsuperscript{55} and other monocyclic derivatives\textsuperscript{9,16,17} have been prepared to date (seq 35, p. 74).

At the outset of this work, no attempt at the preparation of molecules 86-89 had appeared and only two examples of sulfur containing four-membered rings with exocyclic double bonds were known. Both were cyanothiamine derivatives with the following structures.\textsuperscript{56}
Since all of the members of the series of compounds starting with methylenecyclobutane and methylenecyclobutene have been prepared and are stable for a short time in the absence of air, the synthesis of molecules 86-89 appeared attractive. The stability and highly crystalline nature of the sulfones observed in part I influenced us to choose first the preparation of 87 and 89. The steric compression caused by the introduction of the exocyclic methylene group in these two molecules and the electron deficiency imparted to the strained diene chromophore by the sulfone group in 82 was expected to lead to interesting spectral properties and chemical reactivity in comparison with thiete dioxide (85) and the all-carbon analogs. This section of the dissertation describes the synthetic routes to 87 and 89 and, in particular, the successful preparation of two derivatives of 89 and their reactions.
Sequence 35

\[
\begin{align*}
\text{CH}_2\text{Cl} & \xrightarrow{\text{H}_2\text{S}, \text{OH}^-} \text{HO} & \xrightarrow{\text{H}_2\text{O}_2} \text{HOSO}_2 \\
\text{SOCl}_2 & \rightarrow \text{Cl} & \xrightarrow{\text{Et}_3\text{N}} \text{85} \\
\end{align*}
\]

\[
\begin{align*}
\text{(CH}_3\text{)}_2\text{NCH} = \text{C(CH}_3\text{)}_2 & \xrightarrow{\text{CH}_2 = \text{SO}_2} \text{(CH}_3\text{)}_2\text{NCH} = \text{C(CH}_3\text{)}_2 \\
\end{align*}
\]

1) \(\text{CH}_3\text{I}\) \\
2) \(\text{Ag}_2\text{O}, \text{H}_2\text{O}\)
A priori, three synthetic pathways were considered plausible. These were (a) the retro Diels-Alder route; (b) the Hofmann elimination approach, and (c) the N-oxide route. The results of these studies will now be discussed.
Results and Discussion

The retro Diels-Alder route

One of the steps used in the preparation of methylenecyclobutene (64) was the retro Diels-Alder reaction of an anthracene adduct wherein the exocyclic double bond was introduced into the framework of the pyrolysis product. Analogously, if the synthesis of the proper sulfone-containing adduct could be achieved then pyrolysis of this material might achieve the same objective. Such a scheme is outlined in Charts IX-XI.

The reaction sequence begins with the preparation of the known adduct (91) of anthracene and acrolein. The crystalline pyrrolidino

\[(\text{57}) \text{ F. Weiss and R. Rusch, Bull. soc. chim. France, 550 (1964).}\]
enamine 92 was obtained by refluxing aldehyde 91 with an excess of pyrrolidine in toluene solution under a Dean-Stark trap. When a cold (-10°) tetrahydrofuran solution of 92 and triethylamine was treated with an equimolar amount of methanesulfonyl chloride, there was isolated the highly crystalline cycloaddition product 93. The dimethylamino enamine 94 was prepared (admixed with the original aldehyde) by reacting a tetrahydrofuran solution of 91 with dimethylamine and magnesium sulfate under a nitrogen atmosphere at ambient temperature. Exposure of this mixture to sulfene-forming conditions gave

\[(\text{58}) \text{ H. Stucki, unpublished observations.}\]
CHART IX

\[ \text{CH}_2 = \text{CHCHO} \rightarrow \text{CHO} \]

\[ R_2\text{NH} \]

\[ \text{CH-NR}_2 \]

\[ R'\text{CH} = \text{SO}_2 \]

\[ R' = \text{C}_6\text{H}_5 \]

92, \( R_2 = -\text{CH}_2(\text{CH}_2)_2\text{CH}_2- \)

94, \( R = \text{CH}_3 \)

93, \( R_2 = -\text{CH}_2(\text{CH}_2)_2\text{CH}_2- \)

\( R' = \text{H} \)

95, \( R = \text{CH}_3 \)

\( R' = \text{H} \)

96, \( R_2 = -\text{CH}_2(\text{CH}_2)_2\text{CH}_2- \)

\( R' = \text{C}_6\text{H}_5 \)
CHART X

1) CH₃I
2) Ag₂O
3) Δ

93 → 97

(CH₃)₂N·

95

H

96

H

H₂O₂

HOAc, Ac₂O
R.T.

98
CHART XI

$\text{SO}_2$ $\rightsquigarrow 300^\circ \text{C} \rightarrow$ anthracene $+ \left( \begin{array}{c} \text{H}_2\text{C} \\ \text{SO}_2 \end{array} \right) \quad \text{89}$

$\text{H}_2/\text{Pd}$

$\text{SO}_2$ $\rightsquigarrow 400^\circ \text{C} \rightarrow$ anthracene $+ \left( \begin{array}{c} \text{H}_2\text{C} \\ \text{SO}_2 \end{array} \right) \quad \text{87}$

$\text{LAH}$

$\text{SO}_2$ $\rightarrow \Delta \rightarrow \text{H}_2\text{C} \quad \text{86}$

$\text{C}_6\text{H}_5$ $\rightsquigarrow 300^\circ \text{C} \rightarrow$ anthracene $+ \left( \begin{array}{c} \text{H}_2\text{C} \\ \text{SO}_2 \end{array} \right) \quad \text{101}$
the cycloadduct \( \text{95} \). In like fashion, \( \text{92} \) afforded \( \text{96} \) when treated with phenylsulfene (see Chart IX). The indicated trans relationship of the pyrrolidino and phenyl groups in \( \text{96} \) is assigned on the basis of the nmr coupling constant (10.0 Hz) of the thietane dioxide ring protons.\(^{59}\) In this regard, the hetero four-membered ring is

\[ \text{(59) The validity of the Karplus correlation as applied to the thietane dioxide ring system has been established: L. A. Paquette, J. Org. Chem., 29, 2854 (1964).} \]

assigned a puckered conformation with the two groups occupying trans-equatorial positions and the protons possessing a dihedral angle of approximately 180°.

Some measure of further support for the structural assignments for \( \text{93, 95, and 96} \) came from their degradation. Thus, Hofmann elimination of the methiodides of \( \text{93 and 95} \) yielded the identical olefin \( \text{97} \). The cycloadduct \( \text{96} \) would not form a methiodide salt but N-oxide degradation of this material readily afforded the phenyl substituted thiete dioxide \( \text{98} \) (see Chart X). Olefin \( \text{97} \) was hydrogenated to the thietane dioxide \( \text{99} \) which on treatment with lithium aluminum hydride in tetrahydrofuran gave a small amount of an oily liquid with a sulfide-like odor. However, none of the desired thietane \( \text{100} \) nor any other material could be characterized from this mixture (see Chart XI).

The pyrolysis of \( \text{97 and 98} \) at approximately 300° and at atmospheric or reduced pressure under a stream of nitrogen gave anthracene, sulfur dioxide, an intractable yellow solid (in the cold traps) and a brittle, black glassy residue. Adduct \( \text{99} \) merely distilled with some
decomposition at 300°; at 400°, however, similar decomposition products were observed. In all three cases a retro Diels-Alder reaction did occur as evidenced by the formation of anthracene but none of the desired methylene substituted four-membered rings (87, 89, and 101) could be isolated. The adducts would not decompose at lower temperatures.

The reason for the failure of this method will become apparent when the physical properties of derivatives of 89 are discussed (vide infra). The origin of the sulfur dioxide cannot be established with certainty; it may originate from the adducts or from the postulated four-membered ring pyrolysis products. The inability to obtain the desired compounds by this retro Diels-Alder approach necessitated a new route for their synthesis.

**Hofmann elimination approach**

The reactions of sulfenes with 1,3-bis(dialkylamino)-1-alkenes produce a mixture of products from which substituted thietane dioxides such as 29 and 34 can, in certain cases, be isolated (see Part I). It will be noted that the tertiary amino groups in both

![Diagram](image-url)
compounds are disposed in such a manner that conversion of these functions to good leaving groups and double elimination would afford derivatives of 89. However, exposure of 29 to methyl iodide in methanol at room temperature gave by direct crystallization a mixture of the monomethiodide 102 and tetramethylammonium iodide. Chromatographic workup on neutral alumina of the noncrystalline residue afforded two additional crystalline solids, 59 and 103 (see Chart XII). The structure for 102 was derived from its elemental analysis and ultraviolet absorption in ethanol [266 mμ (ε 8,080)]. The amino sulfone 59 has already been characterized in Part I. Michael addition of dimethylamine to 59 and subsequent quaternization of the product with methyl iodide yielded 103. Thus, this transformation, accompanied by the usual spectral data and analytical analysis for 103, secured its structural assignment. Passage of 102 through an Amberlite IRA-400 ion exchange column (hydroxide form) and removal of the water led to the formation of 2-(benzylsulfonyl)-N,N-dimethylethylamine (32) as the only characterizable product.

A similar ring cleavage was observed in the attempted quaternization of 34 with methyl iodide. A methiodide 104 was obtained by direct crystallization but the material decomposed on attempted recrystallization from aqueous methanol. However, an analysis for iodine showed that only one of the nitrogens was quaternized. Careful chromatography of the noncrystalline residue on neutral alumina permitted isolation of the already reported vinyl enamino sulfone 33 and tetramethylammonium iodide. Hofmann degradation of 104 afforded only the demethylation product 34 (Chart XIII).
These results indicate that the attempted degradations of 29 and 34 are related in two ways, namely the preference for demethylation of their methiodides and the ring cleavage encountered in the preparation of these materials. The fragmentation of these rings has already been described in Chart VII (where E now equals a methyl group) and in equation 22.
That the transformation of 102 to 32 with basic ion exchange resin also involves a demethylation step (as in Chart XIII) is made evident when its mechanism is considered (eq 36). The loss of methanol must occur from one of the three indicated intermediates and not from 32 since the methiodide of the latter readily undergoes elimination and addition of water to give the known alcohol 105 under the reaction conditions (see sequence 36). Further support for this mechanism lies in the realization that both thiete dioxide and 3-hydroxythietane-1,1-dioxide undergo ring cleavage in base.51

\[
\begin{align*}
\text{CH}_3\text{SO}_2\text{CH}_2\text{CHO} & \xrightarrow{0\text{H}^-} \text{CH}_3\text{SO}_2\text{CH}_3 + \text{HCO}_2^- \\
\text{SO}_2 & \xrightarrow{0\text{H}^-} \text{SO}_2 \\
\end{align*}
\]
Sequence 36

\[
\begin{align*}
\text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{CH}_2\text{CH}_2\text{N(CH}_3)_2 & \xrightarrow{-\text{CH}_3\text{I}} \text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{N(CH}_3)_2 \\
\text{H}_2\text{O} & \xrightarrow{\text{IRA-400}} \text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{N(CH}_3)_2
\end{align*}
\]

\[
\begin{align*}
\text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{CH}_2\text{CH}_2\text{N(CH}_3)_2 & \xrightarrow{1) \text{CH}_3\text{I}} \text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{CH}_2\text{CH}_2\text{OH} \\
\text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{CH}_2\text{CH}_2\text{N(CH}_3)_2 & \xrightarrow{2) \text{IRA-400}} \text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{CH}_2\text{CH}_2\text{OH}
\end{align*}
\]
Hydrogenation of the double bond in 102 would prevent this adverse Michael addition of water. The resulting saturated methiodide would represent a potential precursor of a 2-methylenethietane dioxide. However, all attempts to hydrogenate 102 gave only starting material.

\[ \begin{align*}
\text{N-Oxide route} \\
\text{Synthesis of the methylene thiete dioxide system}
\end{align*} \]

Treatment of either 29 or 34 with hydrogen peroxide in methanol solution gave in each case a brown oily liquid which could not be converted to a picrate and decomposed when heated in a vacuum. However, when 29 was treated with excess 30% hydrogen peroxide in acetic acid-acetic anhydride solution at room temperature for one day and the resulting mixture was worked up in the usual fashion, \textsuperscript{22a,60} there resulted an oily residue which after chromatography on neutral alumina gave 101 in good yield (eq 37). The methylene thiete

\[ \begin{align*}
\end{align*} \]
dioxide structure (101) was assigned on the basis of its spectral
dioxide structure (101) was assigned on the basis of its spectral
parameters, elemental analysis, and chemical transformations. All
parameters, elemental analysis, and chemical transformations. All
of the spectra were recorded on freshly prepared samples of 101 for
of the spectra were recorded on freshly prepared samples of 101 for
this sulfone slowly becomes colored at room temperature and polymerizes
to a solid which is insoluble in all of the common organic solvents.
to a solid which is insoluble in all of the common organic solvents.
The material is soluble in chloroform and acetonitrile but only
The material is soluble in chloroform and acetonitrile but only
slightly soluble in carbon tetrachloride; however, these solutions
slightly soluble in carbon tetrachloride; however, these solutions
quickly turn red in color on standing and the sulfone cannot be recovered.
quickly turn red in color on standing and the sulfone cannot be recovered.
This decomposition is at a minimum in ether from which 101 can be re-
This decomposition is at a minimum in ether from which 101 can be re-
crystallized. The ultraviolet spectrum of this material was consistent
crystallized. The ultraviolet spectrum of this material was consistent
for a 1-phenylbutandienyl function and is compared in Table III with
for a 1-phenylbutandienyl function and is compared in Table III with
the reported values of two close analogs.
the reported values of two close analogs.

The mass spectrum of 101 shows a molecular ion (m/e 192) and
The mass spectrum of 101 shows a molecular ion (m/e 192) and
a base peak at m/e 128. This fragmentation can be explained by the
a base peak at m/e 128. This fragmentation can be explained by the
sequential loss of the elements of sulfur monoxide (m/e of 144 - 68%
sequential loss of the elements of sulfur monoxide (m/e of 144 - 68%
of base) and oxygen. The ion corresponding to the base peak appears
of base) and oxygen. The ion corresponding to the base peak appears
TABLE 3

Comparison of the Ultraviolet Spectra of 101, 68, and 74

<table>
<thead>
<tr>
<th></th>
<th>Ether</th>
<th>Isooctane</th>
<th>Isooctane</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda_{\text{max}} )</td>
<td></td>
<td>( \lambda_{\text{max}} )</td>
<td>( \lambda_{\text{max}} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( 212 \text{ m}\mu \ (\epsilon 4,600) )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( 219 \ (3,760) )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( 225 \ (3,960) )</td>
<td>( 228 \text{ m}\mu \ (\epsilon 12,000) )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( 233 \ (3,640) )</td>
<td>( 235 \ (9,120) )</td>
</tr>
<tr>
<td>( 291 \text{ m}\mu \ (\epsilon 33,400) )</td>
<td>( 291 \ (7,250) )</td>
<td>( 292 \ (26,900) )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( 302 \ (25,100) )</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( 316.5 \ (\text{sh}) \ (13,200) )</td>
</tr>
</tbody>
</table>
to fragment to acetylene and phenylacetylene (see p. 91). A cyclic sulfinate is proposed as an intermediate in this process since the same has been postulated as occurring in the pyrolysis and in the mass spectrum of dibenzothiophene 5,5-dioxide and such an inter-


mediate has actually been isolated in the pyrolysis of a thiete dioxide. 52d, 62


Another derivative of this ring system was prepared by treating the following thietane dioxide (106) with the same reagents (eq 38).

\[
\begin{align*}
\text{SO} & \quad \text{HOAc-AcO} \\
\text{H}_2\text{O}_2 & \quad \text{HOAc-AcO} \\
106 & \quad \text{H} \\
107 & \\
\end{align*}
\]

The synthesis of 106 was achieved by reacting phenylsulfene with 1,3-bis(1-piperidino)-3-phenyl-1-propene (108); 1-(benzylsulfonyl)piperidine (109) and the enaminosulfone 110 accompanied 106 (eq 39).
Fragmentation Pattern for 101

<table>
<thead>
<tr>
<th>m/e</th>
<th>relative abundance</th>
</tr>
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<tbody>
<tr>
<td>192</td>
<td>34</td>
</tr>
<tr>
<td>144</td>
<td>68</td>
</tr>
<tr>
<td>129</td>
<td>12</td>
</tr>
<tr>
<td>128</td>
<td>100</td>
</tr>
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<td>127</td>
<td>26</td>
</tr>
<tr>
<td>126</td>
<td>10</td>
</tr>
<tr>
<td>105</td>
<td>28</td>
</tr>
<tr>
<td>102</td>
<td>43</td>
</tr>
</tbody>
</table>

\[
\text{m/e 192 (molecular ion)}
\]

\[
\begin{align*}
\text{m/e 192} & \\
\text{shown only} & \\
\text{for this one} & \\
\text{etc.} & \\
\text{m/e 102} & \\
\end{align*}
\]

\[
\text{base peak (m/e 128)}
\]
The methylene thiete dioxide 107 is completely stable under normal laboratory conditions. This sulfone is insoluble in ether and carbon tetrachloride but is soluble in chloroform and can be recrystallized from tetrahydrofuran. Its nmr spectrum was consistent for the assigned structure but, since the ring vinyl proton was under the aromatic envelope and the other vinyl proton was a broad singlet, a definite assignment of the geometric configuration of the molecule was not possible. Therefore, 107 is formulated as shown on steric grounds alone. That the indicated structure possesses a diphenylbutadienyl chromophore is apparent from its ultraviolet spectrum in chloroform [366 µm (sh) (ε 23,450), 349 (40,200), 337 (38,800),
240 (12,850), and end absorption [which is comparable to that reported for 1,4-diphenyl-1,3-butadiene (see p. 31 of this dissertation).

The mass spectrum of 107 displays a fragmentation pattern analogous to that of 101. Again, the molecule rearranges to a sulfinate which loses sulfur monoxide and oxygen to afford a fragment which splits into two phenylacetylene units (base peak of 102) (see p. 94).

