The Reaction of Sulfenes with 1,3-Bis(dimethylamino)-1-alkenes. Mechanistic Dichotomy as a Function of Substitution[1,2]

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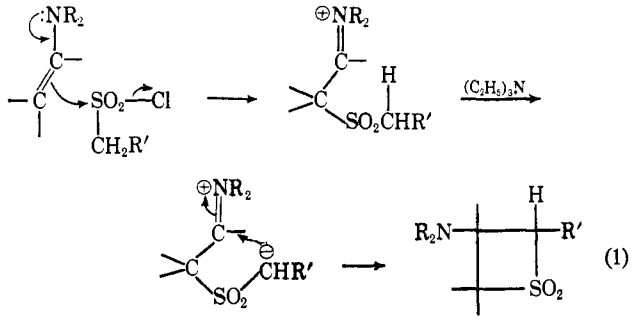
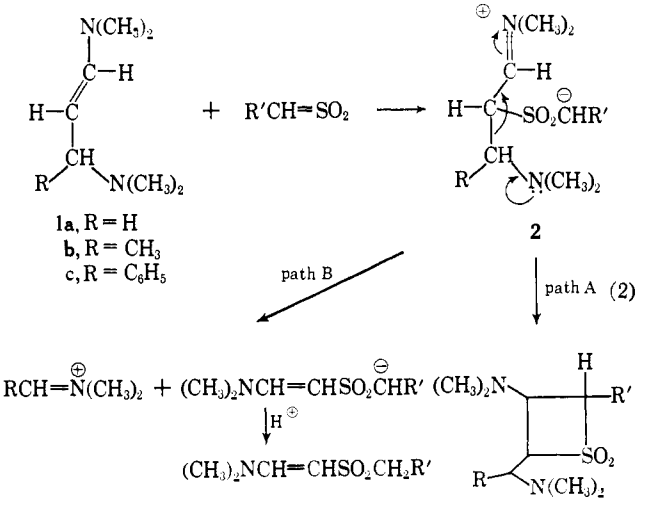
Abstract: The reactions of N,N,N′,N′-tetramethylpropene-1,3-diamine (**1a**), N,N,N′,N′-tetramethyl-1-butene-1,3-diamine (**1b**), and 1,3-bis(dimethylamino)-3-phenyl-1-propene (**1c**) with sulfene and phenylsulfene, generated *in situ* by the action of triethylamine on the appropriate sulfonyl chloride, occurred readily at −10 to −15° in tetrahydrofuran solution to give a wide variety of products. The mechanisms of formation of a large number of these substances were investigated and are discussed. An analysis of these results has provided strong evidence for the nonconcerted addition of sulfenes to enamines, at least in the case of phenylsulfene. The probable causative factors responsible for certain of the deep-seated rearrangements which were encountered are presented.

The formation of sulfenes ($R_2C{=}SO_2$) in the alcoholysis of alkanesulfonyl chlorides in various basic media has been ascertained on the basis of the exclusive formation of the monodeuterated sulfonate esters (no di- or trideuteration observed) in the presence of OD-labeled alcohols under such reaction conditions.[4,5] When an alkanesulfonyl chloride is treated with triethylamine in the presence of electron-rich olefins, such as enamines, a considerable propensity for cycloaddition exists and thietane 1,1-dioxides generally result.[6,7] The intermediacy of sulfenes has also been invoked in such processes because the most plausible alternative mechanism for the formation of such four-membered heterocycles (eq 1) has been ruled out by the data of several groups of workers.[6d,8,9] Although the conclusion that sulfene formation does intervene in thietane dioxide formation rests on this indirect evidence, it does not suffer from lack of analogy.



(1)

In view of recent general interest in the concerted or nonconcerted nature of cycloaddition reactions, we have attempted to establish the timing of the sulfene–enamine cyclization process. At the outset, the possibility was considered that heterocyclic ring formation does proceed by a two-step addition mechanism. If such is the case, then replacement of a simple enamine by a 1,3-bis(dimethylamino)-1-alkene such as **1** would lead, upon interaction with a sulfene, to a zwitterionic intermediate such as **2**. This bifunctional intermediate (**2**) might be expected to undergo partitioning between two possible subsequent reactions, one (path A) leading to thietane dioxide formation, and a second (path B) leading to cleavage (eq 2). Path B would be expected



(2)

to be favored substantially in those instances where R and R′ would assist in the stabilization of the respective fragments. The present report presents the results of such a study. It will be seen that the considerations outlined above are complicated by additional mechanistic possibilities.

(1) Unsaturated Heterocyclic Systems. XXVIII. For the previous paper, see L. A. Paquette and R. W. Begland, *J. Org. Chem.*, **32**, in press.

(2) Supported in part by a grant from the National Science Foundation, GP-5977.

(3) Alfred P. Sloan Foundation Research Fellow.

(4) J. F. King and T. Durst, *J. Am. Chem. Soc.*, **87**, 5684 (1965).

(5) W. E. Truce and R. W. Campbell, *ibid.*, **88**, 3599 (1966).

(6) Enamines: (a) G. Stork and I. J. Borowitz, *ibid.*, **84**, 313 (1962); (b) G. Opitz and H. Adolph, *Angew. Chem.*, **74**, 77 (1962); (c) W. E. Truce, J. R. Norell, J. E. Richman, and J. P. Walsh, *Tetrahedron Letters*, 1677 (1963); (d) G. Opitz and K. Fisher, *Z. Naturforsch.*, **18b**, 775 (1963); (e) L. A. Paquette, *J. Org. Chem.*, **29**, 2851, 2854 (1964); (f) D. C. Dittmer and F. A. Davis, *ibid.*, **29**, 3131 (1964); (g) L. A. Paquette, *ibid.*, 30, 629 (1965); (h) G. Opitz and K. Rieth, *Tetrahedron Letters*, 3977 (1965); (i) G. Opitz, H. Schempp, and H. Adolph, *Ann.*, **684**, 92 (1965); (j) L. A. Paquette and M. Rosen, *Tetrahedron Letters*, 311 (1966); (k) J. N. Wells and F. S. Abbott, *J. Med. Chem.*, **9**, 489 (1966); (l) J. J. Looker, *J. Org. Chem.*, **31**, 2973 (1966); (m) G. Opitz and D. Bücher, *Tetrahedron Letters*, 5263 (1966).

(7) Ketene acetals and aminals: (a) W. E. Truce, J. J. Breiter, D. J. Abraham, and J. R. Norell, *J. Am. Chem. Soc.*, **84**, 3030 (1962); (b) W. E. Truce and J. R. Norell, *ibid.*, **85**, 3231 (1963); (c) R. H. Hasek, P. G. Gott, R. H. Meen, and J. C. Martin, *J. Org. Chem.*, **28**, 2496 (1963); (d) W. E. Truce and P. N. Son, *ibid.*, 30, 71 (1965); (e) R. H. Hasek, R. H. Meen, and J. C. Martin, *ibid.*, 30, 1495 (1965); (f) G. Opitz and H. Schempp, *Ann.*, **684**, 103 (1965); (g) G. Opitz, K. Rieth, and G. Walz, *Tetrahedron Letters*, 5269 (1966).

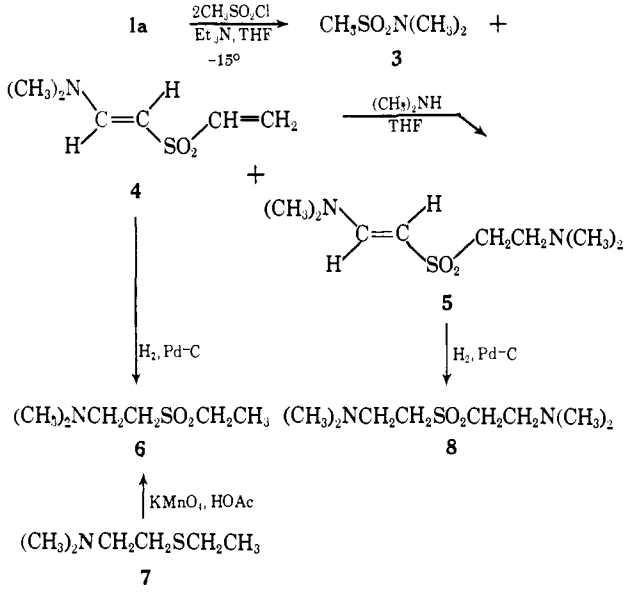
(8) R. Fusco, S. Rossi, and S. Maiorana, *Chim. Ind.* (Milan), **44**, 873 (1962).

(9) I. J. Borowitz, *J. Am. Chem. Soc.*, **86**, 1146 (1964).

Results

N,N,N′,N′-Tetramethylpropene-1,3-diamine (1a). The addition of 2 equiv[10] of methanesulfonyl chloride to a cold (−15°) tetrahydrofuran solution of **1a** gave a dark viscous oil which, when chromatographed on Florisil, afforded three characterizable products (**3**–**5**) as outlined in Chart I. The spectral data (infared and nmr) and elemental analyses of these materials were consistent with the assignments and are summarized in the Experimental Section. Solid confirmation of structure **4** was obtained by hydrogenation to 1-dimethylamino-3-thiapentane 3,3-dioxide (**6**), which was prepared in unequivocal fashion by permanganate oxidation of 1-dimethylamino-3-thiapentane (**7**). Michael addition of dimethylamine to **4** readily yielded **5**, thus interrelating these two compounds. In addition, **5** was reduced to **8** which proved identical in all respects with an authentic sample.

