(39) Cf. C. D. Ritchie, *J. Phys. Chem.*, **65**, 2091 (1961).
(40) R. W. Taft, Jr., N. C. Deno, and P. S. Skell, *Annu. Rev. Phys. Chem.*, **9**, 287 (1958).
(41) S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Prog. Phys. Org. Chem.*, **10**, 1 (1973).
(42) Since the monoprotonation of *N,N,N'*-trimethylethylenediamine does not take place entirely at the secondary amino group (but most of it probably does), the pK_a for this amine has a slightly different meaning from that for the other secondary amines. However, no correction to pK_{ac} has been made on this basis because the diamine was never studied kinetically at a pH high enough for any significant concentration of the conjugate base of its carbinolamine to be present.

Geometry of the Adducts of 2,4-Hexadienes with *N*-Sulfinylarylsulfonamides. A Stereospecific but Nonconcerted Diels–Alder Reaction[1a]

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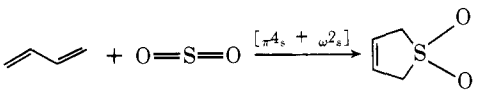
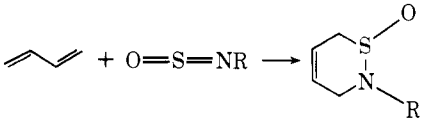
Abstract: The isomeric 2,4-hexadienes were allowed to react with *N*-sulfinyl-*p*-toluenesulfonamide, yielding 3,6-dihydro-3,6-dimethyl-2-(*p*-tolylsulfonyl)-2*H*-1,2-thiazine 1-oxides. The following correlations were observed: (*E,E*)-C_6H_{10} → **1** and **2** (diastereomeric suprafacial adducts); (*E,Z*)-C_6H_{10} → **3** (suprafacial adduct); (*Z,Z*)-C_6H_{10} → **4** (antarafacial adduct). The structures of **1–4** follow from oxidation to sultams (**5, 6**) and from NMR induced shift studies. An adduct with cyclohexadiene was demonstrated to be a diastereomeric mixture (**7**). Analogous adducts (**9, 10**) were obtained with *N,N'*-bis(*p*-tolylsulfonyl)sulfur diimide. The stereochemical results are best accommodated by a nonconcerted (two-step) dipolar mechanism of addition, as specifically required for **4** (which arises from an overall trans addition to the diene).

The stereochemistry of the cycloadditions and eliminations between sulfur dioxide and conjugated dienes (sulfolene reaction) has been quantitatively established; it is a linear cheletropic, suprafacial (cis), *concerted* process.[2] The



isoelectronic imines of sulfur dioxide might be expected to react analogously; however, in actuality, they afford six-membered dihydrothiazine oxides.[3] As part of a broad in-

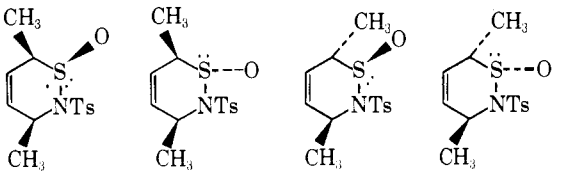


(R = aryl, arylsulfonyl, etc.)

vestigation into the mechanism of the sulfolene and related reactions, we have examined the stereochemistry of this latter cycloaddition. In this report, the reactions of the three isomeric 2,4-hexadienes (trans,trans, cis,trans, cis,cis) with *N*-sulfinyl-*p*-toluenesulfonamide have been found to produce, stereoselectively, all possible configurationally isomeric adducts. From correlations between reactants and products, it is possible to infer a *nonconcerted* mechanism for the thiazine oxide forming reaction, as will be shown.

Results

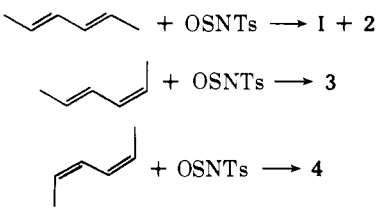
Cycloadditions with OSNTs. Taking into consideration the pyramidal hybridization of sulfur in sulfinamides,[4] there are only four possible diastereomers of the adduct between 2,4-hexadiene and *N*-sulfinyl-*p*-toluenesulfonamide (OSNTs). These are designated **1–4.**



1 **2** **3** **4**

Each of these structures (full name; 3,6-dihydro-3,6-dimethyl-2-(*p*-tolylsulfonyl-2*H*-1,2-thiazine 1-oxide) was obtained from one or another of the hexadienes according to Scheme I. From *trans,trans*-hexadiene and OSNTs, a major isomer (mp 110°) and a minor isomer (mp 115°)

