Registry No.—11 (R_1 = 5-Cl; R_3 = CH_3), 16867-42-8; 11 (R_1 = 3-CH_3; R_3 = C_2H_5), 16867-43-9; 11 (R_1 = 3-CH_3; R_3 = CH_3), 16878-13-0; 11 (R_1 = 3,5-di-Br; R_3 = CH_3), 16867-44-0; 12 (R_1 = 4-CH_3; R_2 = CH_3), 16867-45-1; 12 (R_1 = 5-CH_3; R_2 = CH_3), 16867-46-2; 12 (R_1 = 6-CH_3; R_2 = CH_3), 16867-47-3; 12 (R_1 = 4-CH_3; R_2 = C_6H_5), 16867-48-4; 12 (R_1 = 5-CH_3; (R_2 = C_6H_5), 16867-49-5; 12 (R_1 = 6-CH_3; R_2 = C_6H_5), 16867-50-8; 12 (R_1 = 5-Cl; R_2 = C_6H_5), 16867-51-9; 12 (R_1 = 5-Br; R_2 = C_6H_5), 16867-52-0; 15 (R = 3-CH_3), 16878-15-2; 15 (R = 5-Cl), 16867-57-5; 15 (R = 5-Br), 16867-58-6.

Acknowledgment.—One of us (S. S. I.) wishes to thank the South African Council for Scientific and Industrial Research for the award of an assistantship.

Unsaturated Heterocyclic Systems. XL. Evaluation of Spiro[9,10-ethanoanthracene-11,2′-thietane] S,S-Dioxides and 2-α-Dialkylaminoalkyl-3-dialkylaminothietane 1,1-Dioxides as Precursors of 2-Methylenethiete 1,1-Dioxide Derivatives[1,2]

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Received March 14, 1968

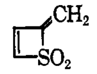
Three synthetic approaches to the highly strained 2-methylenethiete 1,1-dioxide ring system have been evaluated. The retro Diels–Alder route wherein the 9,10-ethanoanthracene moiety was employed as a blocking group for the exocyclic double bond met with failure when it was recognized that the temperatures required to liberate anthracene were well above those at which the desired tetravalent sulfur heterocycles decomposed. The Hofmann degradation approach suffered from the fact that 2α-dialkylaminoalkyl-3-dialkylaminothietane 1,1-dioxides such as **13** and **14** displayed a propensity for ring cleavage when treated with methyl iodide. Two intermediate methiodides, could, however, be isolated. When subjected in turn to the conditions of Hofmann elimination, these methiodides were found to be especially prone to demethylation. Alternatively, N-oxide degradation of 2α-dialkylaminoalkyl-3-dialkylaminothietane 1,1-dioxides, although not an entirely general procedure, was found to give rise to two methylenethiete dioxides. Pertinent mechanistic implications of the above reactions and the physical and spectral properties of the title sulfones are presented in some detail.

A common and fundamental property of unsaturated four-membered-ring heterocycles such as **1a–c** is the

1a, X = NR
b, X = O
c, X = S
d, X = SO_2

ease with which these molecules undergo electrocyclic bond reorganization with ring cleavage. Numerous past investigations have suggested the intermediacy of molecules such as **1** in a variety of chemical and photochemical transformations, but, in general, attempts at isolation have been unsuccessful and rearrangement products have resulted. Recently, however, the isolation of thiete (**1c**)[5a] and a bicyclic thiete derivative[5b] has been described; as expected, both substances have proven to be quite reactive at ambient temperatures.

It was recognized several years ago that the heterocyclic system in question, **1**, was uniquely stabilized when the hetero ring substituent was the sulfone group. Since the preparation of thiete 1,1-dioxide (**1d**) was first described and its chemical behavior examined in a preliminary fashion,[6] the chemistry of this ring system has received considerable attention[7] and a number of stable derivatives are now known.[7,8] It was our intent to investigate in some detail the synthesis and properties of exocyclic methylene derivatives of thiete dioxide, *e.g.*, **2**, in order to examine the effects which are produced by extension of the π-electron system in the indicated manner. That molecules such as **2** would be reactive and be subject to diverse types of reactions was anticipated on the basis of analogy to the chemical behavior of methylenecyclobutenes. For example, hydrocarbons **3–5** are known to polymerize readily and



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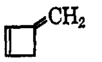

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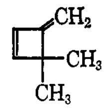
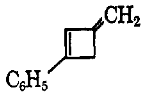


4



5

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[1] For paper XXXIX of this series, see L. A. Paquette and M. K. Scott, *J. Org. Chem.*, **33**, 2379 (1968).

[2] This work was generously supported by Grant GP-5977 from the National Science Foundation.

[3] Alfred P. Sloan Foundation Research Fellow.

[4] National Science Foundation Undergraduate Research Participant, summer 1966.

[5] (a) D. C. Dittmer, K. Takahashi, and F. A. Davis, *Tetrahedron Lett.*, 4061 (1967); (b) D. C. Dittmer and F. A. Davis, *J. Amer. Chem. Soc.*, **87**, 2064 (1965).

[6] (a) D. C. Dittmer and M. E. Christy, *J. Org. Chem.*, **26**, 1324 (1961); (b) D. C. Dittmer and M. E. Christy, *J. Amer. Chem. Soc.*, **84**, 399 (1962).

[7] (a) D. C. Dittmer and N. Takashina, *Tetrahedron Lett.*, 3809 (1964); (b) L. A. Paquette, *J. Org. Chem.*, **30**, 629 (1965); (c) L. A. Paquette and T. R. Phillips, *ibid.*, **30**, 3883 (1965); (d) L. A. Paquette and M. Rosen, unpublished results; (e) D. C. Dittmer and F. A. Davis, *ibid.*, **32**, 3872 (1967).

[8] (a) W. E. Truce, J. R. Norell, J. E. Richman, and J. P. Walsh, *Tetrahedron Lett.*, 1677 (1963); (b) R. H. Hasek, P. G. Gott, R. H. Meen, and J. C. Martin, *J. Org. Chem.*, **28**, 2496 (1963); (c) G. Opitz and H. Schempp, *Z. Naturforsch.*, **19b**, 78 (1964); (d) W. E. Truce and J. R. Norell, *J. Amer. Chem. Soc.*, **85**, 3236 (1963); (e) D. C. Dittmer and F. A. Davis, *J. Org. Chem.*, **29**, 3131 (1964); (f) G. Opitz and H. Schempp, *Ann.*, **684**, 103 (1965); (g) R. H. Hasek, R. H. Meen, and J. C. Martin, *J. Org. Chem.*, **30**, 1495 (1965); (h) J. N. Wells and F. S. Abbott, *J. Med. Chem.*, **9**, 489 (1966); (i) L. A. Paquette and M. Rosen, *J. Amer. Chem. Soc.*, **89**, 4102 (1967); (j) L. A. Paquette and M. Rosen, *J. Org. Chem.*, **33**, 2130 (1968).

spontaneously at room temperature.[9] As the degree of substitution on **3** is significantly increased, however, the carbocycle is seen to acquire moderate stability as gauged by the behavior of 3-methylene-1,4-diphenyl-2-methylcyclobutene.[10]