Chart I



A similar reaction of **1a** with phenylmethanesulfonyl chloride and triethylamine led to a different spectrum of products as shown in Chart II. The structure of cycloadduct **10** was readily derived from its nmr spectrum (see Experimental Section). Structure **12** has been assigned on the basis of spectral characteristics and by subsequent hydrogenation of this unsaturated sulfone to the known 2-(benzylsulfonyl)-N,N-dimethylethylamine (**13**). Interestingly, the yields of the various products were observed to vary dramatically with the relative amount of added phenylmethanesulfonyl chloride. Two such experiments are documented in Table I. The increased amount of *trans*-stilbene formed when larger quantities of phenylsulfene were generated is easily rationalized on the basis of the known dimerization of this reactive intermediate to *trans*-stilbene with accompanying expulsion of sulfur dioxide.[11] More important, however, is the surprising fact that the greater quantity of phenylsulfene effectively destroys the initially formed thietane dioxide **10** in a process which does not produce a characterizable product other than a small increase in the yield of **11**. This observation has been more conclusively verified by treating **10** independently with the phenylsulfene reagent under the identical reaction conditions; chromatographic workup of the resulting dark viscous gum afforded only **9** and a small quantity of **11**.[12]

Chart II

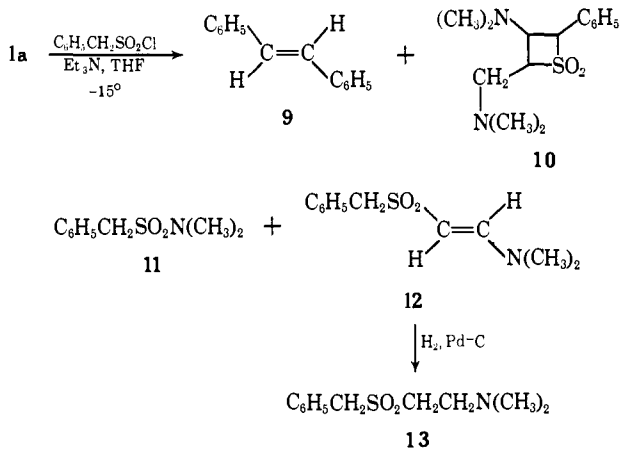
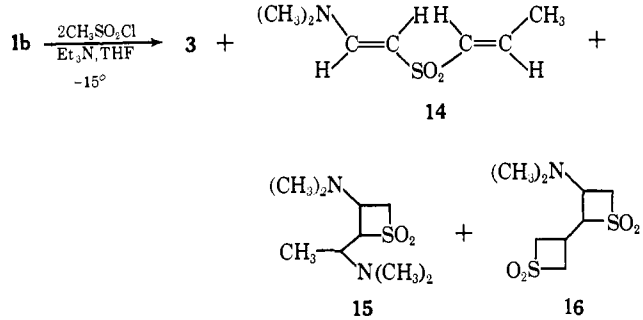


Table I. Variation in Product Yields Observed in the Addition of Phenylmethanesulfonyl Chloride and Triethylamine to **1a**

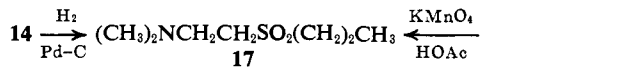
Rel molar proportions, $C_6H_5CH_2SO_2$-Cl-Et_3N/**1a**	% yield			
	9	**10**	**11**	**12**
1.0	Trace	30.7	8.5	4.5
2.0	30.3	Trace	16.8	1.8

N,N,N′,N′-Tetramethyl-1-butene-1,3-diamine (1b). Reaction of **1b** with 2 equiv each of methanesulfonyl chloride and triethylamine in cold (−15°) tetrahydrofuran led to a further variety of products (Chart III).

Chart III



The structure and stereochemistry of **14** were confirmed by a combination of nmr spectroscopy and catalytic hydrogenation to **17**, which was prepared unequivocally in the manner outlined in eq 3. The nmr spectrum of



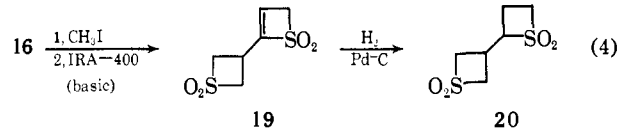
(3)

(10) In the examples considered, maximum yields were generally observed (with **1a** and **1b**) when 2 equiv of the sulfene was utilized. The probable reasons for this phenomenon will be explored in the Discussion.

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

(12) It has, however, been established that **10** does react with methanesulfonyl chloride–triethylamine to produce characterizable products (see Discussion).

15 was that of a substituted 3-dimethylaminothietane dioxide, and not of an open-chain compound; the presence of the 1-dimethylaminoethyl substituent was further dictated by this spectrum (see Experimental Section). The structure of the highly crystalline disulfone **16** was likewise derived from its nmr spectrum which indicated the presence of a *lone* upfield, multiply coupled, proton.[13] Some measure of further support for this assignment came from a partial degradation of **16** (eq 4). Thus, Hofmann elimination of its methiodide gave rise to the α,β-unsaturated sulfone **19** which still displayed one upfield hydrogen but, in addition, incorporated the elements of one vinyl proton into its nmr spectrum. Hydrogenation of **19** afforded **20**; the presence in the spectrum of **20** of three upfield protons was consistent with the 2,3′-bithietane tetroxide structure.



(4)

19 **20**

Attention is called to the fact that the yields of **3**, **14**, **15**, and **16** were also very dependent upon the quantity of sulfene utilized and upon the duration of reaction (Table II). Of particular significance in this

Table II. Product Composition in the Condensation of **1b** with Varying Quantities of Methanesulfonyl Chloride and Triethylamine

Rel molar proportions, CH_3SO_2Cl–Et_3N/**1b**	% yield			
	3	**14**	**15**	**16**
1.0	35.9	...[a]	...[a]	8.8
2.0	33.0	4.5	2.6	24.3
3.0	34.7	5.5	Trace	29.1
2.0[b]	...[c]	...[c]	15.4	13.3

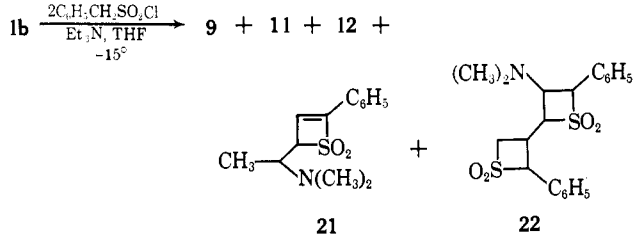
[a] Not observed. [b] In this run, the work-up was commenced 1 hr after completion of the sulfonyl chloride addition instead of after the customary reaction period of 12 hr. [c] Not examined.

instance is the fact that appreciable quantities of the monocyclic thietane dioxide **15** can be isolated after short reaction periods, but that prolonged exposure of this heterocyclic system to the reaction conditions results in its destruction. Indeed, when **15** was independently resubmitted to the original reaction conditions, **3** and **14** were obtained.

When a cold (−15°) tetrahydrofuran solution of **1b** and triethylamine was treated with 2 equiv of phenylmethanesulfonyl chloride, there could be isolated upon chromatography not only the anticipated *trans*-stilbene (**9**) and N,N-dimethylphenylmethanesulfonamide (**11**), but also **12**, the thiete sulfone **21**, and the bithietane tetroxide **22** (Chart IV). In agreement with structure **21**, this cycloaddition product exhibited strong ultraviolet absorption in ethanol at 256 mμ (ϵ 17,800) and an appropriate nmr spectrum. Compound **22** was endowed with spectral parameters completely

(13) The nmr spectra of the various bithietane tetroxides described in this paper were of inferior quality because of the very limited solubility of these substances in organic solvents.

Chart IV

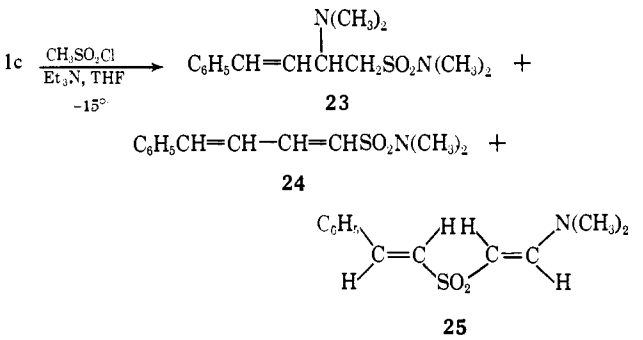


21 **22**

analogous to those displayed by **16**; therefore, its structure was considered secured.

1,3-Bis(dimethylamino)-3-phenyl-1-propene (1c).[14] The preparation of **1c** was achieved by treating an ethereal solution of cinnamaldehyde with dimethylamine and powdered potassium carbonate under a nitrogen atmosphere at ambient temperature.[15] Sulfene addition to **1c** in cold tetrahydrofuran yielded upon direct crystallization a 51% yield of **23** (Chart V).

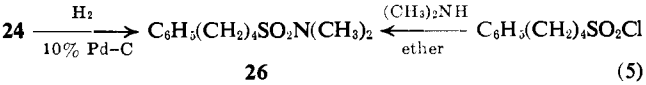
Chart V



25

Careful chromatography of the noncrystalline residue on neutral alumina permitted isolation of two additional crystalline solids, **24** (2–3%) and **25** (3–4%). Initially, the molecular frameworks of **23** and **24** were shown to be similar. Chromatography of **23** on neutral alumina led to the formation of **24**. Indeed, it was found that **24** was an artifact of the sulfene reaction and arose because small quantities of **23** remained in the noncrystalline residue. The sensitivity of **23** to β elimination is not unexpected.

That the major component (**23**) incorporated sulfonamide and styryl groups in its gross structure was evident from its various spectra (see Experimental Section). The presence of the 1-phenylbutadienyl function in **24** was derived from its ultraviolet spectrum [λ_{max}^{EtOH} 301 mμ (ϵ 38,700)], a characteristic of this chromophoric system.[16] The structures of both **23** and **24** were firmly ascertained by catalytic hydrogenation of **24** to N,N-dimethyl-4-phenyl-1-butanesulfonamide (**26**), which was synthesized in unequivocal fashion from the known 4-phenyl-1-butanesulfonyl chloride and dimethylamine (eq 5).



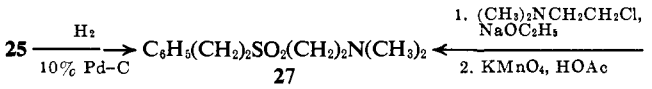
26 (5)

(14) A portion of these results has been previously communicated: L. A. Paquette and M. Rosen, *Tetrahedron Letters*, 703 (1967).

(15) This procedure represents a modification of the preparative details reported for the dipiperidino analog: C. Mannich, K. Handke, and K. Roth, *Chem. Ber.*, **69**, 2112 (1936).

(16) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, Spectrum No. 129.

