Dehydration of 37.—A mixture of 500 mg (1.83 mmol) of **37** and 15 ml of polyphosphoric acid was heated on a steam bath for 3 hr with occasional stirring. After standing overnight at room temperature, this mixture was added to 80 ml of ice water. The organic product was extracted with four 75-ml portions of chloroform and the combined organic layers were washed with water. The solution was dried and evaporated, and the residue was chromatographed on 10 g of alumina. Elution with ether–hexane (1:1) gave 387 mg (83%) of **38**, mp 138.5–139° (from benzene–hexane); ir $\nu_{\max}^{\mathrm{CHCl_3}}$ 1690 cm^{-1}; $\lambda_{\max}^{\mathrm{C_2H_5OH}}$ 261 (ϵ 4500), 269 (ϵ 5600), 279 (ϵ 5600), and 289 mμ (ϵ 3400); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 3.00 and 3.62 (centrosymmetric A_2B_2 pattern, 2 H each), 3.72 (s, 3 H), and 7.46 (characteristic m for 2,3-disubstituted naphthalene).

Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.40; H, 6.71; N, 5.45.

Addition of 2,5-Dimethyl-4,5-diphenylcyclopentadienone to 1H-Azepines.—A solution of 3.30 g (20.0 mmol) of 1-carbethoxyazepine and 5.22 g (10.0 mmol) of **41**[43] in 40 ml of benzene was refluxed under nitrogen with magnetic stirring for 20 hr. The solvent was evaporated under reduced pressure and the residue was chromatographed carefully on Florisil. Elution with 2% ether in hexane gave 3.0 g of recovered **41**, mp 186–187° dec. Elution with 5% ether in hexane gave 1.45 g (41.4%) of **42**, mp 140–141° dec (from ether). Elution with 10% ether in hexane and 25% ether in hexane gave 1.75 g (50%) of **43**, mp 146–147° (from ether–hexane).

42 had $\nu_{\max}^{\mathrm{Nujol}}$ 1765, 1725, and 1680 cm^{-1}; uv $\lambda_{\max}^{\mathrm{C_2H_5OH}}$ 251 (ϵ 11,800) and 281 mμ (ϵ 15,850); for nmr, see text.

Anal. Calcd for $C_{28}H_{27}NO_3$: C, 79.03; H, 6.40; N, 3.29 Found: C, 78.84; H, 6.24; N, 3.04.

43 had ir $\nu_{\max}^{\mathrm{Nujol}}$ 1670, 1665, and 1460 cm^{-1}; uv $\lambda_{\max}^{\mathrm{C_2H_5OH}}$ 227 (ϵ 27,850) and 270 sh mμ (ϵ 6700); for nmr, see text.

Anal. Calcd for $C_{28}H_{27}NO_3$: C, 79.03; H, 6.40; N, 3.29. Found: C, 78,75; H, 6.04; N, 3.06.

From 5.2 g (10 mmol) of **41** and 3.42 g (20 mmol) of N-methanesulfonylazepine in 40 ml of benzene (reflux, 20 hr), there was obtained 1.2 g of recovered **41** and 2.74 g (42%) of **45**, fine white needles from methylene chloride–pentane, mp 158° dec; ir $\nu_{\max}^{\mathrm{CHCl_3}}$ 1760, 1350, and 1155 cm^{-1}; uv $\lambda_{\max}^{\mathrm{CH_2Cl_2}}$ 222 sh (ϵ 20,700) and 253 sh mμ (ϵ 9200); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 1.39 (s, 3 H), 2.90 (s, 3 H), *ca.* 2.90 (m, 2 H), 5.00 (br d, J = 10.5 Hz, 2 H), 6.70–7.2 (m, 12 H, aromatic and α-vinyl protons).

Anal. Calcd for $C_{26}H_{25}NO_3S$: C, 72.37; H, 5.84; N, 3.25. Found: C, 72.35; H, 5.89; N, 3.14.

