tor leaving a yellow solid. Recrystallization from 95% ethanol gave 10.1 g (87%) of *trans*(?)-3,6-dimethyl-1,1,3,6-tetrahydro-2-(*p*-tolylsulfonyl)-1-[(*p*-tolylsulfonyl)imino]-2*H*-1,2-thiazine (**10**): mp 205–208° dec; ir (KBr) λ 7.3, 7.4, 7.7, 8.55, and 8.7 μ; NMR ($CDCl_3$) δ 1.05 (d, 3, J = 7 Hz, CH_3 at the ring carbon adjacent to S), 1.25 (d, 3, J = 7 Hz, CH_3 at the ring carbon adjacent to N), 2.40 (s, 3, aromatic CH_3 group), 2.50 (s, 3, aromatic CH_3 group), 3.3–3.8 (m, 1, methine adjacent to S), 4.2–4.7 (m, 1, methine adjacent to N), 5.9 (broad singlet, 2, olefinic protons), 7.25–8.0 ppm (aromatic rings). Anal. Calcd for $C_{20}H_{24}N_2O_4S_3$: C, 53.09; H, 5.35; N, 6.19. Found: C, 53.08; H, 5.17; N, 6.08.

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Dipolar and Concerted Mechanisms in the Diene Reactions of *N*-Sulfinylsulfonamides[1a]

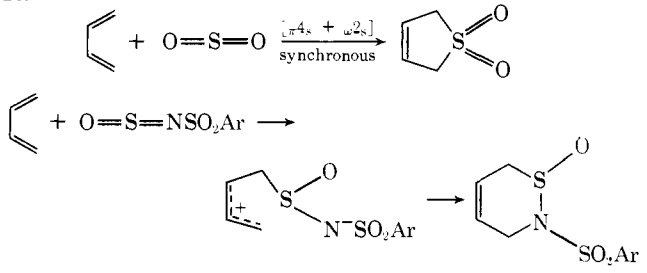
William L. Mock*[1b] and Richard M. Nugent

Contribution from the Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213. *Received February 24, 1975*

Abstract: The *N*-mesylsulfoximine analog of sulfolene, 3,4-dehydro-*N*-(methylsulfonyl)-*S,S*-tetramethylenesulfoximine (**6**), was prepared via a seven-step synthesis, which also yielded the 2,3-dehydro isomer (**7**). By conventional cycloaddition, 3,6-dihydro-2-(methylsulfonyl)-2*H*-1,2-thiazine 1-oxide (**8**) was prepared. Upon heating (100°), **6** rearranged to **8**. Thermolysis of **6** in SO_2 solution produced only sulfolene by capture of liberated butadiene, indicating a dissociation-recombination mechanism for **6** → **8**. It is concluded that, while cheletropic cycloreversion in the case of **6** is concerted, the Diels–Alder cycloaddition yielding **8** proceeds through a dipolar, two-step sequence. A theoretical rationalization for this behavior is presented, based on orbital symmetry concepts.

In earlier articles in this series, two apparently incongruous conclusions were reached. For the sulfolene reaction, the reversible cheletropic addition of sulfur dioxide to a conjugated diene, a concerted transition state with near synchronous bond formation was favored over a sequential process by a substantial margin.[2] However, in the case of the closely analogous cycloaddition of the imines of sulfur dioxide, leading to thiazine oxides, clear stereochemical evidence for a nonconcerted mechanism was documented (see Scheme I).[3]

