25 ml of water and the solution was made slightly basic with solid $NaHCO_3$. The aqueous mixture was then extracted with chloroform (4 × 50 ml). The organic extracts were combined, dried ($MgSO_4$), and concentrated to give 5.1 g (56%) of crude solid. Sublimation at 100° (0.05 mm) gave 3.30 g (36%) of **12**: mp 111–115°; ^1H NMR ($CDCl_3$) δ 1.44 (d, $^2J_{PH}$ = 12 Hz, PCH_3), 1.72 (d, $^2J_{PH}$ = 13 Hz, PCH_3), 1.90–3.62 (complex m, $-CH_2-$), 6.28 (d, $^3J_{PH}$ = 28 Hz, $-C=CH-$), 7.04–7.76 (4 H, aromatic); ^{31}P NMR (D_2O, 2 *M*) δ −77.7 (71%) and −71.2 (29%); ir (Nujol) 1200 cm^{-1} (P=O).

Anal. Calcd for $C_{13}H_{15}OP$: C, 71.55; H, 6.88; P, 14.20. Found: C, 71.49; H, 6.94; P, 14.41.

***trans*- (13a) and *cis*- (13b) 1-Methyl-$\Delta^{3(3a)}$-2,4,5,6,7,7a-hexahydro-1(*H*)-phosphindole.** To a solution of 5.1 g (30 mmol) of **3a** (60%) and **3b** (40%) in 200 ml of dry benzene at 0° was added a solution of 13.1 ml (130 mmol) of trichlorosilane in 25 ml of benzene over a 1-hr period. The ice bath was removed and the mixture was refluxed for 12 hr. It was cooled and carefully hydrolyzed by addition of 50 ml of a 20% NaOH solution. The layers were separated and the aqueous layer was extracted with benzene (4 × 25 ml). The organic extracts were combined and dried ($MgSO_4$) and the benzene was distilled off at atmospheric pressure. The remaining yellow oil was distilled to give 3.1 g of the isomers of **13** (68%) as a colorless liquid: bp 104–106° (16 mm); ^1H NMR ($CDCl_3$) δ 0.73 and 0.88 (each d, $^2J_{PH}$ = 3.5 Hz, PCH_3 for **13b** and **13a**, respectively), 1.10–2.85 (m, $-CH_2-$), 5.15–5.65 (m, $>C=CH-$); ^{31}P NMR (neat) δ +26.2 (**13a**, 56%) and +28.6 (**13b**, 44%).

The methiodide **14** was prepared by treating a small amount of the phosphine with excess methyl iodide. Recrystallization from methanol–ether gave white needles, mp 265° dec.

Anal. Calcd for $C_{10}H_{18}IP$: C, 40.54; H, 6.08; P, 10.47. Found: C, 40.71; H, 5.95; P, 10.28.

1-Methylperhydrophosphindole 1-Oxide (15a and 15b). A mixture of 1 g (5.8 mmol) of **6**, 100 ml of absolute ethanol, and 500 mg of 5% rhodium on alumina was placed in a Parr pressure bottle and shaken under H_2 (50 psi) for 13 hr. The catalyst was removed by filtration and the ethanol by rotary evaporation. The residual oil solidified and was sublimed at 70° (0.01 mm) to give 725 mg of **15** (73%): mp 88–94°; ^1H NMR (D_2O δ 1.57 and 1.62 (each d, $^2J_{PH}$ = 13 Hz, PCH_3), 1.15–2.60 (m, $-CH_2-$); ir (Nujol) 1160 cm^{-1} (P=O); ^{31}P NMR (50% in D_2O) δ −82.8 (49.5%) and −78.8 (50.5%).

Anal. Calcd for $C_9H_{17}OP$: C, 62.79; H, 9.88; P, 18.02. Found: C, 62.95; H, 10.05; P, 17.88.

Acknowledgment. We are grateful to Mr. William L. Orton for the preparation of **6** by the direct cycloaddition method.

Registry No.—**3a**, 57065-62-0; **3b**, 57065-63-1; **6**, 57065-64-2; *trans*-**8**, 57065-65-3; *cis*-**8**, 57065-66-4; *trans*-**9**, 57065-67-5; *cis*-**9**, 57065-68-6; **10**, 54781-35-0; **11** isomer A, 57065-69-7; **11** isomer B, 51728-59-3; **11** isomer C, 57128-60-6; **11** isomer D, 57128-61-7; **12**, 57065-70-0; **13a**, 57065-71-1; **13b**, 57065-72-2; **14**, 57065-73-3; **15a**, 57065-74-4; **15b**, 57128-62-8; 1-vinylcyclohexene, 2622-21-1; methylphosphonous dichloride, 676-83-5; 1-(α-bromovinyl)-1-cyclohexene, 57065-75-5; 1-(α-chlorovinyl)cyclohexene, 57065-76-6; 1-acetylcyclohexene, 932-66-1; chlorotrimethylsilane, 1,2-dihydro-4-vinylnaphthalene, 57065-77-7.

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Scope of the 1,6 Addition of Sulfur Dioxide to *cis*-3-Hexatrienes

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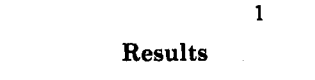
Reaction between *cis*-3-hexatriene and sulfur dioxide yields an adduct, 2,7-dihydrothiepin 1,1-dioxide. Similarly prepared were the seven-membered-ring sulfones with the following substituents: 3-isopropyl-6-methyl, 3,5-dimethyl, 2,4,6-trimethyl, and 3-acetoxymethyl. Sulfolenes only were obtained from *cis*-1,2-dicyclohex-1-enylethylene and 1,3,5-cyclooctatriene, as well as from 4,6-dimethyl-2,3,5-heptatriene. The structure of the adducts is described, and the influence of substituents on the course of the addition reaction is discussed.