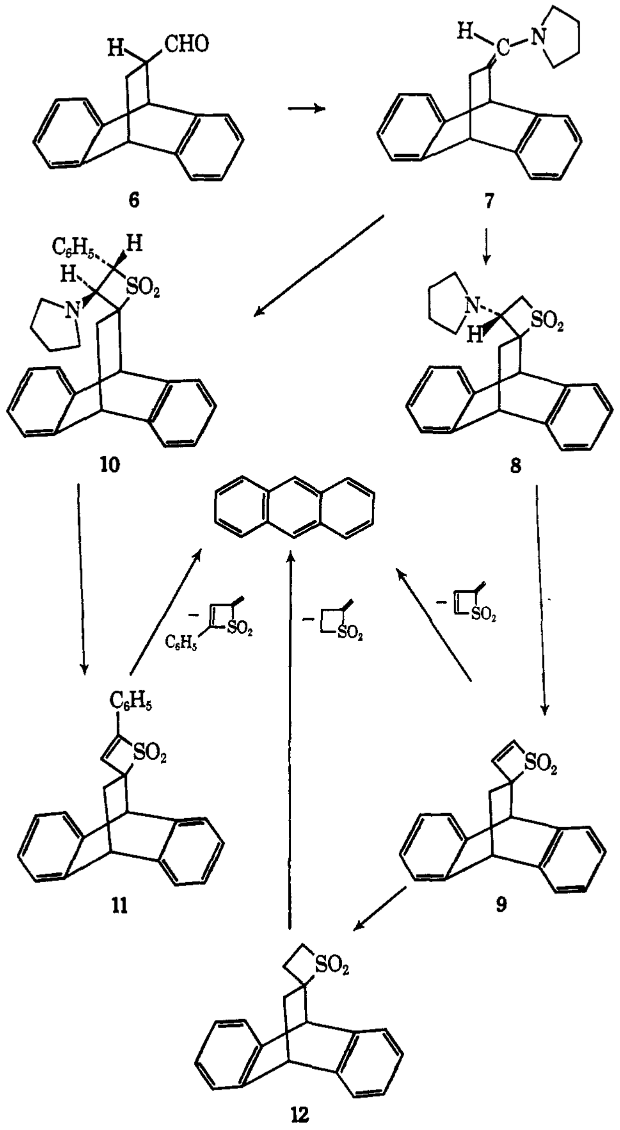
The present paper delineates the various synthetic approaches which have been examined in the preparation of **2** and its derivatives, whereas the ensuing article[11] describes various chemical reactions of this unsaturated heterocyclic system.[12]

Results

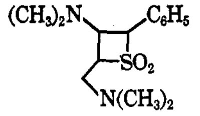
The Retro Diels–Alder Route.—Our initial approach was designed to take advantage of the fact that 9,10-ethanoanthracene derivatives decompose at somewhat elevated temperatures to generate anthracene and unsaturated compounds. Specifically, the intent was to construct a thiete dioxide derivative which incorporated the partially reduced anthracene ring as a blocking group for the exocyclic double bond. This reactive site of unsaturation was then to be introduced at the final stage of the synthesis. The synthesis is outlined in Scheme I. The stereochemistry of **8** was assigned subsequent to consideration of nonbonded strain minimization available to each of the two possible transition states leading to cycloaddition. The *trans* relationship of the pyrrolidino and phenyl groups in **10** is assigned on the basis of the nmr coupling constant (10.0 Hz) of the four-membered sulfone ring protons. Earlier, application of the Karplus correlation[13] to the thietane dioxide ring system was shown to be reliable.[14] The stereochemical assignment depends further upon recognition of the fact that the small heterocyclic ring exists in a puckered coformation[15] with the two substituents in question occupying *trans* equatorial positions and the protons exhibiting a dihedral angle of approximately 180°.[16] The spatial arrangement of the pyrrolidino and phenyl groups relative to the ethanoanthracene superstructure in **10**, although somewhat less convincing, is believed to be as indicated in Scheme I on the basis of steric factors operating in the cycloaddition process and because **10** does not form a methiodide salt.

Sulfones **9**, **11**, and **12** were found to be quite stable to 250°. Pyrolysis of **9** and **11** at approximately 300° under a nitrogen atmosphere at various reduced pressures resulted in the vigorous liberation of anthracene and sulfur dioxide, and formation of an intractable yellow solid (in the cold traps) and a brittle, black glassy residue. Under these conditions, **12** merely distilled with slight decomposition; at 400°, however, similar decomposition products were observed. As will become apparent, the failure of this synthetic scheme can be traced to the instability of the four-membered-ring sulfones at the temperatures required to remove the anthracene blocking group.

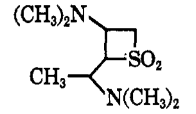
SCHEME I



The Hofmann Degradation Approach.—The reaction of sulfenes with 1,3-bis(dialkylamio)-1-alkenes is now recognized to produce a mixture of products from which 2-α-dialkylaminoalkyl-3-dialkylaminothietane 1,1-dioxides such as **13** and **14** can be isolated under strictly controlled conditions.[8i] In view of the disposition of the tertiary amino groups in these sulfones, a study of the Hofmann degradation of their derived methiodides was initiated in the expectation that derivatives of methylenethiete dioxide would result.



13



14

Exposure of **13** to methyl iodide in methanol solution at room temperature resulted in a gradual exothermic reaction and precipitation of a yellow crystalline solid (*ca.* 41% yield) which consisted of a mixture of monomethiodide **15** and tetramethylammonium iodide (see Scheme II). Chromatographic work-up of the non-

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[9] (a) D. R. Howton and E. R. Buchman, *J. Amer. Chem. Soc.*, **78**, 4011 (1956); (b) D. E. Applequist and J. D. Roberts, *ibid.*, **78**, 4012 (1956).

[10] A. T. Blomquist and Y. C. Meinwald, *ibid.*, **81**, 667 (1959).

[11] L. A. Paquette and M. Rosen, *J. Org. Chem.*, **33**, 3027 (1968).

[12] Portions of this work were presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, p S14.

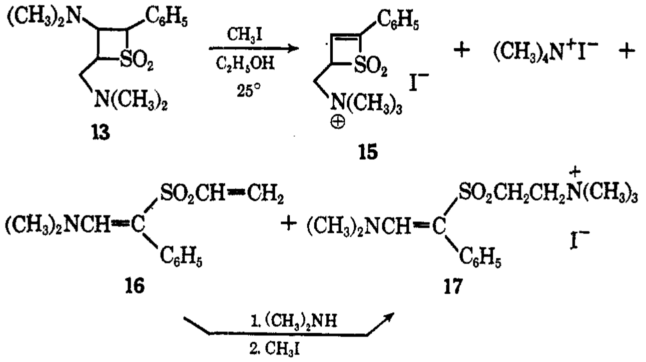
[13] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2871 (1963).

[14] L. A. Paquette, *J. Org. Chem.*, **29**, 2854 (1964).

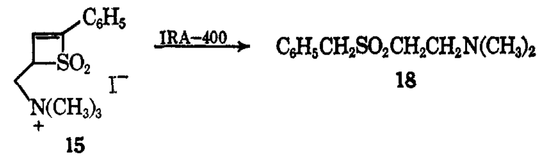
[15] For a summary of the data pertaining to this question, see footnotes 17–21 of ref 8i.

[16] Because of the fact that puckering of the thietane dioxide ring had not been conclusively established when ref 14 appeared, the assignments of configuration in this paper (structures V and VI) should be reversed to compensate for this conformational bias.