Scheme I

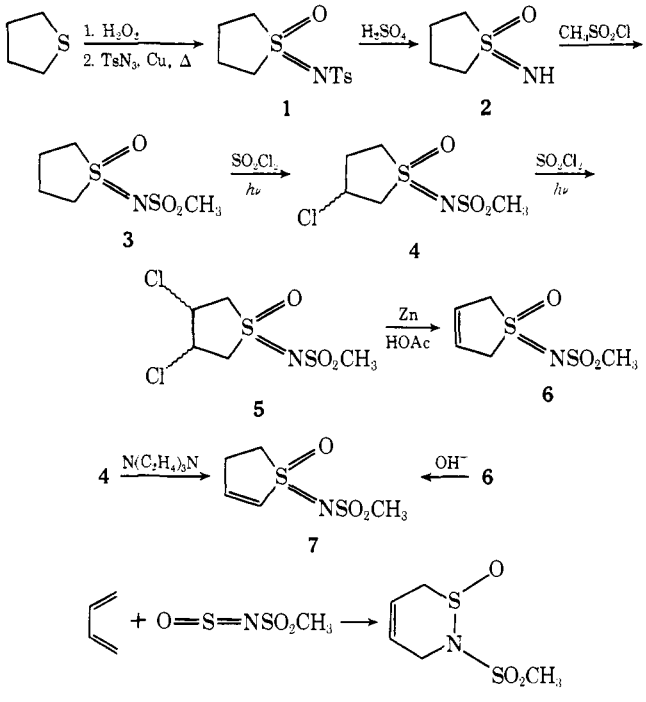


Since the dienophilic reactants are not identical, such disparity in transition state structure is tolerable. However, the similarity is such as to call into question the validity of one or the other of the previous mechanistic conclusions. In an attempt to reconcile what appeared to be contradictory behavior in nearly isoelectronic systems, the imino analog of a sulfolene (**6**) was synthesized. This key substance potentially bridges the reaction manifolds for the preceding two reactions. That its rearrangement and cycloreversion support the dichotomous nature of the respective transition states as previously proposed is the substance of this report.

Results

Synthesis. Preparation of the necessary sulfoximine is summarized in Scheme II. The intermediate **1** had previously been prepared from tetrahydrothiophene as indicated (hydrogen peroxide oxidation to a sulfoxide, followed by copper catalyzed imine transfer from tosyl azide).[4,5] For subsequent manipulations, a mesyl group was substituted for the tosyl group (**1** → **2** → **3**). Sulfuryl chloride haloge-

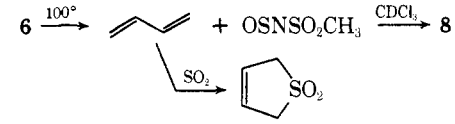
Scheme II



nation provided a monochloride **4** (isolation and purification of which was necessary) and then a dichloride (**5**). Selectivity in this free radical chlorination is a consequence of a pronounced destabilization of radical centers adjacent to a sulfone group, whence only the 3- and 4-positions of the ring are attacked. Dehalogenation (**5** → **6**) completed the sequence, giving the *N*-mesylsulfoxime analog of sulfolene as a crystalline substance, stable at room temperature. Dehydrohalogenation of **4** yielded **7**, an isomer of **6**. Attempts to convert **7** to **6** by base catalyzed isomerization were unsuccessful (no change); in fact, **6** was isomerized to **7** (with concomitant degradation) in aqueous sodium hydroxide. The relative stabilities of **6** and **7** are converse to the corresponding sulfolenes, for which the unconjugated isomer is favored (by 3:2).[6] For purposes of comparison, the thiazine oxide **8** was prepared in conventional fashion by cycloaddition between butadiene and *N*-sulfinylmethanesulfonamide. (No **6** could be detected in this material.)

Thermolyses. Solutions of **6** in deuteriochloroform solution are apparently stable at temperatures up to 60°. However, *at 100° **6** is isomerized to **8*** (90% conversion after 24 hr). It follows that the five-membered ring is thermodynamically disfavored relative to the six membered in this series.

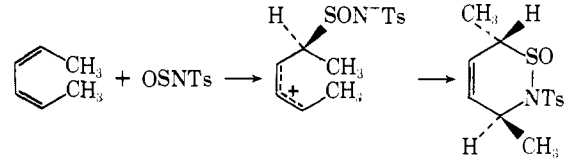
In the decisive experiment, **6** was heated to 100° in *sulfur dioxide* solvent (for 1 half-life, ca. 5 hr). The exclusive products were sulfolene and *N*-sulfinylmethanesulfonamide. No more than 2% of **8** could have been present in the thermolysis mixture (NMR, TLC analysis). In a control experiment it was established that **8** was stable in sulfur dioxide solution (100°, 24 hr). Therefore, **8** could not have been an intermediate in the conversion of **6** to sulfolene. Consequently, we surmise that the most probable mechanism for the isomerization **6** → **8** is dissociation-recombination.