The sulfolene reaction (the addition of sulfur dioxide to a conjugated diene) provides a valuable synthesis of five-membered-ring sulfones. Since the reaction is fully reversible, the sulfones have been exploited as intermediates for the modification and purification of dienes.[2] We have reported that the reaction between hexatriene and sulfur dioxide yields a seven-membered-ring sulfone, 2,7-dihydrothiepin 1,1-dioxide (**1**).[3] This transformation is also reversible. In this article we examine the generality of the cycloaddition with variously substituted trienes. The details of the mechanism of the reaction are considered elsewhere.[4]



1

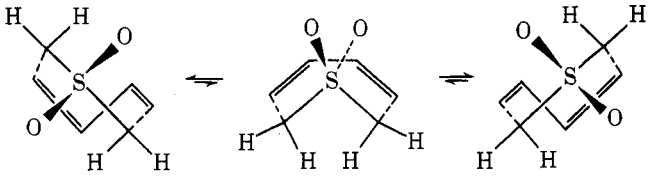
Results

2,7-Dihydrothiepin 1,1-Dioxide (1). The reaction of *cis*-hexatriene with excess sulfur dioxide gives an excellent

yield of 1. Its characterization has previously been described;[3] details are in the Experimental Section.[5] Several properties of this substance are worthy of comment. The adduct dissociates cleanly in the melt at 150–160° to regenerate *cis*-hexatriene (which distills from the reaction vessel) and less than 1% of *trans*-hexatriene or cyclohexadiene. Since 1 has an indefinite shelf life, it represents an attractive method of storing small quantities of this reactive triene for subsequent use. The kinetics and stereochemistry of the decomposition process have been examined.[4c,d]

Exchange in basic deuterium oxide yields α,α'-tetradeuterio-1, the availability of which facilitated analysis of the NMR spectrum of 1 (Experimental Section). In addition to providing a source of the specifically labeled triene, this demonstrates that 1 is the most stable of the isomeric dihydrothiepin dioxides, a result which has been confirmed by the conversion of 4,5-dihydrothiepin 1,1-dioxide into 1 under mildly basic conditions.[6]

Since the ring system of 1 is relatively unfamiliar, a comment regarding its possible conformations seems in order. Molecular models strongly suggest that the dihydrothiepin system exists exclusively in a twist form (**1a**), but that



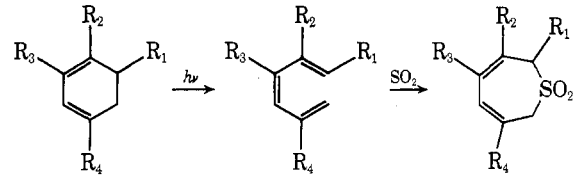
1a **1b** **1a′**

there should be a reasonably favorable pathway for its interconversion with an enantiomeric twist form (**1a′**).[7] In the course of this ring flipping it passes through a folded planar form (**1b**) which may represent a slight minimum (intermediate) on the energy profile for this process. Spectroscopic data supports this analysis. The ultraviolet absorption, uv max 227 nm (ϵ 5850), exhibits an attenuated intensity, attributable to nonplanarity in the diene. In this respect it resembles 1,3-cyclooctadiene, for which uv max 228 nm (ϵ 5600).[8] In support of this conformation is the NMR coupling constant between the 4 and 5 position protons, J = 4 Hz, which is reasonable for the presupposed dihedral angle (ca. 60°) between the planes of the double bonds in **1a**.[9] If the molecule were frozen in one of the twist forms (**1a** or **1a′**), then the geminal protons of methylene groups might be expected to experience different chemical environments.[7] However, this is not reflected in the NMR spectrum at temperatures as low as −50°. (The resonance of these protons remains a sharp doublet.) It can only be concluded either that these protons are accidentally magnetically equivalent ($\Delta\nu \ll J$) or that the barrier to ring flipping is lower than could be detected. Comparison with analogous systems[7] suggests that an activation energy for configurational inversion in the range of 10–20 kcal/mol would be reasonable for **1**.

In agreement with the foregoing analysis is chemical evidence, specifically, the reluctance with which the conjugated system of **1** reacts with dienophiles. Diels–Alder addition could not be observed with maleic anhydride or tetracyanoethylene at temperatures below that which effected dissociation of 1. However, an adduct formed slowly in refluxing benzene with the highly reactive dienophile *N*-methyltriazolinedione. We suggest that cycloaddition to 1 proceeds through conformation **1b**, which is sparsely populated (or proceeds nonconcertedly).

Substituted Hexatrienes. As a class, 3-*cis*-hexatrienes represent a rather inaccessible and highly reactive type of

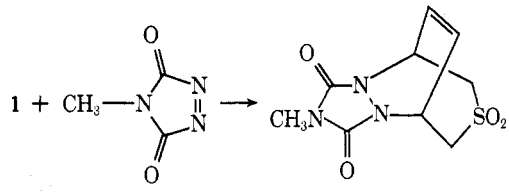
Table I
Substituted 2,7-Dihydrothiepin 1,1-Dioxides



2-5

Compd	R_1	R_2	R_3	R_4	Yield,[a] %
2	H	CH_3	H	i-C_3H_7	4
3	H	H	CH_3	CH_3	8
4	CH_3	H	CH_3	CH_3	6
5	H	CH_2OAc	H	H	14

[a] Yields are for both steps, and are based upon amount of cyclic diene submitted to the sequence.

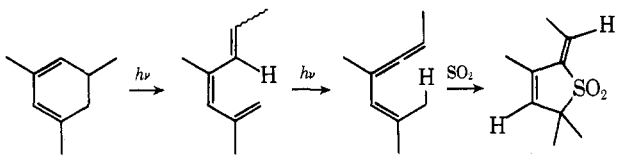


chemical entity. The characteristics of 1 suggested that the dihydrothiepin dioxide ring would be of synthetic utility in this regard. With this in mind, and with the intention of probing the mechanism of the cycloaddition, we undertook to examine sulfur dioxide addition with several trienes.