The stability of the methylene thiete dioxide system is obviously enhanced by phenyl substitution. In an attempt to prepare the parent of this series (89), the thietane dioxide 111 was synthesized in the usual way by treating 1,3-bis(1-piperidino)-1-propene (112) with sulfene (eq 40). Chromatography of the non-crystalline residue
Fragmentation Pattern for 107

<table>
<thead>
<tr>
<th>m/e</th>
<th>relative abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>268</td>
<td>23</td>
</tr>
<tr>
<td>220</td>
<td>10</td>
</tr>
<tr>
<td>204</td>
<td>32</td>
</tr>
<tr>
<td>203</td>
<td>15</td>
</tr>
<tr>
<td>202</td>
<td>20</td>
</tr>
<tr>
<td>105</td>
<td>30</td>
</tr>
<tr>
<td>103</td>
<td>10</td>
</tr>
<tr>
<td>102</td>
<td>100</td>
</tr>
<tr>
<td>101</td>
<td>10</td>
</tr>
</tbody>
</table>

\[
\text{[C}_6\text{H}_5\text{C} \equiv \text{CH}]^+ + \text{[C}_6\text{H}_5\text{C} \equiv \text{CH}]^+ 
\]  

\[\text{m/e 102 (base peak)}\]
on neutral alumina gave the usual side products which are described in the Experimental Section. When 111 was subjected to the N-oxide conditions described earlier, a small amount of yellow oil was isolated which had an infrared spectrum indicative of an enamine component and nmr absorptions consistent with the presence of a piperidino group. In the same way, 34 afforded an oily mixture which was shown to have analogous physical and spectral properties.

\[
\begin{align*}
\text{HOAc-AC}_2O & \quad \text{H}_2\text{O}_2 \\
\text{SO}_2 & \quad \text{S}_{\text{O}_2}
\end{align*}
\]
In both cases, the ring system is probably cleaved in a manner analogous to the rupture caused by methyl iodide. In order to test this hypothesis, the synthesis of 114, an isomer of 101, was attempted. The phenyl group in 113 is placed at a position which can be expected to favor ring opening. Thietane dioxide 113 was obtained from the appropriate enamine 108 and sulfene (seq 41).

\[
\begin{align*}
&\text{open-chained products} + \\
&\begin{pmatrix}
\text{C}_6\text{H}_5\text{SO}_2 \\
\text{C}_6\text{H}_5\text{SO}_2
\end{pmatrix}
\end{align*}
\]
Preliminary examination of the results of its N-oxide degradation has shown that the products are derived from ring rupture and still contain nitrogen; no methylene thiete dioxide could be isolated. Presumably initial N-oxide formation occurs at the side-chain nitrogen leading to a conjugated styrene system produced by the fragmentation indicated in sequence 41.

Reactions of the methylene thiete dioxide system

The methylene thiete dioxide 101 was converted by catalytic hydrogenation at atmospheric pressure to thiete dioxide 115 and at 50 psig of hydrogen to thietane dioxide 116. The structural assignment for 101 was considered secured by its conversion with dimethylamine into an isomer of 29 (seq 42). However, the stereochemistry of this substance (117) could not be assigned with certainty since model spectra for nmr correlations were lacking.
Sequence 42

\[ \text{H}_2, \text{Pd} \rightarrow \text{atmospheric pressure} \]

\[ 115 \]

\[ \text{H}_2, \text{Pd} \rightarrow 50 \text{ psig} \]

\[ 116 \]

\[ (\text{CH}_3)_2\text{NH} \rightarrow \]

\[ (\text{CH}_3)_2\text{N} \]

\[ 117 \]

(isomer of 29)
Diels-Alder addition of 101 and 107 to 1,3-diphenylisobenzofuran (118) afforded exclusively the adducts 119 and 120, respectively (eq 43). Endoxysulfone 119 was reversibly protonated in hot polyphosphoric acid (80% recovery after quenching in water), but was transformed into a mixture of 122 and 123 when refluxed with glacial acetic acid containing anhydrous hydrogen bromide (seq 44, p. 100). An analogous acid-catalyzed dehydrative expulsion of sulfur dioxide from a thietane dioxide of related structure had been observed.52c The main product of this reaction was 122 but the presence of 123
Sequence 44

\[ \text{Reactivity: HOAc, HBr} \]

\[ \begin{align*}
\text{119} & \quad \text{121} & \quad \text{122} \\
\text{C}_6\text{H}_5 & \quad \text{C}_6\text{H}_5 & \quad \text{C}_6\text{H}_5 \\
\text{C}_6\text{H}_5 & \quad \text{C}_6\text{H}_5 & \quad \text{C}_6\text{H}_5 \\
\text{C}_6\text{H}_5 & \quad \text{C}_6\text{H}_5 & \quad \text{C}_6\text{H}_5 \\
\text{C}_6\text{H}_5 & \quad \text{C}_6\text{H}_5 & \quad \text{C}_6\text{H}_5 \\
\end{align*} \]

\[ \text{123} \]
was indicated by an elemental analysis and mass spectrum (m/e of 456-462 - complex pattern for bromine isotopes - molecular ion of 122 and ca 542 - complex pattern, molecular ion of 123). The acetylene 121 is proposed as an intermediate in this transformation; in the presence of hydrogen bromide, however, hydrobromination is evidenced. An unequivocal synthesis of 121 was attempted (seq 45). The known thiol 124\(^{52a}\) was condensed with benzyl chloride

\[
\text{ArCH}_2\text{SH} + \text{C}_6\text{H}_5\text{CH}_2\text{Cl} \xrightarrow{\text{NaOEt}} \text{ArCH}_2\text{SCH}_2\text{C}_6\text{H}_5
\]

\[\text{124} \rightarrow \text{125}\]

\[
1) \text{SOCl}_2 \rightarrow \text{ArCH}_2\text{SO}_2\text{Cl} + \text{C}_6\text{H}_5\text{Cl} \xrightarrow{\text{KOTBu}} \text{ArC=CC}_6\text{H}_5
\]

\[\text{121} \rightarrow \text{121}\]

\[
\text{Ar} \equiv \begin{array}{c}
-\text{C}_6\text{H}_5 \\
| \\
-\text{C}_6\text{H}_5
\end{array}
\]

(45)
and the sulfide 125 was isolated. Conversion of this material to the indicated dichloro compound followed by treatment with base was anticipated to give 121 via a precededent Ramberg-Backlund rearrangement.49c However, several attempts to prepare this dichlorosulfone by the indicated route were unsuccessful.

Exposure of a dilute ether solution of 101 to a Hanovia 200-w mercury arc for 5 days gave a single highly crystalline photodimer 126 in low yield. The dimeric nature of this material was derived from its elemental analysis and mass spectrum. The latter possessed a molecular ion at m/e 384 (18% of base), a peak at m/e 192 (47% of base) corresponding to the molecular ion of the monomer, and two peaks at m/e 144 (base) and 128 (86% of base) which result from the loss of sulfur monoxide and oxygen, respectively. The nmr spectrum indicated the presence of two vinyl protons and the ultraviolet absorption pattern confirmed the presence of a styrene chromophore. These properties of 126 indicated that reaction had occurred exclusively at the exocyclic methylene group. On the basis of this analysis, four possible structures for this dimer are theoretically possible; they are depicted in equation 46, (p. 103). The 1,3 isomer (126c or 126d) would be expected to display a sharp singlet for the cyclobutane protons in its nmr spectrum since these can be expected to be magnetically equivalent through rapid inversion of the puckered cyclobutane ring at room temperature.63 However, this was not the case; the peak for these protons was a very broad multiplet which was

---

Equation 46

\[ \text{cis} (126a) \]

\[ \text{trans} (126b) \]

\[ \text{cis} (126c) \quad \text{and} \quad \text{trans} (126d) \]
observed not to be greatly altered with temperature. The dipole moment of the dimer was 2.7±0.5D in benzene. This fact likewise eliminates 126d from further consideration, for it would be expected to have canceling bond moments. The calculated value for 126a and 126c approximates 8D.64 Thus, the dimer was assigned the 1,2-trans structure 126b. The material has a small, but significant dipole moment since the two hetero rings cannot achieve a conformation where the two dipoles are completely opposed. Detailed Raman and infrared spectral studies were inconclusive for the two halves of the molecule are essentially identical, except for spatial relationships, and the coupling between the two thiete dioxide rings should be very weak in the olefinic double-bond region of these spectra.

A similar irradiation of 107 gave no characterizable products when performed under analogous conditions and in a separate experiment for two hours. The yellow oils which resulted in these attempts contained no sulfonyl absorption in their infrared spectra.

Both 101 and 107 afforded recovered starting material when refluxed in benzene or toluene solution with diiron enneacarbonyl. No characterizable products were found on attempted cyclopropanation with trimethylsulfonium bromide and potassium t-butoxide in dimethyl sulfoxide solution at room temperature. In addition, 101 gave no reaction when refluxed in benzene with anthracene (sequence 47 summarizes these results).
Thus, methylene thiete dioxides are stable substances and undergo Michael addition, give Diels-Alder cycloaddition products with a reactive diene, can be hydrogenated to two different compounds, are photochemically labile, and react in most cases at the exocyclic double bond position.
PART III

PRELIMINARY STUDIES CONCERNING THE PREPARATION OF
BICYCLIC AND FUSED AROMATIC DERIVATIVES OF
THIETE DIOXIDE

Introduction

The chemistry of fused-aromatic thiete dioxides

The 3-ethoxy, 3-amino, 3-N,N-dimethylamino and 3-phenyl-
mercapto derivatives of thietane dioxide were obtained by
respective additions of ethanol, ammonia, dimethylamine, and
thiophenol to thiete dioxide (e.g., eq 48). The reactions of

\[
\text{SO}_2 + \text{C}_6\text{H}_5\text{SH} \rightarrow \text{C}_6\text{H}_5\text{S}\text{SO}_2
\]

(48)

with aqueous base and anthracene have already been discussed.
Also, further exploration into its dienophilic properties has been
initiated by reaction with isobenzofurans. Condensation of
diphenylisobenzofuran 118 with 85 gave adduct 127 which was dehydrated
with acid to the fused naphthothiete dioxide 128. The thiete deriva-
tive of 128 was not obtained by lithium aluminum hydride reduction;
instead the mercaptan $124$ was formed by over-reduction (seq 49).

\[
\begin{align*}
\text{SO}_2 + & \quad \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \\
\text{S} & \quad \text{C}_6\text{H}_5 \\
\text{C}_6\text{H}_5 & \quad \text{C}_6\text{H}_5
\end{align*}
\]

However, a similar Diels-Alder condensation-dehydration sequence with 2,2-dimethylthiete dioxide ($90$) gave the fused thiete dioxide which did afford the thiete derivative on reduction.$^{52a}$

In an attempt to ascertain whether any substantial degree of double bond fixation exists in the naphthothiete system the synthesis of $133$ was attempted (seq 50). Condensation of isobenzofuran ($129$) with $90$ afforded adduct $130$ in good yield. Although the material
Sequence 50

\[
\begin{align*}
\text{129} & \quad \text{+} \quad \text{90} \\
\text{130} & \\
\text{133} & \\
\text{131} & \\
\text{132} &
\end{align*}
\]
proved to be remarkably resistant to acid hydrolysis, it did yield an aromatic hydrocarbon (132) when heated in polyphosphoric acid. The driving force for this expulsion of sulfur dioxide presumably is in the formation of the tertiary carbonium ion 131 (seq 50). This mechanistic scheme was tested by subjecting thiete dioxide (85) to the same reaction. If the same mechanistic sequence is followed, a primary carbonium ion would necessarily be generated. This high-energy restriction caused only normal dehydration to produce 134 as outlined in sequence 51.

The nmr and ultraviolet spectra of 134 provided evidence for the lack of double bond fixation and suggested that the fusion of the thiete dioxide ring to the 2,3-bond of naphthalene does not significantly alter the ground state of the aromatic system.
Since it is well known that the α,β-bonds of naphthalene have appreciable more double bond character than the β,β-bonds\(^{65}\)


and a very high degree of double bond fixation in the α,β-positions has been observed in a naphtho[b]cyclobutadiene\(^{66}\), the synthesis

\[\text{(66) M. P. Cava, B. Hwang, and J. P. Van Meter, J. Am. Chem. Soc., 85, 4032 (1963).}\]

of naphthothiete dioxides \(^{135}\) and \(^{136}\) and a study of their properties seemed desirable. The results of this study will be presented and in particular the properties of \(^{135}\) will be discussed.

Further experimentation with thiete dioxides

The reactions of thiete dioxides with nucleophilic reagents, reactive dienophiles, and with reducing agents\(^{51}\) have been extensively considered. However, one important aspect of their chemistry has not been examined, namely, their reaction with electron-rich olefins. In view of the electrophilic nature of the olefinic
double bond of thiete dioxides and the established propensity of 1-dialkylamino-1,3-butadienes and simple enamines for cycloaddition, reactions of such substrates and other electron-rich olefins with thiete dioxides were investigated. A good analogy for these transformations lies in similar studies with diphenylcyclopropenone (137). Thus, 1-diethylamino-1,3-butadiene (138) afforded 2,7-diphenyltropone on reaction with 137 (eq 52).67


Similar ring enlargement products resulted from the treatment of 137 with enamine 139 (eq 53).

If thiete dioxides react in a similar manner then the [2.2.0] and [4.2.0] bicyclic derivatives of 140 and 141, respectively, might be intermediates or stable entities. If these materials proved to be isolable, 140 would represent the first

\[
\begin{align*}
\text{R} & \quad \text{R'} \\
\text{R}_2\text{N} & \quad \text{SO}_2 \\
\text{R} & \quad \text{R'} \\
\text{NR}_2 & \quad \text{SO}_2
\end{align*}
\]

example of a thiabicyclo[2.2.0]hexane and 141 could serve as a possible precursor for benzothiete dioxide (142). Hofmann elimination of the thietane dioxide 143 gave rise to the expected bicyclic
Equation 52 and Equation 53

\[ \text{N(C}_2\text{H}_5\text{)}_2 + \text{C}_6\text{H}_5\text{-}\text{C}_3\text{H}_5\text{O} \xrightarrow{\text{C}_6\text{H}_6\text{ reflux}} \]

\[ \text{138} \quad \text{137} \]

\[ \text{N(C}_2\text{H}_5\text{)}_2 \]

\[ \text{C}_6\text{H}_5\text{-C}_3\text{H}_5\text{O} \]

\[ \text{C}_6\text{H}_5 \]

\[ \text{139} \quad \text{137} \]

\[ \text{139} \quad \text{137} \]

\[ \text{139} \quad \text{137} \]

\[ \text{139} \quad \text{137} \]

\[ \text{139} \quad \text{137} \]
thiete sulfone $\text{144}$ but attempts to aromatize this material to obtain $\text{142}$ have not been successful (seq 54).$^{52a,60}$

![Chemical structures](image)

The investigations in this area to be described herein are preliminary in nature and are presently under continued study in this laboratory. However, notable advances have been made and these will now be reported.
Results and Discussion

Preparation of the naphthothiete dioxide ring system

The synthesis of the naphthothiete dioxide 135 utilized the precededented cycloaddition reaction of sulfenes with enamines (Chart XIV). Enamine 146 was prepared by refluxing a mixture of α-tetralone (145) and pyrrolidine in toluene under a Dean-Stark trap. This material afforded naphthothietane dioxide 147 when treated with sulfene. Exposure of 147 to 30% hydrogen peroxide solution in glacial acetic acid-acetic anhydride yielded a mixture of naphthothiete doxides (148 and 149). Equilibration of the inseparable mixture with potassium hydroxide gave a solid that was enriched in 148 but still contained 149. Repetition of the equilibration experiment gave the same mixture (nmr comparisons). The equilibrated or non-equilibrated solid mixture could be readily brominated with N-bromosuccinimide; hydrogen bromide was eliminated as the reaction proceeded and the naphthothiete dioxide 135 was obtained directly. The nmr spectra of 134 and 135 in dimethyl sulfoxide-d₆ solution displayed the α-sulfonyl protons as a singlet at τ 4.50 and the aromatic protons as a complex multiplet below τ 2.5. By analogy to the work of Cava and coworkers, 66 the nmr chemical shift of the aromatic protons at the designated α and β positions of 135 should appear considerably upfield from the remainder of the vinyl hydrogens if any double-bond fixation exists. Therefore, 135, like 134, is devoid of this phenomenon and fusion...
Chart XIV

145 → 146

CH₂ = SO₂ → 147

N-oxide degradation

148 and 149 → 135

mixture

NBS - HBr
of a thiete dioxide ring to the α,β bond of naphthalene does not significantly alter the ground state of the aromatic moiety. This is also reflected in the great degree of similarity in the ultraviolet spectra of 135, 134, and methyl 2-naphthyl sulfone (see Table 4).


The mass spectrum of 135 has a molecular ion at m/e 204 and a base peak at m/e 140. This pattern corresponds to the fragmentation observed for the methylene thiete dioxides in Part II of this dissertation. Excellent analogy for the rearrangement of 135 to a cyclic sulfinate exists in the isolation of a similar material from the pyrolysis of the naphthothiete dioxides 128 and 150 (seq 55).
TABLE 4
Comparison of the Ultraviolet Spectra of 135, 134, and Methyl 2-Naphthyl Sulfone

<table>
<thead>
<tr>
<th>135</th>
<th>134</th>
<th>SO₂CH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image-url" alt="Image" /></td>
<td><img src="image-url" alt="Image" /></td>
<td><img src="image-url" alt="Image" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>EtOH</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; (mμ)</th>
<th>EtOH</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; (mμ)</th>
<th>EtOH</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; (mμ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>(ε 1,200)</td>
<td>327</td>
<td>(ε 1,550)</td>
<td>325</td>
<td>(ε 1,380)</td>
</tr>
<tr>
<td>315</td>
<td>(620)</td>
<td>319</td>
<td>(sh) (1,110)</td>
<td>--</td>
<td>a</td>
</tr>
<tr>
<td>308</td>
<td>(800)</td>
<td>313</td>
<td>(1,640)</td>
<td>311</td>
<td>(1,000)</td>
</tr>
<tr>
<td>290</td>
<td>(2,670)</td>
<td>294</td>
<td>(4,240)</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>279</td>
<td>(3,730)</td>
<td>289</td>
<td>(4,440)</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>272</td>
<td>(3,470)</td>
<td>284</td>
<td>(4,630)</td>
<td>277</td>
<td>(4,470)</td>
</tr>
<tr>
<td>263</td>
<td>(2,670)</td>
<td>272.5</td>
<td>(sh) (5,470)</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>230</td>
<td>(63,300)</td>
<td>233</td>
<td>(69,000)</td>
<td>229</td>
<td>(85,000)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>214</td>
<td>(sh) (30,600)</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>

* a Inflections in the curve were not reported but are obvious in the published spectrum (reference 68).
Sequence 55

\[
\begin{align*}
\text{C}_6\text{H}_5 & \quad \Delta \quad \text{C}_6\text{H}_5 \\
\text{C}_6\text{H}_5 & \quad \Delta \quad \text{C}_6\text{H}_5 \\
\text{SO}_2 & \quad \Delta \quad \text{SO} \\
\text{O-SO} & \quad \Delta \quad \text{O-SO} \\
\text{128} & \\
\text{150} & \\
\text{135} & \quad \text{molecular ion} & \quad \text{[O-SO]}^+ \\
\text{(or other possibility)} &
\end{align*}
\]
A similar synthetic scheme was proposed for the preparation of 135 (eq 56). However, the enamine 151 gave no detectable naphthothietane dioxide upon treatment with sulfene.

\[
\text{CH}_2\equiv\text{SO}_2 \quad \rightarrow \quad \text{N}
\]

\[
151 \quad \rightarrow \quad 136
\]

(56)

Lithium aluminum hydride reduction of 134 or 135 in ether solution was exothermic and a small amount of impure material with a sulfide-like odor was isolated in each case. The identity of the materials is currently under study; however, none of the anticipated naphthothietes were observed.
The reactions of thiete dioxides with electron-rich olefins

The first example of a thiabicyclo[2.2.0]hexane was obtained by heating a benzene solution of thiete dioxide (134) and enamine 152 (eq 57). No evidence for any loss of dimethylamine from the thietane dioxide 153 was observed. That the structure is bicyclic and not open-chain in nature was ascertained from its nmr spectrum. In like fashion, 2,2-dimethylthiete dioxide (135) and thiete dioxide undergo cycloaddition with 1-dialkylamino-1,3-butadienes and afford the indicated [4.2.0]bicyclic systems (eq 58).
Sequence 57

Sequence 58

56, R=CH₃
138, R=C₂H₅
85, R'=H
90, R'=CH₃
154, R=R'=CH₃
155, R=C₂H₅, R'=CH₃
156, R=CH₃, R'=H
The Hofmann and N-oxide degradations of these compounds are currently under study.