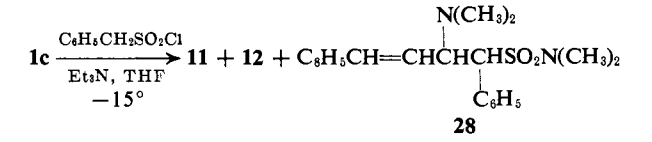
Compound **25** was defined as a styryl enamino sulfone on the basis of its spectral characteristics and by virtue of its catalytic hydrogenation to **27**, which was independently synthesized by the condensation of β-phenethyl mercaptan with β-dimethylaminoethyl chloride and subsequent permanganate oxidation of the resulting sulfide (eq 6).



(6)

In like fashion, the interaction of phenylmethanesulfonyl chloride, triethylamine, and **1c** under the same conditions led principally to the formation of **28** (48%), in addition to lesser quantities of **11** (22%) and **12** (3%) (Chart VI). The structure of **28** was ascertained by

Chart VI



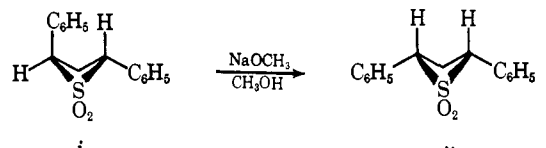
elemental and spectral analysis and by additional chemical transformations similar to those employed in the case of **23** (see Experimental Section).

Discussion

The data described above, with its plethora of products, would tend to suggest that the reaction of sulfenes with 1,3-bis(dimethylamino)-1-alkenes such as **1** was dictated predominantly by the nature of the additional substituent at C_3. Although this conclusion is endowed with some degree of verity, complete analysis of the results will demonstrate that a number of additional important factors play significant roles in affecting the outcome of these sulfene additions.

An examination of Charts I and III indicates that the addition of sulfene to **1a** and **1b** leads to the formation of two common products, namely the sulfonamide **3** and the vinyl enamino sulfones **4** and **14**. The isolation of **3** bears testimony to the fact that dimethylamine is eliminated from **1a** and **1b** at some stage in the reaction. The proposed course of these transformations is outlined in Chart VII.[17] The sequence of events is triggered in both cases by the anticipated[6] formation of a cycloadduct such as **29** which serves as the key intermediate. The quasi-equatorial orientation of the two substituents in **29** and **30** is to be expected irrespective of whether four-membered ring formation is concerted or nonconcerted. Reversible protonation of **29** and **30** [which differ only in the configuration of the potentially asymmetric (when R = CH_3) side-chain carbon atom] at the relatively unhindered tertiary nitrogen atom[22,23] (see Chart VII) serves to generate an electron-deficient center which can be ejected (as dimethylamine when $E^+ = H^+$) by a migration of electrons from the 3-dimethylamino substituent with synchronous rupture of the thietane dioxide ring, as illustrated. The prime driving force in this process is perhaps the relief of strain involved in rupture of the four-membered ring; however, another very important consideration is found in the fact that the geometrical relationship between the electron pair of the 3-dimethylamino group and the departing ammonium ion is such that assisted ionization in the fragmentation reaction may be expected.[24] Because synchronous fragmentation reactions are manifested only when certain geometrical relationships between the nitrogen electron pair and the departing group are met,[24] only ions **31** and **32** have been considered. Inspection of these ions suggests that **32** should possess higher ground-state energy than **31**; therefore, when R = H, **31** may be expected to predominate. On the other hand, when R = CH_3, the presence of both possible configurational isomers precludes this possibility and both **31** and **32** must be present. In fact, steric considerations in the case of **32** may favor the preponderance of an alternative rotamer. In this regard it is interesting, and perhaps significant, to note that with **1a** no such thietane dioxide can be isolated even under conditions of rapid work-up, whereas in the case of **1b** such a product (**15**) is obtained readily. This result is conceivably a reflection of the inability of **32** to achieve readily the geometry demanded for the synchronous fragmentation (*i.e.*, the stereoisomer illustrated; however, see below).

(17) Throughout the Discussion, the thietane 1,1-dioxides are depicted as pronouncedly puckered four-membered rings. Recent spectroscopic investigations of thietane[18a] and several of its derivatives[18b,c] have clearly shown that this heterocyclic system is puckered (angle between the planes, *ca.* 30°), in contrast to the well-recognized planar configuration of oxetane[18d] in its lower vibrational states.[19] 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. 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 which the molecule can best alleviate by maintaining the puckered conformation.[20] The strong conformational preference for a puckered thietane 1,1-dioxide ring has been indicated by the fact that *cis*-2,4-diphenylthietane dioxide (ii) is more stable than the *trans* isomer (i).[21]



i ii

(18) (a) D. O. Harris, H. W. Harrington, A. C. Luntz, and W. D. Gwinn, *J. Chem. Phys.*, **44**, 3467 (1966); (b) W. D. Kelley, T. R. Lusebrink, and C. H. Sederholm, *ibid.*, **44**, 782 (1966); (c) S. Allenmark, *Arkiv Kemi*, **26**, 73 (1966); (d) S. I. Chan, J. Zinn, J. Fernandez, and W. D. Gwinn, *J. Chem. Phys.*, **33**, 1643 (1960).

(19) Unfortunately, a recent comprehensive review of thietane chemistry is badly outdated with respect to the stereochemistry of the thietanes: Y. Etienne, R. Soulas, and H. Lumbroso in "The Chemistry of Heterocyclic Compounds," A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, Chapter 5.

(20) Compare cyclobutane: J. B. Lambert and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 3884, 3891 (1965); K. B. Wiberg and G. M. Lampman, *ibid.*, **88**, 4429 (1966).

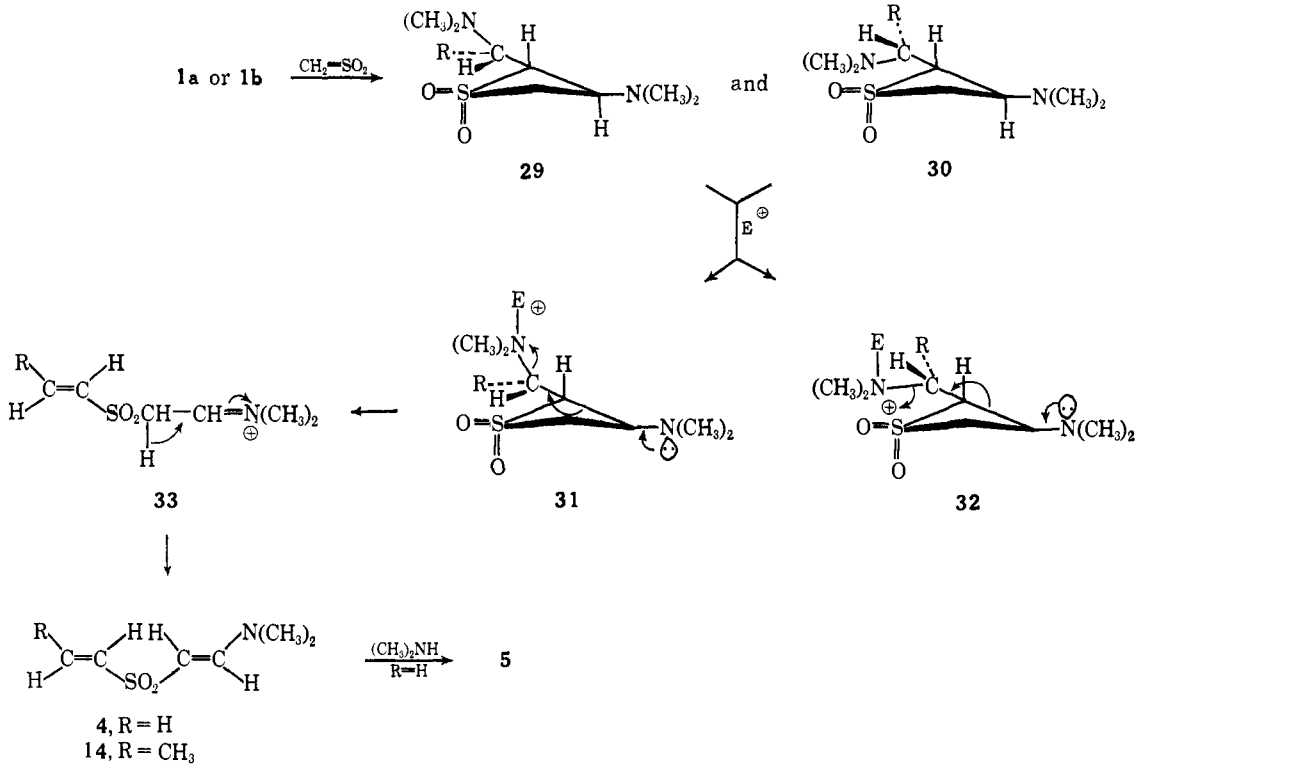
(21) R. M. Dodson and G. Klose, *Chem. Ind.* (London), 450 (1963).

(22) An ample source of protons is generated in the medium by elimination of the elements of hydrogen chloride from the methanesulfonyl chloride. It is understood, of course, that under the reaction conditions which were utilized, a significant quantity of liberated acid is precipitated from solution as the triethylamine salt.

(23) In actual fact, any available electrophile could accomplish the same objective. In addition to the proton, the remaining potential electrophiles are sulfene and methanesulfonyl chloride. If either of these species are utilized, **3** results directly. However, in order to account for the formation of **5** (see text), the involvement of protons in this step must occur to a significant extent.

(24) (a) C. A. Grob, *Experientia*, **13**, 126 (1957); (b) C. A. Grob in "Theoretical Organic Chemistry, Papers Presented to the Kekule Symposium," Buttersworth and Co. (Publishers) Ltd., London, 1959, pp 114–126; (c) C. A. Grob, *Bull. Soc. Chim. France*, 1360 (1960); (d) C. A. Grob, *Gazz. Chim. Ital.*, **92**, 902 (1962); (e) R. D'Arcy, C. A. Grob, T. Kaffenberger, and V. Krasnobajew, *Helv. Chim. Acta*, **49**, 185 (1966); (f) C. A. Grob, R. M. Hoegerle, and M. Ohta, *ibid.*, **45**, 1823 (1962); (g) H. O. House and W. M. Bryant, III, *J. Org. Chem.*, **31**, 3482 (1966).