The paucity of methods for the preparation of acyclic trienes in which the central bond possesses cis geometry is well known to workers having need for such substances.[10] Most of our examples are based on photochemical ring opening of more readily available cyclohexadienes as listed in Table I. There is an inherent limitation in this approach, however. Cyclohexadienes and *cis*-hexatrienes absorb ultraviolet light at approximately the same wavelengths; although the ring opening proceeds with a satisfactory quantum efficiency, a steady state is soon achieved in which the cyclohexadiene component of the photoproduct mixture predominates (because the triene has a characteristically higher extinction coefficient). A further limitation is that thermal closure of the triene back to a cyclohexadiene may also take place (see Discussion). With certain substitution patterns on the triene, this may be so rapid (unimolecular reaction) as to compete effectively with cycloaddition by sulfur dioxide (bimolecular reaction). Our yields are low because of these factors and because no special effort to secure optimum conditions was attempted. In general, photolyses of cyclohexadienes were carried out with a 450-W mercury arc in ca. 0.03 M solution in ether at −20° until the reaction mixture showed no further rapid change upon irradiation as evidenced by uv or GLC analysis. Conditions for the addition of sulfur dioxide depended upon the propensity of the triene to reclose. After the reaction had gone to completion the product was generally obtained by column chromatography on silicic acid.

In the first example, the cyclohexadiene utilized was α-terpinene. In actuality the material submitted to photolysis was a commercial mixture containing ca. 25% of α-terpinene and the balance isomeric terpenes and aromatics as shown by GLC. The triene intermediate was quite unstable, reclosing to diene in a few minutes at room temperature. However, it was successfully intercepted with sulfur dioxide to give 3-isopropyl-6-methyl-2,7-dihydrothiepin 1,1-dioxide (**2**). Trienes from other components in the reaction mixture may have been present, but they did not lead

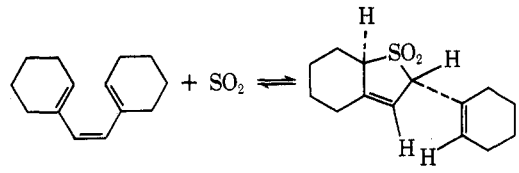
to isolable amounts of adducts. The next two cyclohexadienes were prepared by addition of methyl Grignard reagent to an appropriate ketone, followed by dehydration. In each case this led to a mixture of exocyclic and endocyclic dienes, which were submitted to photolysis without separation. A single product, 3,5-dimethyl-2,7-dihydrothiepin 1,1-dioxide (3), was obtained in the first instance. The intermediate triene did not recyclize so rapidly as in the case of the previous example. From the next cyclohexadiene and anticipated product, 2,4,6-trimethyl-2,7-dihydrothiepin 1,1-dioxide (4), was obtained as an oil, accompanied by a crystalline isomer. The latter was identified as 2-ethylidene-3,5,5-trimethyl-2,5-dihydrothiophene 1,1-dioxide (6). It most probably arose due to overphotolysis, since there is precedent for the production of an allene intermediate in this manner.[11] The orientation (cis–trans) of the ethylidene group is based upon steric considerations in the transition state, and the assignment is supported by a 1.5-Hz coupling (NMR) between the olefinic protons; this is reasonable for a five-bond coupling in a coplanar zigzag ("W") pattern. This product (6) is noteworthy on several



6

counts; it is a sulfolene derived from a vinylallene and as a sulfolene it possesses double substituents in an α position. Both of these features are novel; we have undertaken a broader investigation of allene–sulfur dioxide cycloadditions.[12] Thermal decomposition of the anticipated adduct, 4, gave back 2,4-dimethyl-1,*cis*-3,*trans*-5-heptatriene, indicating preferential formation of a triene with a trans terminal double bond as might be expected on steric or thermodynamic grounds.[4c] The final example in Table I (5) demonstrates the compatibility of the synthetic process with additional functionality, namely an acetoxyl group. The requisite cyclohexadiene was secured from the Diels–Alder adduct of 1-(diethylamino)butadiene and acrolein by diethylamine elimination followed by reduction and acetylation. We describe this route in detail in the Experimental Section since it would appear to be quite general and capable of modification to generate a variety of cyclohexadienes. The photolysis procedure with this diene gave 3-acetoxymethyl-2,7-dihydrothiepin 1,1-dioxide (5).

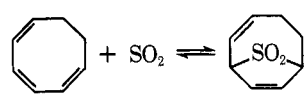
Finally, we shall briefly describe SO_2 adducts of two more trienes, which do not correspond to dihydrothiepin dioxide formation. The chief alternative synthesis of *cis*-hexatrienes involves partial hydrogenation over a poisoned catalyst of a dialkenylacetylene (or precursor thereof, such as an alkenylalkynylcarbinol[10c]). This method has severe practical limitations as regards yields and control of stereospecificity. Partial success is here demonstrated with the single example of dicyclohexenylacetylene. Hydrogenation of this material, brought about by Lindlar catalyst,[10a,c,d] afforded in our hands a complex mixture of hydrocarbons. Without attempted separation, these were treated directly with an excess of sulfur dioxide and the crude product mixture was submitted to column chromatography. By this sequence of operations low yields (<1%) of a sulfone of the correct composition ($C_{14}H_{20}O_2S$) could be obtained, although in several attempts no product at all was recovered. Spectral data for this material immediately demonstrated that it could not be a dihydrothiepin dioxide derivative. It lacked a uv absorption for the conjugated diene, and the NMR spectrum exhibited different chemical shifts for each of the two olefinic protons and for each of two methinyl protons occurring (probably) adjacent to the sulfonyl group. Consequently, the material is formulated as a 1,4 adduct (7). It was established that this material was not an