Registry No.—**19,** 20678-91-5; **25,** 20629-04-3; **26,** 20629-05-4; **30,** 20629-06-5; **31,** 20629-07-6; **32,** 20629-08-7; **36a,** 20629-09-8; **36b,** 20629-10-1; **36c,** 20629-11-2; **36d,** 20678-92-6; **37,** 20629-12-3; **38,** 20629-13-4; **41,** 13360-84-4; **42,** 20629-15-6; **43,** 20629-16-7; **45,** 20629-17-8; N-acetylazepine, 20629-18-9; N-acetyl derivative of 1,2-iminocyclohex-4-ene, 20629-19-0.

Acknowledgment.—The authors wish to thank the National Institutes of Health and the Ciba Corporation for grants employed in the financial support of this research.

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[43] F. W. Gray, *J. Chem. Soc.*, **95**, 2131 (1909); C. F. H. Allen and J. A. Van Allan, *J. Amer. Chem. Soc.*, **64**, 1260 (1942).

Unsaturated Heterocyclic Systems. LVI. The Reaction of a Mesocyclic Dienamine with Sulfene[1]

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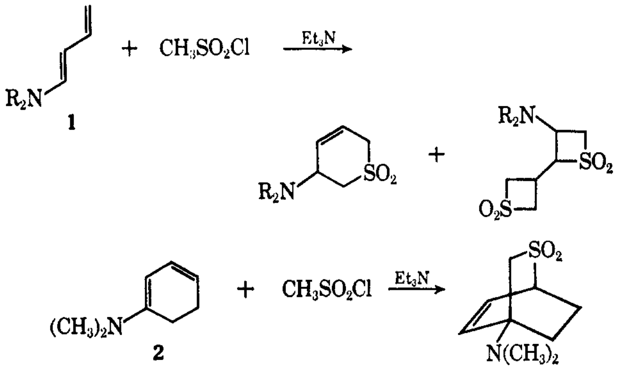
Reaction of 1-dimethylamino-1,3-cyclooctadiene (**3**) with sulfene, generated *in situ* from methanesulfonyl chloride and triethylamine, in tetrahydrofuran solution was found to yield seven crystalline sulfones after chromatographic work-up. The product composition was seen to be dependent upon temperature, rate of addition of the sulfonyl chloride, rate of elution from the chromatography column, and adsorbent. The structure of each of the adducts has been assigned on the basis of elemental analysis, spectral (particularly nmr) data, and chemical transformations in a number of instances. 3-Aminothietane dioxide **7** was shown to be the precursor of sulfones **8**, **9**, **10**, and **11**; the mechanisms of these transformations are presented. Pathways for the formation of **6** and **12** are also proposed. The particular role played by the medium-sized ring of **3** in these reactions is discussed.

Although a stable free sulfene remains to be isolated,[2] the transient generation of these reactive intermediates in the reaction of numerous alkyl, cycloalkyl, and aralkyl sulfonyl chlorides with tertiary amines has been widely accepted and has attracted much recent attention.[3–5] The chemical reactivity of sulfenes is characterized chiefly by their propensity for (2 + 2) cycloaddition to electron-rich double and triple bonds. With dienamines of type **1** and **2**, (4 + 2) cycloaddition is found to compete favorably with the formation of bithietane tetroxides.[5–7] In a significant number of instances, the sulfene–enamine condensation has been observed to produce open-chain products;[8] also, rearrangement products have been isolated from the reaction of sulfenes with certain 1,3-bis(dimethyl-



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[1] For the previous paper in this series, see L. A. Paquette, D. E. Kuhla, J. H. Barrett, and L. M. Leichter, *J. Org. Chem.*, **34**, 2888 (1969).

[2] For a more extensive discussion of this topic, see L. A. Paquette, J. P. Freeman, and R. W. Houser, *ibid.*, **34**, 2901 (1969).

[3] T. J. Wallace, *Quart. Rev.*, **20**, 67 (1966).

[4] G. Optiz, *Angew. Chem. Intern. Ed. Engl.*, **6**, 107 (1967).

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

[6] G. Opitz and F. Schweinsberg, *Angew. Chem.*, **77**, 811 (1965); *Angew. Chem. Intern. Ed. Engl.*, **4**, 786 (1965).

[7] G. Opitz and F. Schweinsberg, unpublished results noted in footnote 121 of ref 4.

[8] Consult, for example, (a) G. Opitz, H. Schempp, and H. Adolph, *Ann.*, **684**, 92 (1965); (b) J. J. Looker, *J. Org. Chem.*, **31**, 2973 (1966); A. M. Hamid and S. Trippett, *J. Chem. Soc., C*, 1612 (1968).