Chart VII

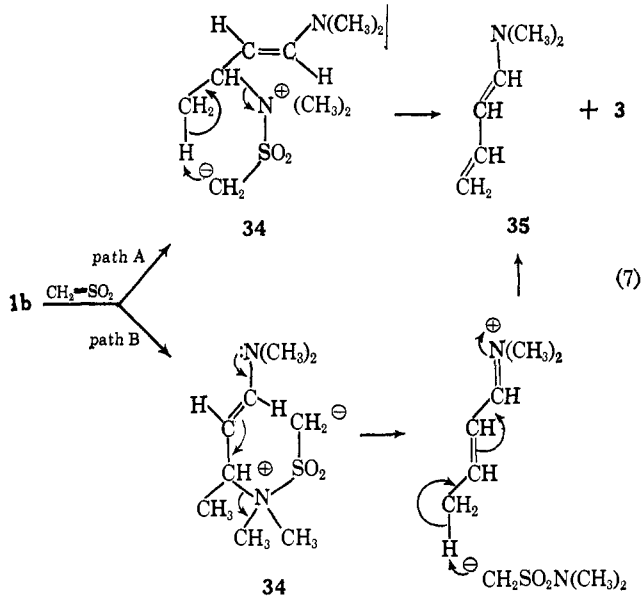


The *trans* configuration about the vinylsulfonyl group in **14** most probably results in the elimination step, whereas the *trans* nature of the enamino sulfone group is established later in the mechanistic sequence.[25]

Evidence confirming the entire mechanistic picture was obtained from the observation that when the previously isolated **15** was resubmitted to the original reaction conditions (for 12 hr), **3** and **14** were obtained. Apparently, therefore, reaction *via* ion **32** is also energetically feasible.

Compound **5** most probably arises by Michael addition to **4** of the elements of dimethylamine shortly after its elimination and prior to the time when it is converted by excess sulfene to **3**, perhaps by virtue of a solvent cage effect. Traces of a similar material from the reaction of **1b** with sulfene have been observed (but not fully characterized) after extensive and careful chromatography. The lower yield of such a Michael product in this case might be expected due to the added steric interference produced by the additional methyl group.[26]

That bithietane tetroxide **16** arises by virtue of initial elimination of dimethylamine from **1b** to give 1-dimethylaminobutadiene (**35**) followed by a double addition of sulfene has been shown to be feasible by independently submitting **35** to the same reaction conditions (see Experimental Section).[27] The formation of **35** from **1b** can be derived mechanistically by invoking initial attack of the sulfene at the nonenamine tertiary nitrogen atom to give zwitterion **34**. Passage of **34** into **35** may occur either *via* an intramolecular six-centered transition state with concomitant loss of sulfonamide **3** (path A), or by a process which involves preliminary expulsion of the anion of N,N-dimethylmethanesulfonamide (**3**) by the enamine system followed by neutralization of charge. Because we have not yet differentiated between these two mechanistic possibilities, further discussion at this time would be pointless.

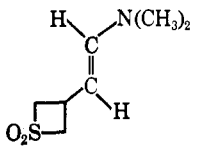


A mechanistic rationalization of the double addition of sulfene to **35** necessitates that the initial sulfene molecule attacks the terminus of the diene system to produce intermediate **36** rather than the alternative possibility **37**. This requirement is demanded by

(25) The isolation of *trans*-enamino sulfones conveys no mechanistic significance because of the facility with which *cis*-enamino sulfones are converted to their more stable geometric counterparts at room temperature: W. E. Truce and D. G. Brady, *J. Org. Chem.*, **31**, 3543 (1966).

(26) The possibility that vinyl sulfones such as **4** could have resulted by retro-Michael degradation of an initially formed β-dimethylaminoethyl precursor such as **5** was considered and discarded when it was found that **6** could be recovered quantitatively after treatment with excess sulfene at room temperature.

(27) While this work was in progress, G. Opitz and F. Schweinsberg [*Angew. Chem.*, 77, 811 (1965)] reported on their study of the addition of sulfene to 1-dialkylamino-1,3-butadienes. Their independent work corroborates our observations.



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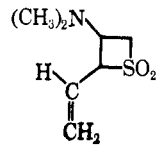
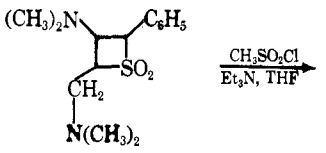


37

the fact that sulfenes undergo cycloaddition only in the presence of an electron-rich olefinic center[6,7] such as is present in **36**, but not in **37**. The good yield of bithietane tetroxide **16** that is obtained from **35** (50%) suggests that the δ-carbon of **35**, *i.e.*, the center most remote from the nitrogen atom, is endowed with appreciable nucleophilicity.[28,29]

When the results of the addition of phenylsulfene to **1a** and **1b** are examined, several questions arise as a result of the observations described above. First, the factors which have contributed in the previous instances to the formation of vinyl enamino sulfones (*i.e.*, **4** and **14**) are absent in the present examples. Rather, 2-dimethylamino-1-phenylmethanesulfonylethylene (**12**) is isolated. One can entertain at least two reasons why phenylsulfene addition prefers to lead to **12**, while the not too dissimilar sulfene chooses vinyl enamino sulfone formation. A first consideration suggests that the cleavage of an initially formed phenyl-substituted thietane dioxide does not parallel the mechanism outlined earlier. Although such a thietane dioxide (**10**) has been obtained in one instance, it has been found not to give a characterizable product upon further reaction with phenylsulfene. In contrast, however, the action of methanesulfonyl chloride and triethylamine on **10** afforded vinyl enamino sulfone **38**[32] in low yield (eq 8). Thus, it does not seem likely that **12** results from a four-membered ring precursor. The second, and much more probable, explanation of



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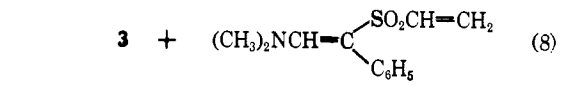

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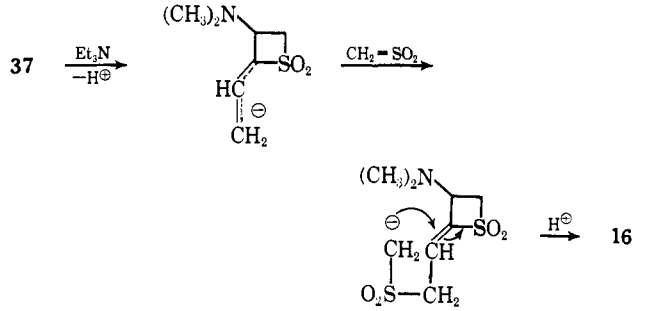
(8)

the genesis of **12** lies in the realization that *the addition of phenylsulfene to* **1a** *and* **1b** (*and also* **1c**; *see below*) *is nonconcerted.* More specifically, stepwise reaction of phenylsulfene with either substrate must lead to **2**, a zwitterion in which the presence of a phenyl group at R′ would effectively stabilize the resulting α-sulfonyl carbanion to an extent sufficient to permit the realization of path B (see eq 2), that is, cleavage of this zwitterion ultimately to afford **12**. It is quite clear that **12** should result irrespective of the nature of the substitution at R (in **2**), and the results bear out this conclusion (see Charts II, IV, and VI). In the foregoing examples, therefore, the increased lifetime of **2** can be diagnosed by virtue of the fact that a mechanistic alternative other than mere cycloaddition is available to the system; this single additional parameter strongly suggests the nonconcertedness of sulfene–enamine interactions, at least in those cases where phenylsulfene is involved.[33,34]

A second point of difference resides in the isolation of **10** in the case of **1a**, but no analogous product with **1b**, a result completely opposite to the observations recorded earlier with sulfene. We have concluded that this apparent discrepancy is attributable to experimental difficulties which developed during the addition of phenylsulfene to **1b** (see Experimental Section), and therefore no significance can be placed on this fact.

A third factor relates to the source of N,N-dimethylphenylmethanesulfonamide (**11**). This substance finds its origin, at least in the case of **1b**, predominantly in the protonation of the carbanionic moiety formed in the

(28) The following mechanism, although without precedent, was considered a reasonable pathway for converting the hypothetical **37** to



16, and therefore evidence bearing on this question was sought. Phenyl propenyl sulfone ($CH_3CH{=}CHSO_2C_6H_5$)[30] was utilized as a model substrate; after treatment with methanesulfonyl chloride and excess triethylamine, this substance could be recovered in high yield as the only isolatable product.

(29) Examination of the literature reveals that 1-dialkylaminobutadienes generally are prone to undergo 1,4 addition to reactive olefins.[31a-c] However, the lone example of the condensation of such a dienamine with ketene suggests that 1,2 addition to the α- and β-carbon atoms predominated;[31d] this latter mode of behavior lies in direct contrast to the manner in which 1-alkoxybutadienes react with ketenes to give cyclobutanones through linkage at the γ- and δ-carbons,[31e] and remains to be explained.

(30) W. E. Parham, F. D. Blake, and D. R. Theissen, *J. Org. Chem.*, 27, 2415 (1962).

(31) (a) S. Hünig and H. Kahanek, *Chem. Ber.*, 90, 238 (1957); (b) J. Ciabattoni and G. A. Berchtold, *J. Am. Chem. Soc.*, 87, 1404 (1965); (c) H. Prinzbach, U. Fischer, and R. Cruse, *Angew. Chem. Intern. Ed. Engl.*, 5, 251 (1966); (d) R. H. Hasek, P. G. Gott, and J. C. Martin, *J. Org. Chem.*, 31, 1931 (1966); (e) J. C. Martin, P. G. Gott, V. W. Goodlett, and R. H. Hasek, *ibid.*, 30, 4175 (1965).

(32) The structure of **38** has been confirmed by elemental and spectral analyses and by catalytic hydrogenation (see Experimental Section).