Scheme I

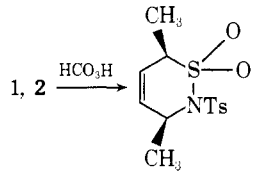


were obtained. As will subsequently be shown, they have structures **1** and **2,** respectively. From *cis,trans*-hexadiene, a single product was obtained (mp 121°), for which structure **3** will be demonstrated. From *cis,cis*-hexadiene and OSNTs, a small amount of the remaining isomer (mp 100°) was obtained; it will be assigned structure **4.**

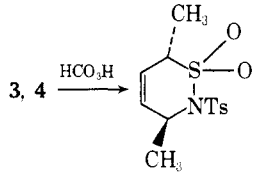
Structural Assignments (1–4). The relative configurations of the isomers ensues from two lines of evidence: (1) correlations between the corresponding sultams produced by oxidation, and (2) paramagnetic shifts induced in the NMR spectra of **1–4** by tris(dipivalomethanato)europium(III) [Eu(dpm)$_3$].

Of the three asymmetric centers in the molecules **1–4,** one may be selectively removed by oxidation of the sulfinyl

function to a sulfonamide. Upon treatment of **1** with performic acid,[5] a sultam (mp 161°) was obtained, for which the structure **5** may be provisionally assigned. The identical substance (**5**) was also obtained from **2**. Similar oxidation of **3** gave a different sultam (mp 168°), which must be assigned structure **6**. From **4** was likewise produced **6**. The only conclusion which can rigorously be drawn from these conversions is that the relative configurations of the methyl groups (cis or trans) must be identical between **1** and **2** and between **3** and **4**; if **5** (**1**, **2**) is cis, then **6** (**3**, **4**) must be trans (or vice versa). The presumed assignments of **5** and **6** are based upon recognition that **1**, **2**, and **3** may thusly be rationalized by a normal suprafacial cycloaddition to a cisoid diene; then only **4** requires a special explanation (antarafacial addition; see Discussion). Reversal of the assignments of **5** and **6** appears relatively less probable. Fortunately, NMR induced shifts confirm the given configurations.

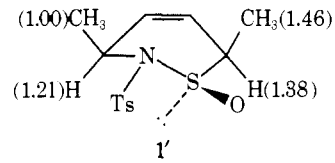


5

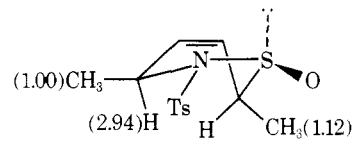


6

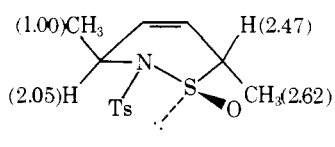
Complete NMR spectral information for the substances **1–6** is given in tabular form in the Experimental Section. We provide here an abstraction of the relevant data which allows structural assignments for **1–4.** The unshifted spectra of the thiazine oxides were too similar to provide relative configurations. However, in the presence of $Eu(dpm)_3$, sizable downfield shifts of most protons occurred in **1–3.** An internally consistent interpretation is summarized in structures **1′–4′**. The numbers adjacent to the methyl and methine positions represent the *relative magnitude* of the induced shift of the respective protons (i.e., the slope of a plot of Δ (Hz) vs. concentration of $Eu(dpm)_3$, normalized to the least strongly shifted resonance in each case). Our interpretation contains two assumptions: (1) that the site of coordination of the lanthanide is sulfinyl *oxygen* (for which adequate precedent exists[6]), and (2) that the molecules exist predominantly in the conformations depicted. Regarding the latter supposition, examination of molecular models reveals that our conformations are indeed the most reasonable from the point of view of minimizing nonbonded interactions. Furthermore, we have considered alternatives (configuration and conformation), all of which provided less satisfactory agreement with the spectra than the given structures.