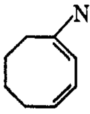
TABLE I

PRODUCT COMPOSITIONS IN THE CONDENSATION OF 1-DIMETHYLAMINO-1,3-CYCLOOCTADIENE WITH SULFENE

Conditions employed	CH_3SO_2Cl, equiv	Chromatog adsorbent	Yield, % 6	7	8	9	10	11	12
THF, −10°	1	Alumina	3.3		17.2			0.8	3.1
THF, −10°	2	Alumina	0.7		10.2	9.4		0.8	8.3
THF, −10°, heated briefly on steam bath with adsorbent prior to chromatography	1	Alumina			41.8			0.7	4.9
Same as above	2	Alumina			35.6			0.5	13.5
THF, −10°, sulfonyl chloride added over 3 hr instead of 30 min	1	Alumina	15.8		14.7				
THF, 25°	1	Alumina				2.4		5.6	
THF, −10°	2	Silica gel			8.9		34		3.3
THF, −10°	2	Florisil					33		7.5
Eluted immediately and rapidly with ether	2	Florisil		5.2			36.8		5.3

amino)-1-alkenes.[5] These apparent anomalies very likely reflect the intervention of zwitterions at some point along the reaction profile.

With this information as background, we set out to examine the addition of sulfene to a mesocyclic dienamine.[9] 1-Dimethylamino-1,3-cyclooctadiene (**3**) was selected for this purpose because of its ready availability.[10] An electron-rich medium-sized-ring diene such as **3** was expected to offer new insight into our limited knowledge of sulfene–dienamine interactions. Thus, the conjugated diene unit in **3** is considerably distorted from planarity, this twisting being enforced by the substantially lower energy of its "tub" conformation (**4**). As a result, transmission of electron density from the nitrogen atom at C-1 to the 4 position as in **5** can be expected to be reduced significantly relative to molecules such as **1** and **2** which can readily adopt planar conformations. Also, the geometry of medium-sized rings is such that substantial nonbonded steric compression between transannular groups exists, and this strain was expected to promote unprecedented reactions.



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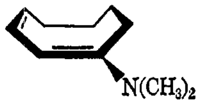

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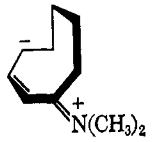

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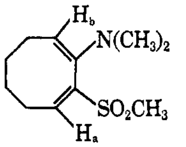
Results

In the generalized procedure, a solution of **3** in tetrahydrofuran containing 1–2 equiv of triethylamine was treated dropwise with a corresponding equivalence of methanesulfonyl chloride. The resulting viscous oils, when chromatographed on alumina, Florisil, or silica gel, afforded a total of seven crystalline sulfones. The yields of these products were found to be quite dependent upon the reaction temperature, the rate of addition of methanesulfonyl chloride, the rate of elution from the chromatography column, and the adsorbent employed. Table I summarizes the available data.

Structural Assignments.—Sulfone **6** was shown to be a monoaddition product by combustion analysis. This substance exhibited infrared bands at 1618 and 1635 cm^{-1}, indicative of an enamine function, and ultraviolet absorption in isooctane at 204 (ϵ 9900) and 286 mμ (ϵ 1350) due to extended conjugation. In agreement with the assigned formulation, the nmr spectrum diplayed a one-proton doublet of doublets (J = 9.3 and 7.3 Hz) at δ 7.00, a one-proton triplet (J = 7.9 Hz) at δ 4.90,[11] a three-proton singlet at δ 2.78 characteristic of a methanesulfonyl group, a six-proton singlet at δ 2.58 for the dimethylamino residue, and a complex multiplet (8H) in the δ 1.0–2.5 region. To eliminate from consideration structures similar to **6** in which the two vinyl protons were adjacent, the nmr spectrum was spin decoupled. Irradiation of H_a (δ 7.00) produced no change in the H_b pattern, and *vice versa*. In contrast, irradiation of the δ 2.0–2.1 absorption caused both H_a and H_b to appear as slightly broadened singlets. This combination of data agrees only with the 2-dimethylamino-3-methanesulfonyl-1,3-cyclooctadiene assignment.