Thiete dioxide and 2,2-dimethylthiete dioxide do not undergo cycloaddition reactions with 1,1-di(l-piperidinyl)ethylene, N,N-dimethyl-2-phenylethynylamine, and N,N,N',N'-tetramethyl-1,3-butadiene-1,4-diamine. Further investigations concerning the reaction of electron-rich olefins with thiete dioxides are in progress.
Experimental

Melting points and boiling points are uncorrected. The infrared spectra were obtained with a Perkin-Elmer Model 237 Infracord spectrometer fitted with sodium chloride prisms. The microanalyses were determined by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. The nmr spectra were determined with a Varian A-60 spectrometer [tetramethylsilane (TMS) and 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (TPSS) as internal standards] purchased with funds made available from the National Science Foundation. Ultraviolet measurements were made with a Cary Model 14 recording spectrometer.

Part I

Reaction of N,N,N',N'-Tetramethylpropene-1,3-diamine (20a) with sulfene.—To a rapidly stirred solution of 31.2 g (0.31 mole) of triethylamine and 20.0 g (0.156 mole) of 20a in 50 ml of dry tetrahydrofuran cooled to -15° was added dropwise under a nitrogen atmosphere a solution of 35.6 g (0.31 mole) of methanesulfonyl chloride in 50 ml of the same solvent. The addition required one hour. Upon completion of the addition, the mixture was permitted to warm slowly to room temperature and was stirred at that temperature for 2 hours. The dark-colored mixture was

filtered to remove the precipitated triethylamine hydrochloride and evaporation of the filtrate afforded a dark oil, which was chromatographed on Florisil. Elution of the column with hexane-

(70) Dissolution of this salt in water and extraction of the aqueous solution with methylene chloride gave no additional material. Basification of the aqueous phase and reextraction likewise gave no additional product(s).

(71) A magnesia-silica gel adsorbent.

ether (1:1) and ether afforded 3.1 g (16.2%) of N,N-dimethyl-
methanesulfonamide (22), mp 49° (lit. mp 50-51).

(72) O. Eisleb, German Patent 735,866 (April 22, 1943); Chem. Abstr., 38, 4101 (1944).

Further elution with ether-methylene chloride (1:1) and methylene chloride gave 1.2 g (4.8%) of trans-1-dimethylamino-3-thia-1,4-pentadiene 3,3-dioxide (23), mp 75-76° (from ether);

\[ \nu_{\text{max}}^{\text{CDCl}_3} \]

6.15 (C=C-N<), 7.65, 7.87, and 8.90-9.05 \( \mu \) (SO2-); \( \nu_{\text{TMS}}^{\text{CDCl}_3} \)

7.08 (singlet, 6H, (CH3)2N-), 5.28, 2.82 (doublets, J=12.5 Hz, 1H each, vinyl protons at C1 and C2), 4.27 (doublet, J=9.0 Hz,

(73) That a coupling constant of this order of magnitude demands a trans configuration has been well established; see reference 31 and R. C. Pink, R. Spratt, and C. J. M. Stirling, J. Chem. Soc., 5714 (1965).

1H, \( \text{H} \uparrow \text{H} \text{C=C} \text{H} \), 3.90 (doublet, J=17.0 Hz, 1H, \( \text{H} \uparrow \text{H} \text{C=C} \text{H} \)), and 3.32

(doublet of doublets, J=9.0 and 17.0 Hz, 1H, \( \text{H} \uparrow \text{H} \text{C=C} \text{H} \)).
Anal. Calcd. for C₁₁H₁₈NO₂S: C, 44.69; H, 6.88; N, 8.69; S, 19.89. Found: C, 44.75; H, 7.03; N, 8.35; S, 19.49.

Continued elution with methylene chloride-methanol (9:1) led to the isolation of 1.85 g (5.75%) of **trans-1,5-bis-(dimethylamino)-3-thia-1-pentene 3,3-dioxide** (24), mp 69-70° (from ligroin);

\[ \text{v} \left( \text{C} = \text{N} \right) \text{max} 6.15 (\text{C} = \text{N} \prec), 7.70, 7.85 \text{ and } 9.05 \mu \left( -\text{SO}_2^- \right) ; \]

\[ \text{f} \left( \text{C} = \text{N} \right) \text{max} 7.78 \text{ (singlet, } 6\text{H, saturated dimethylamino group), 7.17} \]

(singlet, 6H, α,β-unsaturated dimethylamino group), 7.18 (somewhat overlapping on previous peak, complex multiplet, 2H, -CH₂CH₂-), 5.21 (doublet, J=12.5 Hz, 1H, vinyl proton), 2.92 (doublet, J=12.5 Hz, 1H, vinyl proton).

Anal. Calcd. for C₁₈H₁₈N₂O₂S: C, 46.57; H, 8.79; N, 13.58; S, 15.54. Found: C, 46.79; H, 8.85; N, 13.65; S, 15.50.

Further washing of the column with more polar solvent systems gave only very dark non-characterizable gums.

Partial hydrogenation of 23.—A solution of 1.0 g (6.0 mmoles) of 23 in 50 ml of tetrahydrofuran containing 200 mg of platinum oxide was shaken under 45 psig of hydrogen for 24 hr at room temperature. The catalyst was removed by filtration, and the filtrate was concentrated to give an oily solid. Recrystallization
of this material from ether afforded 0.6 g (60%) of 1-dimethyl-

(74) The filtrate from this recrystallization possessed a carbonyl band in its infrared spectrum, thereby suggesting that a certain amount of the enamine had hydrolyzed during the course of the hydrogenation.

amino-3-thia-1-pentene 3,3-dioxide as a white solid, mp 59-60°;

\[ \nu_{\text{CCl}_4} 6.12 \text{ (C=C-N\textsuperscript{-})}, 7.68, 7.86, 8.90, \text{ and } 9.00 \mu \text{ (-SO\textsuperscript{2}-)}; \nu_{\text{CCl}_4}^{\text{max}} 8.83 \text{ (triplet, 3H, CH\textsubscript{3}CH\textsubscript{2}^-)}, 7.18, \text{ (quartet, 2H, CH\textsubscript{3}CH\textsubscript{2}^-)}, 7.12 \text{ (singlet, 6H, (CH\textsubscript{3})\textsubscript{2}N^-)}, 5.32 \text{ (doublet, J=12.5 Hz, 1H, vinyl proton)}, \text{ and } 2.98 \text{ (doublet, J=12.5 Hz, 1H, vinyl proton)}. \]

Anal. Calcd. for C\textsubscript{16}H\textsubscript{13}NO\textsubscript{3}S: C, 44.14; H, 8.03; S, 19.65. Found: C, 44.09; H, 8.19; S, 19.36.

Complete hydrogenation of 22. -- A solution of 1.85 g (0.012 mole) of 22 in 100 ml of tetrahydrofuran containing 0.4 g of 10% palladium on charcoal was hydrogenated as above. After three hours, an additional 0.4 g of catalyst was added, and shaking was continued for 12 hours. The catalyst was filtered, and the filtrate was evaporated to give 1.55 g (81.7%) of a very pale yellow liquid.

A portion of this sample was treated with ethereal hydrogen chloride to give 1-dimethylamino-3-thiapentane 3,3-dioxide (25)
hydrochloride, mp 191-2\(^\circ\) dec. (from 95% ethanol).

Anal. Calcd. for \(\text{C}_6\text{H}_{16}\text{ClNO}_2\text{S}\): C, 35.72; H, 8.00; S, 15.90.

Found: C, 35.67; H, 7.99; S, 16.18.

The remainder of the oil was treated with ethanolic perchloric acid to give the perchlorate of \(25\), mp 91-2\(^\circ\) (from 95% ethanol).

Anal. Calcd. for \(\text{C}_6\text{H}_{16}\text{ClNO}_6\text{S}\): C, 27.12; H, 6.07; S, 12.07.

Found: C, 27.30; H, 6.14; S, 12.12.

Preparation of authentic 1-dimethylamino-3-thiopentane 3,3-dioxide (25).—To a solution of the sodium salt of ethyl mercaptan in ethanol [prepared by the addition of 16.8 g (0.27 mole) of ethyl mercaptan to a cooled solution of 6.2 g (0.27 g-atom) of sodium in 200 ml of absolute ethanol] was added 28.9 g (0.27 mole) of 2-dimethylaminoethyl chloride \(^75\) in one portion. The mixture


was carefully warmed and finally refluxed for 1 hour. Upon cooling, the precipitated sodium chloride was filtered, and the filtrate was concentrated \textit{in vacuo} below 50\(^\circ\). The residue was extracted with ether, and the ethereal solution was fractionally distilled to give
20.7 g (57.2%) of 1-dimethylamino-3-thiapentane (26) as a colorless liquid, bp 76-78° (35 mm) [lit 76 bp 66° (20 mm)].


A solution of 11.0 g (0.083 mole) of 1-dimethylamino-3-thiapentane (26) in 40 ml of 50% aqueous acetic acid was treated dropwise with cooling at 10-20° with a solution of 16.5 g (0.105 mole) of potassium permanganate in 250 ml of 50% aqueous acetic acid during 1 hour. The solution was decolorized with gaseous sulfur dioxide, filtered and evaporated to near dryness in vacuo at 50-60°. The residue was rendered alkaline with 100 ml of 20% aqueous sodium carbonate solution and the liberated oil was extracted with ether. The organic phase was dried and concentrated. Distillation of the residue afforded 5.1 g (45.6%) of 25 as a clear liquid, bp 100° (0.5 mm), n_26^D 1.5040. This sample and its hydrochloride, mp 198-200° dec., 77 were identical in all respects with the material isolated above.

(77) As is customary, the decomposition point of this salt was found to be dependent upon the rate of heating.
Michael addition of dimethylamine to 23.—Into a cold (-10°) solution of 150 mg of 23 in 20 ml of tetrahydrofuran was bubbled gaseous dimethylamine. When the solution was saturated, the flask was stoppered and allowed to stand at room temperature for 10 hours. The solvent was evaporated in vacuo, and the residue was recrystallized from ligroin to yield 0.146 g (79.0%) of 24, mp 69-70°. This material displayed infrared and nmr spectra superimposable upon those of a sample of 24 isolated above.

Hydrogenation of 24.—Hydrogenation of 0.47 g (2.0 mmoles) of 24 was accomplished over 500 mg of 10% palladium on carbon in 30 ml of dry tetrahydrofuran at approximately 60 psig at 25° for 35 hours. Additional 500 mg charges of catalyst were introduced after 14 and 23 hours. Workup as before gave an oil (0.45 g) which was directly converted to its dihydrochloride salt. Recrystallization of this highly crystalline white solid from ethanol gave pure 1,5-bis(dimethylamino)-3-thiapentane 3,3-dioxide (27) dihydrochloride, mp 235°.
Preparation of authentic 27.—A 12.65 g (0.072 mole) sample of 1,5-bis(dimethylamino)-3-thiapentane\(^78\) was oxidized with 15.2 g of potassium permanganate as described above. The resulting sul­
fone, bp 111-2\(^\circ\) (0.3 mm), \(n^D_{25}\) 1.4709, was obtained in 49.5\% yield. The dihydrochloride salt was prepared and melted at 233\(^\circ\).

Reaction of \(N,N,N',N''\)-tetramethylpropene-1,3-diamine (20a) with phenylsulfene.—A stirred solution of 10.0 g (0.078 mole) of 20a and 7.9 g (0.078 mole) of triethylamine in 50 mL of anhydrous tetrahydrofuran under a nitrogen atmosphere was treated at -15\(^\circ\) with a solution of 14.85 g (0.078 mole) of phenylmethanesulfonyl chloride in 50 mL of the same solvent as described above. A similar workup\(^70\) gave a viscous oil which was diluted with 30 mL
of ether and caused to crystallize at 0° with scratching. Recrystal-
ization of the pale yellow solid from ether-hexane afforded 6.75 g
(30.7%) of 2-phenyl-3-dimethylamino-4-dimethylaminomethylthietane
1,1-dioxide (29), mp 91-93°. Further purification with ether-
petroleum ether yielded pure 29 as a highly crystalline white solid,
mp 95-60°; ν CC l 4 7.40 and 8.60 μ (-SO₂ -); δ CDCl₃ 8.05 and 7.70 (two
singlets, 6H each, dimethylamino groups), 0α 7.0 (multiplet, 3H,
CH₂NMe₂ and CHNMe₂ ), 5.50 (doublet of triplets, 1H, non-benzylic
α-sulfonyl proton), 4.80 (doublet, J=9.0 Hz, 1H, benzylic proton),
and 2.61 (singlet, 5H, phenyl group).

Anal. Calcd. for C₃₄H₄₂N₂O₂S: C, 59.54; H, 7.85; N, 9.92;

All filtrates and insoluble residues up to and including
that from the first recrystallization were combined and chromato-
graphed on neutral alumina. Elution with petroleum ether afforded
a very small quantity of trans-stilbene (28), mp 122-3°.

Continued elution with petroleum ether-ether (9:1) led to
the isolation of 1.4 g (8.85%) of N,N-dimethylphenylmethanesul-
fonamide (20), mp 100-1° (from ether) (lit 79 mp 100-1°).

(79) O. Martensson and E. Nilsson, Acta Chem. Scand., 14,
1151 (1960).

The use of petroleum ether-ether (3:1) gave 0.8 g. (4.5%)
of trans-2-dimethylamino-1-phenylmethanesulfonylethylene (31),
mp 77-78°. Additional recrystallizations of this material from
carbon tetrachloride gave pure 31 as a white solid, mp 85°, (lit\textsuperscript{22a} mp 85-86°); ν\textsubscript{CCL\textsubscript{4}} 6.10 (C=C-N\textsuperscript{•}), 7.70-7.90 and 9.10 μ (-SO\textsubscript{2}−);
ν\textsuperscript{\textsuperscript{CDCl\textsubscript{3}}} 7.20 (singlet, 6H, (CH\textsubscript{3})\textsubscript{2}N\textsuperscript{•}), 5.83 (singlet, 2H, PhCH\textsubscript{2}-).
5.40 and 3.18 (doublets, J=12.5 Hz, 1H each, vinyl protons), 73 and 2.68 (singlet, 5H, phenyl group).

Anal. Calcd. for C\textsubscript{11}H\textsubscript{15}NO\textsubscript{2}S: C, 58.64; H, 6.71; N, 6.22; S, 14.23. Found: C, 58.43; H, 6.58; N, 5.74; S, 14.04.

Further elution of the column with solvents of higher polarity gave only dark intractable gums.

When the same reaction was repeated with double the quantity of phenylsulfene and the dark reaction mixture was worked up as above, the following percentage yields of products were obtained: 29, trace; trans-stilbene, 30.3%; 30, 16.8%; and 31, 1.8%.

Hydrogenation of 31 to 2-(benzylsulfonyl)-N,N-dimethyl-ethylamine (32).—A 0.5 g (2.0 mmoles) sample of 31 was hydrogenated over 10% palladium on carbon in tetrahydrofuran solution as described above. The resulting oil was treated with ethereal hydrogen chloride and the hydrochloride salt was obtained, mp 185-7° dec. (from aqueous methanol) (lit\textsuperscript{80} mp 184-6°). Regeneration of the

(80) Ju-Shih Tsung and Ju-Yün Chi, Hua Hsueh Hsueh Pao, 26, 31 (1960); Chem. Abstr., 55, 17635 (1960).
free base from the pure hydrochloride gave a white solid, mp 68-9° (from ether-petroleum ether) (lit\textsuperscript{80} mp 68-9°), identical in all respects with an authentic sample.

**Reaction of $N,N,N',N'$-tetramethyl-1-butene-1,3-diamine (20b) with sulfene.**—A stirred solution of 20\textsuperscript{b} and triethylamine (81) The yields of the various products resulting from changes in the proportions of reactants are tabulated in Table 2.


in tetrahydrofuran was treated dropwise under nitrogen at -15\textdegree with a solution of methanesulfonyl chloride in the same solvent. The resulting suspension was allowed to warm slowly to room temperature and was stirred at that temperature for 12 hours. The reaction mixture was worked up as in the case of 20a. Addition of anhydrous ether to the viscous dark residue and cooling resulted in the precipitation of a solid. This material identified as the bithietane tetroxide (25), was obtained in pure form by recrystallization.
from methanol, white solid, mp 148-50° dec.; $\nu_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ 7.55, 8.20, 8.41, and 8.82 $\mu$ (-SO$_2$-). Its nmr spectrum (in DMSO-d$_6$) displayed only one extensively-coupled upfield proton.

**Anal.** Calcd. for C$_8$H$_{15}$NO$_4$S$_2$: C, 37.93; H, 5.97; N, 5.53; S, 25.31

Found: C, 37.78; H, 6.02; N, 5.52; S, 25.10.

