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Stereochemical Consequences of Orbital Symmetry Control in the Reversible Combining of Sulfur Dioxide with Conjugated Systems (Sulfolene Reactions)

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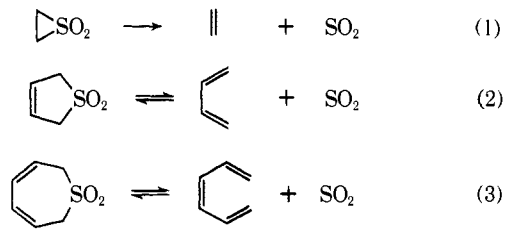
Abstract: The syntheses of the cis and trans stereoisomers of 2,5-dimethyl-2,5-dihydrothiophene 1,1-dioxide (**1** and **2**) and 2,7-dimethyl-2,7-dihydrothiepin 1,1-dioxide (**3** and **4**), the latter pair via a novel ring expansion, are recorded. Thermolysis of these two heterocycles into sulfur dioxide plus 2,4-hexadienes and 2,4,6-octatrienes, respectively, was observed to occur stereospecifically: **1** → (*E*,*E*)-C_6H_{10}; **2** → (*Z*,*E*)-C_6H_{10}; **3** → (*Z*,*Z*,*E*)-C_8H_{12}; **4** → (*E*,*Z*,*E*)-C_8H_{12}. The cheletropic cycloregression proceeded suprafacially in the smaller ring (>99.9%) and antarafacially in the larger ring (>97%) with respect to the hydrocarbon product. Some mechanistic implications regarding these apparently concerted transformations are discussed.

The well known, reversible formation of the sulfolene (2,5-dihydrothiophene 1,1-dioxide) structure from sulfur dioxide plus a conjugated diene comprises a reaction which has occasionally been exploited for synthetic purposes and which also offers challenges of a mechanistic nature having to do with valence shell expansion of sulfur. We attempt here and in the following paper in this issue[2] to summarize our recent and continuing inquiry into the mechanistic details of the chemical interaction of sulfur dioxide with conjugated systems, with specific and especial consideration of orbital symmetry concepts. In this connection, the sulfolene cycloadditions are to be considered as members of a family of cheletropic reactions (eq 1–3). It is from a comparison of structure–reactivity relationships within this sequence that mechanistic inferences may be drawn.



(1)

(2)

(3)

At the inception of this inquiry, episulfone fragmentation (eq 1) had received some study[3] and the sulfolene reaction (eq 2) considerably more thorough examination.[4] The 1,6 addition (eq 3) was found in the course of this investigation.[5] There was for the second and third reactions, however, lack of definitive stereochemical evidence regarding the mode of sulfur dioxide addition and elimination. In this article, we shall describe and comment upon the stereochemical course of fragmentation in the latter set of transformations (eq 2,3). In the following paper in this issue,[2] we describe additional evidence of a kinetic and thermodynamic nature which has bearing on the mechanisms of these reactions.

Adequate documentation exists to establish that fragmentation of the three-membered ring episulfones (eq 1) proceeds cleanly suprafacially with respect to the alkene

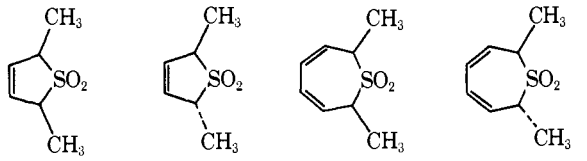
produced.[3] Similarly, it has been known for some time that the sulfolene reaction (eq 2) *could* proceed suprafacially. The evidence is the successful formation of sulfolenes from cyclic dienes (most specifically, 1,3-cycloheptadiene) in which the existence of an antarafacial mode of addition is sterically not feasible.[6] This observation is of a permissive nature only, however, and fails to distinguish between a stereospecific suprafacial addition and a nonstereospecific alternative. Indeed, conclusions from previous studies have favored sequential bond breaking processes for the retroreaction (eq 2).[7] It was apparent that pertinent evidence could be obtained by examination of the decomposition of *cis*- and *trans*-2,5-dimethylsulfolene, in which an unambiguous correlation between the stereochemistry of diene and sulfolene may be drawn. The stereospecific nature of this reaction was reported in a preliminary communication;[8] further details are given below.