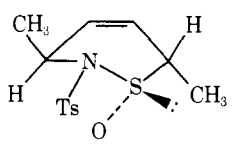
1′



2′



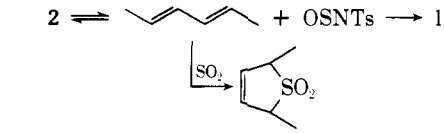
3′



4′

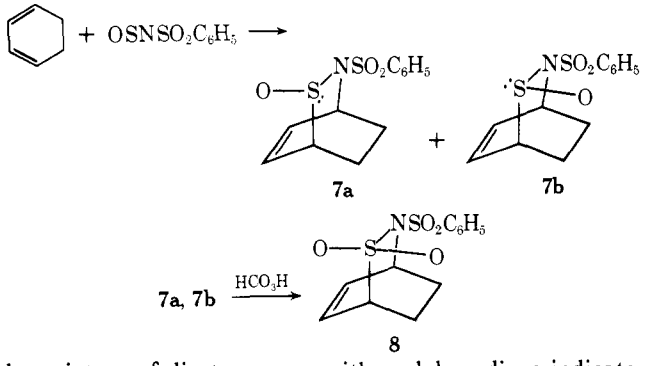
For **1**, the pertinent observation is that the methyl group and methine proton adjacent to sulfur are approximately equally shifted, and are both more strongly affected than the distal methyl-methine combination. We therefore assign a half-chair conformation (as typical for cyclohexene derivatives)[7] with the sulfinyl oxygen in an equatorial position, nearly gauche to both the proximal methyl and methine. In **2** (which must have the same relative configuration between methyl groups as **1**—*cis*), the pertinent observation is that *both* methines are strongly shifted and relatively more so than the methyls. We are forced to assume a boat[8] conformation for **2**, with the methyls in unhindered "equatorial" (bow) positions and the sulfinyl oxygen again in an "equatorial" (gunwale) position (in this case, spatially close to the methine hydrogens). For **3**, a half-chair conformation seems again to best accommodate the induced shifts. In this case, the trans related methyl groups would be expected to adopt pseudo-equatorial positions to the exclusion of other conformations. As in the case of **1**, the sulfinyl oxygen is positioned equatorially, whence the lanthanide equally influences the adjacent methyl and methine positions. Finally in **4**, we are confronted with the fact that only an insignificant induced shift could be observed with the concentrations of $Eu(dpm)_3$ employed for **1–3.** This is rationalized by the assumption of a locked half-chair conformation (forced by the pseudo-equatorial *trans*-methyls as in **3**, in which the sulfinyl oxygen is required to adopt an axial position. We surmise that steric hindrance by the ring (and adjacent *cis*-methyl group) prevents coordination with $Eu(dpm)_3$ in this case. While the foregoing analysis is not rigorous in the sense of absolutely ruling out alternative configurational assignments, we are convinced that it is by far the most plausible, especially when taken with mechanistic considerations (see Discussion). In any event, it is only the cis-trans relationship between the methyl groups which is essential to our conclusions.

Relative Thermodynamic Stabilities. Since the respective abundance of the isomers **1–4** produced from the several hexadienes is the foundation of our mechanistic interpretation, it was of interest to establish their relative stabilities by interconversion. It was found that, when **2** was heated at 100° in chloroform solution for 1 hr, it was converted completely to **1**, clearly indicating that **1** is the thermodynamically favored isomer. A mechanism for this isomerization may be inferred from the observation that, when the conversion was attempted in sulfur dioxide solvent, the exclusive products (>95%) were 2,5-dimethylsulfolene and OSNTs (<5% of **1**). Since the intermediacy of **1** in the latter transformation may be excluded (**1** is converted only ca. 50% to dimethylsulfolene after 6 hr at 100° in SO_2 solution), a dissociation-recombination mechanism seems most plausible for **2** → **1**. (We would make the reservations that interception of a zwitterionic intermediate cannot be excluded; see Discussion.)

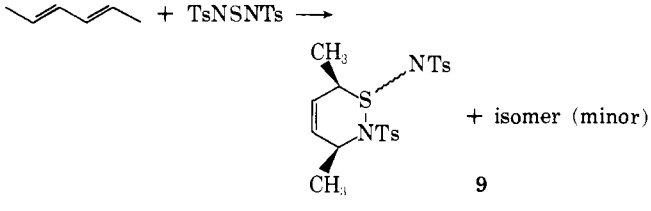


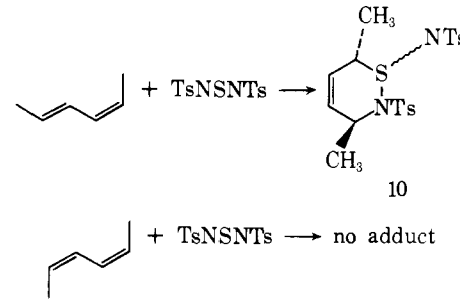
Parallel experiments were attempted with **3**; however, no change (to an isomer or to dimethylsulfolene) was noted when **3** was heated in sulfur dioxide solution at 100° (48 hr) or 120° (3 hr). Unfortunately, **4** was only available in limited quantities and was not submitted to equilibration as above. Upon prolonged heating, all isomers are converted to uncharacterizable (dark) material.