Chromatography of the remaining dark oil on neutral alumina afforded, upon elution with petroleum ether-ether (1:1), 2-(a-dimethylaminoethyl)-3-dimethylaminothietane 1,1-dioxide (24) as a colorless crystalline solid, mp 38° (from petroleum ether);

$\nu_{\text{max}}^{\text{CDCl}_3}$ 7.58, 8.42, and 8.80 $\mu$ (-SO$_2$-); $\gamma_{\text{TMS}}^{\text{CDCl}_3}$ 8.88 (doublet, J=7.0 Hz, 3H, CH=$\text{CH_2}$), 7.73 and 7.68 (two singlets, 6H each, both dimethylamino groups), ca 6.79 (multiplet, 2H, both CH-N=C), and ca 5.92 (multiplet, 3H, a-sulfonyl protons).

**Anal.** Calcd. for C$_9$H$_{20}$N$_2$O$_2$S: C, 49.06; H, 9.15; N, 12.72; S, 14.55. Found: C, 49.10; H, 9.31; N, 12.64; S, 14.47.

Continued elution with ether led to the isolation of N,N-dimethylmethanesulfonamide (22), mp 49°.

Further elution with ether and ether-methylene chloride (1:1) afforded trans,trans-1-dimethylamino-3-thia-1,4-hexadiene 3,3-dioxide (33) as a colorless solid, mp 58° (from ether); $\nu_{\text{max}}^{\text{CDCl}_3}$ 6.15 (C=N=C-N<), 7.65, 7.89, 8.95, and 9.05 $\mu$ (-SO$_2$-); $\gamma_{\text{TMS}}^{\text{CDCl}_3}$ 8.12 (doublet, J=6.0 Hz, 3H, CH$_2$CH=), 7.07 (singlet, 6H, (CH$_3$)$_2$N-), 5.25 and 2.81 (doublets, J=12.5 Hz, 1H each, -CH=CHNMe$_2$), 3.72 (doublet, J=15.0 Hz, 1H, CH$_3$CH=CH-), and 3.30 (doublet of quartets, J=15.0 and 6.0 Hz, 1H, CH$_3$CH=).
1-Dimethylamino-3-thiahexane 3,3-dioxide (36). A. Catalytic hydrogenation of 33.—Hydrogenation of 0.28 g of 33 in tetrahydrofuran over 10% palladium on charcoal was effected in the previously described manner. The resulting oil was converted directly to its methiodide, mp 166° dec.

**Anal.** Calcd. for C_{8}H_{12}NO_{2}S: C, 29.91; H, 6.28; N, 4.36.

Found: C, 29.93; H, 6.20; N, 4.37.

B. From propyl mercaptan.—In a manner analogous to the preparation of 36, 20.5 g (0.27 mole) of n-propyl mercaptan was condensed with 28.9 g (0.27 mole) of 2-dimethylaminoethyl chloride. There was obtained 25.8 g (65%) of 1-dimethylamino-3-thiahexane (37), bp 85° (25 mm), n_{D}^{27} 1.4621.

A 12.2 g (0.083 mole) sample of 37 was oxidized with 16.5 g (0.105 mole) of potassium permanganate in the presdescribed manner to give 7.05 (47.1%) of sulfone 36, bp 110° (0.75 mm), n_{D}^{27} 1.5040.

The methiodide of 36 was prepared in the usual fashion, mp 165-6° dec.

The infrared and nmr spectra of 36 and its methiodide were identical to those of the samples obtained in part A.
Hofmann degradation of bithietane tetroxide (35).—The methiodide salt of 35 was prepared with methyl iodide in refluxing methanol in 85% yield, mp 189° dec. (from aqueous methanol).

Anal. Calcd. for C_{9}H_{18}INO_{4}S_{2}: C, 27.35; H, 4.59; S, 16.22.

Found: C, 27.15; H, 4.62; S, 16.06.

A solution of 6.0 g (0.016 mole) of this methiodide in hot water was passed through a column of Amberlite IRA-400 ion exchange resin (basic form). The total eluate was boiled for 30 minutes, cooled, and extracted with methylene chloride to yield 1.2 g (36.4%) of 38 as white crystals, mp 143-4° (from methanol).

Anal. Calcd. for C_{9}H_{8}O_{4}S_{2}: C, 34.60; H, 3.87; S, 30.79.

Found: C, 34.44; H, 3.94; S, 30.39.

2,3'-Bithietane tetroxide (39).—A solution of 0.5 g (2.4 mmoles) of 38 in 80 ml of methanol containing 0.2 g of 10% palladium on charcoal was hydrogenated on a Parr shaker for 9 hours. The catalyst was filtered, and the solvent was evaporated.
Recrystallization of the residue from methanol gave 0.4 g (80%) of pure 39, mp 187-8°.

**Anal. Calcd.** for C_{6}H_{10}O_{4}S_{2}: C, 34.27; H, 4.79; N, 30.50.

**Found:** C, 34.21; H, 4.70; S, 30.30.

Attempts to further reduce this material through the agency of lithium aluminum hydride invariably led to tar formation.

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**Reaction of N,N,N',N'-tetramethyl-1-butene-1,3-diamine (20b) with phenylsulfene**—A solution of 26.7 g (0.14 mole) of phenylmethanesulfonyl chloride in 100 ml of dry tetrahydrofuran was added dropwise under a nitrogen atmosphere to a cold (-15°) stirred solution containing 10.0 g (0.07 mole) of 20b and 14.2 g (0.14 mole) of triethylamine in 100 ml of the same solvent. When the addition was completed, the reaction mixture was allowed to warm to room temperature during one hour. Then, after filtration of the triethylamine hydrochloride (which contained no additional products) and concentration of the filtrate, the black oily residue was chromatographed on neutral alumina. Elution with petroleum ether gave 1.58 g (12.7%) of trans-stilbene (28), mp 122-3°.
Elution with petroleum ether-ether (1:1) and ether afforded 0.95 g (6.8%) of N,N-dimethylphenylmethanesulfonamide (39), mp 100-1°.

Continued elution with ether led to the isolation of 0.17 g (1%) of 2-phenyl-4-(α-dimethylamino)ethylthiete sulfone (40), mp 123-5° dec (from ether-petroleum ether); νCl  7.60 and 8.60 μ (-SO2-); λmax StOH 256 mµ (ε 17,800); TCDCl 3 8.88 (doublet, J=6.0 Hz, 3H, CH2CH2), 7.74 (singlet, 6H, (CH3)2N-), ea 6.8 (multiplet, 1H, CH3CH2), ea 5.5 (multiplet, 1H, CH-SO2), 2.90-3.00 (multiplet, 1H vinyl proton) and 2.59 (broadened singlet, 5H, phenyl group).

Anal. Calcd. for C13H17NO2S: C, 62.12; H, 6.82; N, 5.57. Found: C, 62.10; H, 6.82; N, 5.27.

Further elution with ether-methylene chloride (9:1) gave 1.35 g (8.5%) of trans-2-dimethylamino-1-phenylmethanesulfonyl-ethylene (31), mp 85°.

Elution with ether-methylene chloride (1:1) and methylene chloride afforded 2.75 g (9.7%) of bithietane tetroxide (41), mp 160-1° dec with prior sintering at 155° (from methanol); νClmax 7.50 and 8.70 μ (-SO2-); TCDCl 3 7.95 (singlet, 6H, (CH3)2N-), ea 6.7 (multiplet, 2H, H3 and H3'), 5.60 (multiplet, 3H, non-benzylic α-sulfonyl protons), ea 4.6 (multiplet, 2H, benzylic α-sulfonyl protons), 2.68 and 2.57 (singlets, 5H each, phenyl protons).

1,3-Bis(dimethylamino)-3-phenyl-1-propene (20c).—A solution of 120 g (0.91 mole) of cinnamaldehyde and 150 ml of ether was added dropwise in a nitrogen atmosphere with stirring to a cold (-20°) mixture of 100 g (2.22 mmoles) of dimethylamine and 60 g of anhydrous potassium carbonate in 100 ml of ether. The mixture was allowed to warm to room temperature, and stirring was continued for 24 hours. The solid was removed by filtration and the ether and other volatiles were removed in vacuo at 50°. The resulting viscous light yellow liquid (141 g, 76%) was used directly because it decomposed on attempted distillation in vacuo; ν \text{Cl}4 6.00 μ (C=N<); ν max \text{Cl}4 7.85 (singlet, 6H, (CH\text{3})\text{2}N-), 7.63 (singlet, 6H, (CH\text{3})\text{2}N-), 6.52 (doublet, J=8.5 Hz, 1H, C\text{6}H\text{5}CH<), 5.80 (quartet, J=13.0 and 8.5 Hz, 1H, vinyl proton at C\text{2}), 4.08 (doublet, J=13.0 Hz, 1H, vinyl proton at C\text{1}), and 2.80 (complex multiplet, 5H, phenyl group).

Reaction of 20c with sulfene.—To a nitrogen-blanketed stirred solution of 20.0 g (0.098 mole) of 20c and 10.0 g (0.098 mole) of triethylamine was added dropwise at -15° a solution of 11.2 g
(0.098 mole) of methanesulfonyl chloride in 100 ml of the same solvent. The reaction mixture was allowed to warm to room temperature and was stirred for 5 hours. The triethylamine hydrochloride was filtered and washed with cold tetrahydrofuran. The filtrate and washings were combined and evaporated to give a viscous yellow oil which, upon trituration with ether, and cooling deposited 14.0 g (51.0%) of pale yellow solid, mp 81-3°. Further recrystallization of this material from ether afforded pure N,N-dimethyl-2-dimethylamino-4-phenyl-3-butene-1-sulfonamide (42) as a highly crystalline white solid, mp 83°; \( \nu_{\text{Cl}1} \) max \( 7.50, 8.70, \) and 10.30 \( \mu \) (\( -\text{SO}_2\text{N}^- \)); \( \lambda_{\text{EtOH}} \) max 251 (\( \epsilon \) 20,300), 282 (sh) (3,800), and 292 (sh) \( \mu \) max (2,800); \( \gamma_{\text{CDCl}_3} \) max 7.70 (singlet, 6H, \((\text{CH}_3)_2\text{N}\)), 7.15 singlet, 6H, \(-\text{SO}_2\text{N}(\text{CH}_3)_2\)), 6.10-7.00 (complex pattern, 3H, methylene protons), 3.15-3.95 (complex pattern, 2H, vinyl protons), and 2.55 (broadened singlet, 5H, phenyl group).

Anal. Calcd. for C\(_{14}\)H\(_{22}\)N\(_2\)O\(_2\)S: C, 59.54; H, 7.85; N, 9.92; S, 11.36. Found: C, 59.58; H, 7.94; N, 9.87; S, 11.34

The filtrate from the trituration was chromatographed on Florisil. Elution with petroleum ether-ether (1:3) afforded 0.55 g (2.3%) of N,N-dimethyl-4-phenyl-1,3-butadiene-1-sulfonamide (42), mp 91° (from ether-petroleum ether); \( \nu_{\text{Cl}1} \) max \( 6.10, 6.30 \) (C=C), and 7.40, 8.70, 10.40 \( \mu \) (\( -\text{SO}_2\text{N}^- \)); \( \lambda_{\text{EtOH}} \) max 224 (\( \epsilon \) 8,400), 229 (10,950), 236 (8,400), and 301 \( \mu \) max (38,700); \( \gamma_{\text{CDCl}_3} \) TMS max 7.25 (singlet, 6H, \((\text{CH}_3)_2\text{N}\)) and 2.6-3.9 (complex pattern, 9H, vinyl and phenyl protons).
Anal. Calcd. for C_{12}H_{15}NO_{2}S: C, 60.73; H, 6.37; N, 5.90; S, 13.51. Found: C, 60.97; H, 6.60; N, 6.13; S, 13.69.

Further elution with ether-chloroform (1:1) and chloroform gave 0.80 g (3.4%) of **trans.trans-1-dimethylamino-3-thia-5-phenyl-1,4-pentadiene 3,3-dioxide (44)**, mp 107-8° (from carbon tetrachloride); νCCl_{4} max 6.10 (C=C-N<), 7.60, 9.00, and 10.40 μ (-SO_{2}N<); 7^{1}CDCl_{3} 7.13 (singlet, 6H, (CH_{3})_{2}N-). 5.19 and 3.20 (doublets, J=13.0 Hz, 1H each, C=C-), 3.00 (doublet, J=9.0 Hz, 1H, C_{6}H_{5}CH=), and 2.68 (complex multiplet, 6H, -SO_{2}CH=CHC_{6}H_{5}).

Anal. Calcd. for C_{12}H_{15}NO_{2}S: C, 60.73; H, 6.37; N, 5.90; S, 13.51. Found: C, 60.91; H, 6.32; N, 5.63; S, 13.61.

**Chromatography of 42 on neutral alumina.**—A 5.0 g (0.018 mole) sample of 42 was placed on 40 g of neutral alumina. Elution with petroleum ether-ether (3:1) afforded 0.6 g of 43, mp 91°, and 3.75 g (60% recovery) of starting material (42). The yield of 43 was 35.7% when based on unrecovered starting material.

**Catalytic hydrogenation of 42.**—To a solution of 1.0 g (3.5 mmoles) of 42 in 50 ml of tetrahydrofuran was added 3 g of 10% palladium on charcoal and the mixture was hydrogenated at 55 psig
and 25° for 72 hours. The catalyst was filtered and the filtrate was evaporated in vacuo. The residue was recrystallized from ether to give 0.95 g (95.0%) of pure N,N-dimethyl-2-dimethylamino-4-phenyl-1-butanesulfonamide, mp 83-4°; ν max CCl 4 7.50, 8.70, and 10.40 μ (-SO2-N); λ EtOH 261 (ε 230), 264 (180), and 268 μ (185); 7 CDCl3 TMS 7.81 (singlet, 6H, (CH3)2N-), 7.30 (singlet, 6H, -SO2N(CH3)2), 6.9-7.5 (complex multiplet partly overlapping previous peak, 7H, methylene protons), and 2.87 (singlet, 5H, phenyl group).

Anal. Calcd. for C14H24N2O2S: C, 59.12; H, 8.51; N, 9.85; S, 11.27. Found: C, 58.98; H, 8.53; N, 9.69; S, 11.29

N,N-Dimethyl-4-phenyl-1-butanesulfonamide (45). A. Catalytic hydrogenation of 43.—A 0.3 g (1.3 mmoles) sample of 43 in 25 ml of tetrahydrofuran was hydrogenated over 10% palladium on charcoal as described above. Recrystallization of the residue from ether-petroleum ether gave pure 45 as a colorless solid, mp 48°; ν max CCl 4 7.50, 9.70, and 10.40 μ (-SO2-N); λ EtOH 242 (ε 80), 240 (130), 253 (190), 259 (230), 261 (230), 264 (180), and 268 μ (185); 7 CDCl3 TMS 8.0-8.4 (broad multiplet, 4H, saturated methylene groups), 7.0-7.6 (broad multiplet, 10H, benzyl and a-sulfonyl protons, -SO2N(CH3)2), and 2.85 (singlet, 5H, phenyl protons).
Anal. Calcd. for C_{12}H_{19}NO_{2}S: C, 59.71; H, 7.93; N, 5.81; S, 13.29. Found: C, 59.70; H, 7.92; N, 5.73; S, 13.01.

B. From 4-Phenyl-1-butanesulfonyl chloride.--Into a solution of 0.5 g of 4-phenyl-1-butanesulfonyl chloride in 20 ml of anhydrous ether cooled to -10° was bubbled a thin stream of gaseous dimethylamine until the precipitation of dimethylamine hydrochloride had ceased. The solid was removed by filtration and the filtrate was evaporated. The residue was recrystallized from ether-petroleum ether to give 4.73 g (91.0%) of 45, mp 48°, identical in all respects with the above sample.


1-Dimethylamino-3-thia-5-phenylpentane 3,3-dioxide (46).

A. Catalytic hydrogenation of 44.--The hydrogenation of 0.082 g (0.3 mmole) of 44 was accomplished over a catalytic quantity of 10% palladium on carbon in 20 ml of tetrahydrofuran at 50 psig and 25° for 7 hours. The oil which resulted upon workup was divided equally and the methiodide and hydrochloride were prepared by conventional methods.
The hydrochloride was obtained as white crystals from methanol-ether, mp 148-50°.

The methiodide was obtained as white prisms from methanol, mp 190-1° dec.  

(86) The melting point of this derivative was dependent upon the duration of the heating process and varied from 185 to 191° dec. 

Anal. Calcd. for C_{13}H_{22}INO_{2}S: C, 40.73; H, 5.79; N, 3.66; S, 8.37. Found: C, 40.76; H, 5.78; N, 3.34; S, 8.79.

B. From phenylethyl mercaptan.—To a stirred solution of the sodium salt of β-phenylethyl mercaptan [prepared by the addition of 12.9 g (0.093 mole) of β-phenylethyl mercaptan\(^{87}\) to a cooled solution of 2.14 g (0.093 g-atom) of sodium in 70 ml of absolute ethanol] was added 10.0 g (0.093 mole) of 2-dimethylaminoethyl chloride\(^{75}\) in one portion. The mixture was carefully heated to reflux in which state it was maintained for one hour. After cooling, the mixture was filtered, and evaporated. Distillation of the residue afforded 15.9 g (81.5%) of 1-dimethylamino-3-thia-5-phenylpentane, bp 91-2° (0.1 mm), \(n^D_27\) 1.5330. 

\(^{87}\) Obtained from the Wateree Chemical Company, Lugoff, South Carolina.
A solution of 13.4 g (0.064 mole) of 1-dimethylamino-3-thia-
5-phenylpentane in 40 ml of 50% aqueous acetic acid was treated
dropwise with stirring at 10-20° with 14.0 g (0.088 mole) of potas-
sium permanganate in 250 ml of 50% aqueous acetic acid. The solution
was decolorized with sulfur dioxide gas, filtered, and evaporated
in vacuo below 60°. The residue was rendered alkaline with 100 ml
of a 20% aqueous sodium carbonate solution. The liberated oil was
extracted with ether. The combined ether layers were dried, fil-
tered, and evaporated. Distillation of the residue gave 8.80 g
(57.0%) of \( \text{ZnOH}_2 \), bp 155-70° (0.03 mm), \( n^D \) 1.5250; \( v^\text{Cl}_4 \) 7.60,
8.70, and 8.90 \( \mu \) (SO\(_2\)); \( \tau^\text{Cl}_4 \) 7.87 (singlet, 6H (CH\(_3\)\(_2\))N\(_2\)),
6.7-7.6 (multiplet, 8H, methylene protons), and 2.85 \( \mu \) (singlet,
5H, phenyl group).