SCHEME II

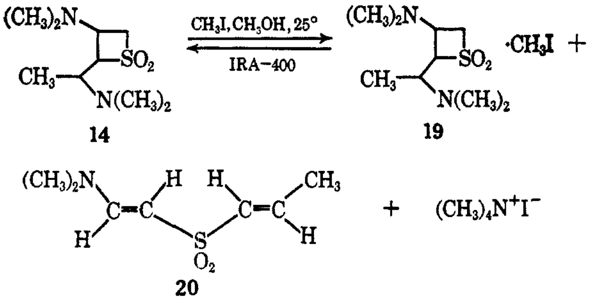


crystalline residue on neutral alumina afforded two additional crystalline solids, **16** (17%) and **17** (6.5%). Elution of **15** through an Amberlite IRA-400 ion-exchange column (hydroxide form) and careful removal of water gave 2-(benzylsulfonyl)-N,N-dimethylethylamine (**18**) as the only characterizable product.



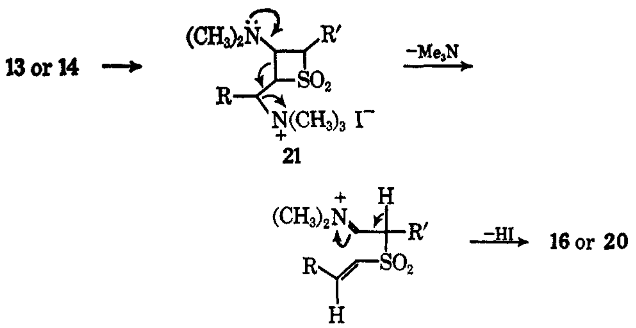
A similar ring cleavage was noted in the attempted quaternizaton of **14** with methyl iodide. In addition to a crystalline monomethiodide (**19**) which was deposited from the solution in 67% yield, careful chromatography of the noncrystalline residue also permitted isolation of the known vinyl enamino sulfone **20** (15%) and a small quantity of tetramethylammonium iodide (Scheme III). Hofmann degradation of **19** afforded only the demethylation product **14**.

SCHEME III



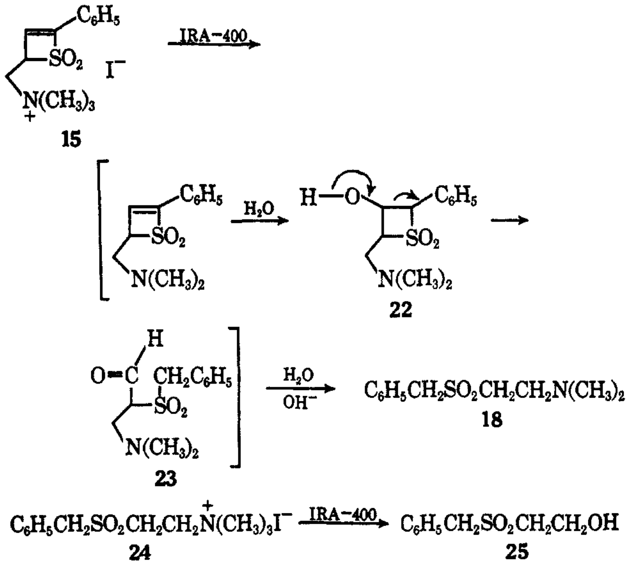
Such results indicate that **13** and **14** exhibit a marked propensity for ring cleavage under the conditions of quaternization. A mechanistic rationalization of this phenomenon demands that the 2α-amino substituent be the more nucleophilic nitrogen center and thus be subject to more rapid quaternization. This newly generated electron-deficient site (see **21**) is now subject to ready ejection (as trimethylamine) by migration of electrons from the 3-amino substituent with synchronous rupture of the four-membered ring as shown in Scheme IV.[17]

SCHEME IV

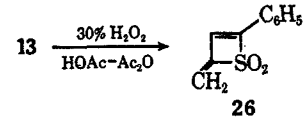


Undoubtedly the most surprising result was the strong preference exhibited by **15** and **19** for demethylation under the Hofmann elimination conditions. In this regard, we propose that **18** arises by loss of methanol directly from **15** or from the methiodides of intermediates **22** and **23** and not from **24** since the latter is rapidly transformed into alcohol **25** under the reaction conditions (see Scheme V). The remainder of the proposed mechanism receives support from the fact that thiete dioxide and 3-hydroxythietane 1,1-dioxide likewise undergo ring cleavage to dimethyl sulfone in basic solution.[6b]

SCHEME V



The N-Oxide Route.—Treatment of either **13** or **14** with hydrogen peroxide in methanol solution gave in each case a brown oily liquid which could not be converted into a picrate and decomposed when heated *in vacuo*. However, when **13** was treated with excess 30% hydrogen peroxide in acetic acid–acetic anhydride solution at room temperature for 1 day, there resulted an oily residue which after chromatography on neutral alumina gave the methylenethiete dioxide **26** in 37% yield. All spectra were recorded on freshly prepared samples of **26** for this sulfone gradually becomes colored at room temperature and polymerizes to a solid which is insoluble in all of the common organic solvents. We have observed that **26** is soluble in chloroform and acetonitrile but only slightly soluble in carbon tetrachloride; however, these solutions quickly turn red in color on standing and the sulfone cannot be recovered. De-



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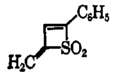
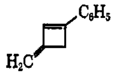
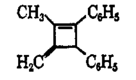
[17] Precedent for this mechanism has been described recently: L. A. Paquette and M. Rosen, *Tetrahedron Lett.*, 311 (1966).

composition was noted to be minimal in ether from which **26** can be recrystallized. The ultraviolet spectrum of this material was consistent with a 1-phenylbutadienyl chromophore and is compared in Table I with the reported values of two carbocyclic analogs.

TABLE I
COMPARISON OF THE ULTRAVIOLET SPECTRA OF **26** WITH TWO METHYLENECYCLOBUTENES

		
26	**5**	**27**
$\lambda_{\max}^{\text{ether}}$, mμ (ε)	$\lambda_{\max}^{\text{isooctane}}$,[a] mμ (ε)	$\lambda_{\max}^{\text{isooctane}}$,[b] mμ (ε)
...	212 (4,600)	...
...	219 (3,760)	...
...	225 (3,960)	228 (12,000)
...	233 (3,640)	235 (9,120)
291 (33,400)	291 (7,250)	292 (26,900)
...	...	302 (25,100)
...	...	316.5 (sh) (13,200)

[a] Reference 9. [b] Reference 10.