Adduct with Cyclohexadiene. The stereochemical orientation of the sulfinyl oxygen in **1–4** must be accommodated in any mechanism of cycloaddition. Toward this end, we reexamined the reaction between *N*-sulfinylarylsulfonamides and 1,3-cyclohexadiene. An adduct with *N*-sulfinyl-*p*-toluenesulfonamide has been reported[9] with no mention of the orientation of the oxygen relative to the olefin (exo-endo?). For the purpose of convenience in NMR analysis, we prepared the cycloadduct using *N*-sulfinylbenzenesulfonamide and 1,3-cyclohexadiene (**7**). It was obvious from the high-field (250 MHz) NMR spectrum that a 50:50 mixture of exo and endo isomers was formed. In the region of the olefinic proton resonances, four triplets at δ 6.10, 6.25, 6.34, and 6.70 were observed. For each triplet, the coupling was 8.4 Hz and each resonance upon integration corresponded to ca. 0.5 proton in the sample. The spacing between the triplets was 44, 24, and 108 Hz; these are too large to be couplings and must represent different chemical shifts of four protons in different environments (**7a** and **7b**). A similar doubling was observed for the bridgehead positions. The isomers could not be separated by recrystallization or chromatography. The mixture apparently gave a single sultam (**8**) upon performic acid oxidation. Production of a equimolar mixture of diastereomers with cyclohexadiene indicates to us that there is no strong *electronic* factor producing the sulfinyl stereoselectivities observed in **1–4**. Hence, in those cases exo or endo addition must result from steric factors intrinsic to the respective 2,4-hexadienes (see Discussion). In the case of cyclohexadiene, such factors apparently are absent or at least are neutralized (as is plausible considering the similar spatial requirements of the etheno and ethano bridges in **7**).



Cycloadditions with TsNSNTs. The bisimine analogs of sulfur dioxide are known to give six-membered ring counterparts of the thiazine oxides.[3] We attempted to extend our investigation of the cycloadducts of hexadiene to this series. Unfortunately, only two (**9** and **10**) of the possible four diastereomers could be isolated in crystalline form (plus a minor amount of a third as an oil). No correlations between isomers could be established. Based on analogy with **1–4**, our results are summarized as follows:

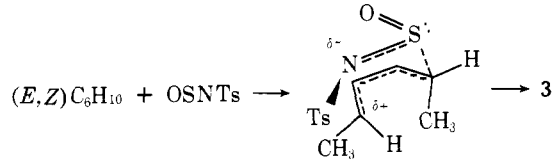




Discussion

The unique stereoselectivities observed in the formation of **1–4** allow a definitive interpretation of the mechanism of this particular variant of the Diels–Alder reaction. We shall consider the anamolous case of **4** separately from the other isomers.

Mechanism for 1, 2, and 3. The first two products, produced from *trans,trans*-hexadiene, require little comment. They both correspond to normal (for the diene synthesis) suprafacial addition to the cisoid conformation of the conjugated system. The major product (**1**) also corresponds to endo addition (i.e., the sulfinyl oxygen adopts an orientation which would place it in proximity to the π electron density of diene for a concerted reaction, rather than distal). However, we discount the likelihood of any secondary orbital overlap considerations in the transition state as being responsible in this case. The minor product (**2**, the exo adduct) is also *thermodynamically* disfavored; the relative exothermicity of the reactions leading to **1** and **2** is sufficient explanation for the kinetic predominance of **1**. Furthermore, formation of an equal mixture of exo and endo adducts (**7a, 7b**) from cyclohexadiene, in which a steric influence would be expected to be neutral, also controverts any electronic stereodirective factor.



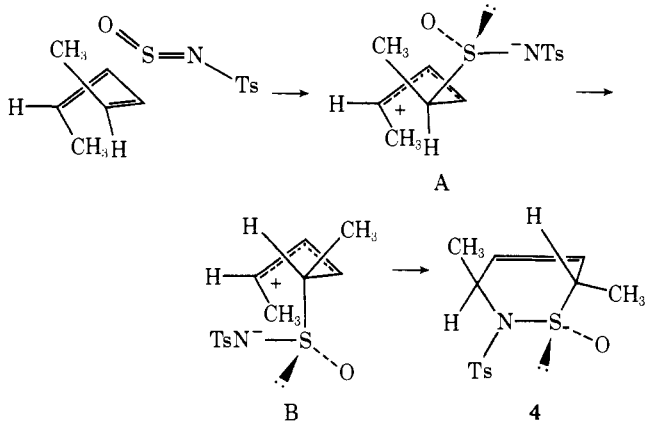
For the isomer **3**, produced exclusively from *cis,trans*-hexadiene, a more complex analysis is feasible. Our interpretation is that **3** is the expected product from an *endo addition which is initiated by C–S bond formation at the cis olefin of the diene.* Were this the case, the resulting configuration (methyl groups trans, sulfinyl oxygen trans to adjacent methyl) would be in accord with the postulated stereochemistry of **3**.[10] Literature precedents may be cited in support of this interpretation. Both 1- and 2-alkyl substituted butadienes give products (6- and 5-substituted 3,6-dihydro-1,2-thiazine 1-oxides) suggesting a dipolar[11] intermediate or transition state corresponding to initial C–S bond formation.[12] (In the former case, diastereomers are formed.) The alkyl group adopts the position yielding maximal stabilization of such an intermediate as that depicted. In the case of *cis,trans*-hexadiene, initial attack at the cis olefin is to be anticipated since a transoid ("sickle") rather than a cisoid ("U-form") allylic moiety may thereby be produced.[13] The endo orientation of sulfinyl oxygen (in **3**) could not have been predicted but, at least, is consistent with the behavior of *trans,trans*-hexadiene (which yields predominantly **1**).