Even with the rigorous establishment of the favored stereochemical course of the five-membered ring cheletropic[9] cycloregression, a question of the magnitude of stereoelectronic factors (orbital symmetry) for the system still remained unanswered. As discussed later, this is because other considerations also may be implicated as stereodirective. For this reason, an analogous examination of the seven-membered ring cheletropic reaction (i.e., eq 3, sulfur dioxide elimination from 2,7-dimethyldihydrothiepin 1,1-dioxide) was also incorporated in this study as described below.[10]

Results

Synthesis of Dimethylsulfolene Isomers. Both stereoisomers of 2,5-dimethylsulfolene may be prepared by cycloaddition of the appropriate diene with sulfur dioxide.[8] The previously known isomer[11] has the cis configuration (**1**). Details for the isolation of the trans isomer (**2**) are given in the Experimental Section. It should be noted that, in the case of **2**, the cycloaddition is not cleanly stereospecific, probably because of preliminary diene isomerization. The assignment of relative configuration to the isomers rests upon independent synthesis of the hydrogenation product of **1**,[8b] and the symmetry properties as revealed by NMR of the dibromides and epoxides of **1** and **2**.[8a,12]

Syntheses of Dimethyldihydrothiepin Dioxide Isomers. No sulfone could be isolated upon attempted cycloaddition of sulfur dioxide with octatriene stereoisomers.[5b] Consequently *cis*- and *trans*-2,7-dimethyl-2,7-dihydrothiepin 1,1-dioxide (**3** and **4**, respectively) were obtained by an indirect synthesis. The preparation (from dimethyl 3,3′-thiodibutyrate) has been previously outlined;[10] details may be found in the Experimental Section. The stereochemical assignments follow explicitly from the symmetrical geometry of certain key intermediates in the synthesis of **3** and **4** as revealed by NMR[10] (see Experimental Section).



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

Fragmentation of Sulfones. In the case of 2,5-dihydrothiophene 1,1-dioxides (sulfolenes), the cycloregression, decomposition of **1** or **2** into sulfur dioxide and a hexadiene, may conveniently be carried out either in the "vapor" phase by injection into the intensely heated inlet of a gas chromatograph[8b] or in the liquid phase simply by heating the melt to an appropriate temperature (80–150°).[8a] We feel that the latter method gives the more definitive results, in that equilibrium conditions are more nearly approached. The hydrocarbon product from such pyrolyses was collected in a cold trap and subsequently submitted to GLC analysis. Extraordinarily clean results were obtained; **1** gave exclusively *trans,trans*-2,4-hexadiene, whereas **2** gave only *cis,trans*-2,4-hexadiene. In each case, stereospecificity exceeded 99.9% (Table I). It follows that the elimination had proceeded entirely suprafacially in each case.

Table I. Hydrocarbon Pyrolysate of 2,5-Dimethyl-2,5-dihydrothiophene 1,1-Dioxides (Dimethylsulfolenes)

Diene product	% from 1[a]	% from 2[b]
trans, trans-C_6H_{10}[c]	>99.9	<0.1
cis, trans-C_6H_{10}[c]	<0.1	>99.9
cis, cis-C_6H_{10}[c]	<0.1	<0.1

[a] Pyrolysis temperature 100°. [b] Pyrolysis temperature 150°. [c] C_6H_{10} = 2,4-hexadiene.