The mass spectrum of **26** (see Table II) shows a molecular ion (*m/e* 192) and a base peak at *m/e* 128. This fragmentation can be explained by the sequential loss of the elements of sulfur monoxide (*m/e* 144) and oxygen from an intermediate cyclic sulfinate such as **28** or **29** (see Scheme VI). The ion corresponding to the base peak appears to fragment to acetylene and phenylacetylene. Precedence for the intervention of a cyclic sulfinate ester has been found in the pyrolysis and electron impact of dibenzothiophene 5,5-dioxide[18] and in the thermal rearrangement of two thiete dioxides.[19]

SCHEME VI
MASS SPECTRAL CRACKING PATTERN FOR **26**

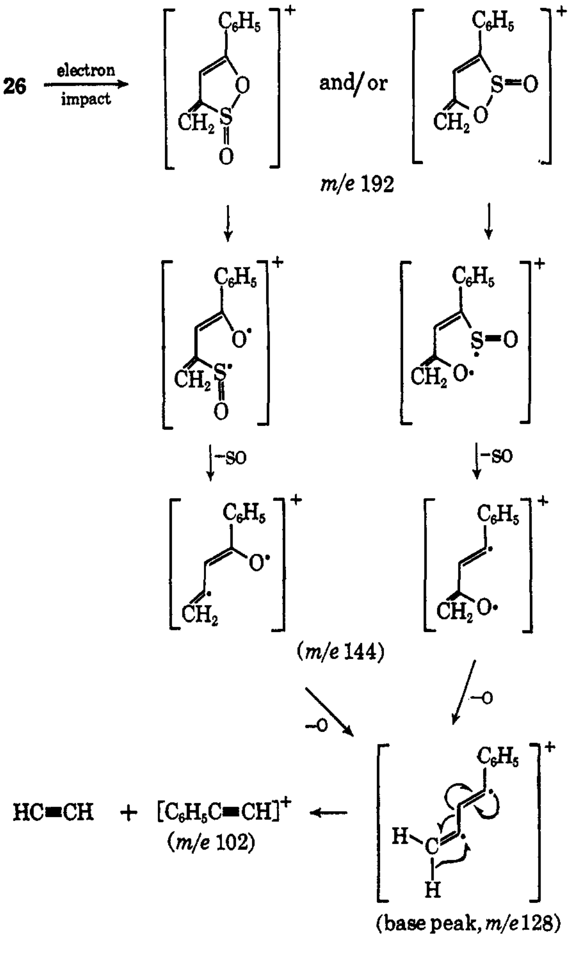
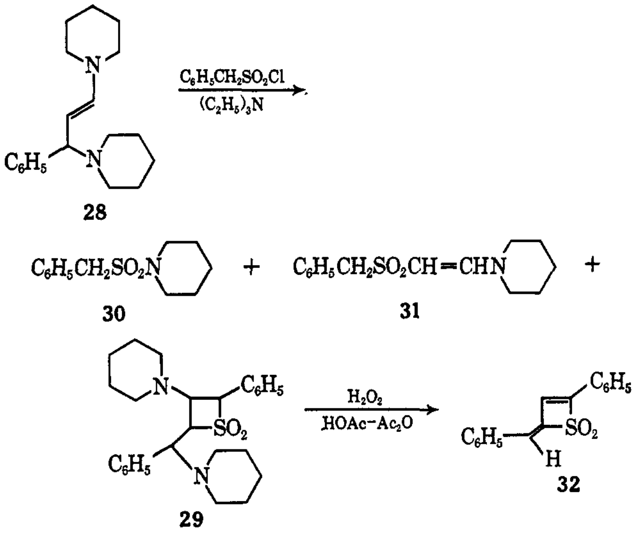


TABLE II
PRINCIPAL MASS SPECTRAL PEAKS IN 2-METHYLENETHIETE 1,1-DIOXIDES **26** AND **32**

26		**32**	
m/e	Relative abundance, %	*m/e*	Relative abundance, %
192	34	268	23
144	68	220	10
129	12	204	32
128	100	203	15
127	26	202	20
126	10	105	30
105	28	103	10
102	43	102	100
		101	10

The successful preparation of methylenethiete dioxide **26** by the N-oxide route prompted an examination of the generality of the procedure. Accordingly, our attention was next turned to the degradation of thietane dioxide **29**. The synthesis of **29** was achieved by treating 1,3-bis(1-piperidino)-3-phenyl-1-propene (**28**) with phenylsulfene; it should be noted that 1-(benzylsulfonyl)piperidine (**30**) and the enamino sulfone **31** accompanied the production of **29**, as anticipated from earlier work[8i] (see Scheme VII). When an acetic acid–acetic anhydride solution of **29** was treated with 30% hydrogen peroxide, the methylenethiete dioxide **32** was produced in 85% yield. This strained heterocycle is quite stable under normal laboratory conditions. The sulfone is insoluble in ether and carbon tetrachloride but soluble in chloroform, and is easily crystallized from tetrahydrofuran. The nmr spectrum of **32** is consistent with the gross structure; however, because the ring vinyl proton resides under the aromatic envelope and the second vinyl proton is a broad singlet, a definitive

SCHEME VII



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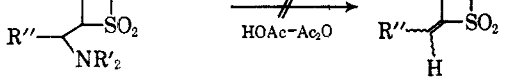
[18] E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **88**, 2836 (1966); *cf.* also ref 7e.

[19] (a) D. C. Dittmer, R. S. Henion, and N. Takashina, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, p O101; (b) R. W. Hoffmann and W. Sieber, *Ann.*, **708**, 96 (1967).

assignment of the geometric configuration about the exocyclic double bond was not possible on the basis of such a spectral analysis. However, consideration of steric factors at play in the elimination step, coupled with an analysis of the nmr spectral properties of the Diels–Alder adduct of **32** with 1,3-diphenylisobenzofuran,[11] permit the conclusion that **32** is of the indicated stereochemistry. That this methylenethiete dioxide possesses a diphenylbutadienyl chromophore is apparent from its ultraviolet spectrum in chloroform (see Experimental Section); this spectrum is roughly comparable with that reported for *trans,trans*-1,4-diphenyl-1,3-butadiene.[20] The mass spectrum of **32** displays a fragmentation pattern analogous to that of **26** (see Table II).

The first indication that the N-oxide degradation pathway was not completely general came from an attempt to prepare the parent of the methylenethiete dioxide series (**35**). The synthesis of the requisite thietane dioxide **34** was effected from the known 1,3-bis(1-piperidino)-1-propene (**33**) and sulfene; treatment of **34** with hydrogen peroxide in the usual manner gave a small amount of yellow oil which displayed an infrared spectrum indicative of the presence of an enamine function and nmr absorptions consistent with the presence of a piperidino group. This material could not be obtained crystalline and was not characterized further.



34, $R_2 = R'_2 = (CH_2)_5$, $R'' = H$
14, $R = R' = R'' = CH_3$
37, $R_2 = R_2' = (CH_2)_5$, $R'' = C_6H_5$

35, $R'' = H$
36, $R'' = CH_3$
38, $R'' = C_6H_5$

In the same way, **14** and **37** afforded oily mixtures, the components of which still contained nitrogen. In these latter examples, the ring system is apparently cleaved in a manner analogous to the sequence of events triggered by methyl iodide. A reasonable hypothesis is that N-oxide formation occurs initially at the 2α-nitrogen atom; if the resulting N-oxide is endowed with appreciable stability, the remaining nitrogen is subsequently oxidized and the methylenethiete dioxide ultimately formed. If the intermediate mono-N-oxide is prone to cleavage in order to relieve the strain inherent in the four-membered ring, then the desired unsaturated heterocycles are not produced.

In summary, the synthesis of the first derivatives of the highly strained methylenethiete dioxide system has been achieved. It is apparent that the stability of this group of heterocycles is markedly dependent upon substitution, particularly phenyl substitution. In this respect, a favorable comparison with the properties of methylenecyclobutenes can be seen.[9,10] Methylenethiete dioxides now join thiirene dioxides[21] in the growing list of strained and reactive tetravalent sulfur heterocycles which have been recently synthesized or recognized as reaction intermediates.