The free base was spectrally identical with the sample ob-
tained in part A. Furthermore, the spectra of its methiodide, mp
186° dec., 86 and its hydrochloride, mp 148-50°, likewise were
superimposable upon those of the same derivatives in part A.

Reaction of 20c with phenylsulfene.--To a nitrogen-blanketed
stirred solution of 10.0 g (0.049 mole) of 20c and 5.0 g (0.049 mole)
of triethylamine in 75 ml of dry tetrahydrofuran was added dropwise
a solution of 9.35 g (0.049 mole) of phenylmethanesulfonyl chloride
in 75 ml of tetrahydrofuran. Workup was accomplished as in the previous sulfene example. Chromatography of the residue on Florisil gave upon elution with petroleum ether-ether (9:1) 2.1 g (21.5%) of \( \text{N,N-dimethylphenylmethanesulfonamide (29)} \), mp 100-1°.

Further elution with petroleum ether-ether (1:1) afforded 8.5 g (48.3%) of \( \text{N,N-dimethyl-2-dimethylamino-1,4-diphenyl-3-butene-1-sulfonamide (47)} \), mp 146-7° (from ethyl acetate); \( \nu_{\text{max}}^{\text{CCl}_4} \) 7.50, 8.70, and 10.40 μ (-SO\(_2\)-N\(\cdot\)); \( \lambda_{\text{EtOH}}^{\text{max}} \) 253 (ε15,800), 284 (sh) (7,500), and 293 (sh) μ (6,200); \( \gamma_{\text{TMS}}^{\text{CDCl}_3} \) 7.65 (singlet, 6H \(\text{(CH}_3\)\(\cdot\)\(\cdot\)\(\cdot\)N\(\cdot\)\)), 7.45 (singlet, 6H, \(-\text{SO}_2\)N\(\text{CH}_3\))\(\cdot\)), 5.40-6.15 (complex pattern, 2H, protons on C\(\cdot\) and C\(\cdot\)), 3.55-4.50 (complex pattern, 2H, vinyl protons), 2.90 and 2.75 (singlets, 5H each, phenyl groups).

Anal. Calcd. for \( \text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_2\text{S} \): C, 67.00; H, 7.31; N, 7.82; S, 8.95. Found: C, 66.67; H, 7.33; N, 7.60; S, 9.14.

Continued elution with ether and ether-chloroform mixtures led to the isolation of 0.35 g (5.5%) of \( \text{trans-2-dimethylamino-1-phenylmethanesulfonylethylene (31)} \), mp 85°.

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Chromatography of 47 on neutral alumina. A 9.0 g (0.025 mole) sample of 47 was placed on 270 g of neutral alumina. Elution with ether gave 2.25 g of \( \text{N,N-dimethyl-1,4-diphenyl-1,3-butadiene-1-sulfonamide (157)} \), mp 104-5° (from ether-petroleum ether);
\[ \nu_{\text{Cl}} 4.61 \ (C=O), \ 7.40, \ 8.70, \ \text{and} \ 10.30 \ \mu \ (-\text{SO}_2\text{N}) \]; \ \lambda_{\text{max}} \ \text{EtOH} \ 226 \\
(6.10, 450), \ 231 \ (12, 300), \ 237 \ (10, 900), \ \text{and} \ 315 \ \mu \ (37, 700); \]
\[ \gamma_{\text{TMS}} \ \text{CDCl}_3 \ 7.38 \ \text{(singlet, 6H, \ (CH}_3)_2\text{N-)}, \ 3.0-3.6 \ \text{(complex multiplet, 1H, vinyl proton at C}_3\text{)}, \ 2.45-2.68 \ \text{(broadened singlets with overlapping multiplets, 12H, phenyl protons and vinyl protons at C}_2\text{ and C}_4\text{).} \]

**Analytical:** Calcd. for C_{18}H_{19}NO_{2}S: C, 68.98; H, 6.11; N, 4.47; S, 10.23. Found: C, 69.19; H, 6.18; N, 4.51; S, 10.39.

Further elution of the column afforded recovered 47.

**Partial hydrogenation of 157:** A solution of 0.5 g (1.6 mmoles) of 157 in 25 ml of tetrahydrofuran was hydrogenated at 50 psig and 25° over 10% palladium on charcoal for 21 hours. After the usual workup, there was obtained 0.5 g (100%) of \( N,N\text{-dimethyl-1,4-diphenyl-1-butene-1-sulfonamide (158)} \), mp 78-90° with prior sintering at 75° (from ether-petroleum ether); \[ \nu_{\text{Cl}} 7.50, \ 8.70, \ \text{and} \ 10.40 \ \mu \ (-\text{SO}_2\text{N}) \]; \ \lambda_{\text{max}} \ \text{EtOH} \ 315 \ \mu \ (6, 750); \]
\[ \gamma_{\text{TMS}} \ \text{CDCl}_3 \ 7.55 \ \text{(singlet, 6H, \ -SO}_2\text{N(CH}_3)_2\text{), 7.3-7.8 (complex multiplet overlapping previous peak, 4H, methylene protons), 2.6-3.2 (complex multiplet, 11H, both phenyl groups and the vinyl proton).} \]

**Analytical:** Calcd. for C_{18}H_{21}NO_{2}S: C, 68.54; H, 6.71; N, 4.44; S, 10.17. Found: C, 68.76; H, 6.90; N, 4.58; S, 10.40.
Reaction of 34 with sulfone. To a stirred solution of 10.0 g (0.045 mole) of 34 and 4.55 g (0.045 mole) of triethylamine in 50 ml of tetrahydrofuran was added dropwise a solution of 5.2 g (0.045 mole) of methanesulfonyl chloride in 50 ml of the same solvent. After 12 hours at room temperature, the precipitated triethylamine hydrochloride was filtered, and the filtrate was evaporated. The residue was chromatographed on neutral alumina to give 3.1 g (30% recovery) of 34 and 0.4 g (7.3%) of 1-dimethylamino-3-thia-1,4-hexadiene 3,3-dioxide (33), mp 56-8°. Further elution of the column gave a trace of 22 and a quantity of uncharacterizable viscous gums.

Reaction of 1-dimethylamino-1,3-butadiene (56) with sulfene.—Five grams (0.052 mole) of 1-dimethylamino-1,3-butadiene 82 was treated in the customary manner with two equivalents of sulfene at -15° under nitrogen. After 4 hours at room temperature, the reaction mixture was filtered, and the filtrate was concentrated in vacuo to give a brown oil. Addition of small amounts of methanol to this oil and cooling resulted in the separation of 0.65 g of bithietane.
tetroxide \textsubscript{35}, mp 143-50\degree. The original precipitate was slurried in water and the insoluble solid was filtered and dried to afford an additional 3.65 g of product. Extraction of the aqueous filtrate with methylene chloride gave an additional 1.90 g of product [total yield, 6.2 g (47.3\%)]. The reaction mixture was not examined further.

\textbf{2-Phenyl-3-dimethylamino-4-dimethylaminoethylthietane 1,1-dioxide (29) reaction with excess sulfene.}—To a stirred solution of 4.0 g (14 mmoles) of 29 and 5.4 g (53 mmoles) of triethylamine in 40 ml of tetrahydrofuran was added dropwise a solution of 6.0 g (53 mmoles) of methanesulfonyl chloride in 25 ml of the same solvent. The customary workup followed. Chromatography of the reaction mixture on neutral alumina gave 200 mg (6.0\%) of 1-dimethylamino-2-phenyl-3-thia-1,4-pentadiene 3,3-dioxide (59), mp 102-3\degree (from carbon tetrachloride); $\gamma_{\text{CCl}_4}^{\text{max}}$ 6.14 (C=C-N\textsuperscript{2}), 7.68 and 8.88 \mu (-SO\textsubscript{2}-); $\lambda_{\text{EtOH}}^{\text{max}}$ 283 m\textmu ($\epsilon$ 20,650); $\gamma_{\text{TMS}}^{\text{CDCl}_3}$ 7.33 (singlet, 6H, (CH\textsubscript{3})\textsubscript{2}N). 4.40 (doublet, J=9.0 Hz, 2H, =CH\textsubscript{2}), 4.06 (singlet, 1H, Me\textsubscript{2}NCH=), 3.56 (doublet of doublets, 1H, -SO\textsubscript{2}CH=), and 2.74 (singlet, 5H, phenyl group).
Anal. Calcd. for $C_{15}H_{15}NO_2S\frac{1}{2}H_2O$: C, 58.51; H, 6.55; N, 5.69; S, 13.02. Found: C, 58.40; H, 6.12; N, 5.66; S, 13.22.

$N,N$-Dimethylmethanesulfonamide (22) was the only remaining characterizable product.

Hydrogenation of 59.— A 0.16 g (0.65 mmole) sample of 59 in 25 ml of tetrahydrofuran was hydrogenated in the manner described above. There was isolated upon workup 0.10 g (62.5%) of 1-dimethylamino-2-phenyl-3-thia-1-pentene 3,3-dioxide (159) as a white solid, mp 129-30° (from ether-petroleum ether); $\nu_{C=O}^{\text{max}}$ 6.10 (C=O-N<), 7.70 and 8.90 $\mu$ (-SO$_2$-); $\lambda_{\text{EtOH}}$ 254 (€ 14,265), and 266 (sh) m$_u$ (9,650); $\nu_{\text{TMS}}^{\text{CDCl}_3}$ 8.70 (triplet, J=7.5 Hz, 3H, -CH$_2$CH$_3$), 7.41 (singlet, 6H, (CH$_3$)$_2$N<), 7.34 (quartet, J=7.5 Hz, 2H, -CH$_2$CH$_3$), 2.86 (singlet, 1H, Me$_2$NCH=), and 2.78 (singlet, 5H, phenyl group).

Anal. Calcd. for $C_{12}H_{17}NO_2$: C, 60.22; H, 7.16; N, 5.85; S, 13.40. Found: C, 60.49; H, 7.40; N, 5.82; S, 13.40.

1-Dimethylamino-3-methoxy-1-butene (61).—To a rapidly stirred mixture of 26.2 g (0.58 mole) of dimethylamine and 40 g of anhydrous magnesium sulfate in 150 ml of anhydrous ether previously cooled to -70° was added dropwise a solution of 30.0 g (0.29 mole) of $\beta$-methoxybutyaldehyde in
100 ml of ether. The reaction mixture was stirred overnight at room temperature. The magnesium sulfate was filtered and washed with ether. The combined filtrate and washings were concentrated in vacuo at 25°. Distillation of the residue afforded 27.5 g (73.5%) of 61 as a colorless liquid, bp 44-5° (7 mm), n_D 1.4479; v_CCl_4 6.05 μ (C=C-N<); v_CCl_4 6.17 (doublet of doublets, J=13.0 and 2.0 Hz, 1H, vinyl proton at C_2), and 4.07 (doublet, J=13.0 Hz, 1H, vinyl proton at C_1).

**Reaction of 61 with sulfene.**—To a solution of 10.0 g (0.077 mole) of 61 and 7.9 g (0.078 mole) of triethylamine in 75 ml of dry tetrahydrofuran there was added with stirring at -10° under nitrogen a solution of 8.82 g (0.077 mole) of methanesulfonyl chloride in 50 ml of the same solvent. The reaction mixture was allowed to warm to room temperature and was stirred for an additional 5 hours. The precipitated triethylamine hydrochloride was filtered and the filtrate was concentrated in vacuo to give a brown oil. Distillation of this material afforded 13.15 g (82.2%) of 62 as a colorless liquid, bp 110-12° (0.1 mm); v_CCl_4 7.60 and 8.80 μ (-SO_2-);
The infrared spectra of the crude and distilled substances were identical. Furthermore, in a second run the crude product was chromatographed on Florisil; this type of workup also afforded 62 in high yield as the lone characterizable product.

\[^{1}C_DCl\_3\] 8.75 (doublet, J=6 Hz, 3H, CH\_3CH\_2\), 7.78 (singlet, 6H, \((CH\_3)_2N\)), ca 7.1 (multiplet, 1H, Me\_2NCH\_2\), 6.68 (singlet, 3H, -OCH\_3\), ca 6.1 (complex multiplet, 4H, CH\_3O-CH\_2\ and a-sulfonyl protons).

The aminothietane dioxide was characterized as its picrate, mp 169-70° (from aqueous ethanol).

**Anal. Calcd.** for C\(_{14}\)H\(_{20}\)N\(_4\)O\(_{10}\)S: C, 38.52; H, 4.62; N, 12.84; S, 7.35. **Found:** C, 38.63; H, 4.77; N, 12.96; S, 7.37.

**Hofmann degradation of 62.**—A solution of 5.0 g (0.024 mole) of 62 and 7.0 g (0.049 mole) of methyl iodide in 30 ml of methanol was allowed to stand at room temperature for 24 hours. The precipitated solid was filtered and dried. One recrystallization from aqueous methanol gave 7.6 g (90.4%) of the pure methiodide, mp 196° dec.

**Anal. Calcd.** for C\(_9\)H\(_{20}\)INO\(_3\)S: C, 30.95; H, 5.77; S, 9.18. **Found:** C, 30.71; H, 5.76; S, 9.19.
A solution of 4.0 g (0.011 mole) of this methiodide salt in 25 ml of warm water was passed through a column of Amberlite IRA-400 ion exchange resin (basic form). A total of 500 ml of eluate was collected and concentrated in vacuo to ca 100 ml. This aqueous solution was extracted with three 100-ml portions of chloroform and the combined organic layers were dried, filtered, and evaporated. The residual oil was distilled in a molecular still at 0.02 mm (bath temperature 60-70°) to give 1.2 g (64.5%) of pure 63 as a colorless liquid; ν<sub>max</sub> <sup>CCl<sub>4</sub></sup> 7.60 and 8.80 μ (-SO<sub>2</sub>−); ν<sub>max</sub> <sup>TMS</sup> 8.62 (doublet, J=6.0 Hz, 3H, CH<sub>2</sub>CH<sub>2</sub>′), 6.68 (singlet, 3H, -OCH<sub>3</sub>), 5.82 (quartet with additional small coupling, J=6.0 Hz, 1H, CH<sub>2</sub>O-CH<sub>2</sub>′), 5.65 (broadened singlet, 2H, α-sulfonyl protons), and 3.05 (broadened singlet, 1H, vinyl proton).

Anal. Calcd. for C<sub>6</sub>H<sub>10</sub>O<sub>3</sub>S: C, 44.42; H, 6.21; S, 19.77.

Found: C, 44.24; H, 6.21; S, 19.90.
1-[(9,10-Dihydro-9,10-ethanoanthracen-11-ylidene)methyl]pyrrolidine (92).—A solution of 150.0 g. (0.64 mole) of 9,10-dihydro-9,10-ethanoanthracene-11-carboxaldehyde (91)\(^57\) and 58.0 g (0.96 mole) of pyrrolidine in 550 ml of toluene was heated under a Dean-Stark trap at reflux for 2 hours. The mixture was cooled and concentrated in vacuo to give a yellow solid which was dissolved in 1200 ml of anhydrous ether. This solution was concentrated to ca 600 ml and cooled to give 140.2 g (76.3\%) of a light yellow crystalline solid, mp 118-20\(^0\). Recrystallization from ether yielded flakes of 92, mp 125-127; \(\nu_{\text{CCL}}\)\(^4\) 6.02 \(\mu\) (\(\text{C}=\text{C}-\text{N}\)); \(\nu_{\text{CDCl}}\)\(^3\) max \(\text{TMS}\) 8.26-8.56 (complex pattern, 4H, \(-\text{CH}_2-\) of pyrroldino group), 7.48 and 7.43 (merging doublets, \(J=2.5\) Hz, 2H, \(-\text{CH}_2-\text{C}=-\text{C}\)), 6.86-7.19 (complex pattern, 4H, \((\text{CH}_2)_2\)\(^\text{N}\) of pyrroldino group), 5.66 (triplet, \(J=2.5\) Hz, 1H, \(\text{CH}-\text{CH}_2\)), 5.51 (singlet, 1H, \(\text{CH}=-\text{C}=-\text{CH}-\text{N}\)), 3.83 (broad singlet, 1H, vinyl proton), and 2.46-3.06 (complex pattern, 8H, aromatic ring protons).

1-(9,10-Dihydrospiro[9,10-ethanoanthracene-11,2'-thietan]-3'-yl)pyrrolidine S,S-dioxide (23).--A stirred solution of 90.0 g (0.314 mole) of 92 and 33.0 g (0.327 mole) of triethylamine in 500 ml of dry tetrahydrofuran under a nitrogen atmosphere was treated dropwise at -10° with a solution of 37.0 g (0.323 mole) of methanesulfonyl chloride in 120 ml of the same solvent in 45 minutes. Upon completion of the addition, the mixture was allowed to warm slowly to room temperature and was stirred at that temperature for 6 hours. Filtration of the mixture afforded a solid mixture of triethylamine hydrochloride and adduct. The solid mixture was dissolved in water and the insoluble material was filtered and washed with water, methanol, and ether to yield 71.2 g of a slightly colored solid, mp 232-3° dec. The reaction mixture filtrate was concentrated in vacuo and the resulting solid was slurried with methanol, filtered, and washed further with methanol, acetone, and ether to afford 27.8 g of a light brown solid, mp 192-4° dec. The total yield of crude 22 was 99.0 g (86.1%). One recrystallization of the combined solids from acetone-methanol gave 85.0 g (74.1%) of colorless 23, mp 237-8° dec. An analytical sample was obtained from acetone as fine white crystals, mp 246.5° dec; $\nu_{\text{max}}$ 7.70 and
8.80 μ (-SO₂-); the compound was too insoluble in organic solvents for useful nrar studies.

Anal. Calcd. for C₂₂H₂₅NO₂S: C, 72.03; H, 6.34; S, 8.77
Found: C, 72.29; H, 6.32; S, 8.71.