Table II. Hydrocarbon Pyrolysate of 2,7-Dimethyl-2,7-dihydrothiepin 1,1-Dioxides

Triene product	% from 3[a]	% from 4[b]
trans, cis, trans-C_8H_{12}[c]	2.2	>98.0
cis, cis, trans-C_8H_{12}[c]	97.7	<1
cis, cis, cis-C_8H_{12}[c]	<0.1	<0.1
trans, trans, trans-C_8H_{12}[c,d]	<0.1	<1

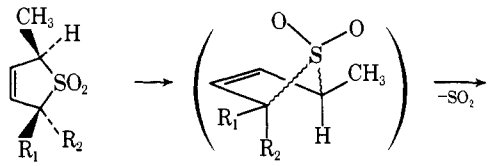
[a] Pyrolysis temperature 195°. [b] Pyrolysis temperature 240°. [c] C_8H_{12} = 2,4,6-octatriene. [d] GLC peaks attributable to other geometrical isomers were in general not detected; however, overlap cannot be excluded (see Experimental Section).

At this point, a strong inference could be drawn about orbital symmetry control in this reaction; however, the mechanism is beclouded by the observation that the episulfone ring (eq 1) also decomposes stereospecifically and suprafacially.[3] It was for this reason that an examination was undertaken of the preferential stereochemical course of the 2,7-dihydrothiepin 1,1-dioxide decomposition (eq 3). For **3** and **4**, insufficient quantities of material were available for liquid phase pyrolysis in the manner of **1** and **2**. Hence, recourse was made to "vapor" phase cracking in a GLC inlet with subsequent direct analysis of the pyrolysate. Stereospecific formation of octatrienes was observed. The product distribution is given in Table II. Identity of trienes (through relative retention times) was aided greatly by data kindly supplied by Professor E. N. Marvell[13] since an authentic sample of only *trans,trans,trans*-2,4,6-octatriene was available. For **4**, an injection port temperature of 225–240° was required. The major hydrocarbon product was *trans,-cis,trans,*-2,4,6-octatriene (>98%). Of the minor components of the pyrolysate, *cis,cis,trans*-2,4,6-octatriene was found in no greater abundance than was the all-trans isomer, lending credence to the suggestion that these may be secondary rearrangement products. (Alternatively, some may have come from *cis,cis,cis*-2,4,6-octatriene; see below.) The requirement for flash pyrolysis (necessary to get a good GLC trace) is that the decomposition temperature be substantially above the minimum (ca. 130°) necessary to effect the transformation. Under these conditions, it is not unreasonable that the initially formed product might undergo isomerization, especially if there were substantial inhomogeneity of actual pyrolysis conditions throughout the region of sample decomposition. This proviso also applies to the elimination of sulfur dioxide from **3**, for which a temperature (GLC inlet) of 195° sufficed. In this case, the major product was *cis,cis,trans*-2,4,6-octatriene (97.7%). The minor isomer, *trans,cis,trans*-2,4,6-octatriene (2.2%), may also have arisen in part from a contaminating amount of **4** in the sulfone submitted to pyrolysis. Further purification of **3** was impractical because of its limited availability. As noted subsequently, cross-contamination of this sort is a

major experimental limitation in the determination of stereospecificities. At higher pyrolysis temperatures, the fragmentation of **3** gave substantially increased quantities of *cis,cis,cis*-2,4,6-octatriene; at 260°, the ratio of the latter to *cis,cis,trans*-2,4,6-octatriene was 1:5.9. This may be easily explained. Marvell, Caple, and Schatz have observed that these isomers readily equilibrate above 100°, presumably interconverting through sequential 1,7 sigmatropic hydrogen migrations.[13] The equilibrium ratio has been reported as 1:5.5, a fact which further supports the identification of trienes as assigned. It may be conservatively concluded that fragmentation of these dihydrothiepin dioxides proceeds at least 97% stereospecifically in an antarafacial sense with respect to the hydrocarbon component.