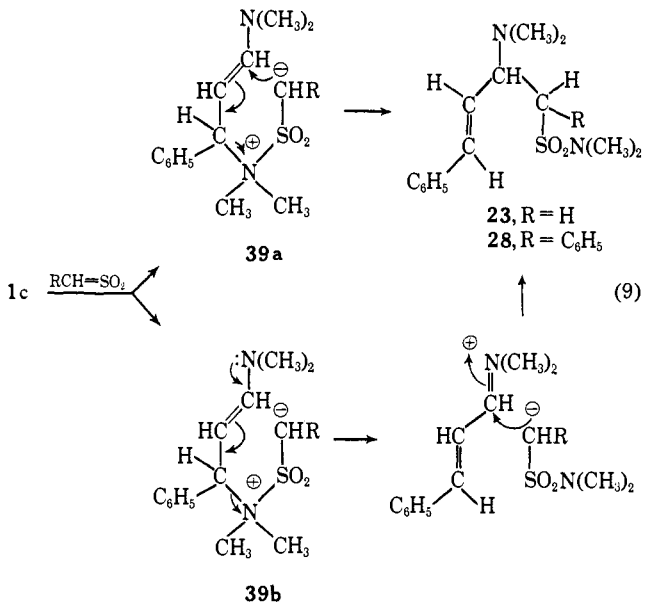
(33) It should be clear that a simple nucleophilic attack by the nucleophilic β-carbon atom of the enamine at the tetravalent sulfur atom of phenylmethanesulfonyl chloride could lead, on the mechanistic level, to **12** without the need of invoking the intermediacy of phenylsulfene or also zwitterions of type **2**. We regard this rationale as untenable for the following reasons: (a) no analogous products were isolated when methanesulfonyl chloride was employed, presumably because the latter substance is converted very rapidly to sulfene under the reaction conditions and no free methanesulfonyl chloride is available for direct condensation (the anticipated product, $CH_3SO_2CH{=}CHN(CH_3)_2$, is stable to the reaction conditions and work-up); (b) the increased acidity of the α-sulfonyl protons in phenylmethanesulfonyl chloride would be expected additionally to favor phenylsulfene formation; (c) an increase in the amount of added phenylmethanesulfonyl chloride does not result in an increase in the yield of **12** (see Table I, for example), as might be expected if phenylsulfene formation was being by-passed in the formation of **12**.

(34) A number of cases have been reported in which acylic sulfones result in certain additions of sulfenes to enamines.[8i,k,1,7d] With but one exception,[7d] these phenomena were interpreted on the basis of initial thietane dioxide formation, followed by a mechanistically unprecedented (at least with triethylamine as base) cleavage of the heterocyclic ring. The rationale was advanced that these observations paralleled the results obtained in the addition of ketenes to enamines.[35] However, in contrast to the unstable 3-aminocyclobutanones, 3-aminothietane dioxides are stable and have proven to be useful synthetic intermediates.[6] As an alternative, we propose that these acylic products may perhaps arise because of the initial formation of a zwitterion *via* a nonconcerted pathway, followed by a prototropic shift to give the observed products.

(35) (a) R. H. Hasek and J. C. Martin, *J. Org. Chem.*, 28, 1468 (1963); (b) G. A. Berchtold, G. R. Harvey, and G. E. Wilson, *ibid.*, 30, 2642 (1965).

fragmentation of an intermediate analogous to **34**.[36] However, there exists a variety of other molecular pathways by which **11** could form in less significant quantity.

As is apparent from Charts V and VI, the addition of sulfene and phenylsulfene to **1c** results in unprecedented rearrangement of the carbon framework. The genesis of **23** and **28** can be derived in a mechanistically plausible fashion by invoking initial attack of the sulfenes predominantly at the benzylic nitrogen atom.[37] The conversion of the resulting dipolar species (**39**) to the rearrangement products can result either by the intramolecular attack of the nucleophilic α-sulfonyl carbanion at the α position of the enamine system with

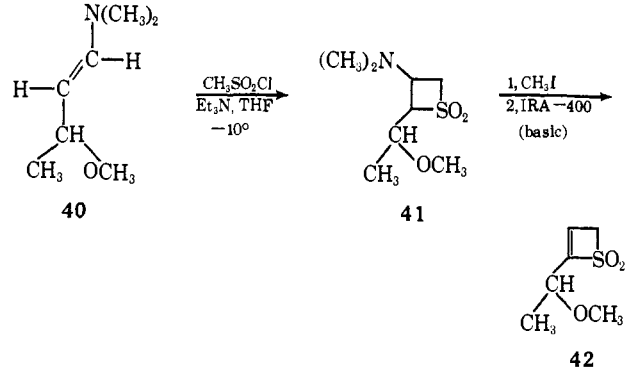


synchronous double-bond migration and cleavage of the bond to positively charged nitrogen (*via* six-centered transition state **39a**) or by a cleavage–recombination process (**39b**; see eq 9).[38] Contributing to the favorable energetics of this rearrangement is the fact that such a double-bond migration leads to a conjugated styrene system.

The formation of **25** can be attributed to a small amount of cycloaddition leading to a substituted 3-aminothietane dioxide which undergoes cleavage in the manner described above. Enamino sulfone **12** again arises by virtue of the fact that the addition of phenylsulfene to **1c** is nonconcerted.

In connection with the broader question of the effect of electronegative substituents disposed at C_3 of the enamine system on the cycloadditive propensity of sulfenes, it was deemed worthwhile to examine the chemical behavior of 1-dimethylamino-3-methoxy-1-butene (**40**) in this regard. When **40** was exposed to methanesulfonyl chloride and triethylamine under the conditions employed earlier, the cycloadduct **41** was obtained in high yield (Chart VIII). Further chemical transformation of **41** to **42** served to corroborate the structural assignment.

Chart VIII



Thus, we can conclude that the unusual transformations observed with the 1,3-bis(dimethylamino)-1-alkenes (**1a–c**) are engendered by the high order of nucleophilicity and basicity of the 3-amino substituent as well as by the customary mobility associated with the unbonded nitrogen electron pair.

Experimental Section[39]

Reaction of N,N,N′,N′-Tetramethylpropene-1,3-diamine (1a) with Sulfene. To a rapidly stirred solution of 31.2 g (0.31 mole) of triethylamine and 20.0 g (0.156 mole) of **1a**[40] 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 1 hr. Upon completion of the addition, the mixture was permitted to warm slowly to room temperature and was stirred at that temperature for 2 hr. The dark-colored mixture was filtered to remove the precipitated triethylamine hydrochloride,[41] and evaporation of the filtrate afforded a dark oil, which was chromatographed on Florisil. Elution of the column with hexane–ether (1:1) and ether afforded 3.1 g (16.2%) of **N,N-dimethylmethanesulfonamide (3)**, mp 49°, (lit.[42] mp 50–51°).

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 (4)**, mp 75–76° (from ether); $\nu_{max}^{CCl_4}$ 6.15 (C=CN<), 7.65, 7.87, and 8.90–9.05 μ (-SO_2-); $\tau_{TMS}^{CDCl_3}$ 7.08 (singlet, 6 H, (CH_3)$_2$N–), 5.28, 2.82 (doublets, J = 12.5 cps, 1 H each, vinyl protons at C_1 and C_2),[43] 4.27 (doublet, J = 9 cps, 1 H, *trans*-*H*HC=CH–), 3.90 (doublet, J = 17 cps, 1 H, *cis*-H*H*C=CH–), and 3.32 (doublet of doublets, J = 9 and 17 cps, 1 H, H_2C=C*H*–).

Anal. Calcd for $C_6H_{11}NO_2S$: 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.

(36) This mechanistic pathway also represents the genesis of bithietane tetroxide **22**, as discussed earlier for **16**.

(37) The predominance of attack of the sulfenes at the benzyl nitrogen atom, rather than at the β-carbon atom of the enamine system, is undoubtedly a reflection of the generally greater basicity of benzylamines relative to simpler aliphatic amines (usually about 1 pK_a unit).

(38) Unfortunately, the point at issue in deciding between these two alternative pathways revolves about the timing of the attack of the α-sulfonyl carbanion at the C_1 position, a question for which it is always very difficult to obtain a proper solution. However, at this point in time, we tend to favor the cyclic mechanism (**39a**), for it appears somewhat improbable on the basis of our earlier considerations that the carbanionic terminus could sever itself from the remainder of the molecule and subsequently recombine in at least 50% yield without confronting one of the many species present in the solution (especially H^+) with which it could react readily (in the absence of a powerful solvent cage effect).

(39) 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 as internal standard) purchased with funds made available from the National Science Foundation. Ultraviolet measurements were made with a Cary Model 14 recording spectrometer.

(40) R. C. Doss and A. M. Schnitzer, U. S. Patent 2,800,509 (July 23, 1957); *Chem. Abstr.*, **51**, 17979 (1957).

(41) 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).

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

(43) That a coupling constant of this order of magnitude demands a *trans* configuration has been well established; see ref 25 and R. C. Pink, R. Spratt, and C. J. M. Stirling, *J. Chem. Soc.*, 5714 (1965).

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 (5)**, mp 69–70° (from ligroin); $\nu_{max}^{CCl_4}$ 6.15 (C=CN<), 7.70, 7.85, and 9.05 μ (–SO_2–); $\tau_{max}^{CCl_4}$ 7.78 (singlet, 6 H, saturated dimethylamino group), 7.17 (singlet, 6 H, α,β-unsaturated dimethylamino group), 7.18 (somewhat overlapping on previous peak, complex multiplet, 4 H, –CH_2CH_2–), 5.21 (doublet, J = 12.5 cps, 1 H, vinyl proton), and 2.92 (doublet, J = 12.5 cps, 1 H, vinyl proton).

Anal. Calcd for $C_8H_{16}N_2O_2S$: 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 noncharacterizable gums.

Partial Hydrogenation of 4. A solution of 1.0 g (6.0 mmoles) of **4** 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[44] afforded 0.6 g (60%) of **1-dimethylamino-3-thia-1-pentene 3,3-dioxide** as a white solid, mp 59–60°; $\nu_{max}^{CCl_4}$ 6.12 (C=CN<), 7.68, 7.86, 8.90, and 9.00 μ (–SO_2–); $\tau_{TMS}^{CCl_4}$ 8.83 (triplet, 3 H, CH_3CH_2–), 7.18 (quartet, 2 H, CH_3CH_2–), 7.12 (singlet, 6 H, $(CH_3)_2N$–), 5.32 (doublet, J = 12.5 cps, 1 H, vinyl proton), and 2.98 (doublet, J = 12.5 cps, 1 H, vinyl proton).