1-(9,10-Dihydro-4'-phenylspiro[9,10-ethanoanthracene-11,2'-thietan]-3'-yl)pyrrolidine S,S-dioxide (96).—To a rapidly stirred solution of 26.0 g (0.091 mole) of 92 and 9.5 g (0.094 mole) of triethylamine in 150 ml of dry tetrahydrofuran cooled to -10° was added dropwise under a nitrogen atmosphere in 30 minutes a solution of 17.5 g (0.092 mole) of benzylsulfonyl chloride in 75 ml of the same solvent. After the addition, the mixture was warmed to room temperature and stirred for 6 hours. The triethylamine hydrochloride was filtered and the filtrate was concentrated in vacuo to give a yellow froth which, when slurried with 250 ml of methanol at room temperature, gave 28.0 g of 96 as a light brown solid, mp 178-180° dec. (second crop, wt.=4.70 g, mp 165-177° dec. - total yield of 96 was 81.8%). An analytical sample was obtained from acetone-methanol, mp 184-185° dec.; νCHCl₃max 7.65, 8.70 and 9.00 μ (-SO₂-); ¹CDCl₃ 8.25-9.00 (multiplet with a superimposed singlet at ~8.9, SH, pyrrolidino group), 7.24 and 7.19 (merging doublets,
J=2.5 Hz, 2H, $\text{CH-CH}_2^\text{C}$, 6.40 (doublet, $J=10.0$ Hz, 1H, $\text{N-CH}_2^\text{C}$), 5.50 (triplet, $J=2.5$ Hz, 1H $\text{CH-CH}_2^\text{C}$), 5.00 (singlet, 1H, $\text{CH}_2^\text{C}$), 4.58 (doublet, $J=10.0$ Hz, 1H, $\alpha$-sulfonyl proton), and 2.28-2.98 (complex pattern, 13H, aromatic ring protons).

Anal. Calcd. for C$_{28}$H$_{27}$NO$_2$S: C, 76.15; H, 6.16; N, 3.17; S, 7.26. Found: C, 75.82; H, 6.30; N, 2.98; S, 7.30.

9,10-Dihydrospiro[9,10-ethanoanthracene-11,2'-[2H]thiete] 1,1'-dioxide (97).-- The methiodide of 93 was prepared by reaction with excess methyl iodide in refluxing acetone. The salt was filtered from the warm reaction mixture and was obtained as a light brown solid, mp 186-188° dec. (frothing). Concentration of the filtrate in vacuo gave unreacted starting material which can be reutilized in the methiodide preparation. The methiodide was not purified for analysis and was used directly for the next reaction.

A stirred slurry of 10.0g (0.019 mole) of this methiodide, ca 5 g (0.022 mole) of freshly prepared silver oxide, and 600 ml water was refluxed for 2 hours. A reaction was evidenced

by the presence of free amine and a color change of brown to black in the reaction vessel. The mixture was cooled and the solid filtered and extracted with chloroform. The chloroform solution was dried and filtered through Celite to afford, after removal of the chloroform, a light brown solid. Recrystallization of this solid from acetone gave 4.95 g (88.7%) of 27, mp 220-222° dec. An analytical sample was obtained from acetone, mp 226-228° dec;

\[
\nu_{\text{CHCl}}\text{max } 7.69 \text{ and } 8.65 \mu (\text{-SO}_2-); \quad \gamma_{\text{CDCl}}\text{ 3 } 1.04 \text{ and } 7.30 [\text{AB quartet (further split by } J=2.5 \text{ Hz), } J=14.0 \text{ Hz, } 2\text{H, } -\text{CH}_2-], 5.59 (\text{triplet, } J=2.5 \text{ Hz, } 1\text{H, } CH-CH_2-), 5.24 (\text{singlet, } 1\text{H, CH-C} \text{ }, 3.59 (\text{doublet, } J=4.0 \text{ Hz, } 1\text{H, non-\text{-sulfonyl vinyl proton, }} 3.32 (\text{doublet, } J=4.0 \text{ Hz. } 1\text{H, a-sulfonyl vinyl proton, and } 2.42-2.97 \text{ (complex pattern, } 8\text{H, aromatic ring protons). }

**Anal. Calcd. for C_{18}H_{14}O_{2}S:** C, 73.44; H, 4.79; S, 10.87

**Found:** C, 73.60; H, 4.89; S, 11.00.
during which a colorless solid was seen to crystallize from the solution. The solid was filtered and washed with methanol and ether to yield 7.7 g (76.5%) of colorless 98, mp 240-242° dec. An analytical sample was obtained from acetone-methanol, mp 250-251° dec.;

\[ \nu_{\text{max}}^{\text{CHCl}_3} \] 7.69 and 8.71 \( \mu \) (-SO\(_2\)-); \( \tau_{\text{CDCl}_3}^{\text{TMS}} \) 5.16 (singlet, 1H, \( \text{CH}-\text{C}^< \)), 3.62 (singlet, 1H, vinyl proton), 2.50-2.95 (complex pattern, 13H, aromatic ring protons), and the other three protons (\( \text{C-CH}_2-\text{CH}^< \)) are within the high noise level but the integration is 2:1.

Anal. Calcd. for C\(_{24}\)H\(_{18}\)O\(_2\)S: C, 77.81; H, 4.90; S, 8.66.

Found: C, 77.69; H, 4.96; S, 8.58.

9,10-Dihydrospiro[9,10-ethanoanthracene-11,2'-thietane] 1',1'-dioxide (99).--A mixture of 6.0 g (0.02 mole) of 97, 250 ml of acetone, and 1.0 g of 10% palladium on carbon was shaken under 50 psig of hydrogen for 25 hours at room temperature. The catalyst was filtered, and the filtrate evaporated to a colorless solid. Recrystallization from methanol gave 5.50 g (91.3%) of 99, mp 208-209°.

Pure 99 was obtained from methanol, mp 207.5-208.5° (slight coloration); \[ \nu_{\text{max}}^{\text{CHCl}_3} \] 7.62, 8.63 and 8.85 \( \mu \) (-SO\(_2\)-); \( \tau_{\text{CDCl}_3}^{\text{TMS}} \) 7.72-8.72 [complex pattern, 3H, \( \text{CH-CH}_2-\text{C}^< \) (just one of these protons) and \( -\text{CH}_2-\text{CH}_2-\text{SO}_2- \)], 7.17 [low field portion of an AB quartet (further split by \( J=2.5 \) Hz), \( J=14.0 \) Hz, 1H, \( \text{CH-CH}_2-\text{C}^< \) (just one of these protons)], 6.29 (doublet of triplets, \( J=9.0 \) and 2.5 Hz, 2H, \( \alpha \)-sulfonyl
protons), 5.63 (multiplet, 1H, $\text{CH}-\text{CH}_2$), 5.22 (singlet, 1H, $\text{CH}-\text{C}^-$), and 2.41-3.09 (complex pattern, 8H, aromatic ring protons).

**Anal. Calcd. for C$_{18}$H$_{16}$O$_2$:** C, 72.94; H, 5.44; S, 10.82

**Found:** C, 72.89; H, 5.49; S, 10.76.

Reaction of 2-phenyl-3-dimethylamino-4-dimethylaminomethyl thietane 1,1-dioxide (29) with methyl iodide.—Addition of 4.5 g (0.032 mole) of methyl iodide to a stirred solution of 3.0 g (0.0105 mole) of 29 in 20 ml of methanol resulted in a gradual exothermic reaction. After the initial reaction had subsided, the mixture was kept at room temperature for one day during which time there precipitated 1.7 g (40.8%) - based on pure 102) of a yellow crystalline solid, mp 204-205° dec. 77 (residue remained mp $>250^\circ$). Recrystallization of this material from aqueous methanol yielded pure 2-phenyl-4-dimethylaminomethyl-2-thiete-1,1-dioxide, methiodide-monohydrate (102) [examination of the filtrates afforded tetramethylammonium iodide, mp $>250^\circ$, (lit$^{91}$ mp $>230^\circ$)]

as a colorless highly crystalline solid, mp 204-5° dec; \( \nu_{\text{nujol}} \) max 2.90 (H2O) and 7.55 and 8.85 \( \mu \) \( (-\text{SO}_2^-) \); \( \lambda_{\text{max}} \) EtCH 266 \( \mu \) \( (6 \ 8,080) \).

**Anal.** Calcd. for C_{13}H_{18}NO_{12}S.H_2O: C, 39.30; H, 5.07; N, 3.53; S, 8.07. Found: C, 39.09; H, 5.38; N, 3.33; S, 8.14.

The filtrate from the removal of 102 and tetramethylammonium iodide was concentrated under reduced pressure and chromatographed on neutral alumina. Elution of the column with ether yielded 0.45 g (17.4%) of 1-dimethylamino-2-phenyl-3-thia-1,4-pentadiene 3,3-dioxide (59), mp 101-3° (from carbon tetrachloride).

Continued elution with methanol-chloroform (1:1) gave an oily solid which afforded 0.3 g (6.46%) of pure 1,5-bis(dimethylamino)-2-phenyl-3-thia-1-pentene 3,3-dioxide, 5-methiodide-monohydrate (103) upon trituration with ether, mp 220-1° (methanol);

\( \nu_{\text{nujol}} \) max 2.90 (H2O), 6.10 (-C=C-N\( \equiv \)), 7.70 and 8.90 \( \mu \) \( (-\text{SO}_2^-) \);

\( \lambda_{\text{max}} \) EtCH 2.47 \( (6 \ 14,140) \) and 266 (sh) \( \mu \) \( (10,450) \).

**Anal.** Calcd. for C_{15}H_{25}INO_{12}S.H_2O: C, 40.72; H, 6.15; N, 6.33; S, 7.25. Found: C, 39.91; H, 6.03; N, 6.52; S, 7.06.
Michael addition of dimethylamine to 59 and subsequent quaternization of the product with methyl iodide. — A cooled \((-10^\circ)\) solution of 0.02 g (0.08 mmols) of 59 in 5 ml of dry tetrahydrofuran was treated with excess dimethylamine. After remaining at 0\(^\circ\) for one day, the mixture was concentrated to an oil which was immediately reacted with methyl iodide in refluxing methanol solution for 2 hours. On cooling, there was deposited 0.03 g (84.0\%) of a crystalline material, mp 220-1\(^\circ\) (methanol), identical in all respects to 103.

Further Hofmann degradation of 102. — A solution of 6.45 g (0.016 mole - based on pure 102) of the mixture of 102 and tetramethylammonium iodide in hot water was passed through a column of Amberlite IRA-400 ion exchange resin (basic). The total eluate was concentrated to ca 50 ml \textit{in vacuo} and extracted with chloroform to yield 1.7 g (46.1\% - based on pure 102) of an oily crystalline
solid. Recrystallization from ether-petroleum ether gave rod-like crystals of 2-(benzylsulfonyl)-N,N-dimethylethylamine (22), mp 59-61° (methiodide, mp 194-5° dec. from methanol). 92

(92) Comparison of this material with authentic 32 indicates an inconsistency in the melting points of both the parent base and its methiodide. The infrared spectra of the samples from both sources are entirely comparable except for the presence of a medium intensity band at 6.1 μ in the spectrum of the material isolated from the experiment. However, the nmr spectrum of impure 32 shows no vinyl protons and the material gave a correct analysis. Chromatography of this material on neutral alumina gave pure 32, mp 69-70° (ether-petroleum ether), identical in all respects to the authentic sample.

Anal. Calcd. for C11H17NO2S: C, 58.11; H, 7.54; N, 6.16; S, 14.11. Found: C, 58.27; H, 7.60; N, 6.10; S, 13.99.

Reaction of 2-(a-dimethylaminoethyl)-3-dimethylaminothietane 1,1-dioxide (34) with methyl iodide.—Addition of 10.0 g (0.07 mole) of methyl iodide to a solution of 5.0 g (0.022 mole) of 34 in 50 ml of methanol resulted in a gradual exothermic reaction. After the initial reaction had subsided, the mixture was kept at room temperature for one day during which time there precipitated a colorless solid. The solid [5.5 g (67.1%), mp 168-9° dec.] was filtered from the mixture and the filtrate was saved. All attempts at
recrystallization of this material from aqueous methanol-ether gave 10% recovery of the solid, mp 173-5° dec. Analysis of the unpurified material for iodine identified it as the monomethiodide 104.

Analytical data for C_{10}H_{23}IN_{2}O_{2}S: I, 35.03

Found: I, 35.49.

The above filtrate was concentrated in vacuo and chromatographed on neutral alumina. Elution of the column with ether afforded 0.6 g (15.1%) of an oil which was identical in all respects (except for its non-crystalline form) to 1-dimethylamino-3-thia-1,4-hexadiene 3,3-dioxide (33). The oil was hydrogenated over 10% palladium on carbon and a methiodide was prepared from the hydrogenated material mp 166° dec. This derivative was identical in all respects to the methiodide of 36.

Continued elution with methanol-chloroform (1:4) gave 0.1 g of tetramethylammonium iodide, mp > 250°.

Further Hofmann degradation of 104.--A solution of 4.0 g (0.011 mole) of 104 in hot water was passed through a column of Amberlite IRA-400 ion exchange resin (basic form). The total alkaline eluate was reduced to one-half its volume in vacuo at 60-70°. The remaining solution was concentrated under reduced pressure at -70° to 1.5 g (61.6%) of a brown oil. The oil was similar in all respects to 34.
(infrared spectrum had medium intensity absorption at 6.1 μ - enamine) and a methanol solution of this material gave on reaction with methyl iodide the above methiodide \((104)\), mp 165-6° dec.

**Hofmann degradation of 32**.--The methiodide salt of 32 was prepared with methyl iodide in refluxing methanol in 93.4% yield, mp 212-3° dec. (from aqueous methanol).

A solution of 10.0 g (0.027 mole) of this methiodide in hot water was passed through a column of Amberlite IRA-400 ion exchange resin (basic). The total eluate was concentrated in vacuo and extracted with chloroform to yield 2.3 g (43.4%) of a colorless solid. Recrystallization from ethyl acetate-petroleum ether gave flakes of 2-(benzylsulfonyl)ethanol \((105)\), mp 74° (lit. 93, mp 97° - needles from water); \(\nu_{max}^{CHCl_3}\) 2.90 (-OH) and 7.60 and 8.96 μ (-SO₂-);

\(\gamma_{CHCl_3}\) 6.98 (triplet, \(J=5.5\ Hz, 2H, -SO_2CH_2CH_2-\)), 6.80 (singlet, 1H, -CH₂OH), 6.05 (triplet, \(J=5.5\ Hz, 2H, -CH_2OH\)), 5.70 (singlet, 2H, benzylic protons), and 2.67 (singlet, 5H, phenyl group).

**Anal. Calcd.** for C₁₉H₁₂O₃S: C, 53.98; H, 6.03; S, 16.02

**Found:** C, 54.14; H, 6.05; S, 15.71.
2-Methylene-4-phenyl-2H-thiote 1,1-dioxide (101).—A solution of 29 (7.0 g, 0.025 mole) in 15 ml of glacial acetic acid and 15 ml of acetic anhydride contained in a 100-ml round-bottom flask equipped with a magnetic stirring bar and cooled to -10° was treated dropwise with stirring during 10 minutes with 14.0 g (0.123 mole) of 30% hydrogen peroxide. The reaction mixture was stirred at 0° for an additional 30 minutes and at room temperature for 17 hours, again cooled in ice, and neutralized with a 25% sodium hydroxide solution. Three runs as above were combined and concentrated in vacuo for 1.5 hours at 60° and at 30° to proximate dryness. The solid residue was dissolved in a minimum amount of water and the solution was extracted with chloroform. The organic extract was separated, dried over anhydrous potassium carbonate and concentrated to a brown oil. Chromatography of this oil on neutral alumina yielded upon elution with ether-petroleum ether (1:1) and ether 5.40 g (37.6 %) of a light yellow crystalline solid, mp 83-5° dec.94 Rapid recrystallization

(94) The combined eluates were concentrated to a small volume and the solid crystallized from the solution. Petroleum ether was added to cause further crystallization and the material was removed by filtration. In this way, pure 101 could be isolated and its decomposition was at a minimum.
from ether-petroleum ether gave pure 2-methylene-4-phenyl-2H-thiete 1,1-dioxide (101) as a colorless, highly crystalline solid, mp 86-8°
dec95; νmaxnujol 7.66, 8.40, 8.67 and 8.90 μ (-SO2-); λmaxether 291 μ.

(95) This material decomposes slowly at room temperature and rapidly in acetonitrile, carbon tetrachloride, and chloroform. Decomposition is slow in ether but it can be recovered by adding petroleum ether.

(€ 33,400); TCDCl3 2.53 (singlet, 6H, phenyl group and styrene proton), 4.45 (doublet of doublets, J=4.0 and 1.0 Hz, 1H, methylene proton), and 4.66 (doublet, J=4.0 Hz, 1H, methylene proton).

Found: C, 62.34; H, 4.47; S, 16.34.

2-Phenyl-3-(1-piperidino)-4-(1-piperidinophenylmethyl)-thietane 1,1-dioxide (106).--To a rapidly stirred solution of 18.6 g (0.065 mole) of 108 and 6.8 g (0.067 mole) of triethylamine in

100 ml of dry tetrahydrofuran cooled to -10° was added dropwise under a nitrogen atmosphere a solution of 12.5 g (0.066 mole) of benzylsulfonyl chloride in 100 ml of the same solvent. Upon completion of the addition, the mixture was permitted to warm to room temperature and was stirred at that temperature for 4 hours. The triethylamine hydrochloride70 was filtered from the reaction
mixture and evaporation of the filtrate afforded a brown oily solid, which was chromatographed on neutral alumina. Elution of the column with petroleum ether-ether (3:1) gave 9.45 g of a brown solid. Two recrystallizations of this material from ether afforded 6.0 g (20.7%) of \( \text{106} \) as a light brown solid, mp 166-7°. Further purification from ether gave pure \( \text{106} \), mp 161-2°; \( \nu_{\text{max}}^{\text{CCl}_4} 7.59, 8.56, 8.84 \) and 9.06 μ (-SO₂-); \( \delta_{\text{CDCl}_3} \) 8.57 (multiplet, 12H, -CH₂- of piperidino groups), 7.22-7.83 (multiplet, 8H, \{CH₂\}_2N- of piperidino groups), 6.32 (broad triplet, J=8.0 Hz, 1H, \( \sim \text{CH-N} \)), 5.77 (broad doublet, J=11.0 Hz, 1H, non-benzylic \( \alpha \)-sulfonyl proton), 4.62 (broad doublet, J=8.0 Hz, 1H, benzylic \( \alpha \)-sulfonyl proton), and 2.70 (singlet, 10H, phenyl groups).