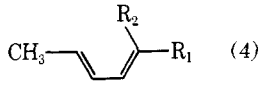
Discussion

The stereochemical results regarding the elimination of sulfur dioxide from the sulfones described in this article may be summarized as follows. For the case of the five-membered ring (sulfones **1** and **2**), fragmentation is cleanly (99.9%) a suprafacial (cis elimination) process with respect to the hydrocarbon (diene) component (eq 4, A, wherein ⇝



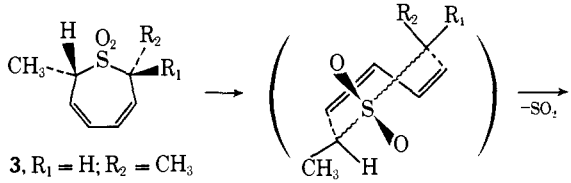
1, $R_1 = CH_3$; $R_2 = H$
2, $R_1 = H$; $R_2 = CH_3$

A



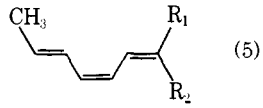
(4)

denotes bond rupture). In contrast, for the seven-membered ring (dihydrothiepin dioxides **3** and **4**), extrusion of sulfur dioxide preferentially proceeds antarafacially (>97% trans elimination) with respect to the hydrocarbon (triene) fragment (eq 5, B).



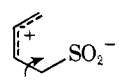
3, $R_1 = H$; $R_2 = CH_3$
4, $R_1 = CH_3$; $R_2 = H$

B



(5)

The first conclusion which can be drawn from these results is that in each case there is being observed a *concerted* reaction (or nearly so). The alternative would be a two-step mechanism involving dipolar[7] or diradical intermediates (e.g., **5** or **6**). There is adequate precedent to suggest that,



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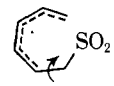
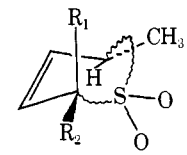
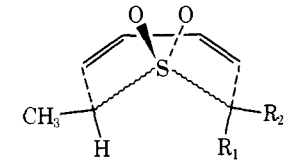


6

should either of such species intervene, *with an appreciable lifetime*, rotation about the bond shown would result in crossover (e.g., such that more than one hexadiene should arise from either dimethysulfolene), in contradistinction to observation.[14] Conversely, should other evidence indicate (for example) a polar nature (**5**) of the transition state, it must be specified that the energy barrier to decomposition of an intermediate such as **5** is less than the rotational barrier about the single bond adjacent to the unsaturated assemblage.[15] Therefore, our working definition of concertedness is an observational one;[15] the reservation is made that considerable nonsynchrony in the order of bond breaking is compatible with experimental observation. Cognate conclusions which follow from the stereochemical results have to do with the geometry of the transition states, which must resemble the species in eq 4 and 5, respectively. Alternative transition states such as shown (A′, B′) must be excluded as



A′



B′

inconsistent with the correlations between sulfones and dienes or trienes.

Application of the principles of orbital symmetry conservation[9] to these cheletropic cycloeliminations satisfactorily rationalizes the stereochemical results. Space does not allow recapitulation of Woodward and Hoffmann's description of the pertinent molecular orbital interactions, for which the comprehensive article is best consulted.[9] However, it is relevant to note that a presumption of a *linear* (as opposed to nonlinear[9]) departure of sulfur dioxide is required. (The nonlinear transition state would involve a nonleast motion path corresponding to an antarafacial interaction at sulfur.[2]) Unfortunately, the stereochemical orientation of sulfur dioxide in the activated complex is not imprinted upon the reaction products as is the hydrocarbon configuration. Hence, the incomplete stereochemical data leave legitimate doubt as to the significance of symmetry constraints in these reactions. This mechanistic point is given fuller consideration in the following paper in this issue.[2] What remains for discussion here is a critical evaluation of factors other than symmetry conservation which might tend to produce the observed stereospecificity. Only if conformational and other stereodirective influences can be discounted will a presumption of concertedness be justified.