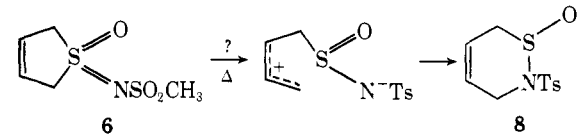
Discussion

General. Several incidental conclusions follow from the isolation and isomerization of **6**. Firstly, sulfoximines are not intermediates in the cycloaddition between conjugated dienes and *N*-sulfinylsulfonamides (e.g., formation of **8**). The stability of **6** is such that it would survive and accumulate in such event. Secondly, in this series at least, the sulfoximine functionality is thermodynamically disfavored relative to the sulfinamide group. Although steric factors (strain in five- vs. six-membered ring) possibly contribute, nevertheless the ordering of stabilities is opposite to that of the oxygen analogs ($RSO\text{-}OR \rightarrow R_2SO_2$).[7,8] Thirdly, the rate of dissociation of **6** is quite similar to that of sulfolene (butadiene sulfone possesses a half-life of ca. 2 hr at 115°).[9] Similar transition states are therefore reasonable. Likely the dissociation of **6** is virtually reversible.

Correlation within Sulfolene and Thiazine Oxide Reaction Manifolds. The behavior of **6**, in conjunction with the previously established mechanism for the formation of **8**, allows an illuminating inference about the energy hypersurfaces for the cheletropic sulfolene reaction and the thiazine oxide Diels–Alder cycloaddition. To recapitulate the evidence from the previous article,[3] the directing effects of diene substituents in general, and the stereochemical crossover in the case of *cis,cis*-hexadiene in particular, lead to the conclusion that a dipolar intermediate intervenes in the six-membered ring forming reaction. We presume that a similar mechanism, at least *verging* on two step, applies to the formation of **8** from butadiene.[10]



Under these circumstances, it would have been a reasonable anticipation that **6** should isomerize to **8** via the same zwitterionic intermediate. Scission of a *single* C–S bond in **6** is all that is *required;* the spatial reorganization necessary

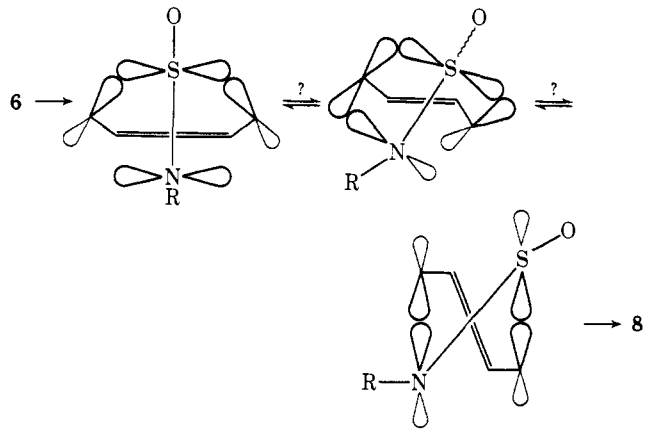


in migrating the ring methylene from sulfur to nitrogen is minimal. A near-concerted process appears reasonable. Attractive as this possibility may seem a priori, the evidence controverts such a mechanism. Attempted rearrangement in sulfur dioxide solution leads cleanly to capture of liberated butadiene by solvent. The most plausible mechanism for the conversion of **6** to **8** is therefore dissociation–recombination. In particular, *in the fragmentation of **6**, any dipolar character in the transition state must be specifically avoided*, for the fate of the zwitterion is collapse to **8**.[11] We wish to emphasize this point; there can be no common single intermediate in the reactions of **6** and **8**.[12] This conclusion is fully in accord with previous evidence on the sulfolene reaction (the stereoelectronic characteristics of which should apply to **6**). For the cheletropic cycloreversion in the five-membered ring sulfones, kinetic data have been obtained leading to the conclusion that a fully synchronous, $[_{\pi}4_s + _{\omega}2_s]$, concerted process is favored relative to any dipolar alternative by at least 10 kcal/mol in free energy of activation.[2]

The picture which emerges is that the energy hypersurface for the interaction of butadiene with *N*-sulfinylsulfonamides contains two *noncontiguous* regions: one leading to (from) thiazine oxide having the characteristics of a zwitterion, and the other leading to (from) sulfoximine having a

symmetric, delocalized (aromatic) geometry. In order to understand why there should be an insurmountable barrier on the energy surface between the saddle regions for these respective reactions (as the evidence indicates), elementary orbital symmetry concepts may be consulted.