Experimental Section[22]

1-[(9,10-Dihydro-9,10-ethanoanthracen-11-ylidene)methyl]-pyrrolidine (7).—A solution of 150.0 g (0.64 mol) of 9,10-dihydro-9,10-ethanoanthracene-11-carboxaldehyde (**6**)[23] and 58.0 g (0.96 mol) of pyrrolidine in 550 ml of toluene was heated under a Dean–Stark trap at reflux for 2 hr. 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 118–120°. Recrystallization from ether yielded flakes of **7**: mp 125–127°; $\lambda_{\max}^{CCl_4}$ 6.02 μ (>C=C–N<); $\tau_{TMS}^{CDCl_3}$ 8.26–8.56 (complex pattern, 4 H, –CH₂– of pyrrolidino group), 7.48 and 7.43 (merging doublets, J = 2.5 Hz, 2 H, –CH₂–C=C), 6.86–7.19 (complex pattern, 4 H, (–CH₂–)₂N– of pyrrolidino group), 5.66 (triplet, J = 2.5 Hz, 1 H, >CH–CH₂–), 5.51 (singlet, 1 H, >CH–C=CH–N<), 3.83 (broad singlet, 1 H, vinyl proton), and 2.46–3.06 (complex pattern, 8 H, aromatic ring protons).

Anal. Calcd for $C_{21}H_{21}N$: C, 87.76; H, 7.37. Found: C, 87.41; H, 7.30.

1-(9,10-Dihydrospiro[9,10-ethanoanthracene-11,2′-thietan]-3′-yl)pyrrolidine S,S-Dioxide (8).—A stirred solution of 90.0 g (0.314 mol) of **7** and 33.0 g (0.327 mol) 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 mol) of methanesulfonyl chloride in 120 ml of the same solvent during 45 min. Upon completion of the addition, the mixture was allowed to warm slowly to room temperature and was stirred at that temperature for 6 hr. Filtration of the slurry 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 232–233° dec. The reaction 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 192–194° dec. The total yield of crude **8** was 99.0 g (86.1%). One recrystallization of the combined solids from acetone–methanol gave 85.0 g (74.1%) of colorless **8**, mp 237–238° dec. An analytical sample was obtained from acetone as fine white crystals: mp 246.5° dec; $\lambda_{\max}^{Nujol}$ 7.70 and 8.80 μ (–SO₂–). The compound was too insoluble in organic solvents for useful nmr studies.

Anal. Calcd for $C_{22}H_{23}NO_2S$: C, 72.03; H, 6.34; S, 8.77. Found: C, 72.29; H, 6.32; S, 8.71.

9,10-Dihydrospiro[9,10-ethanoanthracene-11,2′[2H]-thiete] 1′,1′-Dioxide (9).—The methiodide of **8** 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 was reutilized in the methiodide preparation. The methiodide was not purified for analysis and was used directly for the next reaction.

A stirred slurry of 10.0 g (0.019 mol) of this methiodide, *ca.* 5 g (0.022 mol) of freshly prepared silver oxide, and 600 of water was refluxed for 2 hr. A reaction was evidenced by the presence of free amine and a color change from brown to black in the reaction vessel. The mixture was cooled and the solid was filtered and extracted with chloroform. The chloroform solution was dried and filtered through Celite to afford, after removal of the

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[20] $\lambda_{\max}$ 328 mμ (ε 41,000); see R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, Spectrum No. 129; E. A. Braude, *Ann. Rept. Progr. Chem.* (Chem. Soc. London), **42**, 105 (1945).

[21] (a) L. A. Carpino and L. V. McAdams, III, *J. Amer. Chem. Soc.*, **87**, 5804 (1965); (b) L. A. Carpino and R. H. Rynbrandt, *ibid.*, **88**, 5682 (1966); (c) see also L. A. Paquette and L. S. Wittenbrook, *Chem. Commun.*, 471 (1966); L. A. Paquette and L. S. Wittenbrook, *J. Amer. Chem. Soc.*, **89**, 4483 (1967); L. A. Paquette, L. S. Wittenbrook, and V. V. Kane, *ibid.*, **89**, 4487 (1967).

[22] Melting points were determined with a Thomas–Hoover melting point apparatus and are corrected. Infrared spectra were recorded with a Perkin-Elmer Infracord Model 137 spectrometer fitted with sodium chloride prisms. Ultraviolet spectra were determined with a Cary 14 recording spectrometer. Nuclear magnetic resonance spectra were obtained with a Varian A-60 spectrometer purchased with funds made available through the National Science Foundation. The mass spectrum was measured with an AEI MS-9 mass spectrometer at an ionizing energy of 70 eV. The microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

[23] F. Weiss and R. Rusch, *Bull. Soc. Chim. Fr.*, 550 (1964).

chloroform, a light brown solid. Recrystallization of this solid from acetone gave 4.95 g (88.7%) of **9**, mp 220–222° dec. An analytical sample was obtained from acetone: mp 226–228° dec; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 7.69 and 8.65 μ (–SO$_2$–); $\tau_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 8.04 and 7.30 [AB quartet (further split by J = 2.5 Hz), J = 14.0 Hz, 2 H, –CH$_2$–], 5.59 (triplet, J = 2.5 Hz, 1 H, >CH–CH$_2$–), 5.24 (singlet, 1 H, >CH–C$\lessdot$), 3.59 (doublet, J = 4.0 Hz, 1 H, non-α-sulfonyl vinyl proton), 3.32 (doublet, J = 4.0 Hz, 1 H, α-sulfonyl vinyl proton), and 2.42–2.97 (complex pattern, 8 H, aromatic ring protons).

Anal. Calcd for $C_{18}H_{14}O_2S$: C, 73.44; H, 4.79; S, 10.87. Found: C, 73.60; H, 4.89; S, 11.00.

1-(9,10-Dihydro-4′-phenylspiro[9,10-ethanoanthracene-11,2′-thietan]-3′-yl)pyrrolidine S,S-Dioxide (10).—To a rapidly stirred solution of 26.0 g (0.091 mol) of **7** and 9.5 g (0.094 mol) of triethylamine in 150 ml of dry tetrahydrofuran cooled to −10° was added dropwise under a nitrogen atmosphere during 30 min a solution of 17.5 g (0.092 mol) of phenylmethanesulfonyl chloride in 75 ml of the same solvent. After the addition, the mixture was warmed to room temperature and stirred for 6 hr. The triethylamine hydrochloride[24] 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 **10** as a light brown solid, mp 178–180° dec (second crop, 4.70 g, mp 165–177° dec, total yield 81.8%). An analytical sample was obtained from acetone–methanol: mp 184–185° dec; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 7.65, 8.70, and 9.00 μ (–SO$_2$–); $\tau_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 8.25–9.00 (multiplet with a superimposed singlet at ~8.9, 8 H, pyrrolidino group), 7.24 and 7.19 (merging doublets, J = 2.5 Hz, 2 H, >CH–CH$_2$–C$\lessdot$), 6.40 (doublet, J = 10.0 Hz, 1 H, >N–CH<), 5.50 (triplet, J = 2.5 Hz, 1 H, >CH–CH$_2$–), 5.00 (singlet, 1 H, >CH–C$\lessdot$), 4.58 (doublet, J = 10.0 Hz, 1 H, α-sulfonyl proton), and 2.28–2.98 (complex pattern, 13 H, aromatic ring protons).