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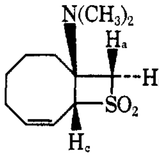

7

Sulfone **7** proved very elusive and was obtained only by rapid elution of the crude reaction mixture from a Florisil column. Its instability was further reflected in the fact that **7** was cleanly converted to **9** upon standing in chloroform solution at ambient temperatures for 2 days. Nmr studies in deuteriochloroform indicated, *inter alia*, the presence of two vinyl protons (multiplet centered at δ 5.83), a dimethylamino substituent (singlet of area 6 at δ 2.42), and four methylene groups (broad multiplet of area 8 at δ 1.1–2.3). Particularly revealing in this instance were the absorptions of the remaining three protons, which were characteristic of a thietane dioxide ring. Thus, the broad one-proton peak at δ 5.17 is properly shifted for the allylic α-sulfonyl environment (H_c), whereas doublets of doublets are seen for H_a (J = 14 and 3 Hz) and H_b

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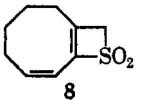
(9) "Mesocyclic" is herein employed as an alternative to "medium-sized ring" [N. J. Leonard, T. W. Milligan, and T. L. Brown, *J. Amer. Chem. Soc.*, **82**, 4075 (1960)].

(10) L. A. Paquette and R. W. Begland, *ibid.*, **88**, 4685 (1966).

(11) The vinyl proton of 1-cyano-2,3-diethyl-1,3-cyclooctadiene is seen as a triplet (J = 7.3 Hz) at δ 5.60: J. G. Atkinson, D. E. Ayer, G. Büchi, and E. W. Robb, *ibid.*, **85**, 2257 (1963).

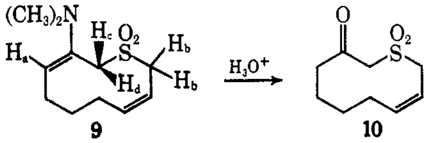
(J = 14 and 1 Hz). H_a (δ 4.32) is downfield shifted relative to H_b (δ 3.42) because of the paramagnetic shielding induced by the proximate *cis*-oriented nitrogen atom. The differences in the diagonal coupling constants (J_{AC} = 3 Hz; J_{BC} = 1 Hz) are in good agreement with values reported for cyclobutane derivatives.[12] From these data, it was clear that structure **7** represented a unique fit to the spectral parameters.

The structure of sulfone **8** was revealed from its elemental analysis, which indicated addition of sulfene ($CH_2{=}SO_2$) and loss of dimethylamine, its ultraviolet spectrum [λ_{max}^{EtOH} 246 mμ (ε 5860)], which denoted extended conjugation, and its nmr spectrum in carbon tetrachloride, which showed a multiplet of area 2 at δ 5.96 for the vinyl protons, a singlet at δ 4.20 for the two protons α to the sulfonyl group, a four-proton multiplet at δ 2.2–2.7 for the allylic hydrogens, and upfield absorption for the remaining four saturated protons.



8

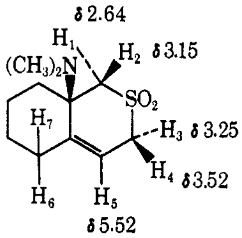
The elemental analysis of sulfone **9** indicated that this substance was isomeric with **7**; the previously mentioned rearrangement of **7** is therefore a true bond reorganization. This colorless solid exhibited pertinent infrared absorption (CCl_4) at 1637 cm^{-1} and an ultraviolet maximum (C_2H_5OH) at 237 mμ (ε 5770) strongly suggestive of the presence of an enamine chromophore. This conclusion was confirmed by acid hydrolysis of **9**, which gave a keto sulfone identical in all respects with **10**. The nmr spectrum of **9** consisted of a two-proton multiplet at δ 5.65 (–CH=CH–), a four-proton multiplet at δ 3.7–4.5 (H_a, 2 H_b, and H_c), and a peak of area 1 at δ 2.92 (H_d), in addition to a singlet (6 H) at δ 2.71 assignable to the dimethylamino group and a high field multiplet of area 6 due to the remaining methylene hydrogens. Dreiding models of **9** clearly show that the upfield shift of the H_d adsorption can be traced to its proximity to the shielding cone of the transannularly disposed double bond. Thus, it may be concluded that the conversion of **7** to **9** is the result of rupture of the bond common to the thietane and cyclooctene rings (see below).