7

isomerized (via extensive hydrogen migration) dihydrothiepin dioxide (several of which might conceivably have given the observed spectra) by the fact that the sulfone readily dissociated on heating to give sulfur dioxide and triene. It might be suspected that the sulfone was formed from *trans*-dicyclohexenylethylene, a likely constituent of the hydrogenation mixture,[10c] since this material could only give a 1,4 adduct. However, the triene obtained upon thermolysis of the sulfone possessed ultraviolet absorption uv max 245 nm, the wavelength corresponding to the (apparently nonplanar) cis triene (trans triene uv max 260, 269, 281 nm).[10a] Consequently, we believe that in this case suprafacial 1,4 addition of sulfur dioxide to *cis*-dicyclohexenylethylene has occurred. However, a reservation must be made; the diversity of the components in the reactant mixture creates the possibility that 7 has an entirely different, unsuspected structure. Nevertheless, there is a strong indication that 1,4 addition of sulfur dioxide may compete effectively with 1,6 addition, depending on the nature of the triene.

The Experimental Section also carries the synthesis and characterization of 8, the product from sulfur dioxide and 1,3,5-cyclooctatriene. In this case formation of the (known[4b]) 1,6 adduct is disfavored by orbital symmetry considerations.[4d] A point of practical interest is that the crystalline adduct provides a particularly advantageous method of purification and storage of cyclooctatriene, since 8 dissociates on mild heating. In this regard it is competitive with the silver nitrate adduct (which we regard as less convenient).[13]



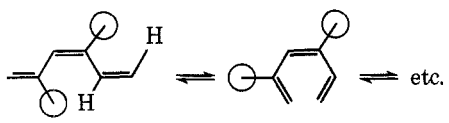
8

Discussion

The limited number of examples cited show that 1,6 cycloaddition of sulfur dioxide to 3-*cis*-hexatrienes apparently is a general reaction. Substituents in the β and γ positions (R_2, R_3, and R_4 in Table I) appear to facilitate the reaction. This is a qualitative observation, based on the fact that these trienes react rapidly in cold (and, in the case of 2, dilute) solution with sulfur dioxide whereas formation of the unsubstituted parent (1) requires more vigorous conditions. Substituents in the α position (R_1 in Table I) appear to suppress the reaction. Whereas a low yield of 4 was obtained with β and γ substituents to offset the effect of the α-methyl group, in several other cases which were attempted with one or two α substituents, either the reaction was diverted to 1,4 addition or no sulfone was obtained.[14] In this regard the reactivity of the trienes toward sulfur dioxide partially parallels the facility with which they recyclize to cyclohexadienes, although the aliphatic substituent effect appears small for the latter reaction (rate factors in the range of 1 to 3 have been suggested[10d]). We tentatively propose that these reactivity trends have a steric origin. The

presence of substituents at the internal positions (β, γ) favors conformations which place the terminal carbons of the triene in proximity; i.e., the cisoid conformation (or an approximating skew orientation) about both of the single bonds in a triene must be obtained before reaction can ensue. In the absence of substituents transoid conformations will be favored; however, steric bulk will destabilize the latter and lead to greater population of the reactive conformations (Scheme I). The retarding influence of the α

Scheme I



substituents (in the SO_2 addition only) may likewise be attributed to a steric origin, since they contribute congestion at the reaction site and possibly destabilize the product as well.[4d] An inductive effect of alkyl substituents might be expected to be relatively more important in the SO_2 reaction. A close correlation of structure–reactivity effects for the two reactions is unexpected in any event; the triene to cyclohexadiene electrocyclization proceeds suprafacially[10c] whereas the cycloaddition of SO_2 occurs antarafacially.[4a,c] The limited data recorded do not warrant further elaboration. Consideration of mechanistic aspects of the cycloaddition has been presented elsewhere.[4d]

Finally, we would mention the synthetic applicability of this reaction. On one hand, the adducts provide excellent precursors for other seven-membered-ring sulfones, particularly for the fully unsaturated thiepin dioxides.[3,15] More generally they appear to have limited use for the isolation and storage of hexatrienes. The most pertinent examples from this work would be the adduct from hexatriene itself (1) and the sulfolene from cyclooctatriene (8). Since the adducts are considerably less reactive than the trienes toward most reagents, the sulfone may be used as a temporarily protected derivative of the triene while manipulation is carried out elsewhere in the molecule. The triene functionality may be recovered subsequently by heating (although this may be accompanied by concomitant cyclization). A preparatively felicitous aspect of this fragmentation is the relative involatility of the sulfones compared to the products; consequently it is a simple matter to distill away the products as formed and thereby prevent (or suppress) their immediate further reaction. One independent and general synthesis (i.e., other than SO_2 addition) of the dihydrothiepin dioxide ring has been described.[4a,c,16] Other, more expeditious schemes, perhaps analogous to the sulfolene forming ylide reactions of McIntosh,[17] might largely overcome current practical restrictions on triene availability.

Experimental Section

General. Elemental analyses were by Galbraith Laboratories, Inc., Knoxville, Tenn., or Micro-Tech Laboratories, Inc., Skokie, Ill. Melting points were determined in open capillaries and are corrected. Nuclear magnetic resonance (NMR) spectra were obtained on a Varian A-60 instrument. Infrared (ir) spectra were obtained on a Perkin-Elmer Model 21 instrument. Ultraviolet (uv) spectra were obtained on a Cary Model 14 instrument. For gas chromatography (GLC) a 1,2,3-tris(2-cyanoethoxy)propane column was used. Photolyses were carried out with a 450-W Hanovia mercury arc with a Vycor filter. The lamp was placed in a water-cooled immersion well which was placed in the reaction vessel (through which was bubbled a stream of inert gas for agitation) which was in turn placed in a refrigerator bath. The standard chromatographic isolation procedure referred to below involved the preparation of a 2.5-cm diameter column of 80 g of Mallinkrodt SilicAR CC7, 200–300 mesh, slurried in carbon tetrachloride. After application of the sample to the column, it was submitted to gradient elution involving in succession the following solvents: CCl_4 (100 ml); CCl_4–$CHCl_3$, 6:1 (70 ml), 2:1 (60 ml), 1:2 (60 ml); $CHCl_3$ (500 ml). Fractions were collected at 10-min intervals. Reactions products were located by TLC and spectroscopic analysis.