Anal. Calcd for $C_{28}H_{27}NO_2S$: 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-Dihydro-4′-phenylspiro[9,10-ethanoanthracene-11,2′[2H]-thiete] 1′,1′-Dioxide (11).—A stirred mixture of **10** (12.0 g, 0.027 mol) in 100 ml of glacial acetic acid and 100 ml of acetic anhydride was treated dropwise during 15 min at −10° with 18.0 g (0.16 mol) of 30% hydrogen peroxide solution. The homogeneous reaction mixture was warmed to room temperature and stirred for 18 hr during which time 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 **11**, mp 240–242° dec. An analytical sample was obtained from acetone–methanol: mp 250–251° dec; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 7.69 and 8.71 μ (–SO$_2$–); $\tau_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.16 (singlet, 1 H, >CH–C$\lessdot$), 3.62 (singlet, 1 H, vinyl proton), and 2.50–2.95 (complex pattern, 13 H, aromatic ring protons).

Anal. Calcd for $C_{24}H_{18}O_2S$: 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′-thiethane] 1′,1′-Dioxide (12).—A mixture of 6.0 g (0.02 mol) of **9**, 250 ml of acetone, and 1.0 g of 10% palladium on carbon was shaken under 50 psig of hydrogen for 25 hr at room temperature. The catalyst was filtered, and the filtrate was evaporated to give a colorless solid. Recrystallization from methanol gave 5.50 g (91.3%) of **12**, mp 207–208°. Pure **12** was obtained from methanol: mp 207.5–208.5° (slight coloration); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 7.62, 8.63 and 8.85 μ (–SO$_2$–); $\tau_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 7.72–8.72 [complex pattern, 3 H, >CH–CH$_2$–C$\lessdot$ (one such proton) and –CH$_2$–CH$_2$–SO$_2$–], 7.17 [low field portion of an AB quartet (further split by J = 2.5 Hz), J = 14.0 Hz, 1 H, >CH–CH$_2$-C$\lessdot$ (one such proton)], 6.29 (doublet of triplets, J = 9.0 and 2.5 Hz, 2 H, α-sulfonyl protons), 5.63 (multiplet, 1 H, >CH–CH$_2$–), 5.22 (singlet, 1 H, >CH–C$\lessdot$), and 2.41–3.09 (complex pattern, 8 H, aromatic ring protons).

Anal. Calcd for $C_{18}H_{16}O_2S$: 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-dimethylaminomethylthietane 1,1-Dioxide (13) with Methyl Iodide.—Addition of 4.5 g (0.032 mol) of methyl iodide to a stirred solution of 3.0 g (0.0105 mol) of **13** 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 1 day during which time there precipitated 1.7 g (40.8% based on pure **15**) of a yellow crystalline solid, mp 204–205° dec. Recrystallization of this material from aqueous methanol yielded pure **2-phenyl-4-dimethylaminomethyl-2-thiete 1,1-dioxide methiodide monohydrate (15)** as a colorless highly crystalline solid: mp 204–205° dec; $\lambda_{\max}^{\mathrm{Nujol}}$ 2.90 (H$_2$O) and 7.55 and 8.85 μ (–SO$_2$–); $\lambda_{\max}^{\mathrm{EtOH}}$ 266 mμ (ϵ 8080). Examination of the filtrates afforded tetramethylammonium iodide, mp >250°.

Anal. Calcd for $C_{13}H_{18}INO_2S \cdot H_2O$: 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 **15** 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 (16)**, mp 101–103° from carbon tetrachloride (lit.[8i] mp 102–103°).

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 (17)** upon trituration with ether: mp 220–221° (methanol); $\lambda_{\max}^{\mathrm{Nujol}}$ 2.90 (H$_2$O), 6.10 (–C=C–N<), 7.70, and 8.90 μ (–SO$_2$–); $\lambda_{\max}^{\mathrm{EtOH}}$ 2.47 mμ (ϵ 14,140), 266 sh (10,450) and end absorption.

Anal. Calcd for $C_{15}H_{25}IN_2O_2S \cdot H_2O$: 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.

Unequivocal Synthesis of 17.—A cooled (−10°) solution of 0.02 g (0.08 mol) of **16** in 5 ml of dry tetrahydrofuran was treated with excess dimethylamine. After remaining at 0° for 1 day, the mixture was concentrated to give an oil which was immediately treated with methyl iodide in refluxing methanol solution for 2 hr. On cooling, there was deposited 0.03 g (84.0%) of a crystalline material, mp 220–221° (methanol), identical in all respects with **17**.

Hofmann Degradation of 15.—A solution of 6.45 g (0.016 mol based on pure **15**) of the mixture of **15** and tetramethylammonium iodide in hot water was passed through a column of Amberlite IRA-400 ion-exchange resin (hydroxide form). The total eluate was concentrated to *ca.* 50 ml *in vacuo* and extracted with chloroform to yield 1.7 g (46.1% based on pure **15**) of an oily crystalline solid. Recrystallization of this material from ether–petroleum ether (bp 60–80°) gave rodlike crystals of **2-(benzylsulfonyl)-N,N-dimethylethylamine (18)**, mp 69–70° (lit.[8i] mp 68–69°).

Anal. Calcd for $C_{11}H_{17}NO_2S$: 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-(α-Dimethylaminoethyl)-3-dimethylaminothietane 1,1-Dioxide (14) with Methyl Iodide.—Addition of 10.0 g (0.07 mol) of methyl iodide to a solution of 5.0 g (0.022 mol) of **14** 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. This solid [5.5 g (67.1%), mp 168–169° dec] was filtered and the filtrate was saved. All attempts to recrystallize this material from aqueous methanol–ether gave poor (10%) recovery of the solid, mp 173–175° dec. Analysis of the unpurified material for iodine identified it as the monomethiodide **19**.

Anal. Calcd for $C_{10}H_{23}IN_2O_2S$: 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 with 1-dimethylamino-3-thia-1,4-hexadiene 3,3-dioxide (**20**). The crude oil was hydrogenated over 10% palladium on carbon and a methiodide was prepared from the hydrogenated material, mp 166° (lit.[8i] mp 166° dec).

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

Attempted Hofmann Degradation of 19.—A solution of 4.0 g (0.011 mol) of **19** in hot water was passed through a column of Amberlite IRA-400 ion-exchange resin (hydroxide 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 **14** (with the exception that its infrared spectrum displayed a medium intensity absorption at 6.1 μ due to small amounts of an enamine impurity). A methanol solution of this material gave on reaction with methyl iodide the above methiodide (**19**), mp 165–166° dec, in good yield.

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[24] 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).

Hofmann Degradation of 18.—The methiodide salt of **18** was prepared with methyl iodide in refluxing methanol in 93.4% yield, mp 212–213° dec (from aqueous methanol).

A solution of 10.0 g (0.027 mol) of this methiodide (**24**) in hot water was passed through a column of Amberlite IRA-400 ion exchange resin (hydroxide form). The total eluate was concentrated *in vacuo* and extracted with chloroform to yield 2.3 g (43.4%) of colorless solid. Recrystallization from ethyl acetate–petroleum ether gave flakes of 2-(benzylsulfonyl)ethanol (**25**): mp 74° (lit.[25] mp 97°, needles from water); $\lambda_{max}^{CHCl_3}$ 2.90 (–OH) and 7.60 and 8.96 μ (–SO_2–); $\tau_{TMS}^{CHCl_3}$ 6.98 (triplet, J = 5.5 Hz, 2 H, –$SO_2CH_2CH_2$–), 6.80 (singlet, 1 H, –CH_2OH), 6.05 (triplet, J = 5.5 Hz, 2 H, –CH_2OH), 5.70 (singlet, 2 H, benzylic protons), and 2.67 (singlet, 5 H, phenyl group).