Regarding the sulfolene fragmentation, the antarafacial process A′ must be regarded as something of a straw man. For a five-membered cycloalkene, clearly ring strain considerations disfavor the latter, and it also appears the relatively greater C–S bond rupture would be required (for A′ vs. A) before appreciable overlap could develop within the incipient conjugated system. Hence, the suprafacial path of sulfolene dissociation (A) represents a "nonrisky orbital symmetry prediction", and mechanistic conclusions based on this stereochemical result alone would consequently be weak. The argument for stereoelectronic control suffers further debilitation by the stereospecific nature of episulfone fragmentation.[3,8a]

Turning to the seven-membered ring sulfones **3** and **4**, a conclusion may be drawn as to the minimal stereodirective influence of ring strain and nonbonded interactions for these fragmentations. The correlation between octatrienes and their precursor sulfones require that the transition state resemble B (eq 5) rather than B′. In contrast to the sulfolene case, here the apparently disfavored suprafacial mode (B′) suffers no obvious steric prohibition. Inspection of molecular models reveals that the required conformation leading to suprafacial fragmentation is likely quite accessible and in fact probably represents a local minimum on the energy profile connecting the two enantiomerically related conformers of the dihydrothiepin system (which resemble B).[5b,16] (We are unable to provide any evidence from NMR

regarding the velocity of the ring inversion process, such as might be ascertained by detection of magnetic nonequivalence at the α position within dihydrothiepin dioxide itself,[5b] within **3**, or within other derivatives we have synthesized.[5b]) Moreover, regarding the feasibility of the unobserved mode of dissociation, π bonding overlap (in the absence of symmetry constraints) appears comparable or superior in B′ relative to B; the carbon atoms in the former are more nearly coplanar, and hence less torsion would be engendered in the incipient double bonds in the course of fragmentation. Nevertheless, it is transition states corresponding to B (eq 5) which are favored. In discounting nonbonded interactions in the transition state as a causative factor for this stereospecificity, behavior of **3** is the more critical. Note that, in the antarafacial decomposition of this substance, one methyl group must be positioned inward, where it may come in contact with the rest of the molecular aggregation. (Note also the minimal amount of *cis,cis,cis*-octatriene produced from **4**.) Such steric repulsions should be relieved for **3** in B′, which nevertheless does not lead to fragmentation. The lower decomposition temperature of **3** relative to **4** is consistent with a slight ground state destabilization of **3** attributable to this origin. By a process of elimination, one is left with orbital symmetry control as the most probable dominant stereodirective factor in these fragmentations (providing some as yet unrecognized influence is not operative). Therefore, these reactions are classified as retro $[_{\pi}4_s + _{\omega}2_s]$ and $[_{\pi}6_a + _{\omega}2_s]$ processes (eq 4 and 5, respectively, linear departure of sulfur dioxide).[17]

While the preceding considerations allow a reasonable inference of stereoelectronic control and hence concertedness, the quantitative limitations of such a conclusion require comment. It is a fact that an observed 99% stereospecificity in a reaction, while preparatively invariably gratifying, maximally represents only 3–4 kcal/mol of activation energy relative to a nonstereospecific course. For the purpose of understanding the importance of orbital symmetry factors, required is the actual magnitude of the activation energy gap between the real transition state and that for other virtual (or perhaps only hypothetical) mechanisms. The experimental difficulties in measuring extreme stereospecificities (>99.9%) are formidable. There is the analytical problem of detecting and correctly identifying a minor reaction product so as to establish its true proportion relative to the major product. The purity of the reactant must be similarly determined (before and after partial reaction), for the minor product may in fact arise from a contaminant or from a competing conversion (isomerization) of the reactant. In the present study, the stereochemical integrity of the samples of the sulfones submitted to pyrolysis cannot be guaranteed to greater than the stereospecificity exhibited in Tables I and II.

Hence, for definitive, quantitative information regarding the various conceivable paths of fragmentation, one must turn to kinetic data. Rate studies described in the following article[2] allow such comparison. Further mechanistic consideration is deferred until that Discussion.

Experimental Section

General. Elemental analyses were by Galbraith Laboratories, Inc., Knoxville, Tenn., or Micro-Tech Laboratories, Inc., Skokie, Ill. Melting points were taken in capillary tubes. Infrared (ir) spectra were obtained with a Perkin-Elmer spectrophotometer, Model 21 or Infracord and nuclear magnetic resonance spectra (NMR) with a Varian A60 or Hitachi Perkin-Elmer Model 20 instrument.