2,7-Dihydrothiepin 1,1-Dioxide (1). To a solution of 9.23 g (0.115 mol) of *cis*-hexatriene[18] (*trans*-hexatriene removed by formation of the maleic anhydride adduct) and 0.1 g of *tert*-butylcatechol in 18 g of ether in a combustion tube was added 40 g of sulfur dioxide at −80°. The container was sealed and the mixture was allowed to stand at room temperature for several weeks (alternatively, it may be heated at 50–55° for 48 hr). The tube was chilled and opened, and the solvent was allowed to evaporate. The residue was taken up in 60 ml of hot benzene and filtered, and was then diluted with 120 ml of hot hexane. Upon cooling the product separated and was collected. Concentration of the mother liquors afforded additional material. The combined product was sublimed at 100° (0.1 mm) to give 14.01 g (84.4%) of 1: mp 107–108°; ir ($CHCl_3$) 1310, 1120 cm^{-1}; uv max (C_2H_5OH) 227 nm (ϵ 5850); MS (70 eV) *m/e* 144. The NMR spectrum is not amenable to complete analysis. However, by comparing the spectra of various substituted dihydrothiepin 1,1-dioxides (here reported and unpublished)[9] chemical shifts and certain of the coupling constants for this ring may be deduced. The α protons (2,7 positions, adjacent to the sulfonyl group) occur at δ 3.5–4.0 ppm in various solvents; in the olefinic region, the β protons (3,6 positions) consistently occur upfield from the γ protons (4,5 positions), δ ca. 6.0 and 6.5 ppm, respectively. Coupling between the α and β positions is 6.8 Hz, that between β and γ is ca. 10 Hz, and that between two γ protons is ca. 4 Hz. All other couplings are ≤1 Hz. The spectrum (especially the methylene protons) was unchanged in $CDCl_3$ solution at temperatures down to −50°.[19] Similarly, nonequivalence in the α protons was not detectable (no broadening of line width at 40° and 60 MHz) in CCl_4, CS_2, C_6H_6, C_5H_5N, $C_6H_5NO_2$, $(CH_3)_2NCHO$, or CF_3CO_2H solutions.

Anal. Calcd for $C_6H_8O_2S$: C, 50.00; H, 5.60. Found: C, 50.00; H, 5.49.

Thermal Decomposition of 1. Quantitative recovery of *cis*-hexatriene from 1 may be carried out by heating the sulfone in a flask (under an inert gas sweep such that the triene is carried into a cold trap) with an oil bath (150–160°) or with a hot air blower. The pyrolysate was found to be free (<1%) of *trans*-hexatriene or 1,3-cyclohexadiene by GLC analysis.

Deuterium Exchange in 1. To a dioxane–deuterium oxide mixture containing 1 was added a catalytic amount of commercial potassium *tert*-butylate. The exchange reaction was conducted in an NMR tube so that it could be monitored. After warming for several hours, 1 was recovered by chloroform extraction and recrystallization from benzene–hexane, mp and mmp 107–108°. It was seen by NMR examination that the methylene hydrogens adjacent to the sulfonyl group (δ 3.7 ppm) were almost completely replaced by deuterium. The olefinic hydrogens remained; the resonance at δ 6.05 ppm was simplified to a broadened doublet.

Hexahydrothiepin 1,1-Dioxide.[20] A solution of hexamethylene sulfide in acetic acid was treated with excess peracetic acid for 24 hr at 25°. Solvent was removed on a rotary evaporator and the residue was recrystallized from benzene–hexane and then sublimed at 70° (2 mm) to give thiepane dioxide: mp 71–71.5° (recorded mp 68°);[20] ir ($CHCl_3$) 1313, 1294, 1120 cm^{-1}.

Anal. Calcd for $C_6H_{12}O_2S$: C, 48.64; H, 8.16. Found: C, 48.74; H, 8.03.

Hydrogenation of 1. Catalyst was prepared by prereducing 13 mg of 10% palladium on charcoal in 10 ml of ethyl acetate. To this was added 62 mg (0.43 mmol) of 1. After 10 min at 32° hydrogen absorption ceased; 2 molar equiv had been consumed. After filtration, evaporation, and recrystallization, hexahydrothiepin 1,1-dioxide (thiepane dioxide) was isolated in good yield, mp and mmp with authentic material 70–71°.

Diels–Alder Adduct of 1. A solution of 0.25 g (1.7 mmol) of 1 and 1.0 g of *N*-methyltriazolinedione in 20 ml of benzene was refluxed for 3.5 hr. After cooling, the precipitate was collected and recrystallized from acetic acid–benzene to give 0.34 g (76%) of the addition product: mp 280–282°; ir (KBr) 1775, 1710, 1330, 1320, 1125 cm^{-1}.

Anal. Calcd for $C_9H_{11}N_3O_4S$: C, 42.03; H, 4.31; N, 16.34. Found: C, 42.00; H, 4.10; N, 16.13.