Anal. Calcd for $C_9H_{12}O_3S$: C, 53.98; H, 6.03; S, 16.02. Found: C, 54.14; H, 6.05; S, 15.71.

2-Methylene-4-phenyl-2H-thiete 1,1-Dioxide (**26**).—A solution of **13** (7.0 g, 0.025 mol) in 15 ml of glacial acetic acid and 15 ml of acetic anhydride contained in a 100-ml, round-bottomed flask equipped with a magnetic stirring bar and cooled to −10° was treated dropwise with stirring during 10 min with 14.0 g (0.123 mol) of 30% hydrogen peroxide. The reaction mixture was stirred at 0° for an additional 30 min and at room temperature for 17 hr, 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 hr 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 83–85° dec.[26] Rapid recrystallization from ether–petroleum ether gave pure **26** as a colorless, highly crystalline solid: mp 86–88° dec; λ_{max}^{Nujol} 7.66, 8.40, 8.67, and 8.90 μ (–SO_2–); λ_{max}^{ether} 291 mμ (ϵ 33,400); $\tau_{TMS}^{CDCl_3}$ 2.53 (singlet, 6 H, phenyl group and styrene proton), 4.45 (doublet of doublets, J = 4.0 and 1.0 Hz, 1 H, methylene proton), and 4.66 (doublet, J = 4.0 Hz, 1 H, methylene proton).

Anal. Calcd for $C_{10}H_8O_2S$: C, 62.48; H, 4.19; S, 16.68. Found: C 62.34; H, 4.47; S, 16.34.

2-Phenyl-3-(1-piperidino)-4-(1-piperidinophenylmethyl)thietane 1,1-Dioxide (**29**).—To a rapidly stirred solution of 18.6 g (0.065 mol) of **28**[27] and 6.8 g (0.067 mol) 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 mol) of phenylmethanesulfonyl 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 hr. The triethylamine hydrochloride[24] was filtered and the filtrate was evaporated to give 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 **29** as a light brown solid, mp 156–157°. Further purification from ether gave pure **29**: mp 161–162°; $\lambda_{max}^{CCl_4}$ 7.59, 8.56, 8.84, and 9.06 μ (–SO_2–); $\tau_{TMS}^{CDCl_3}$ 8.57 (multiplet, 12 H, –CH_2– of piperidino groups), 7.22–7.83 [multiplet, 8 H, (–CH_2–)$_2$-N– of piperidino groups], 6.32 (broad triplet, J = 8.0 Hz, 1 H, >CH–N<), 5.77 (broad doublet, J = 11.0 Hz, C_6H_5–CH–N<), 5.00 (complex pattern, 1 H, nonbenzylic α-sulfonyl proton), 4.62 (broad doublet, J = 8.0 Hz, 1 H, benzylic α-sulfonyl proton), and 2.70 (singlet, 10 H, phenyl groups).

Anal. Calcd for $C_{26}H_{34}N_2O_2S$: 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 **29**. Recrystallization of this material from ether afforded 3.45 g (21.8%) of colorless flakes, mp 125–127°. Further purification from carbon tetrachloride gave pure 1-(benzylsulfonyl)piperidine (**30**), mp 137° (lit.[28] mp 136–138°).

Further elution of the column with chloroform–ether (1:1) gave a brown oil which upon trituration with ether afforded 0.5 g (2.86%) of a brown crystalline solid, mp 86–88°. Recrystallization from ether gave analytically pure 2-(1-piperidino)-1-phenylmethanesulfonylethylene (**31**): mp 91–92°: $\lambda_{max}^{CCl_4}$ 6.16 (C═C–N<), 7.66 and 9.00 μ –SO_2–); $\tau_{TMS}^{CDCl_3}$ 8.47 (multiplet, 6 H, –CH_2– of piperidino group), 6.96 (multiplet, 4 H, (–CH_2–)N– of piperidino group), 5.83 (broad singlet, 2 H, benzylic protons), 5.32 and 3.30 (doublets, J = 13.0 Hz, 1 H each, vinyl protons), and 2.67 (singlet, 5 H, 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; H, 5.17.

2-Benzylidene-4-phenyl-2H-thiete 1,1-Dioxide (**32**).—A stirred mixture of **29** (5.0 g, 11.4 mmol) in 20 ml of glacial acetic acid and 15 ml of acetic anhydride was treated dropwise during 5 min at −10° with 6.0 g (0.053 mol) of 30% hydrogen peroxide. The reaction mixture was permitted to warm to room temperature and was stirred for 19 hr, again cooled in ice, and neutralized with a 25% sodium hydroxide solution. The yellow oily solid which precipitated during neutralization was extracted with chloroform and the organic solution was 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 209–210° 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 208–210° dec. Recrystallization of the combined solids from tetrahydrofuran–petroleum ether afforded pure **32**: mp 212–213° dec; $\lambda_{max}^{CHCl_3}$ 6.02 (>C═C<), 7.63 and 8.70 μ (–SO_2–); $\lambda_{max}^{CHCl_3}$ 366 (sh) mμ (ϵ 23,450), 349 (40,200), 337 (38,800), and 240 (12,850); $\tau_{TMS}^{CDCl_3}$ 3.49 (singlet, 1 H, exocyclic styrene proton), 2.31–2.79 (broad singlet, 11 H, phenyl groups and ring proton).

Anal. Calcd for $C_{16}H_{12}O_2S$: C, 71.61; H, 4.51; S, 11.95. Found: C, 71.39; H, 4.24; S, 12.26.

2-(1-Piperidinomethyl)-3-(1-piperidino)thietane 1,1-Dioxide (**34**).—A solution of 10.00 g (0.099 mol) of triethylamine and 20.0 g (0.096 mol) of 1,3-bis(1-piperidino)-1-propene (**33**)[27] in 50 ml of dry tetrahydrofuran was treated in the usual manner with 11.0 g (0.096 mol) of methanesulfonyl chloride in 50 ml of the same solvent. 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 62–64° (second crop, 2.5 g, mp 58–60°, total yield 67.3%). Recrystallization from ether–petroleum ether gave pure **34**: mp 67–68°; $\lambda_{max}^{CCl_4}$ 7.54, 8.39, 8.78, and 9.07 μ (–SO_2–); $\tau_{TMS}^{CDCl_3}$ 8.50 (broad singlet, 12 H, –CH_2– or piperidino groups), 7.58 [multiplet, 8 H, (–CH_2–)$_2$N– of piperidino groups], 6.92–7.28 [complex pattern (five sharp lines), 3 H, –CH_2N< and >CHN<], 6.08 (doublet, J = 8.0 Hz, 2 H, –CH_2SO_2–), and 5.45–5.85 (multiplet, 1 H, >$CHSO_2$–).

Anal. Calcd for $C_{14}H_{26}N_2O_2S$: 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 concentration of the above mother liquors on neutral alumina gave, on elution of the column with ether, a small quantity of additional **34**, mp 67–68°. Elution with petroleum ether–ether (1:1) gave a mixture of **34** and 1-(methylsulfonyl)piperidine (characteristic $\lambda_{max}^{CCl_4}$ 10.4 μ for sulfonamide but not characterized any further), mp 40–55°. Further elution with chloroform–ether (1:9) gave colored oils which displayed intense absorption in the infrared spectrum at 6.10 μ.