**Anal. Calcd. for \( \text{C}_{26}\text{H}_{34}\text{N}_2\text{O}_2\text{S} \): C, 71.19; H, 7.81; N, 6.39.**  
**Found: C, 71.21; H, 7.91; N, 6.23.**

Continued elution with petroleum ether-ether (3:1 and 1:1) and ether yielded 7.0 g of an oil which contained some \( \text{106} \). Recrystallization of this material from ether afforded 3.45 g (21.8%) of a colorless flaky solid, mp 125-7°. Further purification from carbon tetrachloride gave pure \( 1-(\text{benzylsulfonyl})\text{piperidine} \) (109), mp 137° (lit.72 mp 136-8°).

Further elution of the column with chloroform-ether (1:1) gave a brown oil which afforded 0.5 g (2.86%), upon trituration with ether, of a brown crystalline solid, mp 86-8°. Recrystallization from ether gave analytically pure \( 2-(\text{1-piperidino})\text{1-phenylmethane-sulfonylethylene} \) (110), mp 91-2°; \( \nu_{\text{max}}^{\text{CCl}_4} 6.16 \) (C=O-N<), 7.66 and
9.00 μ (-SO\(_2\)) ; \(\gamma^{1}C\text{DCl}3\) 8.47 (multiplet, 6H, \(-\text{CH}_2\) of piperidino group), 6.96 (multiplet, 4H, \(\text{CH}_2N\) of piperidino group), 5.83 (broad singlet, 2H, benzylic protons), 5.32 and 3.30 (doublets, \(J=13.0 \text{ Hz}, 1\text{H each}, \text{vinyl protons}\)), and 2.67 (singlet, 5H, phenyl group).

Anal. Calcd. for C\(_{14}H_{19}NO_2S\): C, 63.36; H, 7.22; N, 5.28

Found: C, 63.41; H, 7.24; N, 5.17.

2-Benzylidene-4-phenyl-2H-thiete, 1,1-dioxide (107).—A stirred mixture of 106 (5.0 g, 11.4 mmoles) in 20 ml of glacial acetic acid and 15 ml of acetic anhydride was treated dropwise during 5 minutes at -10° with 6.0 g (0.053 mole) of 30% hydrogen peroxide. The reaction mixture was permitted to warm to room temperature and was stirred for 19 hours, again cooled in ice, and neutralized with a 25% sodium hydroxide solution. A yellow oily solid was precipitated during neutralization and was extracted with chloroform and dried over potassium carbonate. (The aqueous layer from the extraction afforded no additional material after concentration to dryness and extraction of the salt-residue with chloroform). The dried chloroform extract was filtered and concentrated in vacuo to give an oily solid which afforded, on trituration with ether, 1.82 g of a yellow solid, mp 209-10° dec. The filtrate
was concentrated and chromatographed on neutral alumina. Elution of
the column with ether gave 0.8 g of the same material (total yield -
85.3%), mp 208-10° dec. Recrystallization from tetrahydrofuran-
petroleum ether afforded pure 107, mp 212-3° dec.; \( \lambda_{\text{max}}^{\text{CHCl}_3} 6.02 \)
\( (\approx \text{C} = \text{C}) \), 7.63 and 8.70 \( \mu \) \( (\approx \text{SO}_2^-) \); \( \lambda_{\text{max}}^{\text{CHCl}_3} 366 \) (sh) \( \mu \) \( ( E 23,450) \),
349 (40,200), 337 (38,800), and 240 (12,850); \( \gamma_{\text{CDCl}_3} \) 3.49
(singlet, 1H, exocyclic styrene proton), 2.31-2.79 (broad singlet,
11H, phenyl groups and ring proton).

**Anal.** Calcd. for \( \text{C}_{16} \text{H}_{12} \text{O}_2 \text{S} \): C, 71.61; H, 4.51; S, 11.95


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2-(1-Piperidinomethyl)-3-(1-piperidino)thietane 1,1-dioxide

(111).---A solution of 10.0 g (0.099 mole) of triethylamine and
20.0 g (0.096 mole) of 1,3-bis(1-piperidino)-1-propene (112)\(^{96}\) in 50 ml
of dry tetrahydrofuran was treated in the usual manner with 11.0 g
(0.096 mole) of methanesulfonyl chloride in 50 ml of the same sol-
vent. Removal of the triethylamine hydrochloride and concentration
of the filtrate yielded an oily liquid which afforded, on trituration
with ether at 0°, 16.0 g of a brown crystalline solid, mp 62-4°
(second crop, 2.5 g, mp 58-60° - total yield, 67.3%). Recrystal-
lization from ether-petroleum ether gave pure 111, mp 67-8°;
$\nu_{\text{max}}^{\text{CCl}_4}$ 7.54, 8.39, 8.78, and 9.07 $\mu$ (-SO$^-_2$); $\tau_{\text{TMS}}^{\text{CDCl}_3}$ 8.50 (broad singlet, 12H, -CH$_2^-$ of piperidino groups), 7.58 (multiplet, 8H, -CH$_2^-$N- of piperidino groups), 6.92-7.28 (complex pattern - 5 sharp lines, 3H, -CH$_2^-$N$^<-CHN$^<-), 6.08 (doublet, $J=8.0$ Hz, 2H, -CH$_2$SO$_2^-$), and 5.45-5.85 (multiplet, 1H, -CHSO$_2^-$).

Anal. Calcd. for C$_{14}$H$_{26}$N$_2$O$_2$S: C, 58.69; H, 9.15; N, 9.78.

Found: C, 58.68; H, 9.23; N, 9.48.

Chromatography of the residues obtained from the concentration of the mother liquors from the purification of 111 on neutral alumina gave, on elution of the column with ether, 111, mp 67-8°.

Elution with petroleum ether-ether (1:1) gave a mixture of 111 and 1-(methylsulfonyl)piperidine (characteristic $\nu_{\text{max}}^{\text{CCl}_4}$ 10.4 $\mu$ for sulfonamide but not characterized any further), mp 40-55°. Further elution with chloroform-ether (1:9) gave colored oils which contained intense absorption in the infrared at 6.10 $\mu$.

2-(1-Piperidinophenylmethyl)-3-(1-piperidino)thietane 1,1-dioxide (113).--A stirred solution of 20.0 g (0.07 mole) of triethylamine in 60 ml of anhydrous tetrahydrofuran under a nitrogen atmosphere was treated dropwise at -10° with a solution of 8.1 g (0.07 mole) of methanesulfonyl chloride in
50 ml of the same solvent. The addition required one hour. Upon completion of the addition, the mixture was permitted to warm slowly to room temperature and was stirred at that temperature for 8 hours. The mixture was filtered to remove the precipitated triethylamine hydrochloride (contained no additional material) and evaporation of the filtrate afforded a brown viscous oil. The oil became crystalline after standing at room temperature for one day. The partially crystalline mixture was mixed with ether and cooled to 0° to afford 14.45 g of yellow solid, mp 125-7°. Further recrystallization of this material from ether-petroleum ether gave pure 113 as a colorless fluffy solid, mp 129-30°; \( \nu_{\text{max}}^\text{CCL} \) 7.50, 8.40, and 9.10 \( \mu \) (\(-\text{SO}_2^-\)); \( ^\text{1H}^\text{CCH} \) 8.11-8.92 (multiplet, 12H, \(-\text{CH}_2\) of piperidino groups), 7.25-8.08 (multiplet, 8H, \( \{\text{CH}_2\}^\text{2N} \) of piperidino groups), 6.56 (broad triplet, J=6.0 Hz, 1H, \( >\text{NCH} \), 6.07 and 5.88 [singlet and doublet (J=3.0 Hz), respectively, 3H, \(-\text{CH}_2\)-SO\(_2^-\) and \( >\text{CH-N} \), resp.], 4.93 and 5.13 (doublet of doublets, J=12.0 and 6.0 Hz, 1H, \( >\text{CH-SO}_2^-\)), and 2.75 (singlet, 5H, phenyl group).

Anal. Calcd. for C\(_\text{20}^\text{30}^\text{22}\)H\(_\text{N}^\text{0}^\text{S}^\text{2}\): C, 66.26; H, 8.34; N, 7.73; S, 8.85. Found: C, 66.49; H, 8.46; N, 7.69; S, 8.97.

All filtrates and insoluble residues from the original reaction mixture and recrystallizations of 113 were combined and chromatographed on neutral alumina. The only material isolated was 113 and the total weight obtained by direct crystallization and through chromatography of the filtrates was 15.5 g (61.0%).
Partial hydrogenation of 101.—A solution of 0.5 g (2.6 mmoles) of 101 in 50 ml of ether containing 300 mg of 10% palladium on carbon was placed in an atmospheric hydrogenation apparatus. The uptake of hydrogen was rapid but ceased before one equivalent was consumed. The catalyst was removed by filtration, and the filtrate was concentrated to give a colorless solid which possessed an unpleasant odor and contained starting material. Recrystallization of this mixture from ether-petroleum ether afforded 0.25 g (49.5%) of 2-methyl-4-phenyl-2H-thiote 1,1-dioxide (115) as a slightly colored solid, mp 104.7°. An analytical sample of 115 was obtained from ether,

(97) Starting material (101) cannot be recovered under these conditions.

mp 111-2°; $\nu$$_{max}^{CCl_4}$ 7.62, 8.47 and 8.80 $\mu$ (-SO$_2$-); $\lambda$$_{max}^{EtOH}$ 255 $\mu$
( $\epsilon$ 17,270); $\gamma$$_{TMS}^{CCl_4}$ 8.48 (doublet, $J$=7.0 Hz, 3H, methyl group), 5.25 (broad quartet, $J$=7.0 Hz, 1H, $\alpha$-sulfonyl proton), 3.10 (singlet - slightly split, $J$=2.0 Hz, 1H, styrene proton), and 2.60 (singlet, 5H, phenyl group).

Anal. Calcd. for C$_{10}$H$_{10}$O$_2$S: C, 61.83; H, 5.18; S, 16.51

Found: C, 61.95; H, 5.32; S, 16.45.
Complete hydrogenation of 101.—A solution of 0.4 g (2.1 mmoles) of 101 in 30 ml ether containing 100 mg of 10% palladium on charcoal was shaken under 50 psig of hydrogen for 4 hours at room temperature. The catalyst was removed by filtration and the filtrate was concentrated to give 0.35 g of an unpleasant smelling colorless solid, mp 91-3° (prior softening at 76°). The melting point did not change on recrystallization of the material from ether-petroleum ether and its nmr spectrum showed that it was a mixture of completely and partially hydrogenated material.

The above mixture (0.2 g) was hydrogenated under the same conditions for 54 hours and afforded 0.2 g (>90%) of a colorless solid, mp 95-7°. Recrystallization from ether-petroleum ether afforded pure 2-methyl-4-phenylthietane 1,1-dioxide (116), mp 107-9°; \( \nu_{\text{max}} \) same as 115, except for fine structure; \( \delta_{\text{CDCl}_3}^{13} \) 8.48 (broad doublet, J=7.0 Hz, 3H, methyl group), 7.25-7.75 (multiplet, 2H, ring methylene protons), 5.55-5.95 (multiplet, 1H, non-benzylic \( \alpha \)-sulfonyl proton), 4.68 (multiplet, 1H, benzylic \( \alpha \)-sulfonyl proton), and 2.60 (singlet, 5H, phenyl group).

Anal. Calcd. for C\(_{10}\)H\(_{12}\)O\(_2\)S: C, 61.19; H, 6.16; S, 16.34
Found: C, 61.18; H, 6.17; S, 16.22.
Reaction of 2-methylene-2-phenyl-2H-thiete 1,1-dioxide (101) with dimethylamine.—Into a cold (-20°) solution of 0.30 g (1.6 mmoles) of 101 in 20 ml ether was distilled excess dimethylamine and the resulting brown mixture was left overnight at 0°. Evaporation of the solution and trituration of the residual brown oil with ether afforded on cooling 0.20 g (45.5%) of an isomer (117) of 2-phenyl-3-dimethylamino-4-dimethylaminomethylthietane 1,1-dioxide (29), mp 76-8°. Recrystallization from ether gave pure 117 (unassigned isomer), mp 84-86; ν<sub>max</sub> <sub>CCl<sub>4</sub></sub> 7.50, 8.55, and 8.67 μ (-SO<sub>2</sub>-); ν<sub>CDCl<sub>3</sub></sub> 7.83 and 7.60 (two singlets, 6H each, dimethylamino groups), 6.90 (doublet, J=6.0 Hz, 2H, -CH<sub>2</sub>NMe<sub>2</sub>), 6.43 (doublet, J=10.0 Hz, 1H, -CH(NMe<sub>2</sub>), 5.55-5.95 (multiplet, 1H, non-benzylic α-sulfonyl proton), 4.82 (doublet, J=10.0 Hz, 1H, benzylic proton), and 2.52 (singlet, 5H, phenyl group).

Anal. Calcd. for C<sub>14</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>S: C, 59.54; H, 7.85; N, 9.92

Found: C, 59.63; H, 7.85; N, 9.57.
3,4-Dihydro-1,4,4'-triphenylspiro[1,4-epoxynaphthalene-2(1H),2'-[2H]thiete] 1',1'-dioxide (119).—A solution of 0.7 g (2.6 mmoles) of 1,3-diphenylisobenzofuran (118) and 0.5 g (2.6 mmoles) of


in 10 ml of benzene was refluxed for 16 hours under an atmosphere of nitrogen. The resulting brown solution was concentrated to an oil which was chromatographed on neutral alumina. Elution of the column with ether-petroleum ether (varying percentages) afforded 1.15 g (79.2%) of colorless adduct, mp 210-2° dec. An analytical sample of 119 was obtained from benzene-petroleum ether, mp 207-9°, with formation of yellow color at 165° (reverse Diels-Alder?); \( \lambda_{\text{max}}^{\text{CHCl}_3} \) 7.67 and 8.69 \( \mu \) (\( \text{SO}_2 \)-); \( \lambda_{\text{max}}^{\text{EtOH}} \) 262 \( \mu \) (\( \varepsilon \) 27,900); \( \gamma_{\text{CDCl}_3} \) 6.67 and 7.17 (\( \text{AB} \) quartet, \( J=13.0 \) Hz, 2H, methylene protons), 3.38 (singlet, 1H, styrene proton), 2.20-3.15 (complex pattern with singlet at 2.68, 17H, fused aromatic ring protons and phenyl groups), and 1.88 (complex pattern, 2H, fused aromatic ring protons).

**Anal.** Calcd. for \( C_{30}H_{22}O_3S \): C, 77.89; H, 4.80; S, 6.93

Found: C, 78.21; H, 4.92; S, 6.74.
3,4-Dihydro-1,3,4,4'-tetraphenylspiro[1,4-epoxynaphthalene-2(1H),2'-[2H]thiete] 1',1'-dioxide (120). A solution of 1.05 g (3.8 mmols) of 1,3-diphenylisobenzofuran (118) and 1.0 g (3.7 mmols) of 107 in 15 ml of toluene was refluxed for one day under an atmosphere of nitrogen. The toluene was removed in vacuo and the yellow residue was chromatographed on neutral alumina. Elution of the column with ether-petroleum ether (1:3) gave 0.4 g (20.0%) of yellow adduct, mp 211-3°C dec. Recrystallization of this material from benzene-petroleum ether gave an analytical sample of 120, mp 216°C, with formation of yellow color at 190°C (reverse Diels-Alder?); $\nu_{\text{max}}$ CHCl$_3$ 7.66 and 8.69 $\mu$ (-SO$_2$); $\lambda_{\text{max}}$ EtCH$_2$ 263 mp (€ 12,970); $\gamma_{\text{CDCl}_3}$ 5.40 (multiplet, 1H, benzylic proton), 3.94 (broad singlet, 1H, styrene proton), 2.28-3.18 (complex pattern with singlet super-imposed at 2.92,22H, fused aromatic ring protons and phenyl groups), and 1.68-1.91 (complex pattern, 2H, fused aromatic ring protons).

Anal. Calcd. for C$_{36}$H$_{26}$O$_3$S: C, 80.27; H, 4.87; S, 5.95.

Found: C, 80.20; H, 4.95; S, 5.94.

Further elution of the column with ether-petroleum ether
(1:1) and ether gave 1.5 g of an oily solid. Recrystallization of this material from benzene-petroleum ether afforded 0.45 g of a mixture of 120, dibenzoyl ethylene (decomposition product of 118), and 107, mp 162-5°.

Treatment of 119 with acidic reagents. (a) Polyphosphoric acid.—A mixture of 0.5 g (1.1 mmoles) of a finely powdered 119 and 10.0 g of polyphosphoric acid was heated at 100° for one day with intermittent stirring. A color change from blue to greenish-blue to dark green was observed in the reaction proper. In fact, each time the above was stirred, this color change was noted in those regions of the mixture where unreacted 119 had accumulated. The green syrup was poured into water, and the organic components were extracted with chloroform. Usual workup of this chloroform solution afforded a brown froth which on trituration with ether, gave 0.4 g (80.0% recovery) of a brown highly crystalline solid, mp 209-11° dec, identical in all respects to 119 (mp 210-2°).

(b) Hydrogen bromide.—A stirred mixture of 0.65 g (1.4 mmoles) of 119 and 10 ml of glacial acetic acid containing 0.5 ml of acetic anhydride was treated with gaseous hydrogen bromide for 5 min. The resulting red solution was refluxed for 16 hours whereupon it turned dark brown. The solution was cooled, poured into water, and the organic components were extracted with chloroform. Usual workup of this solution gave 0.9 g of a brown oil. Chromatography of this material on neutral alumina afforded, on elution
with petroleum ether-ether (3:1), 0.5 g (77.0%) of 122, as a color-
less waxy solid, mp ca 73° (prior softening at 63°). Molecular dis-
tillation at ca 120° (0.02 mm) and recrystallization from methanol
gave pure 122, mp 68-70°; \nu_{\text{max}}^{\text{CCl}_4} 14.33 \mu\text{ (aromatic system)} and lack
of -SO_2- absorption; \lambda_{\text{EtOH}}^{\text{max}} 310 ( \epsilon 20,150), 285 (32,750), 236 \mu\text{ (37,400)}; \gamma_{\text{TMS}}^{\text{310}} 3.16 (\text{singlet, } 1\text{H, vinyl proton}), and 2.10-3.05
(complex pattern, 20\text{H, aromatic protons}).

(99) These calculations are based on the sample being all 122 and ignore the presence of 123.

Anal. Calcd. for C_{30}H_{21}Br: C, 78.09; H, 4.59; Br, 17.32.
Found: C, 77.63; H, 4.21; Br, 19.51.