Anal. Calcd for $C_8H_{13}NO_2S$: C, 44.14; H, 8.03; S, 19.65. Found: C, 44.09; H, 8.19; S, 19.36.

Complete Hydrogenation of 4. A solution of 1.85 g (0.012 mole) of **4** in 100 ml of tetrahydrofuran containing 0.4 g of 10% palladium on charcoal was hydrogenated as above. After 3 hr, an additional 0.4 g of catalyst was added, and shaking was continued for 12 hr. The catalyst was filtered, and the filtrate was evaporated to give 1.55 (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 (6) hydrochloride,** mp 191–192° dec (from 95% ethanol).

Anal. Calcd for $C_6H_{16}ClNO_2S$: 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 **6**, mp 91–92° (from 95% ethanol).

Anal. Calcd for $C_8H_{16}ClNO_6S$: 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-thiapentane 3,3-Dioxide (6). 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[45] in one portion. The mixture was carefully warmed and finally refluxed for 1 hr. Upon cooling, the precipitated sodium chloride was filtered, and the filtrate was concentrated *in vacuo* below 50°. 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** as a colorless liquid, bp 76–78° (35 mm) [lit.[46] bp 66° (20 mm)].

A solution of 11.0 g (0.083 mole) of 1-dimethylamino-3-thiapentane 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 hr. 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 **6** as a clear liquid, bp 100° (0.5 mm), $n^{26}D$ 1.5040. This sample and its hydrochloride, mp 198–200° dec,[47] were identical in all respects with the material isolated above.

Michael Addition of Dimethylamine to 4. Into a cold (–10°) solution of 150 mg of **4** 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 hr. The solvent was evaporated *in vacuo*, and the residue was recrystallized from ligroin to yield 0.146 g (79%) of **5**, mp 69–70°. The material displayed infrared and nmr spectra superimposable upon those of a sample of **5** isolated as above.

Hydrogenation of 5. Hydrogenation of 0.47 g (2.0 mmoles) of **5** was accomplished over 500 mg of 10% palladium on carbon in 30 ml of dry tetrahydrofuran at approximately 60 psig at 25° for 35 hr. Additional 500-mg charges of catalyst were introduced after 14 and 23 hr. Work-up 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 (8) dihydrochloride,** mp 235°.

Preparation of Authentic 8. A 12.65-g (0.072 mole) sample of 1,5-bis(dimethylamino)-3-thiapentane[48] was oxidized with 15.2 g of potassium permanganate as described above. The resulting sulfone, bp 111–112° (0.3 mm), $n^{25}D$ 1.4709, was obtained in 49.5% yield. The dihydrochloride salt was prepared and melted at 233°.[49] The spectra of the free base and the dihydrochloride were superimposable upon the samples prepared above.

Reaction of N,N,N′,N′-Tetramethylpropene-1,3-diamine (1a) with Phenylsulfene. A stirred solution of 10.0 g (0.078 mole) of **1a** and 7.9 g (0.078 mole) of triethylamine in 50 ml of anhydrous tetrahydrofuran under a nitrogen atmosphere was treated at –15° 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 work-up[41] gave a viscous oil which was diluted with 30 ml of ether and caused to crystallize at 0° with scratching. Recrystallization of the pale yellow solid from ether–hexane afforded 6.75 g (30.7%) of **2-phenyl-3-dimethylamino-4-dimethylaminomethylthietane 1,1-dioxide (10)**, mp 91–93°. Further purification with ether–petroleum ether yielded pure **10** as a highly crystalline white solid, mp 95–96°; $\nu_{max}^{CCl_4}$ 7.4 and 8.6 μ (–SO_2–); $\tau_{TMS}^{CDCl_3}$ 8.05 and 7.70 (two singlets, 6 H each, dimethylamino groups), *ca.* 7.0 (multiplet, 3 H, CH_2NMe_2 and >$CHNMe_2$), 5.50 (doublet of triplets, 1 H, nonbenzylic α-sulfonyl proton), 4.80 (doublet, J = 9 cps, 1 H, benzylic proton), and 2.61 (singlet, 5 H, phenyl group).

Anal. Calcd for $C_{14}H_{22}N_2O_2S$: C, 59.54; H, 7.85; N, 9.92; S, 11.36. Found: C, 59.63; H, 7.94; N, 9.85; S, 11.31.

All filtrates and insoluble residues up to and including that from the first recrystallization were combined and chromatographed on neutral alumina. Elution with petroleum ether afforded a very small quantity of *trans*-**stilbene**, mp 122–123°.

Continued elution with petroleum ether–ether (9:1) led to the isolation of 1.38 g (8.85%) of **N,N-dimethylphenylmethanesulfonamide (11)**, mp 100–101° (from ether) (lit.[50] mp 100–101°).

The use of petroleum ether–ether (3:1) gave 0.8 g (4.5%) of *trans*-**2-dimethylamino-1-phenylmethanesulfonylethylene (12),** mp 77–78°. Additional recrystallizations of this material from carbon tetrachloride gave pure **12**, as a white solid, mp 85°;[51] $\nu_{max}^{CCl_4}$ 6.1 (C=CN<), 7.7–7.9 and 9.1 μ (–SO_2–); $\tau_{TMS}^{CDCl_3}$ 7.20 (singlet, 6 H, $(CH_3)_2N$–), 5.83 (singlet, 2 H, $PhCH_2$–), 5.40 and 3.18 (doublets, J = 12.5 cps, 1 H each, vinyl protons),[43] and 2.68 (singlet, 5 H, phenyl group).

Anal. Calcd for $C_{11}H_{15}NO_2S$: 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: **10**, trace; *trans*-stilbene, 30.3%; **11**, 16.8%; and **12**, 1.8%.

Hydrogenation of 12 to 2-(Benzylsulfonyl)-N,N-dimethylethylamine (13). A 0.5-g (2.0 mmoles) sample of **12** 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 185–187° dec (from aqueous methanol) (lit.[52] mp 184–186°). Regeneration of the free base from the pure hydrochloride gave a white

(44) 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.

(45) R. R. Burtner, *J. Am. Chem. Soc.*, 71, 2578 (1949).

(46) G. Tsatsas, C. Sandris, and D. Kontonassios, *Bull. Soc. Chim. France*, 2160 (1963).

(47) As is customary, the decomposition point of this salt was found to be dependent upon the rate of heating.

(48) W. Wienawski, *Acta Polon. Pharm.*, **18**, 269 (1961); *Chem. Abstr.*, **57**, 12303 (1962).

(49) We are at a loss to explain Wienawski's[48] reported melting point of 248° for this dihydrochloride.

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

(51) After completion of this work, **12** was described by J. N. Wells and F. S. Abbott [*J. Med. Chem.*, **9**, 489 (1966)], mp 85–86° (from ether–petroleum ether).

(52) J.-S. Tsung and J.-Y. Chi, *Hua Hsueh Hsueh Pao*, **26**, 31 (1960); *Chem. Abstr.*, **55**, 17635 (1960).

solid, mp 68–69° (from ether–petroleum ether) (lit.[52] mp 68–69°), identical in all respects with an authentic sample.

Reaction of N,N,N′,N′-Tetramethyl-1-butene-1,3-diamine (1b) with Sulfene.[53] A stirred solution of **1b**[54] and triethylamine in tetrahydrofuran was treated dropwise under nitrogen at −15° 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 hr. The reaction mixture was worked up as in the case of **1a**.[55] 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 16,** was obtained in pure form by recrystallization from methanol, white solid, mp 148–150° dec; $\nu_{max}^{CH_2Cl_2}$ 7.55, 8.20, 8.41, and 8.82 μ (–SO_2–). Its nmr spectrum (in DMSO-d_6) displayed only one extensively coupled upfield proton.[13]

Anal. Calcd for $C_8H_{15}NO_4S_2$: 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-(α-dimethylaminoethyl)-3-dimethylaminothietane 1,1-dioxide (15)** as a colorless crystalline solid, mp 38° (from petroleum ether); $\nu_{max}^{CCl_4}$ 7.58, 8.42, and 8.80 μ (–SO_2–); $\tau_{TMS}^{CDCl_3}$ 8.88 (doublet, J = 7 cps, 3 H, CH_3CH<), 7.73 and 7.68 (two singlets, 6 H each, both dimethylamino groups), *ca.* 6.79 (multiplet, 2 H, both CHN<), and *ca.* 5.92 (multiplet, 3 H, α-sulfonyl protons).

Anal. Calcd for $C_9H_{20}N_2O_2S$: 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 (3),** 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 (14)** as a colorless solid, mp 58° (from ether); $\lambda_{max}^{CCl_4}$ 6.15 (C=CN<), 7.65, 7.89, 8.95, and 9.05 μ (–SO_2–); $\tau_{TMS}^{CDCl_3}$ 8.12 (doublet, J = 6 cps, 3 H, CH_3CH=), 7.07 (singlet, 6 H, $(CH_3)_2$N–), 5.25 and 2.81 (doublets, J = 12.5 cps, 1 H each, –CH=$CH$$NMe_2$),[43] 3.72 (doublet, J = 15 cps, 1 H, CH_3CH=CH–), and 3.30 (doublet of quartets, J = 15 and 6 cps, 1 H, CH_3CH=).

Anal. Calcd for $C_7H_{13}NO_2S$: C, 47.97; H, 7.47; N, 7.99; S, 18.30. Found: C, 47.92; H, 7.41; N, 7.76; S, 18.20.

1-Dimethylamino-3-thiahexane 3,3-Dioxide (17). A. Catalytic Hydrogenation of 14. Hydrogenation of 0.28 g of **14** 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 $C_8H_{20}INO_2S$: 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 **7,** 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 (18),** bp 85° (25 mm), n^{27}D 1.4621.

A 12.2-g (0.083 mole) sample of **18** was oxidized with 16.5 g (0.105 mole) of potassium permanganate in the predescribed manner to give 7.05 (47.1%) of sulfone **17,** bp 110° (0.75 mm), n^{27}D 1.5040.

The methiodide of **17** was prepared in the usual fashion, mp 165–166° dec.

The infrared and nmr spectra of **17** and its methiodide were identical with those of the samples obtained in part A.