3-Isopropyl-6-methyl-2,7-dihydrothiepin 1,1-Dioxide (2). A solution of 15 g of a terpene mixture containing ca. 25% of α-terpinene in 1.4 l. of ether was irradiated at 0° for 1.25 hr. After completion of the irradiation 15 g of sulfur dioxide was passed into the

solution, which was maintained at 0° for 3.5 hr and then allowed to warm slowly to 20° during the next 0.75 hr. After removal of the solvent on a rotary evaporator, any unreacted hydrocarbon was removed at 60° (0.1 mm). The remaining residue, a black tar, was taken up in carbon tetrachloride and treated with activated charcoal. After filtration the solution was concentrated to 10 ml and submitted to column chromatography. Fractions containing the product were combined and recrystallized from hexane at low temperature, giving 217 mg (4%) of **2**: mp 67.5–68.5°; ir (KBr) 1315, 1137, 1119 cm^{-1}; NMR ($CDCl_3$) δ 1.13 (d, 6, J = 7 Hz), 2.05 (s, 3), 2.55 (septet, 1, J = 7 Hz), 3.56 (s, 2), 3.62 (s, 2), and 6.21 ppm (s, 2).

Anal. Calcd for $C_{10}H_{16}O_2S$: C, 59.98; H, 8.05. Found: C, 59.91; H, 7.91.

3,5-Dimethyl-2,7-dihydrothiepin 1,1-Dioxide (3). Addition of methylmagnesium chloride to 3-methyl-2-cyclohexenone followed by acidic dehydration gave 1,3-dimethyl-1,3-cyclohexadiene.[21] A solution of 5.0 g (0.046 mol) of the diene in 1.4 l. of ether was irradiated at −10° for 1.25 hr. The solvent was removed upon a rotary evaporator at ca. 0° and the residue was transferred in the cold to a combustion tube. After cooling to −80°, 10 g of sulfur dioxide was added and the vessel was sealed and allowed to warm and maintained at 25° for 7 days. The tube was chilled and opened, and the solvent was allowed to evaporate. The residue was taken up in 10 ml of carbon tetrachloride and submitted to column chromatography by the standard procedure. Fractions containing the product were combined and recrystallized from hexane to give 0.63 g (8%)[21c] of **3**: mp 84–85°; ir (KBr) 1320, 1140, 1120 cm^{-1}; NMR ($CDCl_3$) δ 2.89 (broad s, 3), 2.99 (d, 3, J = 1.5 Hz), 3.58 (s, 2), 3.59 (d, 2, J = 7 Hz), 5.73 (t–q, 1, 7, J = 7, 1.5 Hz), 6.16 ppm (broad s, 1).

Anal. Calcd for $C_8H_{12}O_2S$: C, 55.80, H, 7.03. Found: C, 56.01; H, 7.09.

2,4,6-Trimethyl-2,7-dihydrothiepin 1,1-Dioxide (4) and 2-Ethylidene-3,5,5-trimethyl-2,5-dihydrothiophene 1,1-Dioxide (6). Addition of methylmagnesium chloride to 3,5-dimethyl-2-cyclohexenone followed by acidic dehydration gave a mixture of 1,3,5-trimethyl-1,3-cyclohexadiene[22] and 1,5-dimethyl-3-methylene-1-cyclohexene in approximately equal amounts (GLC analysis). A solution of 5.0 g (0.021 mol of endocyclic component) of diene in 1.4 l. of ether was irradiated at 0° for 1.25 hr. The ether was removed in the cold on a rotary evaporator. The residue was transferred with the aid of 10 ml of ether to a combustion tube and 0.1 g of *tert*-butylcatechol was added. At −80°, 15 g of sulfur dioxide was added and the vessel was sealed. After 24 hr at 25° the mixture was heated to 56° for 72 hr. After chilling the tube was opened and the solvent was allowed to evaporate. The residue was taken up in 10 ml of carbon tetrachloride and submitted to column chromatography by the standard procedure. Fractions containing sulfone product were combined and recrystallized from hexane at 0°. The mother liquors, containing an additional product, were reserved. The crystalline material, 0.70 g (18%), mp 110.5–111.5°, was assigned structure **6**: ir (KBr) 1282, 1155, 1116 cm^{-1}; uv max (C_2H_5OH) 242 nm (ϵ 15000); NMR ($CDCl_3$) δ 1.50 (s, 6), 2.19 (d, 3, J = 8 Hz), 2.27 (s, 3), 4.1 (m, 1), and 6.62 ppm (q–d, 1, J = 8, 1.5 Hz).

Anal. Calcd for $C_9H_{14}O_2S$: C, 58.05; H, 7.58. Found: C, 58.07; H, 7.59.

The hexane mother liquors from the recrystallization of **6** were chilled to −80°, whereupon an oil separated. After decantation the residue was taken up in pentane and the low temperature precipitation was repeated to afford 0.245 g (6%) of **4**, reasonably pure by NMR examination. For analysis the material was evaporatively distilled at 100° (0.01 mm): NMR (CCl_4) δ 1.43 (d, 3, J = 7 Hz), 1.83 (broad s, 3), 2.05 (d, 3, J = 1.5 Hz), ca. 3.3 (m, 1), 3.46 (s, 2), 5.35 (d–q, 1, J = 6, 1.5 Hz), and 6.07 ppm (broad s, 1).

Anal. Calcd for $C_9H_{14}O_2S$: C, 58.05; H, 7.58. Found: C, 58.45; H, 7.70.

Thermal decomposition of **4** was carried out in the manner described for **1**. In addition to sulfur dioxide, a single major hydrocarbon was obtained (GLC analysis), which had spectral properties in accord with its formulation as 2,4-dimethyl-1,*cis*-3,*trans*-5-heptatriene: ir (CCl_4) 970, 895 cm^{-1}; uv max (C_2H_5OH) 257, 267, 277 nm; NMR (CCl_4) δ ca. 1.8 (m, 9), 4.75 (m, 1), 4.92 (m, 1), 5.61 (m, 1), 5.64 (d–d, 1, J = 16, 6.5 Hz), and 6.60 ppm (broad d, 1, J = 16 Hz).