Since we have addressed the question of the geometry of the sulfinyl oxygen in the transition state, some consideration of the configuration of the *N*-sulfinylarylsulfonamide reagent is in order. Two likely possibilities may be entertained (trans and cis). While the question of this type of

isomerism has been examined, both theoretically and experimentally,[14] no firm conclusion can at present be drawn as to which is the *reactive* component in these cycloadditions. (Best available evidence would have them in equilibrium under the conditions of our synthesis.)[14] We favor the trans configuration as more easily accommodated to the apparent steric origin of the endo specificities in **1** and **3**. The arylsulfonyl group is undoubtedly bulkier than the sulfinyl oxygen; steric congestion places the former in the exo position within the product-determining step.

Mechanism for 4. The stereochemistry of the cycloadduct (**4**) obtained from *cis,cis*-hexadiene represents an unprecedented antarafacial (trans) Diels–Alder diene synthesis. In rationalizing its formation, we first exclude a trivial explanation; **4** cannot arise from a preliminary isomerization of *cis,cis*-hexadiene to *cis,trans*-hexadiene followed by normal (suprafacial) 1,4 addition since it has previously been demonstrated that the latter diene gives only **3** (none of which accompanies **4**). Therefore the product-determining step must indeed involve unisomerized *cis,cis*-hexadiene interacting with OSNTs. However, it is not necessary to postulate a concerted process to explain stereospecificity within this reaction.[15] Our preferred rationalization is as shown in Scheme II. The reactive conformation of the diene is cisoid which, due to severe methyl–methyl repulsions, can only

Scheme II. Stereoselective Formation of **4**



achieve a helical skew arrangement as depicted. Attack by OSNTs is upon an exposed end of the helical diene (C–S bond formation, zwitterion A). Direct closure to a thiazine oxide (**1** or **2**) is now blocked, however, by the methyl–methyl repulsions previously alluded to. With the allylic moiety locked in a cisoid ("U-form") configuration, it is impossible to rotate one methyl past the other so as to bring the nitrogen within bonding distance of the other terminus of the diene. Consequently, rotation in the *opposite* direction ensues (requiring only that the methine hydrogen at the newly formed quaternary center pass the blocking methyl group), yielding zwitterion **B**. At this point, there is no barrier to cyclization, and the zwitterion collapses, resulting in stereospecific formation of an antarafacial adduct (**4**). It is fortuitous coincidence that the configuration of sulfinyl oxygen emerges epimeric to that in **3** (although nonbonded interactions as in **1–3** may by analogy rationalize a configuration for A leading to **4**). It follows that a *two-step mechanism* (Scheme II) is the most plausible explanation for the generation of **4**.

Conclusion

Dipolar character in the transition states for thiazine oxide formation has previously been indicated by the orientational effects of alkyl substituents.[12] However, in all such cases, concertedness (initiation of C–N bond formation before completion of C–S bond) could not be excluded since stereospecific suprafacial addition to the diene was not disproved. Indeed, a concerted mechanism adequately explains **1–3.** However, with **4**, a two-step mechanism (C–S and C–N bond formation completely separated in time) is required. It is possible that *two* mechanisms are operative (concerted for **1–3,** sequential for **4**). However, since experimental conditions for the formation of **4** do not differ greatly from those for **1–3,** it seems more economical to us to postulate that there is but one mechanism, namely *two step.* It is necessary and sufficient in the case of **1–3** that ring closure (C–N bond formation) be more rapid than rotation about the C–C bond adjacent to the allylic moiety (as in **4**).[16] We conclude that thiazine oxide formation is nonconcerted.

Experimental Section

General. Elemental analyses were by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points were taken in capillary tubes and are uncorrected. The ir spectra were obtained with a Perkin-Elmer infracord spectrophotometer, Model 137B, and the NMR spectra with a Hitachi Perkin-Elmer, Model R-20 or with a Varian A-60 spectrophotometer. The 250-MHz spectra were obtained at the NMR Facility for Biomedical Research at this University.

The yields and percentage yields were recorded after all purification procedures were complete, unless otherwise noted. The *N*-sulfinyl compounds used were prepared from thionyl chloride and the necessary amide by the method of Kresze et al.,[5] and the corresponding sulfur diimides were prepared from the *N*-sulfinyl compound by treatment with pyridine according to the procedure of Wucherpfennig and Kresze.[17] Commercial chemicals used were of reagent grade quality and were used without purification unless otherwise noted.