9 **10**

Sulfone **10** was obtained only when the crude reaction mixture was chromatographed on Florisil or silica gel, apparently at the expense of **7** and **9**. Suspicion that **10** was the end product of (a) the rearrangement of **7** to **9** (see above) and (b) hydrolysis of the latter sulfone during the chromatographic procedure was confirmed by the finding that the action of dilute acid on **9** readily gave **10**. The presence of a carbonyl function was indicated by an intense infrared band at 1725 cm^{-1} and confirmed by the preparation of a 2,4-dinitrophenylhydrazone derivative. A molecular formula of $C_9H_{14}O_3S$ was derived from the elemental analysis. Again in this situation the nmr spectrum was most enlightening; the multiplet at δ 5.75 was assigned to the –CH=CH– group, the two-proton singlet at δ 4.21 to the methylene group positioned between the carbonyl and sulfonyl functions, and a doublet (J = 8 Hz) of area 2 at δ 3.80 to the allylic α-sulfonyl protons.[13] Two distinctly broader multiplets at δ 2.40–2.65 (2 H) and 1.60–2.35 (6 H) comprise the peaks expected for the remaining allylic and saturated $-CH_2-$ groups.

Monoaddition product **11** was obtained in very low yield. Its infrared spectrum lacked bands usually associated with enamine, carbonyl, and conjugated olefinic groups, and the ultraviolet spectrum was characterized only by end absorption. The 60-MHz spectrum of **11** established the presence of a lone vinyl proton, an α-sulfonyl methylene group, and a $=CH-CH_2SO_2-$ linkage.[13] Substantiation for the assigned structure was found in its spin-decoupled 100-MHz spectrum. On the basis of these measurements, this rearrangement product was deduced to possess a singly unsaturated sulfone-containing six-membered ring bearing a dimethylamino group at a ring juncture position. The various significant coupling constants were seen to be $J_{1,2}$ = 14.5 Hz; $J_{3,4}$ = 16.8 Hz; $J_{3,5}$ = 7.2 Hz; and $J_{4,5}$ = 2.6 Hz. In addition there was also spin–spin interaction (J = 4.3 Hz) between H-1 and H-3, resumably resulting from the W-plan arrangement of the intervening σ bonds.[14] Molecular models show that the nonidentical spin–spin coupling of H-3 and H-4 to H-5 are the result of widely differing dihedral angle relationships.[15] Finally, the H-5 absorption was seen as a doublet of quartets because allylic coupling to H-6 (J = 1.8 Hz) caused the unsymmetrical doublet of doublets pattern due to the X portion of the ABX system to be split further.



11

Sulfone **12** was the only bis addition product isolated. The bright yellow color of its crystals, an intense infrared band at 1545 cm^{-1}, and strong ultraviolet absorption [λ_{max}^{EtOH} 218 (ε 6580), 263 (ε 6580), and 352 mμ (ε 13,200)] suggested a highly conjugated chromophore. The nmr spectrum revealed the presence of a lone vinyl proton (singlet at δ 7.74), two methanesulfonyl groups (singlets of area 3 at δ 3.02 and 2.94), and a dimethylamino group (singlet at δ 3.30), in addition to eight

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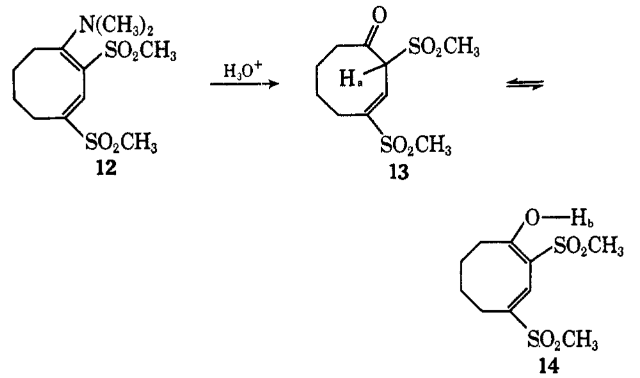
(12) (a) K. Griesbaum, W. Naegele, and G. G. Wanless, *J. Amer. Chem. Soc.*, **87**, 3151 (1965); (b) V. Georgian, L. Georgian, and A. V. Robertson, *Tetrahedron*, **19**, 1219 (1963).