Hofmann Degradation of Bithietane Tetroxide 16. The methiodide salt of **16** was prepared with methyl iodide in refluxing methanol in 85% yield, mp 189° dec (from aqueous methanol).

Anal. Calcd for $C_9H_{18}INO_4S_2$: 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 min, cooled, and extracted with methylene chloride to yield 1.2 g (36.4%) of **19** as white crystals, mp 143–144° (from methanol).

Anal. Calcd for $C_6H_8O_4S_2$: C, 34.60; H, 3.87; S, 30.79. Found: C, 34.44; H, 3.94; S, 30.39.

2,3′-Bithietane Tetroxide (20). A solution of 0.5 g (2.4 mmoles) of **19** in 80 ml of methanol containing 0.2 g of 10% palladium on charcoal was hydrogenated on a Parr shaker for 9 hr. The catalyst was filtered, and the solvent was evaporated. Recrystallization of the residue from methanol gave 0.4 g (80%) of pure **20,** mp 187–188°.

Anal. Calcd for $C_8H_{10}O_4S_2$: C, 34.27; H, 4.79; S, 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.

Reaction of N,N,N′,N′-Tetramethyl-1-butene-1,3-diamine (1b) 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 **1b** 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 1 hr.[56] 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 (9),** mp 122–123°.

Elution with petroleum ether–ether (1:1) and ether afforded 0.95 g (6.8%) of **N,N-dimethylphenylmethanesulfonamide (11),** mp 100–101°.

Continued elution with ether led to the isolation of 0.17 g (1%) of **2-phenyl-4-(α-dimethylamino)ethylthiete sulfone (21),** mp 123–125° dec (from ether–petroleum ether); $\nu_{max}^{CCl_4}$ 7.6 and 8.6 μ (–SO_2–); λ_{max}^{EtOH} 256 mμ (ε 17,800); $\tau_{TMS}^{CDCl_3}$ 8.88 (doublet, J = 6 cps, 3 H, CH_3CH<), 7.74 (singlet, 6 H, $(CH_3)_2$N–), *ca.* 6.8 (multiplet, 1 H, CH_3CH<), *ca.* 5.5 (multiplet, 1 H, >CH-SO_2), 2.9–3.0 (multiplet, 1 H, vinyl proton), and 2.59 (broadened singlet, 5 H, phenyl group).

Anal. Calcd for $C_{13}H_{17}NO_2S$: 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-phenylmethanesulfonylethylene (12),** mp 85°.

Elution with ether–methylene chloride (1:1) and methylene chloride afforded 2.75 g (9.7%) of **bithietane tetroxide 22,** mp 160–161° dec with prior sintering at 155° (from methanol); $\nu_{max}^{CHCl_3}$ 7.5 and 8.7 μ (–SO_2–); $\tau_{TMS}^{CDCl_3}$ 7.95 (singlet, 6 H, $(CH_3)_2$N–), *ca.* 6.7 (multiplet, 2 H, H_3 and H_3'), 5.6 (multiplet, 3 H, nonbenzylic α-sulfonyl protons), *ca.* 4.6 (multiplet, 2 H, benzylic α-sulfonyl protons), and 2.68 and 2.57 (singlets, 5 H each, phenyl protons).

Anal. Calcd for $C_{20}H_{23}NO_4S_2$: C, 59.23; H, 5.71; N, 3.45; S, 15.81. Found: C, 59.23; H, 5.66; N, 3.09; S, 15.77.

1,3-Bis(dimethylamino)-3-phenyl-1-propene (1c). 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 hr. 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*; $\nu_{max}^{CCl_4}$ 6.0 μ (C=CN<); $\tau_{TMS}^{CCl_4}$ 7.85 (singlet, 6 H, $(CH_3)_2$N–), 7.63 (singlet, 6 H, $(CH_3)_2$N–), 6.52 (doublet, J = 8.5 cps, 1 H, C_6H_5CH<), 5.80 (quartet, J = 13 and 8.5 cps, 1 H, vinyl proton at C_2), 4.08 (doublet, J = 13 cps, 1 H, vinyl proton at C_1), and 2.80 (complex multiplet, 5 H, phenyl group).

Reaction of 1c with Sulfene. To a nitrogen-blanketed stirred solution of 20.0 g (0.098 mole) of **1c** 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 hr. The triethylamine hydrochloride was filtered[41] 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 (51.0%) of pale yellow solid, mp 81–83°. Further recrystallization of this material from ether afforded pure **N,N-dimethyl-2-dimethylamino-4-phenyl-3-butene-1-sulfonamide (23)** as a highly crystalline white solid, mp 83°; $\nu_{max}^{CCl_4}$ 7.5, 8.7, and 10.3 μ (–SO_2N<); λ_{max}^{EtOH} 251 mμ (ε 20,300), 282 (sh) (3800), and 292 (sh) (2800); $\tau_{TMS}^{CDCl_3}$ 7.70 (singlet, 6 H, $(CH_3)_2$N–), 7.15 (singlet, 6 H, –SO_2N$(CH_3)_2$), 6.10–7.00 (complex pattern, 3 H, methylene protons), 3.15–3.95

(53) The yields of the various products resulting from changes in the proportions of reactants are tabulated in Table II.

(54) Z. Arnold, *Collection Czech. Chem. Commun.*, **25,** 1308 (1960).

(55) In this present instance, much of the bithietane tetroxide **16** was found to coprecipitate with the triethylamine hydrochloride. Isolation could be achieved simply by slurrying the precipitated solid in water and removing the undissolved **16** by filtration.

(56) These so-called "fast conditions" (see Table II) were necessary in this instance because many of the initially formed products are apparently destroyed on more prolonged exposure to the reaction conditions.

(complex pattern, 2 H, vinyl protons), and 2.55 (boradened singlet, 5 H, phenyl group).

Anal. Calcd for $C_{14}H_{22}N_2O_2S$: 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 (24)**, mp 91° (from ether–petroleum ether); $\nu_{max}^{CCl_4}$ 6.1 and 6.3 (C=C), 7.4, 8.7, and 10.4 μ (-SO_2N<); λ_{max}^{EtOH} 224 mμ (ϵ 8400), 229 (10,950), 236 (8400), and 301 (38,700); $\tau_{TMS}^{CDCl_3}$ 7.25 (singlet, 6 H, (CH_3)$_2$N-) and 2.6–3.9 (complex pattern, 9 H, vinyl and phenyl protons).

Anal. Calcd for $C_{12}H_{15}NO_2S$: 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 (25)**, mp 107–108° (from carbon tetrachloride); $\nu_{max}^{CCl_4}$ 6.1 (C=CN<), 7.6, 9.0, and 10.4 μ (-SO_2N<); $\tau_{TMS}^{CDCl_3}$ 7.13 (singlet, 6 H, (CH_3)$_2$N-), 5.19 and 3.20 (doublets, J = 13 cps, 1 H each, $HC(Me_2N)$=$C(SO_2-)H$-),[48] 3.00 (doublet, J = 9 cps, 1 H, C_6H_5CH=), and 2.68 (complex multiplet, 6 H, -SO_2CH=CHC_6H_5).

Anal. Calcd for $C_{12}H_{15}NO_2S$: 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 23 on Neutral Alumina. A 5.0-g (0.018 mole) sample of **23** was placed on 40 g of neutral alumina. Elution with petroleum ether–ether (3:1) afforded 0.6 g of **24**, mp 91°, and 3.75 g (60% recovery) of starting material (**23**). The yield of **24** was 35.7% when based on unrecovered starting material.

Catalytic Hydrogenation of 23. To a solution of 1.0 g (3.5 mmoles) of **23** 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 hr. The catalyst was filtered and the filtrate was evaporated *in vacuo*. The residue was recrystallized from ether to give 0.95 g (95%) of pure **N,N-dimethyl-2-dimethylamino-4-phenyl-1-butanesulfonamide**, mp 83–84°; $\nu_{max}^{CCl_4}$ 7.5, 8.7, and 10.4 μ (-SO_2N<); λ_{max}^{EtOH} 261 mμ (ϵ 230), 264 (180), and 268 (185); $\tau_{TMS}^{CDCl_3}$ 7.81 (singlet, 6 H, (CH_3)$_2$N-), 7.30 (singlet, 6 H, -$SO_2N(CH_3)_2$), 6.9–7.5 (complex multiplet partly overlapping previous peak, 7 H, methylene protons), and 2.87 (singlet, 5 H, phenyl group).

Anal. Calcd for $C_{14}H_{24}N_2O_2S$: 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 (26). A. Catalytic Hydrogenation of 24. A 0.3-g (1.3 mmoles) sample of **24** 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 **26** as a colorless solid, mp 48°; $\nu_{max}^{CCl_4}$ 7.5, 9.7, and 10.4 μ (-SO_2N<); λ_{max}^{EtOH} 242 mμ (ϵ 80), 248 (130), 253 (190), 259 (230), 261 (230), 264 (180), and 268 (185); $\tau_{TMS}^{CDCl_3}$ 8.0–8.4 (broad multiplet, 4 H, saturated methylene groups), 7.0–7.6 (broad multiplet, 10 H, benzyl and α-sulfonyl protons, -SO_2N-(CH_3)$_2$), and 2.85 (singlet, 5 H, phenyl protons).

Anal. Calcd for $C_{12}H_{19}NO_2S$: 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[57] 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%) of **26**, mp 48°, identical in all respects with the above sample.

1-Dimethylamino-3-thia-5-phenylpentane 3,3-Dioxide (27). A. Catalytic Hydrogenation of 25. The hydrogenation of 0.082 g (0.3 mmole) of **25** was accomplished over a catalytic quantity of 10% palladium on carbon in 20 ml of tetrahydrofuran at 50 psig and 35° for 7 hr. The oil which resulted upon work-up was divided equally and a methiodide and hydrochloride were prepared by conventional methods.

The hydrochloride was obtained as white crystals from methanol–ether, mp 148–150°.

The methiodide was obtained as white prisms from methanol, mp 190–191° dec.[58]

Anal. Calcd for $C_{13}H_{22}INO_2S$: 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[59] 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[45] in one portion. The mixture was carefully heated to reflux in which state it was maintained for 1 hr. 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 91–92° (0.1 mm), n^{27}D 1.5330.