Preparation of 1 and 2. To a solution of 10 g (46 mmol) of *N*-sulfinyl-*p*-toluenesulfonamide in 5 ml of dry benzene at 80° was rapidly added 10 g (0.12 mol) of *trans,trans*-2,4-hexadiene. The reaction mixture was maintained at 80° for 1 min and then rapidly cooled in an ice bath. Volatile material was removed on a rotary evaporator at 25°, leaving a yellow solid. Recrystallization from 95% ethanol gave 10.0 g (73%) of *cis,cis*-3,6-dihydro-3,6-dimethyl-2-(*p*-tolylsulfonyl)-2*H*-1,2-thiazine 1-oxide (**1**): mp 110–111°; ir (KBr) λ 7.4, 8.55, 8.7, 8.8, 9.07, and 10.0 μ; NMR (see Table I). *Anal.* Calcd for $C_{13}H_{17}NS_2O_3$: C, 52.17; H, 5.73; N, 4.68. Found: C, 51.95; H, 5.66; N, 4.35.

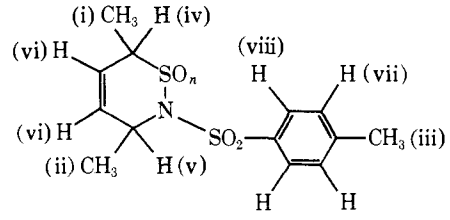
The mother liquors from the recrystallization of **1** were evaporated to dryness on a rotary evaporator, taken up in chloroform, dried with magnesium sulfate, and were again evaporated to dryness. The yellow solid was taken up in a few milliliters of chloroform and submitted to column chromatography on 100 g of silicic acid with chloroform eluent. The fractions containing **2** were resubmitted to column chromatography as above. The product was recrystallized from ether–petroleum ether to give 300 mg (2.2%) of *trans,cis*-3,6-dihydro-3,6-dimethyl-2-(*p*-tolylsulfonyl)-2*H*-1,2-thiazine 1-oxide (**2**): mp 115–117°; ir (KBr) λ 7.4, 8.55, 8.8, 9.0, and 9.15 μ; NMR (see Table I). *Anal.* Calcd for $C_{13}H_{17}NS_2O_3$: C, 52.17; H, 5.73; H, 4.68. Found: C, 52.36; H, 5.62; N, 4.66.

When the cycloaddition was carried out below 60°, only **1** could be isolated (80% yield at 25°).

Preparation of 3. To a solution of 2 g (9.2 mmol) of *N*-sulfinyl-*p*-toluenesulfonamide in 1 ml of dry benzene at 25° was slowly added 2 g (24 mmol) of *cis,trans*-2,4-hexadiene. The reaction mixture was allowed to stand overnight during which time the product crystallized from solution. Volatile material was removed on a rotary evaporator leaving a yellow solid. Recrystallization from 95% ethanol gave 2.3 g (84%) of *cis,trans*-3,6-dihydro-3,6-dimethyl-2-(*p*-tolylsulfonyl)-2*H*-1,2-thiazine 1-oxide (**3**): mp 121–123°; ir (KBr) λ 7.4, 7.5, 8.6, 8.9, 9.1, 9.2, and 9.85 μ; NMR (see Table I). *Anal.* Calcd for $C_{13}H_{17}NS_2O_3$: C, 52.17; H, 5.73; N, 4.68. Found: C, 52.03; H, 5.72; N, 4.73.

Preparation of 4. To a solution of 2.5 g (11.5 mmol) of *N*-sul-

Table I. Proton NMR Chemical Shifts (Including Induced Shifts) for **1**–**6** (*ca.* 0.066 *M* in $CDCl_3$ solution, ppm from Me_4Si)



Proton	1	2	3	4	5	6
i	1.35 (0.076)[a]	1.40 (0.103)[a]	1.20 (0.138)[a]	0.99[b]	1.25	1.05
ii	1.50 (0.052)	1.50 (0.092)	1.30 (0.052)	1.41	1.50	1.55
iii	2.50	2.47	2.48	2.45	2.40	2.40
iv	3.35 (0.072)	3.50 (0.226)	3.50 (0.130)	3.02	3.45	3.50
v	4.60 (0.063)	3.95 (0.270)	4.60 (0.108)	4.53	5.20	5.20
vi[c]	5.70	5.85	5.90	5.57	5.50	5.65
vii	7.40	7.40	7.35	7.30	7.30	7.30
viii	7.90	7.95	7.85	7.73	7.70	7.75

[a] Induced shift (δ) per milligram of $Eu(dpm)_3$ in the range 10–40 mg added lanthanide. [b] Range of induced shifts only 0.0015–0.015 (see Results). [c] Separate olefinic resonances not resolved.