(13) The assignments of chemical shifts given for **9**, **10**, and **11** have been correlated with those of a number of model compounds including, for example, the acyclic sulfones described by C. D. Broaddus, *J. Amer. Chem. Soc.*, **90**, 5504 (1968).

(14) For selected examples of this phenomenon, see J. Meinwald and A. Lewis, *ibid.*, **83**, 2769 (1964); J. Meinwald and Y. C. Meinwald, *ibid.*, **85**, 2514 (1963); K. B. Wiberg, B. R. Lowry, and B. J. Nist, *ibid.*, **84**, 1594 (1962); E. I. Snyder and B. Franzus, *ibid.*, **86**, 1166 (1964).

(15) Similar angular dependences of comparable magnitude have been noted; see, for instance, S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

protons at higher field. Hence this disulfone was considered to have a 1-dimethylamino-1,3-cyclooctadiene skeleton bearing methanesulfonyl groups at C-2 and C-4. Hydrolysis of **12** was found to produce a mixture of ketone **13** (30%) and enol **14** (70%). The infrared spectrum of this mixture exhibited a medium-intensity band at 1700 cm^{-1} for the keto form and strong absorption at 1603 cm^{-1} for the enol form. The nmr spectrum ($CDCl_3$) displayed a peak of intensity 0.3 H at δ 5.00 for H_a of **13** and a peak of area 0.7 at δ 10.61 for H_b of **14**. The predominance of enol form **14** is not unexpected in view of the behavior of the related carbomethoxy derivative.[10]



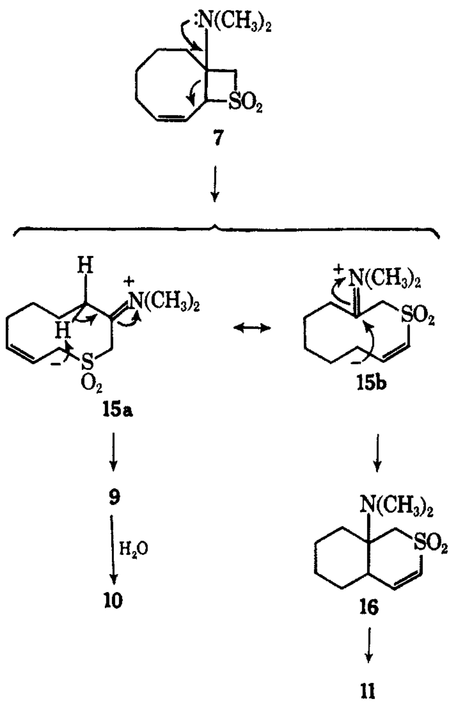
Mechanistic Considerations.—Earlier work has shown that 3-aminothietane dioxides are the customary end products of sulfene–enamine condensations.[3-5] However, in the present study, **7** was isolated only in one instance and in low yield. This observation can be reconciled with the instability of **7**, as noted by its relatively rapid conversion to **9** in chloroform solution at room temperature. When **7** is adsorbed on a chromatographic column packed with such stationary phases as alumina, silica gel, or Florisil, the onset of additional reactions is seen. In fact, only when the crude sulfene reaction mixture was rapidly eluted from a Florisil column to minimize contact time was the direct isolation of **7** possible (Table I).

β elimination of the elements of dimethylamine from **7** can account for the production of **8**. Because the proton which is abstracted is particularly strongly activated owing to its allylic and α-sulfonyl nature, this precedented transformation can be expected to be facile and is probably triggered by the triethylamine present in the sulfene reaction mixture.