Preparation of *cis*- and *trans*-2,5-Dimethyl-2,5-dihydrothiophene 1,1-Dioxides (1 and 2).[8,18] A mixture of 62 g (0.76 mol) of *cis,trans*-2,4-hexadiene, 100 g of sulfur dioxide, and 300 mg of *tert*-butylcatechol was sealed in heavy-walled combustion tubes and heated at 100° for 12 hr. After chilling, the tubes were opened, and the sulfur dioxide was allowed to escape. Analysis (NMR) revealed approximately equal amounts of the two isomeric adducts. The product mixture was heated in an oil bath at 100–110° for 1 hr to effect selective decomposition of one isomer. In the course of the heating, *trans,trans*-2,4-hexadiene distilled from the reaction mixture; removal of hydrocarbon was completed under reduced pressure (30 cm). The recovered diene (16 g) was subsequently reconverted to *cis*-dimethylsulfolene. The residue from the distillation was taken up in ether, diluted with hexane, and chilled to promote crystallization. Purification was best effected by recrystallization from rather large volumes of hexane to give 26 g (23.5%) of *trans*-2,5-dimethyl-2,5-dihydrothiophene 1,1-dioxide (**2**): mp 63–63.5°; ir (KBr) 1304 and 1130 cm^{-1}; NMR (CCl_4) δ 1.35 (d, 6, J = 7.5 Hz), 3.53 (q, 2, J = 7.5 Hz), and 5.85 ppm (s, 2).

Anal. Calcd for $C_6H_{10}O_2S$: C, 49.31; H, 6.90. Found: C, 49.89; H, 6.67.

For the formation of the stereoisomeric sulfolene,[11] a solution of *trans,trans*-2,4-hexadiene (such as recovered in the previous operation) was allowed to stand at ca. 50° for several days in ether solution containing an excess of sulfur dioxide. Removal of the solvent and recrystallization of the residue from pentane at low temperatures gave *cis*-2,5-dimethyl-2,5-dihydrothiophene 1,1-dioxide[11] (**1**): mp 43–44°; ir (KBr) 1302 and 1127 cm^{-1}; NMR (CCl_4) δ 1.33 (d, 6, J = 7.4 Hz), 3.60 (q, 2, J = 7.4 Hz), and 5.82 ppm (s, 2).

Anal. Calcd for $C_6H_{10}O_2S$: C, 49.31; H, 6.90. Found: C, 49.12; H, 6.80.

Dimethylsulfolene Dibromides.[8a] A carbon tetrachloride solution of **1** was allowed to react with an excess of bromine to afford a single dibromide, *cis*-3,*trans*-4-dibromo-2,*cis*-5-dimethyltetrahydrothiophene 1,1-dioxide: mp 123–124°; NMR ($CDCl_3$) δ 1.49 (d, 3, J = 7.2 Hz), 1.53 (d, 3, J = 6.9 Hz), 3.40 (q-d, 1, J = 6.9, 8.6 Hz), 3.64 (q-d, 1, J = 7.2 7.5 Hz), 4.14 (d-d, 1 J = 8.6, 8.6 Hz), and 4.74 ppm (d-d, 1, J = 7.5, 8.6 Hz).

Anal. Calcd for $C_6H_{10}Br_2O_2S$: C, 23.53; H, 3.29. Found: C, 23.57; H, 3.45.

Similar treatment of **2** afforded a mixture of two substances in a ratio ca. 2:1 (as estimated by NMR examination of the reaction mixture). Recrystallization from hexane gave the major isomer, *cis*-3,*trans*-4-dibromo-2,*trans*-5-dimethyltetrahydrothiophene 1,1-dioxide: mp 88–88.5°; NMR ($CDCl_3$) δ 1.53 (d, 6, J = 6.7 Hz), ca. 3.2 (m, 2), and ca. 3.9 ppm (m, 2, J_{cis} ca. $\geq$ 8 Hz).