finyl-*p*-toluenesulfonamide in 5 ml of dry benzene at 25° was slowly added 1 g (12 mmol) of *cis,cis*-2,4-hexadiene. The reaction mixture was allowed to stand at 25° for 1 hr and then was heated to 80° for 2 min followed by cooling rapidly in an ice bath. The orange colored reaction mixture was then placed in a refrigerator overnight. The following day the volatile material was removed on a rotary evaporator leaving a thick red oil, which was taken up in ca. 2 ml of chloroform and submitted to column chromatography on 40 g of silicic acid with chloroform eluent. The majority of the product was a very slow moving tar-like material. The fractions containing the desired material were combined and filtered, and solvent was removed. The product was recrystallized from ether–petroleum ether to give 70 mg (2%) of *trans,trans*-3,6-dihydro-3,6-dimethyl-2-(*p*-tolylsulfonyl)-2*H*-1,2-thiazine 1-oxide (**4**): mp 100–103°; ir (KBr) λ 7.4, 8.6, 9.1, and 9.15 μ; NMR (see Table I). *Anal.* Calcd for $C_{13}H_{17}NS_2O_3$: C, 52.17; H, 5.73; N, 4.68. Found: C, 52.08; H, 5.64; N, 4.51.

Preparation of 5 and 6. This reaction is essentially the procedure of Kresze et al.[5] A solution was prepared from 30 ml of 98% formic acid and 10 ml of acetic anhydride. In 5 ml of this solution were dissolved 1 g (3.3 mmol) of **1** and 1 g (8.9 mmol) of 30% hydrogen peroxide. The reaction mixture was allowed to stand at 25° for 3 days during which time a mass of flat, colorless needles formed. The product was filtered, crushed, and washed with water, ethanol, and ether. The white powder was air dried to give 0.55 g (52%) of *cis*-3,6-dihydro-3,6-dimethyl-3,6-dimethyl-2-(*p*-tolylsulfonyl)-2*H*-1,2-thiazine 1,1-dioxide (**5**): mp 161–163°; ir (KBr) λ 7.3, 7.35, 7.4, 8.55, and 8.65 μ; NMR (see Table I). *Anal.* Calcd for $C_{13}H_{17}NS_2O_4$: C, 49.52; H, 5.44; N, 4.44. Found: C, 49.33; H, 5.41; N, 4.07.

Oxidation of 100 mg (0.33 mmol) of **2** in the same manner gave 30 mg (28%) of **5**: mp 161–163°; no depression of mixture melting point; identical ir.

In 5 ml of the formic–acetic anhydride solution were dissolved 1 g (3.3 mmol) of **3** and 1 g (8.9 mmol) of 30% hydrogen peroxide. The reaction mixture was allowed to stand at 25° for 3 days at which time a mass of colorless plate-like crystals had formed. The product was filtered, crushed, and washed with water, ethanol, and ether. The white powder was air dried to give 0.6 g (57%) of *trans*-3,6-dihydro-3,6-dimethyl-2-(*p*-tolylsulfonyl)-2*H*-1,2-thiazine 1,1-dioxide (**6**): mp 168–169°; ir (KBr) λ 7.30, 7.35, 7.4, 8.5, and 8.6 μ; NMR (see Table I). *Anal.* Calcd for $C_{13}H_{17}NS_2O_4$: C, 49.52; H, 5.44; N, 4.44. Found: C, 49.36; H, 5.35; N, 4.17.

Oxidation of 50 mg (0.16 mmol) of **4** in the same manner gave 10 mg (19%) of **6**: mp 168–169°; no depression of mixture melting point; identical ir.

Preparation of 7 and 8. To a solution of 3 g (14 mmol) of *N*-sulfinylbenzenesulfonamide in 20 ml of benzene of 0° was added 3 g (37.5 mmol) of 1,3-cyclohexadiene in benzene. The reaction mixture was brought to room temperature and then refluxed for several minutes. Volatile material was removed on a rotary evaporator. Recrystallization of the residue from 95% ethanol gave 3.6 g (82%) of *exo*- and *endo*-3,6-dihydro-3,6-ethano-2-benzenesulfonyl-2*H*-1,2-thiazine 1-oxide (**7a, 7b**), mp 116–124° (see Results for NMR proof of diastereomeric mixture).

To a solution of 1 g (3.5 mmol) of **7** in 3.5 ml of 98% formic acid and 1.5 ml of acetic anhydride was added 1.5 ml of 30% hydrogen peroxide. The mixture was allowed to stand overnight at 25°. A crystalline precipitate was collected and washed with water, ethanol, and ether to give 0.9 g (85%) of 3,6-dihydro-3,6-ethano-2-benzenesulfonyl-2*H*-1,2-thiazine 1,1-dioxide (**8**), recrystallized from acetone: mp 185–186°; ir (KBr) λ 7.5, 8.6 μ; NMR (CF_3CO_2H) δ 1.5–3.0 (m, 4, ethanobridge), 4.35 (m, 1, bridgehead), 4.95 (m, 1, bridgehead), 6.45 (m, 2, olefin), and 7.5–8.3 ppm (m, 5, aromatic ring). Anal. Calcd for $C_{12}H_{13}NO_4S_2$: C, 48.16; H, 4.38; N, 4.68. Found: C, 48.40; H, 4.28; N, 4.71.