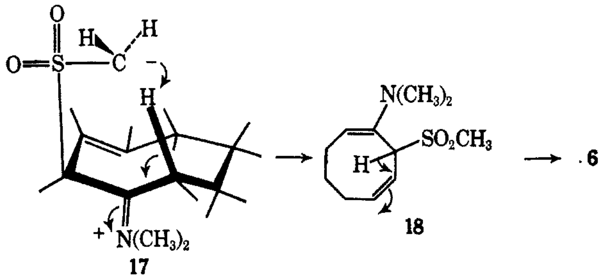
The mechanism that prevails in the rearrangement of **7** to **9** is visualized as due to ring opening of the thiabicyclo[6.2.0]decane system to give dipolar species **15** (Scheme I). The allylic delocalization accorded the α-sulfonyl carbanion upon cleavage of the central bond in **7** may perhaps provide the requisite driving force, although the possibility that relief of steric strain is also influential cannot be discounted. Transannular proton transfer *via* a six-centered transition state completes the passage to **9**.

It seemed likely that zwitterion **15** could also serve as a precursor to **11**. The principal feature of this change involves recyclization to form **16** (Scheme I) and base-catalyzed equilibration of **16** to its β,γ-unsaturated isomer (**11**). Although this suggested pathway may seem controvertible, the facts remain that **7** was tranformed into **9** and **11** when allowed to pass through a column of neutral alumina and that α,β-unsaturated sulfones are frequently less stable than their β,γ-unsaturated counterparts.[13,16]

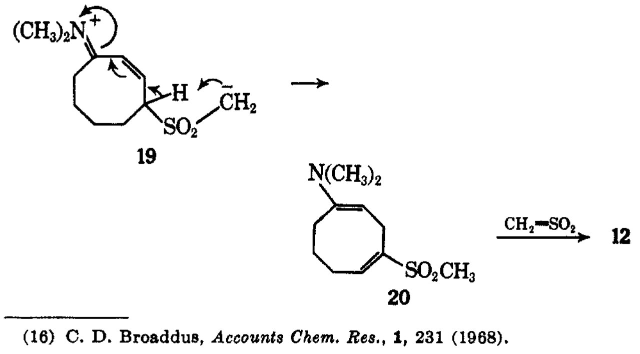
SCHEME I



The formation of **6** can be accommodated by a nonconcerted attack of sulfene at C-2 of the mesocyclic dienamine to produce zwitterion **17**. The carbanionic side chain in **17** can be positioned where it can abstract a proton α to the dimethyliminonium group (as shown) through a six-membered transition state. Isomerization of the double bond in the enamine thus formed (**18**) leads to **6**.



Disulfone **12** may be produced by stepwise bonding of sulfene to C-4 of the dienamine to afford **19**, proton



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(16) C. D. Broaddus, *Accounts Chem. Res.*, **1**, 231 (1968).

transfer in which leads to **20**. Repetition of this reaction sequence at C-2 in **20** gives rise to **12**.[17]

The present work shows that twisting of the π system of a dienamine out of planarity lessens the degree of sulfene bonding at C-4, very likely because of the diminution of nucleophilicity at that position. Furthermore, the isolation of **6** and **12** provides compelling evidence that sulfene reactions may, under certain circumstances, be nonconcerted.[18] Also, since sulfone **7** is the precursor of **8**, **9**, **10**, and **11**, the available evidence is consistent with the fact that 3-aminothietane dioxide formation is again kinetically preferred in the present instance.

Experimental Section

Melting points are corrected. The microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Infrared spectra were recorded with a Perkin-Elmer Model 237 spectrophotometer and ultraviolet spectra were determined with a Cary Model 14 instrument. The nmr spectra were determined with Varian A-60 and HA-100 spectrometers using tetramethylsilane as internal standard.

Reaction of 1-Dimethylamino-1,3-cyclooctadiene (3) with Sulfene.—In a typical experiment, to a stirred solution containing 1 equiv of **3**[10] and 1 or 2 equiv of triethylamine in dry tetrahydrofuran (usually 5 g of **3** in 75 ml of solvent) at $-10°$ under nitrogen was added dropwise during 0.5 hr an equivalence of methanesulfonyl chloride equal to that of the tertiary amine. The resulting slurry was stirred for 1 hr at $-10°$ and for an additional hour at room temperature. The mixture was filtered to remove the precipitated triethylamine hydrochloride and the solvent was evaporated *in vacuo* at room temperature. The resulting oil was chromatographed.

Under various reaction and work-up conditions (see Table I), seven products were obtained.

Sulfone **6** was obtained as white crystals, mp 85–86°, from ether–hexane.