2-(1-Piperidinophenylmethyl)-3-(1-piperidino)thietane 1,1-Dioxide (**37**).—A stirred solution of 20.0 g (0.07 mol) of **28**[27] and 7.3 g (0.07 mol) 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 mol) 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 8 hr. The mixture was filtered to remove the precipitated triethylamine hydrochloride, and evaporation of the filtrate afforded a brown viscous oil. The oil became crystalline after standing at room temperature for 1 day. The partially crystalline mixture was mixed with ether and cooled to 0° to afford 14.45 g of yellow solid, mp 125–127°. Further recrystallization of this material from ether–petroleum ether gave pure **37** as a colorless fluffy solid: mp 129–130°; $\lambda_{max}^{CCl_4}$ 7.50 8.40, and

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(25) E. Fromm and H. Jörg, *Chem. Ber.*, **58B**, 304 (1925).

(26) The combined eluates were concentrated to a small volume and the solid was crystallized from the solution. Petroleum ether was added to cause further crystallization and the material was removed by filtration. In this way, pure **26** could be isolated and its decomposition minimized.

(27) C. Mannich, K. Handke, and K. Roth, *Chem. Ber.*, **69**, 2112 (1936).

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

9.10 μ (-SO_2-); $\tau_{TMS}^{CDCl_3}$ 8.11–8.92 (multiplet, 12 H, -CH_2- of piperidino groups), 7.25–8.08 [multiplet, 8 H, (-CH_2-)$_2$N- of piperidino groups], 6.56 (broad triplet, J = 6.0 Hz, H, >CHN<, 6.07 and 5.88 [singlet and doublet (J = 3.0 Hz), respectively, 3 H, -CH_2-SO_2- and C_6H_5-CH-N<, respectively], 4.93 and 5.13 (doublet of doublets, J = 12.0 and 6.0 Hz, 1 H, >CH-SO_2-), and 2.75 (singlet, 5 H, phenyl group).

Anal. Calcd for $C_{20}H_{30}N_2O_2S$: 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 were combined and chromatographed on neutral alumina. The only material isolated was **37** and the total weight obtained by direct crystallization and chromatography was 15.5 g (61.0%).

Registry No.—**7**, 16808-51-8; **8**, 16808-52-9; **9**, 16808-53-0; **10**, 16808-54-1; **11**, 16808-55-2; **12**, 16808-56-3; **15**, 16808-57-4; **17**, 16808-58-5; **19**, 16793-41-2; **25**, 16793-42-3; **26**, 16793-43-4; **29**, 16791-06-3; **31**, 16790-87-7; **32**, 16790-88-8; **34**, 16790-89-9; **37**, 16790-90-2.

Unsaturated Heterocyclic Systems. XLI. Selected Reactions of 2-Methylenethiete 1,1-Dioxides[1,2]

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Received March 14, 1968

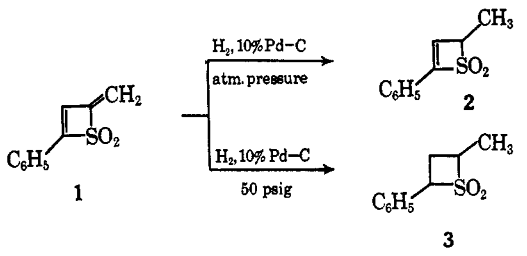
2-Methylene-4-phenyl-2H-thiete 1,1-dioxide (1) could be hydrogenated in two distinct stages to a dihydro and tetrahydro derivative, respectively. This strained sulfone (1) was also found to undergo ready Michael reaction with dimethylamine. When exposed to 1,3-diphenylisobenzofuran, both 1 and its phenyl congener 7 gave rise to Diels–Alder adducts. In each instance, a single adduct was formed. The stereochemistry of the adducts and the stereospecificity of the processes have been assigned on the basis of spectral data and steric considerations. Irradiation of 1 in diethyl ether leads to the formation of a lone (2 + 2π) dimer. Spectral analysis and dipole moment data establish the structure of the dimer as that of the *trans*-1,2-cyclobutane derivative 14. The probable mechanistic pathways for the stereoselective photocycloaddition are discussed.

The preceding paper describes the first synthesis of highly unsaturated and reactive methylenethiete dioxides.[1] The "cross conjugation" of the butadiene chromophore with the sulfonyl group in such molecules, when considered together with the relatively high degree of ring strain, makes the system a particularly suitable subject for experimental evaluation of chemical reactivity, bond hybridization, and involvement of d orbitals at the heteroatom. Although the geometrical parameters (*i.e.*, interorbital and internuclear angles) for a molecule such as 1 have not yet been evaluated, a number of modified physical and chemical properties can be expected because of varied hybridization at the vinylic carbon atoms. Although the four carbon centers fall roughly into two sets of similarly hybridized atoms, their relative reactivities were anticipated to differ significantly and to lend to the molecule properties which are not normally seen in unstrained α,β-unsaturated sulfones or thiete dioxides. The present paper describes the chemical properties of 1 and 7, of which reactions have been selected in an attempt to provide insight into the reactivity differences of the exocyclic and endocyclic double bonds.[4]

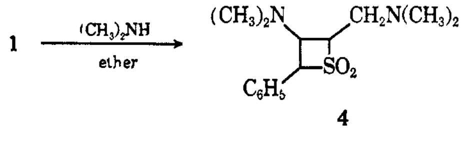
Results and Discussion

When a dilute solution of 1 was hydrogenated at atmospheric pressure over 10% palladium on charcoal, there resulted a rapid uptake of hydrogen which ceased before 1 equiv was consumed. The resulting dihydro derivative was easily identified as 2-methyl-4-phenyl-2H-thiete 1,1-dioxide (2) principally on the basis of its nmr spectrum (see Experimental Section). When the pressure of hydrogen was increased to 50 psig and the catalytic hydrogenation allowed to proceed for 58 hr, thietane dioxide 3 was formed in greater than 90% yield (Scheme I).

SCHEME I



Exposure of 1 to a cold ethereal solution of dimethylamine (eq 1) led to the formation of 2-dimethylaminomethyl-3-dimethylamino-4-phenylthietane 1,1-dioxide (4), mp 76–78°, isomeric with the sulfone of identical gross structure, mp 91–93°,[5] utilized in the preparation of 1.[1] The stereochemical relationship of the two isomers could not be established with certainty owing to unresolvable complexities of certain nmr absorptions and the lack of appropriate model compounds.



(1)

Reaction of equimolar quantities of 1 and 1,3-diphenylisobenzofuran (5) in refluxing benzene solu-

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[1] For part XL of this series, see L. A. Paquette, M. Rosen, and H. Stucki, 33, 3020 (1968).

[2] This work was generously supported by Grant GP-5977 from the National Science Foundation.

[3] Alfred P. Sloan Foundation Research Fellow.

[4] Our intended goal was somewhat beclouded by the fact that, of the two known and available methylenethiete dioxides (1 and 7), only 7 possesses two identically substituted (except for the ring) double bonds. However, as will be seen, the chemical behavior of 1 is sufficiently diagnostic of the divergence in reactivity between the two sites of unsaturation to be of interpretive value.

[5] L. A. Paquette and M. Rosen, *J. Amer. Chem. Soc.*, 89, 4102 (1967).