The most expeditious way to visualize the differences in the orbital symmetry mechanics involved in these processes is to examine a *hypothetical concerted transition state* for the isomerization **6** → **8.** The geometrically most plausible (least motion, electrocyclically allowed) path would require the nitrogen of the sulfoximine to swing toward the *backside* of a methylene bound to sulfur.[13] Synchronous C–N bond formation and C–S bond rupture would carry the five-membered sulfoximine into the six-membered thiazine oxide:



The pertinent point is that *the penultimate precursor to* **8** *in this mechanism does not correspond to the transition state for a suprafacial Diels–Alder reaction.* In fact, by this analysis, the $[_{\pi}4_s + _{\omega}2_s]$ transition state for the sulfolene reaction correlates with the $[_{\pi}4_a + _{\pi}2_a]$ variant of the diene synthesis rather than the normally observed $[_{\pi}4_s + _{\pi}2_s]$ process. The antarafacial geometry of the hypothetical diene–sulfinylamide complex being exorbitantly strained, it follows that a sizable energy barrier should indeed exist between the two modes of cycloaddition (i.e., the intermediate structures depicted represent the ridge separating the accessible regions of the energy hypersurface for interaction of diene with sulfinylamide). Hence, dissociation–recombination is a lower energy path than concerted rearrangement for the exothermic isomerization of **6** to **8.** There being no physical requirement for similar electron distributions in the two thusly separated reaction manifolds, it is perfectly plausible for the cheletropic sulfolene reaction to be a concerted process (dissociation of **6,** retro-$[_{\pi}4_s + _{\omega}2_s]$), while the thiazine oxide variant of the Diels–Alder reaction (formation–dissociation of **8,** nominally $[_{\pi}4_s + _{\pi}2_s]$), should be in fact a sequential (two-step) reaction.[10,14] However, it is a matter of some curiosity that the same two reactants should adopt such disparate mechanisms according to how they come together in chemical combination.

Experimental Section

Preparation of 1. Tetrahydrothiophene was converted to the sulfoxide by oxidation with 30% hydrogen peroxide in acetone.[4] Refluxing a methanolic solution of this material with tolylsulfonyl azide in the presence of copper powder gave *S,S*-tetramethylene-*N*-(*p*-tolylsulfonyl)sulfoximine[5] (**1**), mp 106–107°.

Preparation of 2. A solution of 25 g (0.091 mol) of **1** in 25 ml of concentrated sulfuric acid was heated on a steam bath for 10 min.[15] The pale amber reaction mixture was poured onto 50 g of ice and then neutralized to pH 8 with sodium bicarbonate. The mixture was filtered, and the filtrate was extracted with three 30-ml portions of chloroform. The chloroform extracts were combined, dried with magnesium sulfate, and reduced on a rotary evaporator to give 6.5 g of **2,** as a viscous oil. The oil was dissolved in 5 ml of chloroform and submitted to column chromatography on 100 g of silicic acid with chloroform eluent. The fractions containing **2** were combined and filtered, and the solvent was removed. The product was then distilled under vacuum to give 6.0 g (51%) of *S,S*-tetramethylenesulfoximine (**2**): bp 100–103° (0.3 mm); ir (neat) λ 8.35 and 9.9 μ; NMR ($CDCl_3$) δ 2.2–2.5 (m, 4, β-methylene protons), 3.2 (t, 4, J = 7.0 Hz, α-methylene protons), and 3.3 (s, 1, NH) ppm.

Anal. Calcd for C_4H_9NOS: C, 40.33; H, 7.62. Found: C, 40.34; H, 7.62.

Preparation of 3. To a magnetically stirred solution of 6.5 g (0.055 mol) of **2** in 10 ml of dry pyridine was added (with cooling in an ice bath) 7.0 g (0.067 mol) of methanesulfonyl chloride in 10 ml of dry pyridine at such a rate that the temperature did not exceed 10°.[16] The mixture was allowed to stand overnight during which time the temperature came to 25° and a mass of dark colored crystals formed. The reaction mixture was then poured into 100 ml of water and extracted with three 50-ml portions of chloroform. The chloroform extracts were combined and dried with magnesium sulfate, and the solvent was removed on a rotary evaporator to give a solution of product in pyridine. The pyridine was removed by codistillation at reduced pressure with two 30-ml portions of toluene, and residual solvent was removed under vacuum to give 7.0 g of crude product. Recrystallization from 95% ethanol gave 6.0 g (56%) of *N*-(methylsulfonyl)-*S,S*-tetramethylenesulfoximine (**3**): mp 94–95°; ir (KBr) λ 7.7, 8.35, 8.9, and 9.5 μ; NMR ($CDCl_3$) δ 2.5–2.3 (m, 4, β-methylene protons), 3 (s, 3, CH_3), and 3.1–3.7 (m, 4, α-methylene protons) ppm.