Anal. Calcd for $C_{11}H_{19}NO_2S$: C, 57.62; H, 8.35; N, 6.11; S, 13.96. Found: C, 57.56; H, 8.39; N, 6.02; S, 13.94.

Sulfone **7** was obtained as white crystals, mp 89.5–90.5°, from ether–hexane; $\nu_{\max}^{\mathrm{CCl_4}}$ 1328, 1192, and 1140 cm^{-1} ($-SO_2-$).

Anal. Calcd for $C_{11}H_{19}NO_2S$: C, 57.62; H, 8.35; N, 6.11; S, 13.96. Found: C, 57.56; H, 8.38; N, 5.85; S, 13.97.

Sulfone **8** was obtained as white crystals, mp 94–95°, from ether.

Anal. Calcd for $C_9H_{12}O_2S$: C, 58.66; H, 6.59; S, 17.40. Found: C, 58.66; H, 6.60; S, 17.41.

Sulfone **9** was obtained as white crystals, mp 109–110°, from ether–hexane.

Anal. Calcd for $C_{11}H_{19}NO_2S$: C, 57.62; H, 8.35; N, 6.11; S, 13.96. Found: C, 57.47; H, 8.28; N, 5.94; S, 13.96.

Sulfone **10** was recrystallized from chloroform–hexane to give white crystals, mp 144–145°.

Anal. Calcd for $C_9H_{14}O_3S$: C, 53.46; H, 6.98; S, 15.82. Found: C, 53.43; H, 7.01; S, 15.74.

The 2,4-dinitrophenylhydrazone was obtained as orange crystals, mp 219–220°, from 95% ethyl alcohol.

Sulfone **11** was obtained as white crystals, mp 169.0–170.5°, from ether.

Anal. Calcd for $C_{11}H_{19}NO_2S$: C, 57.62; H, 8.35; N, 6.11; S, 13.96. Found: C, 57.39; H, 8.30; N, 5.75; S, 14.11.

Sulfone **12** was isolated from methanol as yellow crystals, mp 192–193°.

Anal. Calcd for $C_{12}H_{21}NO_4S_2$: C, 46.90; H, 6.89; N, 4.56; S, 20.82. Found: C, 46.63; H, 6.88; N, 4.41; S, 20.78.

Hydrolysis of 9.—A solution of 170 mg (0.74 mmol) of **9** and 0.5 ml of concentrated hydrochloric acid in 2 ml of water was refluxed for 10 min, cooled, and extracted with methylene chloride. The combined organic layers were dried and evaporated to give 120 mg (80%) of **10**, mp 143–145°, identical in all respects with the previously isolated material.

Hydrolysis of 12.—A solution of 1.30 g (4.2 mmol) of **12** and 4 ml of concentrated hydrochloric acid in 10 ml of water was treated as above. There was obtained 1.01 g (86%) of a mixture of **13** and **14**. Recrystallization of this material from chloroform–hexane gave white crystals, mp 133.0–134.5°.

Anal. Calcd for $C_{10}H_{16}O_5S_2$: C, 42.84; H, 5.75; S, 22.87. Found: C, 42.70; H, 5.74; S, 22.73.

Registry No.—Sulfene, 917-73-7; **6**, 20452-33-9; **7**, 20452-93-1; **8**, 20452-34-0; **9**, 20452-35-1; **10**, 20452-36-2; **10** (2,4-dinitrophenylhydrazone), 20452-37-3; **11**, 20452-94-2; **12**, 20452-38-4; **13**, 20500-57-6; **3**, 14833-75-1.

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[17] Alternatively, the formation of **12** can be rationalized in terms of the direct reaction of **8** with methanesulfonyl chloride. Although the point has not been proven unequivocally, we consider this pathway less likely in view of the existing evidence that dehydrohalogenation of methanesulfonyl chloride by a tertiary amine normally proceeds faster than displacement of the sulfur-bound halogen by the β carbon of an enamine: I. J. Borowitz, *J. Amer. Chem. Soc.*, **86**, 1146 (1964).

[18] Further discussion about the concertedness or nonconcertedness of sulfene reactions may be found in ref 5. See also G. Optiz, *Angew. Chem. Intern. Ed. Engl.*, **7**, 646 (1968).