Benzyl 1,4-diphenyl-2-naphthalene sulfide (125).—To a solution
of the sodium salt of 1,4-diphenyl-2-naphthaleneethanethiol (124)\textsuperscript{52a}
in ethanol [prepared by the addition of 1.2 g (3.7 mmoles) of solid
124 to a solution of 0.1 g (4.3 mg-atom) of sodium in 6 ml of absolute
ethanol] was added 0.47 g (3.7 mmoles) of benzyl chloride in one por-
tion. The mixture was refluxed for 0.5 hour. Upon cooling, the
precipitated sodium chloride was filtered, and the filtrate was concen-
trated in vacuo. The residue was extracted with chloroform, and the
resulting organic phase was evaporated at reduced pressure to give
1.65 g (ca 100%) of a yellow oil. Distillation of this material at
ca 200° (0.05 mm) gave a purified substance identified as 125 on the
basis of the following spectral and chemical evidence; \nu_{\text{max}}^{\text{CCl}_4} 14.30 \mu\text{ (aromatic)}; \gamma_{\text{TMS}}^{\text{310}} 6.72 (\text{broad singlet, } 4\text{H, } -\text{CH}_2-\text{S-CH}_2-), 3.22 and 2.37-
3.10 (singlet and complex region respectively, 20\text{H, aromatic protons}).
An ethereal solution of this material was oxidized with ethereal monoperphthalic acid. Usual workup gave a colorless crystalline solid, mp 163-4°C. Recrystallization from ether gave an analytical sample of the sulfone 160, mp 164°C; \( \nu_{\text{max}}^{\text{CHCl}_3} 7.59 \) and 8.95 (-SO\(_2\)-); \( \lambda_{\text{max}}^{\text{EtOH}} 2.98 \) (\( \epsilon \) 8,760), 240 (49,800), and 231 mp (30,150).

**Anal.** Calcd. for C\(_{30}\)H\(_{24}\)O\(_2\)S: C, 80.32; H, 5.39; S, 7.15. Found: C, 80.03; H, 5.38; S, 7.44.

Photolysis of 101 to trans-2,7-diphenyl-1,6-dithiadispiro-[3.0.3.2]deca-2,7-diene 1,1,6,6-tetraoxide (126b).—A stirred solution of 5.1 g (0.027 mole) of 101 in 450 ml ether was irradiated under nitrogen with a Hanovia 200-w mercury arc for 5 days. Workup gave a black oily solid which was chromatographed on neutral alumina. Elution of the column with ether-petroleum ether (1:1) afforded 0.9 g of starting material (101) and, after one recrystallization from acetone, 0.5 g (9.8% overall and 11.9% based on unrecovered 101) of photodimer (126b), mp 231°C dec. An analytical sample of 126b was obtained from acetone, mp 232°C dec (darkened at ca 205°C); \( \nu_{\text{max}}^{\text{CHCl}_3} 7.62 \) and 8.64 \( \mu \) (-SO\(_2\)-); \( \lambda_{\text{max}}^{\text{EtOH}} 258 \) (\( \epsilon \) 36,900) (slight shoulder at 266); \( \gamma_{\text{TMS}}^{\text{DMSO-d6}} 7.27 \) (multiplet, 4H, -(CH\(_2\))\(_2\)), 2.47 (singlet, 10H, phenyl groups), and 2.10 (singlet, 2H, vinyl protons).

**Anal.** Calcd. for C\(_{20}\)H\(_{16}\)O\(_2\)S: C, 62.48; H, 4.20; S, 16.68. Found: C, 62.31; H, 4.29; S, 16.65.
1-(3,4-Dihydro-1-naphthyl)pyrrolidine (146).—A mixture of 20.0 g (0.137 mole) of α-tetralone, 10.5 g (0.148 mole) of pyrrolidine, and 0.2 g of p-toluenesulfonic acid was refluxed in 250 ml of toluene under a Dean-Stark trap in a nitrogen atmosphere for 24 hours. Approximately 2.5 ml of water was collected in the trap and the reaction mixture turned yellow. The solution was cooled and concentrated in vacuo. The residue was distilled at reduced pressure to give 1A6, bp 85-90° (0.25 mm) (15.9 g, 58.2%), nD25 1.5914; νCl4 max 6.15 (-C=O-N<); TCCl4 max 6.0-8.40 (complex pattern, 12H, -CH2CH2- and pyrrolidino group), 5.0 (triplet, J=5.0 Hz, 1H, vinyl proton), and 2.58-3.15 (complex pattern, 4H, aromatic ring protons).

1-(3,4-Dihydro-1H-naphtho[2,1-b]thiet-8b(2eH)-yl)pyrrolidine S,S-dioxide (147).—A solution of 12.6 g (0.063 mole) of 146 in 50 ml of dry tetrahydrofuran was treated in the usual manner with sulfene generated from 6.55 g (0.065 mole) of triethylamine and 7.32 g (0.063 mole) of methanesulfonyl chloride (in 50 ml of the same solvent). Usual workup gave a brown oil and no additional
product was contained in the triethylamine hydrochloride. Tritura-
tion of the oil at 0° yielded 10.1 g (57.8%) of 147 as a colorless
crystalline solid, mp 101-2° (methanol); νCHCl₃ max 3 7.60, 8.09, 8.47,
8.80, and 9.00 μ (-SO₂⁻); 1CDCl₃ 8.10-8.49 (multiplet, 4H, -CH₂-
of pyrrolidino group), 6.95-7.81 (complex pattern, 8H, -(CH₂)N-
and -CH₂-CH₂-), 4.95-5.93 [broad triplet (5.17, J=7.0 Hz) super-
imposed on the low field portion of an AB quartet, J=15.0 Hz, 3H,
a-sulfonyl protons], and 2.58-2.83 (complex pattern, 4H, aromatic
ring protons).

Anal. Calcd. for C₁₅H₁₉NO₂S: C, 64.95; H, 6.90; N, 5.05.
Found: C, 64.63; H, 7.01; N, 4.65.

N-Oxide degradation of 147 and equilibration of the resulting
mixture (148 and 149).--A stirred solution of 6.0 g (0.022 mole) of
147 in 13 ml of glacial acetic acid and 13 ml of acetic anhydride
was treated at -10° with 5.0 g (0.044 mole) of 30% hydrogen peroxide
solution. The mixture was warmed to room temperature and stirred
at that temperature for 12 hours. A colorless solid was seen to
crystallize from the yellow solution and on neutralization with a
25% solution of sodium hydroxide more of the same material was
precipitated. The solid was filtered and washed with cold methanol
and ether to afford 4.1 g (91.1%) of a mixture of thiete dioxides
This material was recrystallized from methanol for analysis as a mixture, mp 142-55° (prior sintering at ca 130°); \( \nu_{\text{CHCl}_3}^{\text{max}} \) 7.65, 8.42, and 8.80 \( \mu \) (-SO\(_2\)) ; \( \lambda_{\text{EtOH}}^{\text{max}} \) 267 ( 12,860), 224 (11,850), 218 (16,290), 212 (14,810), and 207 \( \mu \) (13,750); \( \gamma_{\text{TMS}}^{\text{CDCl}_3} \) 6.81-8.17 (complex pattern, 4H, -CH\(_2\)-CH\(_2\)-), 5.10-5.60 [complex pattern (5.46 - triplet, \( J=3.0 \) Hz, superimposed on a complex pattern), ca 1.4H, \( \alpha \)-sulfonyl protons (except for the vinyl proton)], 3.57 (singlet, ca 0.6 Hz, vinyl proton), and 2.55-3.25 (complex pattern, 4H, aromatic ring protons).

**Anal.** Calcd. for C\(_{11}\)H\(_{10}\)O\(_2\)S: C, 64.05; H, 4.89; S, 15.55.

Found: C, 64.08; H, 5.00; S, 15.62.

The above material (5.0 g, 0.024 mole) in 100 ml of dry tetrahydrofuran was added dropwise with stirring under nitrogen to 6.50 g (0.10 mole) of powdered potassium hydroxide. The reaction mixture became yellow in color when stirred for 8 hours at room temperature. Water (ca 200 ml) was added and the mixture was extracted with chloroform. Usual workup of the chloroform extract afforded 4.2 g (84.0%) of a light yellow solid, mp 159-61°. Recrystallization of this material from methanol gave a different mixture of thiete sulfones (148 and 149), mp 168-70° (slight dec); \( \nu_{\text{CHCl}_3}^{\text{max}} \) 7.62, 8.45, 8.72, 8.80 and 8.91 \( \mu \) (-SO\(_2\)) ; \( \gamma_{\text{TMS}}^{\text{CDCl}_3} \) 6.70-7.90

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(100) This material in tetrahydrofuran was treated with potassium hydroxide for 20 hours and gave on workup the same mixture of sulfones (by nmr comparison).
(complex pattern, 4H, -CH$_2$-CH$_2$-); 4.98-5.48 [complex pattern (5.40 - triplet, J=3.0 Hz, superimposed on a complex pattern), ca 1.75H, α-sulfonyl protons (except for the vinyl proton)],
3.45 (singlet, ca 0.25H, vinyl proton), and 2.40-3.15 (complex pattern, 4H, aromatic ring protons).

l-H-Naphtho[2,1-b]thiete 2,2-dioxide (135).—A mixture of 2.0 g (9.7 mmoles) of the equilibrated material (148 and 149),

(101) This reaction also is successful when non-equilibrated material is used. The yield is not diminished and the workup is the same.

1.74 g (9.8 mmoles) of N-bromosuccinimide, and a catalytic amount of dibenzoyl peroxide in 100 ml of carbon tetrachloride was refluxed for 3 hours. A reaction was evidenced by the formation of succinimide and by the evolution of hydrogen bromide. The mixture was cooled, filtered, and chloroform was added to the filtrate. The solution was transferred to a separatory funnel and washed successively with water, 10% sodium bisulfite solution, and water and dried over magnesium sulfate. Usual workup gave an oily solid residue which afforded, upon trituration with ether and filtration, 1.1 g (55.6%) of 135, mp 174-6°. Pure 135 was obtained from benzene-petroleum ether, mp 188° (slight decomposition);
\[ \gamma_{\text{max}}^{\text{CHCl}_3} 7.60, 8.34, 8.52, 8.66, \text{ and } 8.90 \mu (-\text{SO}_2-); \lambda_{\text{max}}^{\text{EtOH}} 323 \]

\( (\in 1,200), 315 (620), 308 (800), 290 (2,670), 279 (3,730), 272 (3,470), 263 (\text{sh}) (2,670), \text{ and } 230 \text{ mp (63,300); } \tau_{\text{TMS}}^{\text{DMSO-d}_6} 4.50 \)

(singlet, 2H, a-sulfonyl protons) and 1.82-2.58 (complex pattern, 6H, aromatic ring protons).

**Anal.** Calcd. for \( \text{C}_{11}\text{H}_8\text{O}_2\text{S} \): C, 64.68; H, 3.95; S, 15.70.

Found: C, 64.68; H, 3.98; S, 15.39.

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5,5-Dimethyl-6-dimethylamino-2-thiabicyclo-[2.2.0]hexane 2,2-dioxide (153).—A mixture of 3.0 g (0.029 mole) of thiete 1,1-dioxide, \(^{54}3.9\) g (0.039 mole) of 2-methyl-1-dimethylamino-1-propene, \(^{55}5.5\) and 5 ml of dry benzene was refluxed for 24 hours under a nitrogen atmosphere. Chromatography of the concentrated reaction mixture on neutral alumina afforded, on elution with ether-petroleum ether (1:3), 3.5 g (59.8\%) of 153, mp 102-3°. An analytical sample was prepared by recrystallization from ether-petroleum ether, mp 102-3°; \( \gamma_{\text{max}}^{\text{CCl}_4} 7.50, 8.20, 8.27, 8.45, \text{ and } 8.75 \mu (-\text{SO}_2-); \tau_{\text{TMS}}^{\text{CDCl}_3} 8.80 \) (singlet, 6H, \( \geq \text{C(CH}_2)_2 \)), 7.90 (singlet, 6H, \( \text{CH}_3 \)_2N-), 7.53-7.83 (complex pattern, 1H, \( \text{Me}_2\text{C-CH}_2\text{-} \)), 7.00 (doublet, J=6.0 Hz, 1H, \( \geq \text{N-CH}_2 \leq \)), and 5.58-6.13 (complex pattern, 3H, a-sulfonyl protons).

**Anal.** Calcd. for \( \text{C}_{15}\text{H}_{17}\text{NO}_2\text{S} \): C, 53.17; H, 8.43; S, 15.77.

Found: C, 53.43; H, 8.45; S, 15.76.
A methiodide of \( \text{153} \) was prepared in the usual way in 83.0% yield. Recrystallization from methanol-ether gave an analytical sample, mp 225\(^\circ\) dec (prior darkening at 210\(^\circ\)).

**Anal.** Calcd. for \( \text{C}_{10}\text{H}_{20}\text{INO}_{2}\text{S} \): C, 34.79; H, 5.84; S, 9.29.

Found: C, 34.86; H, 5.86; S, 8.90.

5-Dimethylamino-(\text{154}) and 5-diethylamino-8,8-dimethyl-7-thiabicyclo[4.2.0]oct-3-ene 7,7-dioxide (\text{155}).—A mixture of 4.0 g (0.041 mole) of 1-dimethylamino-1,3-butadiene\(^52\) and 5.0 g (0.038 mole) of 2,2-dimethylthiete 1,1-dioxide\(^55\) in 10 ml of dry benzene was left at room temperature under nitrogen for one week and then refluxed for 2 hours. The black solution was concentrated \textit{in vacuo} and the residue was chromatographed on neutral alumina. Elution of the column with petroleum ether and a mixture of same with ether (9:1) gave an oily solid. Recrystallization of this material from ether-petroleum ether afforded 1.7 g (19.5%) of \text{154}, mp 45-8\(^\circ\).

An analytical sample was prepared through the hydrochloride salt, mp 215\(^\circ\) dec (from methanol-ether) and recrystallization of the regenerated \text{154} from ether-petroleum ether, mp 59\(^\circ\); \( \nu_{\text{max}}^{\text{Cl}} \) 3.40 and 3.58 (C-H attached to carbon and nitrogen, respectively), 7.62, 8.52, 8.67, and 8.99 \( \mu \) (\text{-SO}_2\text{-}); \( \gamma_{\text{TMS}}^{\text{CDCl}_3} \) 8.35 and 8.60 (singlets, 3H each, \( \sim \)C(\text{CH}_3)_2), 7.72 (singlet superimposed on a multiplet at
7.83, 9H, \(-N(CH_3)_2\) and \(-C=C-CH_2-CH_\beta\), 6.14-6.35 (multiplet, 1H, Me_2N-CH_\beta\), 5.40-5.75 (multiplet, 1H, \(\alpha\)-sulfonyl bridgehead proton), and 4.12 (broad singlet, 2H, vinyl protons).

**Anal. Calcd. for C_{11}H_{19}NO_2S:** C, 57.61; H, 8.35; N, 6.10; S, 13.98. **Found:** C, 57.62; H, 8.42; N, 5.99; S, 13.64.

The hydrochloride of 154 had the following nmr spectrum:

- 8.32 and 8.57 (singlets, 3H each, \(\geq C(CH_3)_2\)), 7.25-7.90 (multiplet, 3H, \(\geq C-CH_2-CH_\beta\)), 7.10 (singlet, 5H, \(-N(CH_3)_2\)),
- 5.55 (multiplet, 1H, \(\alpha\)-sulfonyl bridgehead proton),
- 4.95 (multiplet, 1H, \(\geq N-CH\)),
- 4.08 (multiplet, 1H, \(-H_2C=CH-\)), and
- 3.62 (multiplet, 1H, \(-CH=CH-CH=CH-\)).

A methiodide salt of 154 was prepared, mp 211° dec (methanol-water).

**Anal. Calcd. for C_{12}H_{22}INO_2S:** C, 38.82; H, 5.97; S, 8.64. **Found:** C, 38.62; H, 5.92; S, 8.42.

The synthesis of 155 was achieved by refluxing a mixture of 0.94 g (7.6 mmoles) of 1-diethylamino-1,3-butadiene\(^{33b}\) and 1.0 g (7.6 mmoles) of 2,2-dimethylthietene 1,1-dioxide in 5 ml of dry xylene under nitrogen for 12 hours. The dark reaction mixture was concentrated and the residue chromatographed on Florisil. Elution of the column with varying percentages of petroleum ether-ether gave a yellow crystalline solid. Recrystallization of this material from petroleum ether yielded 0.4 g (19.5%) of 155, mp 64° (approximately one-fourth of the starting weight of 2,2-dimethylthietene 1,1-dioxide
was recovered); $\nu_{\text{max}}^{\text{CCl}_4}$ 7.62, 8.59, 8.69, and 9.00 μ (−SO₂−).

**Anal. Calcd. for C₁₃H₂₃N₂O₂S: C, 60.66; H, 9.01; N, 5.44; S, 12.46. Found: C, 60.39; H, 8.88; N, 5.40; S, 12.36.**

**5-Dimethylamino-7-thiabicyclo[4.2.0]oct-3-ene 7,7-dioxide (156).**— A solution of 6.35 g (0.061 mole) of thiete 1,1-dioxide, 6.0 g (0.062 mole) of 1-dimethylamino-1,3-butadiene, and 25 ml of dry benzene was stirred at room temperature under nitrogen for 6 days. The black reaction mixture was concentrated in vacuo to give a black oily liquid which was chromatographed on neutral alumina. Elution of the column with petroleum ether, mixtures of the same and ether, and pure ether gave 8.8 g (71.5%) of 156 as a yellow oil. Attempts at purification of 156 through its hydrochloride salt gave a colorless oil with no change in any of its spectral properties; $\nu_{\text{max}}^{\text{CCl}_4}$ 3.40 and 3.60 (C-H attached to carbon and nitrogen, respectively), 7.55, 8.34, 8.50, and 8.85 μ (−SO₂−); $\tau_{\text{TMS}}^{\text{CCl}_4}$ 7.17-8.10 (multiplet with two singlets superimposed at 7.66 and 7.80, 9H, −N(CH₃)₂ and −C=O−CH₂−CH−), 6.26-6.67 and 5.38-6.00 (two complex patterns, 2H each, =N−CH− and the α-sulfonyl protons), and 4.14 (broad singlet, 2H, vinyl protons).

A methiodide of 156 was obtained in 78.0% yield in the usual manner, mp 191° dec (methanol-water).
Anal. Calcd. for $\text{C}_{10}\text{H}_{10}\text{INO}_2$: C, 34.99; H, 5.29; N, 4.08.

Found: C, 34.92; H, 5.35; N, 3.93.