Anal. Calcd for $C_5H_{11}NO_3S_2$: C, 30.44; H, 5.62. Found: C, 30.55; H, 5.58.

Preparation of 4.[17] In a 50-ml round-bottomed flask fitted with a reflux condenser were placed 2 g of **3** and 10 ml of sulfuryl chloride. The flask was placed approximately 3 cm above a sun lamp and irradiated for 2 min. At the end of the first irradiation, a homogenous solution was obtained; however, NMR analysis indicated incomplete reaction. The reaction mixture was further irradiated an additional three times for a period of 2 min each time, for a total of 8 min. The reaction mixture was allowed to cool for 5 min between irradiations. At the end of the fourth irradiation, NMR analysis indicated that **3** had been consumed. The reaction mixture was diluted with 5 ml of carbon tetrachloride and cooled in an ice bath to 0°. A mass of white crystals formed which were filtered and recrystallized from chloroform to give 1.2 g (51%) of 3-chloro-*N*-(methylsulfonyl)-*S,S*-tetramethylenesulfoximine (**4,** stereochemistry unknown): mp 140–142°; ir (KBr) λ 7.7, 8.3, 8.85, and 9.3 μ; NMR ($CDCl_3$) δ 2.4–2.7 (m, 2, β-methylene protons), 3.0 (s, 3, CH_3), 3.1–4.2 (broad m, 4, α-methylene protons), and 4.3–4.6 (methine proton) ppm.

Anal. Calcd for $C_5H_{10}ClNO_3S_2$: C, 25.92; H, 4.35. Found: C, 25.86; H, 4.27.

Preparation of 5.[17] In the same apparatus were placed 10 ml of sulfuryl chloride and 1 g of pure **4.** The mixture was irradiated for 2 min and was then diluted with 5 ml of carbon tetrachloride. The mixture was then irradiated twice more for 2-min periods, in each case allowing 5 min cooling time between irradiations (NMR analysis). All volatile material was removed on a rotary evaporator, and the yellow oil which remained was dissolved in 2 ml of chloroform. The chloroform solution was submitted to column chromatography on 40 g of silicic acid with chloroform eluent. The fractions containing **5** were combined and filtered, and solvent was removed. Recrystallization from ether–petroleum ether gave 0.3 g (26%) of 3,4-dichloro-*N*-(methylsulfonyl)-*S,S*-tetramethylenesulfoximine (**5,** stereochemistry unknown): mp 105–107°; ir (KBr) λ 7.7, 8.2, 8.8, and 9.5 μ; NMR ($CDCl_3$) δ 3 (s, 3, CH_3), 3.3–4.3 (broad m, 4, α-methylene protons), and 4.6–4.8 (m, 2, methine protons) ppm.

Anal. Calcd for $C_5H_9Cl_2NO_3S_2$: C, 22.56; H, 3.41. Found: C, 22.79; H, 3.43.

Preparation of 6. To a solution of 0.6 g (2.2 mmol) of **5** in 10 ml of acetic acid was added 5 g (large excess) of zinc powder. The mixture was heated for 1 hr at 100° with frequent swirling and subsequently filtered. The filtrate was diluted with 100 ml of water and extracted with three 25-ml portions of chloroform. The extracts were washed with sodium bicarbonate solution to pH 7 (aqueous phase). The dried ($MgSO_4$) chloroform solution was

evaporated under reduced pressure. The resulting viscous residual liquid was dissolved in ca. 2 ml of chloroform and submitted to column chromatography on 50 g of silicic acid with chloroform eluent. The fractions containing **6** were combined and filtered, and solvent was removed. Recrystallization from ether gave 0.23 g (51%) of 3,4-dehydro-*N*-(methylsulfonyl)-*S*,*S*-tetramethylenesulfoximine (**6**): mp 82–83°; ir (KBr) λ 7.7, 8.3, 8.8, and 9.35 μ; NMR ($CDCl_3$) δ 3.1 (s, 3, CH_3), 4.0 (d, 2, J = 17 Hz, one of the methylene protons), 4.4 (d, 2, J = 17 Hz, one of the methylene protons), and 6.2 (s, 2, olefinic protons) ppm.