1-Hydroxymethyl-1,3-cyclohexadiene. The following synthesis should be adaptable to give a variety of cyclohexadienes.[23] To a solution of 80.3 g (0.64 mol) of 1-diethylaminobutadiene and 0.1 g of *tert*-butylcatechol in 100 ml of ether in an ice–salt bath and with magnetic stirring was added dropwise over a period of 0.5 hr a solution of 42 g of acrolein in 100 ml of ether. The mixture was stirred for 0.5 hr at 0° and then allowed to warm to 25° and stand for several hours. The ether was removed under vacuum and the residue was diluted with a cold mixture of 100 ml of concentrated hydrochloric acid and 500 ml of water. An aldehyde layer separated and the mixture was warmed briefly to complete diethylamine elimination. Organic material was extracted into ether, which was washed with water and saturated sodium chloride solution. The ether was removed under vacuum to give a residue (62 g) of cyclohexadienecarboxaldehyde,[23] which was submitted to reduction without purification. The product was taken up in 250 ml of methanol and the solution was stirred magnetically at 0° while 10 g of sodium borohydride in dilute sodium carbonate solution was added. After the initial reaction had subsided the mixture was allowed to warm to 25°. After several hours the mixture was diluted with water and extracted three times with ether–pentane. The organic extracts were washed with water and saturated sodium chloride solutions and dried over anhydrous sodium sulfate. The solvent was removed under vacuum and the residue was distilled at reduced pressure through a 20-cm Vigreux column to give 46 g (65%, based on diethylaminobutadiene) of 1-hydroxymethyl-1,3-cyclohexadiene,[23] bp 85–88° (14 mm).

Anal. Calcd for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 76.42; H, 9.17.

A tetracyanoethylene adduct was obtained, mp >200° dec without melting.

Anal. Calcd for $C_{13}H_{10}N_4O$: C, 65.53; H, 4.23; N, 23.52. Found: C, 65.40; H, 4.10; N, 23.59.

1-Acetoxymethyl-1,3-cyclohexadiene. To a mixture of 25 g (0.23 mol) of 1-hydroxymethyl-1,3-cyclohexadiene in 75 ml of pyridine at 0° was added slowly 50 ml of acetic anhydride. The mixture was allowed to come slowly to 25° and then to stand for several hours. The solution was treated with 300 ml of water and the ester was extracted into pentane. The organic extract was washed with dilute hydrochloric acid and with sodium bicarbonate solutions, and then was dried and the pentane was removed under vacuum. The residue was distilled under reduced pressure to give 31.3 g (90.5%) of 1-acetoxymethyl-1,3-cyclohexadiene, bp 58–60° (2 mm).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.94; H, 7.89.

A tetracyanoethylene adduct was obtained, mp 154.5–155°.

Anal. Calcd for $C_{15}H_{12}N_4O_2$: C, 64.27; H, 4.32; N, 19.99. Found: C, 64.26; H, 4.17; N, 20.08.

3-Acetoxymethyl-2,7-dihydrothiepin 1,1-Dioxide (5). A total of 30 g (0.197 mol) of 1-acetoxymethyl-1,3-cyclohexadiene, divided into 6-g batches, each dissolved in 1.4 l. of ether, was irradiated at −10 to −20° for 1.25 hr. From each batch the ether was removed below 20° and the residue was placed in a sealed tube with 15 g of sulfur dioxide, 0.1 g of *tert*-butylcatechol, and sufficient ether to effect transfer. After 4 days at 25° the tubes were opened, solvent was removed from the contents, and the residue was submitted to column chromatography by the standard procedure. Fractions found to contain the product from all batches were combined and recrystallized from large volumes of hexane to give a total of 6.2 g (14.5%) of **5**: mp 65–65.5°; NMR ($CDCl_3$) δ 2.11 (s, 3), 3.65 (d, 2, J = 6 Hz), 3.68 (s, 2), 4.73 (s, 2), 6.1 (m, 1), and 6.5 ppm (m, 2).

Anal. Calcd for $C_9H_{12}O_4S$: C, 50.00; H, 5.60. Found: C, 49.74; H, 5.70.

Adduct of Sulfur Dioxide and Dicyclohexenylethylene (7). This procedure was repeated many times, frequently without success. A solution of 4.61 g (0.025 mol) of dicyclohexenylacetylene[10a] in 50 ml of benzene was hydrogenated using 0.23 g of Lindlar catalyst; hydrogen uptake was interrupted after absorption of ca. 1 molar equiv. After filtration, the benzene was removed under vacuum and the residue, containing *cis*-dicyclohexenylethylene,[10a,c] was transferred with the aid of a little ether to a combustion tube. The vessel was cooled to −80°, 11 g of sulfur dioxide and 0.1 g of *tert*-butylcatechol were added, and the tube was sealed. After standing overnight at 25°, the mixture was heated to 56° for 1.25 hr. The tube was then chilled and opened, and the solvent was allowed to evaporate. The residue was triturated with warm hexane and the insoluble black precipitate was discarded. Removal of the hexane gave 4.84 g of a brown oil, which was submitted to column chromatography by the standard procedure. From appropriate fractions one could occasionally isolate, by low temperature crystallization from hexane, 10–15 mg (<0.2%) of a solid of the expected composition: mp 86–87°; ir (CCl_4) 1310, 1118 cm^{-1}; uv (C_2H_5OH) end absorption only, 235 nm (ϵ 46), 215 (4600); NMR ($CDCl_3$) δ 1–3 (m, 16), 3.5 (m, 1), 4.05 (m, 1), 5.5 (broad q, 1), and

5.65 ppm (m, 1); NMR (C_6H_6) δ 1–2.5 (m, 16), 3.35 (m, 1), 4.1 (m, 1), 5.3 (broad q, 1), and 5.7 ppm (m, 1). The foregoing spectral data exclude a dihydrothiepin dioxide structure for **7** but are in accord with its formulation as *trans*-2-cyclohex-1-enyl-2,4,5,6,7,7a-hexahydrobenzo[*b*]thiophene 1,1-dioxide. The latter sulfolene structure is further supported by the results of thermal decomposition of **7**, which liberates in addition to sulfur dioxide a triene (and/or cyclohexadiene), uv max (C_2H_5OH) 245 nm. This absorption corresponds to that reported for *cis*-dicyclohexenylethylene (uv 248 nm),[10a] and excludes the trans isomer (uv 260, 269, 281 nm)[10a] as the coreactant in the sulfur dioxide cycloaddition.