Preparation of 9 and 10. To a solution of 18.2 g (0.049 mol) of *N,N'*-bis(*p*-tolylsulfonyl)sulfur diimide in 15 ml of benzene at 70° was rapidly added a solution of 4.0 g (0.067 mol) of *trans,trans*-2,4-hexadiene in 5 ml of benzene. The reaction mixture was kept at 70° for 1 min and then was rapidly cooled in an ice bath to 25° and allowed to stand at 25° overnight. Volatile material was removed on a rotary evaporator leaving a yellow semisolid. Recrystallization from 95% ethanol gave 17.1 g (78%) of *cis*(?)-3,6-dimethyl-1,1,3,6-tetrahydro-2-(*p*-tolylsulfonyl)-1-[(*p*-tolylsulfonyl)imino]-2*H*-1,2-thiazine (**9**): mp 157–158°; ir (KBr) λ 7.3, 7.65, 8.55, and 8.7 μ; NMR ($CDCl_3$) δ 1.1 (d, 3, J = 7 Hz, CH_3 at the ring carbon adjacent to S), 1.3 (d, 3, J = 7 Hz, CH_3 at the ring carbon adjacent to N), 2.4 (s, 3, aromatic CH_3 group), 2.5 (s, 3, aromatic CH_3 group), 3.4–3.9 (m, 1, methine adjacent to S), 4.3–4.6 (m, 1, methine adjacent to N), 5.4–6.0 (m, 2, olefinic protons), 7.35–7.94 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, 52.91; H, 5.25; N, 6.28.

The mother liquors from the recrystallization of **9** were evaporated on a rotary evaporator to yield a viscous oil. The oil was dissolved in ca. 4 ml of chloroform and submitted to column chromatography on 100 g of silicic acid with chloroform eluent. Fractions containing an isomer were combined and filtered, and solvent was removed to yield a gummy solid. This material was dissolved in ca. 2 ml of chloroform and resubmitted to column chromatography as above. Again appropriate fractions were combined and filtered, and solvent was removed to give ca. 400 mg (2%) of an isomer as a viscous oil which was not successfully crystallized: NMR ($CDCl_3$) δ 1.0 (d, 3, J = 7 Hz, CH_3 at the ring carbon adjacent to S), 1.5 (d, 3, J = 7 Hz, CH_3 at ring carbon adjacent to N), 2.5 (broad s, 6, aromatic CH_3 groups), 2.9–3.4 (m, 1, methine adjacent to S), 4.6–4.9 (m, 1, methine adjacent to N), 5.7 (s, 2, olefinic protons), 7.3–7.8 ppm (aromatic rings).

To a solution of 9.6 g (0.026 mol) of *N,N'*-bis(*p*-tolylsulfonyl)sulfur diimide in 10 ml of benzene at 70° was rapidly added a solution of 2.0 g (0.033 mol) of *cis,trans*-2,4-hexadiene in 3 ml of benzene. The reaction mixture was kept at 70° for 1 min and then was rapidly cooled in an ice bath to 25° and allowed to stand at 25° overnight. Volatile material was removed on a rotary evapora-

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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References and Notes

(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.
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(16) A similar conclusion applies to C–S bond scission in the retro reaction (dissociation), at least as regards **2**. In the isomerization **2** → **1**, evidently no *cis,trans*-hexadiene (which would yield **3**) is produced.
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Dipolar and Concerted Mechanisms in the Diene Reactions of *N*-Sulfinylsulfonamides[1a]

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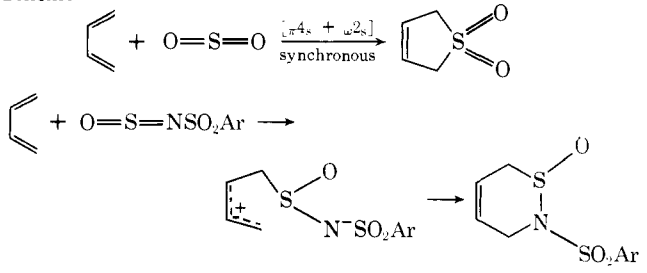
Abstract: The *N*-mesylsulfoximine analog of sulfolene, 3,4-dehydro-*N*-(methylsulfonyl)-*S,S*-tetramethylenesulfoximine (**6**), was prepared via a seven-step synthesis, which also yielded the 2,3-dehydro isomer (**7**). By conventional cycloaddition, 3,6-dihydro-2-(methylsulfonyl)-2*H*-1,2-thiazine 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-