Anal. Calcd for $C_5H_9NO_3S_2$: C, 30.76; H, 4.65; N, 7.17. Found: C, 30.97; H, 4.44; N, 6.91.

Preparation of 7. To a solution of 1 g (4.5 mmol) of **4** in 10 ml of chloroform was added a solution of 0.6 g (5.5 mmol) of 1,4-diazabicyclo[2.2.2]octane in 10 ml of chloroform. The mixture was allowed to stand at 25° for 4 hr during which time the hydrochloride of diazabicyclooctane precipitated. The mixture was filtered, and volatile material was removed from the filtrate on a rotary evaporator. The residue was dissolved in ca. 2 ml of chloroform and submitted to column chromatography on 40 g of silicic acid with chloroform eluent. The fractions containing **7** were combined and filtered, and solvent was removed. Recrystallization from ether gave 0.60 g (71%) of 2,3-dehydro-*N*-(methylsulfonyl)-*S*,*S*-tetramethylenesulfoximine (**7**): mp 75–76°; ir (KBr) λ 7.75, 8.35, 8.8, and 9.4 μ; NMR ($CDCl_3$) δ 3.05 (s, 3, CH_3), 2.95–4.05 (broad, m, 4, methylene protons), and 7.0 (s, 2, olefinic protons) ppm.

Anal. Calcd for $C_5H_9NO_3S_2$: C, 30.76; H, 4.65. Found: C, 30.91; H, 4.64.

After 1 hr in 2 *N* sodium hydroxide solution at 25°, **6** was completely converted to **7** (10% recovery) and degradation products (not characterized).

Preparation of Authentic 8. Into a three-necked flask equipped with an acetone–Dry Ice cold finger condenser, a gas inlet tube, and a magnetic stirrer was placed a solution of 5 g (0.046 mol) of *N*-sulfinylmethanesulfonamide in 5 ml of benzene. Over a period of 30 min, 1,3-butadiene was passed into the solution until the volume of the reaction mixture had increased by ca. 50% and a large excess was present. The condenser was removed, and the reaction mixture was warmed to 25° during which time the excess butadiene was allowed to escape, leaving the product as a white solid suspended in benzene. The product was filtered and recrystallized from 95% ethanol to give 6.7 g (73%) of 3,6-dihydro-2-(methylsulfonyl)-2*H*-1,2-thiazine 1-oxide (**8**): mp 120–121°; ir (KBr) λ 7.5, 7.6, 8.7, 9.1, 9.2, 9.3, and 9.9 μ; NMR ($CDCl_3$) δ 3.0 (s, 3, CH_3), 3.3–3.6 (m, 2, CH_2 adjacent to ring S), 3.9–4.2 (m, 2, CH_2 adjacent to N), and 5.5–6.3 (m, 2, olefinic protons) ppm.

Identity of **8** with the rearrangement product of **6** (see Results) was established by spectral and TLC analysis and by mixture melting point.

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(1) (a) Taken from the Ph.D. Thesis of R. M. Nugent, Carnegie-Mellon University, 1972. (b) Fellow of The Alfred P. Sloan Foundation; address correspondence to this author at the Department of Chemistry, University of Illinois at Chicago Circle, Box 4348, Chicago, Ill., 60680.
(2) W. L. Mock, *J. Am. Chem. Soc.*, **92**, 3807 (1970); **97**, 3673 (1975).
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(10) Cited evidence indicates that diene substituents perturb the mechanism, favoring the more stabilized dipole. Hence, **8** may form through a more concerted process than occurring in the hexadienes.
(11) Clearly closure of a zwitterion must compete efficiently with fragmentation for, in most cases, the cyclization is stereospecific. In particular, the intermediate B in Scheme I of the previous article (ref 3) does not dissociate appreciably.
(12) More generally stated, the transition states for **6** and **8** may both be concerted, or one may be concerted and the other dipolar; what is excluded is that both be dipolar.
(13) A suprafacial migration would be orbital symmetry disallowed.
(14) A complicating ambiguity is the geometry of the sulfinylsulfonamide, which may be cis or trans (ref 3). It is conceivable that one isomer yields cheletropic addition while the other correlates with the six-membered ring.
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