Anal. Calcd for $C_{14}H_{20}O_2S$: C, 66.64; H, 7.99. Found: C, 66.78; H, 8.05.

9-Thiabicyclo[4.2.1]nona-2,7-diene 9,9-Dioxide (8). This sulfone may be obtained from purified 1,3,5-cyclooctatriene prepared by reduction of cyclooctatetraene.[13] The procedure here given makes use of a currently more readily available hydrocarbon. A mixture of 105 g (0.97 mol) of 1,5-cyclooctadiene, 175 g (0.98 mol) of *N*-bromosuccinimide, and 2 g of benzoyl peroxide in 400 ml of carbon tetrachloride was refluxed overnight. After filtration there was obtained by distillation 94 g of "bromocyclooctadienes", bp 75–80° (25 mm). To this material in 260 ml of dimethylformamide at 0° was added portionwise 60 g of commercial potassium *tert*-butylate over 0.5 hr. Dilution with water, extraction with pentane, and distillation gave 37 g of "cyclooctatrienes",[24] bp 70–75° (60 mm). This material was placed in sealed tubes with approximately equal volumes of sulfur dioxide and a trace of *tert*-butylcatechol. After 12 hr at 100°, the tubes were chilled and opened, and the sulfur dioxide was allowed to evaporate. The residue was triturated with pentane and the crystalline material was collected. The filtrate was evaporated and the residual "cyclooctatriene" was again sealed with sulfur dioxide and heated for 12 hr. This was necessary since the reaction fails to go to completion under these preparative conditions (i.e., in the absence of a very large excess of sulfur dioxide).[4d] After several reaction cycles the product was combined and recrystallized from benzene–hexane to give 29.3 g (49% based on "cyclooctatriene") of **8**: mp 134–136° dec (rapid heating); ir ($CHCl_3$) 1308, 1127, 1108 cm^{-1}; NMR ($CDCl_3$) δ 2–3 (m, 4), 3.7 (broad t, 1), 4.05 (d–d–m, 1, J = 8, 4 Hz), ca. 5.6 (m, 1), ca. 5.9 (m, 1), 6.2 (d–d–m, 1, J = 8, 4 Hz), and 6.6 ppm (d–d–m, 1, J = 8, 4 Hz).

Anal. Calcd for $C_8H_{10}O_2S$: C, 56.46; H, 5.92. Found: C, 56.58; H, 5.86.

9-Thiabicyclo[4.2.1]non-7-ene 9,9-Dioxide. Into several combustion tubes were placed a total of 40 g (0.27 mol) of 1,3-cyclooctadiene, 0.5 g of *tert*-butylcatechol, 60 ml of ether, and 55–60 g of sulfur dioxide (at −80°). The tubes were sealed and maintained at 149–150° for 7 days (*caution:* explosion hazard). They were then chilled and opened, and the sulfur dioxide was allowed to evaporate. From the residue a crystalline product was obtained by dissolution in benzene and precipitation with hexane. This material was sublimed at 130° (0.01 mm) and recrystallized from benzene–hexane to give 5.0 g (8%) of adduct, mp 190–191°. This material also has been prepared indirectly from the sulfur dichloride addition product of 1,3-cyclooctadiene,[25] reported mp 190–191°.

Anal. Calcd for $C_8H_{12}O_2S$: C, 55.80, H, 7.03. Found: C, 55.68; H, 7.02.

9-Thiabicyclo[4.2.1]nonane 9,9-Dioxide. The cyclooctatriene–sulfur dioxide adduct (**8**) was hydrogenated in ethyl acetate solution using rather massive amounts of palladium on charcoal catalyst (in order to overcome an apparent poisoning effect). After filtration and solvent removal, the residue was sublimed at 150° (15 mm) to give the saturated bicyclic sulfone, mp 234–235° (reported mp 235–237°).[25] The same material (no mixture melting point depression) was obtained by hydrogenation of the cyclooctadiene adduct described in the preceding paragraph.

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Registry No.—**1**, 16301-86-3; **1** Diels–Alder adduct, 57196-79-9; **2**, 57196-80-2; **3**, 57196-81-3; **4**, 57196-82-4; **5**, 57196-83-5; **6**, 57196-84-6; **7**, 57196-85-7; **8**, 29294-06-2; hexahydrothiepin 1,1-dioxide, 6251-33-8; hexamethylene sulfide, 4753-80-4; *N*-methyltriazolinedione, 13274-43-6; α-terpinene, 99-86-5; 1,3-dimethyl-1,3-cyclohexadiene, 4573-05-1; 1,3,5-trimethyl-1,3-cyclohexadiene, 1731-26-6; 1,5-dimethyl-3-methylene-1-cyclohexene, 57196-86-8; 2,4-dimethyl-1,*cis*-3,*trans*-5-heptatriene, 57196-87-9; 1-hydroxymethyl-1,3-cyclohexadiene, 21203-48-5; 1-diethylaminobutadiene, 14958-13-5; 1-acetoxymethyl-1,3-cyclohexadiene, 32833-06-0; dicyclohexenylacetylene, 3725-09-5; *cis*-dicyclohexenylethylene, 52944-49-7; 1,3,5-cyclooctatriene, 1871-52-9; 9-thiabicyclo[4.2.1]non-7-ene 9,9-dioxide, 6522-52-7; 1,3-cyclooctadiene, 3806-59-5; 9-thiabicyclo[4.2.1]nonane 9,9-dioxide, 6522-53-8; *cis*-hexatriene, 2612-46-6; sulfur dioxide, 7446-09-5.

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