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 potassium 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, filtered, and evaporated. Distillation of the residue gave 8.80 g (57.0%) of **27**, bp 155–157° (0.03 mm), $n^{27.5}$D 1.5250; $\nu_{max}^{CCl_4}$ 7.6, 8.7, and 8.9 μ (-SO_2-); $\tau_{TMS}^{CCl_4}$ 7.87 (singlet, 6 H, (CH_3)$_2$N-), 6.7–7.6 (multiplet, 8 H, methylene protons), and 2.85 μ (singlet, 5 H, phenyl group).

The free base was spectrally identical with the sample obtained in part A. Furthermore, the spectra of its methiodide, mp 186° dec,[58] and its hydrochloride, mp 148–150°, likewise were superimposable upon those of the same derivatives in part A.

Reaction of 1c with Phenylsulfene. To a nitrogen-blanketed stirred solution of 10.0 g (0.049 mole) of **1c** 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 tetahydrofuran. Work-up 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 **N,N-dimethylphenylmethanesulfonamide (11)**, mp 100–101°.

Further elution with petroleum ether–ether (1:1) afforded 8.5 g (48.3%) of **N,N-dimethyl-2-dimethylamino-1,4-diphenyl-3-butene-1-sulfonamide (28)**, mp 146–147° (from ethyl acetate); $\nu_{max}^{CCl_4}$ 7.5, 8.7, and 10.4 μ (-SO_2N<); λ_{max}^{EtOH} 253 mμ (15,800), 284 (sh) (7500), and 293 (sh) (6200); $\tau_{TMS}^{CDCl_3}$ 7.65 (singlet, 6 H, (CH_3)$_2$N-), 7.45 (singlet, 6 H, -$SO_2N(CH_3)_2$), 5.40–6.15 (complex pattern, 2 H, protons on C_1 and C_2), 3.55–4.50 (complex pattern, 2 H, vinyl protons), and 2.90 and 2.75 (singlets, 5 H each, phenyl groups).

Anal. Calcd for $C_{20}H_{26}N_2O_2S$: 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 *trans*-**2-dimethylamino-1-phenylmethanesulfonylethylene (12)**, mp 85°.

Chromatography of 28 on Neutral Alumina. A 9.0-g (0.025 mole) sample of **28** was placed on 270 g of neutral alumina. Elution with ether gave 2.25 g of **N,N-dimethyl-1,4-diphenyl-1,3-butadiene-1-sulfonamide (43)**, mp 104–105° (from ether–petroleum ether); $\nu_{max}^{CCl_4}$ 6.1 (C=C), 7.4, 8.7, and 10.3 μ (-SO_2N<); λ_{max}^{EtOH} 226 mμ (10,450), 231 (12,300), 237 (10,900), and 315 (37,700); $\tau_{TMS}^{CDCl_3}$ 7.38 (singlet, 6 H, (CH_3)$_2$N-), 3.0–3.6 (complex multiplet, 1 H, vinyl proton at C_3), and 2.45–2.68 (broadened singlets with overlapping multiplets, 12 H, phenyl protons and vinyl protons at C_2 and C_4).

Anal. Calcd for $C_{18}H_{19}NO_2S$: 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 **28**.

Partial Hydrogenation of 43. A solution of 0.5 g (1.6 mmoles) of **43** in 25 ml of tetrahydrofuran was hydrogenated at 50 psig and 25° over 10% palladium on charcoal for 21 hr. After the usual work-up, there was obtained 0.5 g (100%) of **N,N-dimethyl-1,4-diphenyl-1-butene-1-sulfonamide (44)**, mp 78–79° with prior sintering at 75° (from ether–petroleum ether); $\nu_{max}^{CCl_4}$ 7.5, 8.7, and 10.4 μ (-SO_2N); λ_{max}^{EtOH} 315 mμ (ϵ 4750) and end absorption; $\tau_{TMS}^{CDCl_3}$ 7.55 (singlet, 6 H, -$SO_2N(CH_3)_2$), 7.3–7.8 (complex multiplet overlapping previous peak, 4 H, methylene protons), and 2.6–3.2 (complex multiplet, 11 H, both phenyl groups and the vinyl proton).

Anal. Calcd for $C_{18}H_{21}NO_2S$: 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 15 with Sulfene. To a stirred solution of 10.0 g (0.045 mole) of **15** 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.

(57) W. E. Truce and J. P. Milionis, *J. Am. Chem. Soc.*, **74**, 974 (1952).

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

(59) Obtained from the Wateree Chemical Co., Lugoff, S. C.

After 12 hr at room temperature, the precipitated triethylamine hydrochloride was filtered (no **16** found admixed with this salt), and the filtrate was evaporated. The residue was chromatographed on neutral alumina to give 3.1 g (30% recovery) of **15** and 0.4 g (7.3%) of **1-dimethylamino-3-thia-1,4-hexadiene 3,3-dioxide (14)**, mp 56–58°. Further elution of the column gave a trace of **3** and a quantity of uncharacterizable viscous gums.

Reaction of 1-Dimethylamino-1,3-butadiene (35) with Sulfene. Five grams (0.052 mole) of 1-dimethylamino-1,3-butadiene[54] was treated in the customary manner with 2 equiv of sulfene at −15° under nitrogen. After 4 hr 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 **16**, mp 148–150°. 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.

2-Phenyl-3-dimethylamino-4-dimethylaminomethylthietane 1,1-Dioxide. Reaction with Excess Sulfene. To a stirred solution of 4.0 g (14 mmoles) of **10** 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 work-up followed. Chromatography of the reaction mixture on neutral alumina gave 220 mg (6.0%) of **1-dimethylamino-2-phenyl-3-thia-1,4-pentadiene 3,3-dioxide (38)**, mp 102–103° (from carbon tetrachloride); $\nu_{max}^{CCl_4}$ 6.14 (C=CN<), 7.68 and 8.88 μ (-SO_2-); $\tau_{TMS}^{CDCl_3}$ 7.33 (singlet, 6 H, $(CH_3)_2N$), 4.40 (doublet, J = 9 cps, 2 H, =CH_2), 4.06 (singlet, 1 H, Me_2NCH=), 3.56 (doublet of doublets, 1 H, -SO_2CH=), and 2.74 (singlet, 5 H, phenyl group); λ_{max}^{EtOH} 283 mμ (ε 20,650).

Anal. Calcd for $C_{12}H_{15}NO_2S \cdot 0.5H_2O$: 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 (3) was the only remaining characterizable product.

Hydrogenation of 38. A 0.16-g (0.65 mmole) sample of **38** in 25 ml of tetrahydrofuran was hydrogenated in the manner described above. There was isolated upon work-up 0.10 g (62.5%) of **1-dimethylamino-2-phenyl-3-thia-1-pentene 3,3-dioxide (45)** as a white solid, mp 129–130° (from ether–petroleum ether); $\nu_{max}^{CCl_4}$ 6.1 (C=CN<), 7.7 and 8.9 μ (-SO_2-); $\tau_{TMS}^{CDCl_3}$ 8.70 (triplet, J = 7.5 cps, 3 H, -CH_2CH_3), 7.41 (singlet, 6 H, $(CH_3)_2N$-), 7.37 (quartet, J = 7.5 cps, 2 H, -CH_2CH_3), 2.86 (singlet, 1 H, Me_2NCH=), and 2.78 (singlet, 5 H, phenyl group); λ_{max}^{EtOH} 245 mμ (ε 15,265) and 266 (sh) mμ (ε 9650).

Anal. Calcd for $C_{12}H_{17}NO_2S$: 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 (40). 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 β-methoxybutyraldehyde[60] 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 **40** as a colorless liquid, bp 44–45° (7 mm), $n^{30}D$ 1.4479; $\nu_{max}^{CCl_4}$ 6.05 μ (C=CN<); $\tau_{TMS}^{CCl_4}$ 6.17 (doublet of doublets, J = 13 and 2 cps, 1 H, vinyl proton at C_2), and 4.07 (doublet, J = 13 cps, 1 H, vinyl proton at C_1).

Reaction of 40 with Sulfene. To a solution of 10.0 g (0.077 mole) of **40** 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 hr. The precipitated triethylamine hydrochloride was filtered,[61] and the filtrate was concentrated *in vacuo* to give a brown oil. Distillation of this material afforded 13.15 g (82.2%) of **41** as a colorless liquid, bp 110–112° (0.1 mm);[61] $\nu_{max}^{CCl_4}$ 7.6 and 8.8 μ (-SO_2-); $\tau_{TMS}^{CDCl_3}$ 8.75 (doublet, J = 6 cps, 3 H, CH_3CH<), 7.78 (singlet, 6 H, $(CH_3)_2N$-), *ca.* 7.1 (multiplet, 1 H, Me_2NCH<), 6.68 (singlet, 3 H, -OCH_3), and *ca.* 6.1 (complex multiplet, 4 H, CH_3O-CH< and α-sulfonyl protons).

The aminothietane dioxide was characterized as its picrate, mp 169–170° (from aqueous ethanol).

Anal. Calcd for $C_{14}H_{20}N_4O_{10}S$: C, 38.53; 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 41. A solution of 5.0 g (0.024 mole) of **41** and 7.0 g (0.049 mole) of methyl iodide in 30 ml of methanol was allowed to stand at room temperature for 24 hr. 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 $C_9H_{20}INO_3S$: 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 **42** as a colorless liquid; $\nu_{max}^{CCl_4}$ 7.6 and 8.8 μ (-SO_2-); $\tau_{TMS}^{CCl_4}$ 8.62 (doublet, J = 6 cps, 3 H, CH_3CH<), 6.68 (singlet, 3 H, -OCH_3), 5.82 (quartet with additional small coupling, J = 6 cps, 1 H, CH_3OCH<), 5.65 (broadened singlet, 2 H, α-sulfonyl protons), and 3.05 (broadened singlet, 1 H, vinyl proton).

Anal. Calcd for $C_8H_{10}O_3S$: C, 44.42; H, 6.21; S, 19.77. Found: C, 44.24; H, 6.21; S, 19.90.

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(60) F. Büttner, *Ann.*, **583**, 184 (1953).

(61) 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 work-up also afforded **41** in high yield as the lone characterizable product.