Anal. Calcd for $C_6H_{10}Br_2O_2S$: C, 23.53; H, 3.29. Found: C, 23.97; H, 3.25.

The minor isomer (not isolated) was assigned its structure, *trans*-3,*trans*-4-dibromo-2,*trans*-5-dimethyltetrahydrothiophene 1,1-dioxide, on the basis of relative couplings and chemical shift of the bromomethine protons: NMR ($CDCl_3$) δ 1.51 (d, 6, J = 6.7 Hz), ca. 3.7 (m, 2), and 4.85 ppm (d, 2, J_{trans} = 4.5 Hz).

Preparation of *cis*- and *trans*-2,7-Dimethyl-2,7-dihydrothiepin 1,1-Dioxide (3 and 4). The following sequence describes the synthesis of the stereoisomeric seven-membered ring sulfones. A summarizing flow sheet has appeared in a preliminary communication.[10]

Dimethyl 3,3′-Thiodibutyrate.[19a] A solution of sodium methoxide, which was prepared by the addition of 39 g (1.7 mol) of sodium to 700 ml of methanol, was saturated with hydrogen sulfide at room temperature. To the solution of sodium sulfhydrylate thus obtained was added 145 g of anhydrous sodium acetate. The mixture was placed in an ice bath and stirred magnetically, while 242 g (1.77 mol) of methyl 3-chlorobutyrate was added dropwise over 1 hr. After completion of the addition, the stirred mixture was maintained at 0° for 0.5 hr, then allowed to stir at 25° for 18 hr, and finally was heated to reflux for 3 hr (with stirring). The cooled mixture was poured into 2 l. of water. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic extracts were washed with water and with saturated sodium chloride solution and were dried over calcium chloride. After removal of the ether, the residue was distilled at reduced pressure to give 170 g (82%) of dimethyl 3,3′-thiodibutyrate, bp 105° (0.5 mm), recorded[19a] bp 114–117° (1.5 mm).

3-Carbomethoxy-2,6-dimethyltetrahydro-1,4-thiapyrone. A discussion of the utilization of Dieckmann condensation for obtaining 1,4-thiapyrones is given by Barkenbus, Midkiff, and Newman.[19b] The reaction was conducted according to their recommendations.

Sodium methoxide was prepared by dissolving 17 g of sodium in 350 ml of methanol. Excess methanol was removed under vacuum, finally at 100° (20 mm). The residue (under argon atmosphere) was covered with diethyl ether to which was added 84.2 g (0.36 mol) of dimethyl 3,3′-thiodibutyrate. The mixture was refluxed with magnetic stirring for 18 hr. The mixture was then poured into sufficient dilute acetic acid to neutralize the base, and organic materials were extracted into ether. Upon removal of solvent, a residual oil was obtained which was taken up in hexane and chilled, whereupon a crystalline product separated. Additional material could be secured by reduced pressure distillation of the residue obtained from the mother liquors followed by crystallization from hexane as before. There was obtained a total of 35.75 g (49%) of 3-carbomethoxy-2,6-dimethyltetrahydro-1,4-thiapyrone, mp 80–85°, recorded[19b,c] mp 83.5°, 86°. The material so obtained was used without further purification. As subsequently shown, the methyl groups must possess a cis relationship in this substance. The stereoisomer(s), if present, apparently did not crystallize.

3-Carbomethoxy-2,6-dimethyltetrahydro-1,4-thiapyrone 1,1-Dioxide. To a solution of 34.56 g (0.17 mol) of the preceding sulfide in 400 ml of acetic acid was added slowly with cooling an excess (50 ml) of 40% peracetic acid in acetic acid. After standing for 24 hr at 25°, the mixture (containing a crystalline precipitate) was heated briefly to ensure complete oxidation. The solvent was removed at reduced pressure, and the residue was recrystallized from a large volume of benzene to give 35.2 g (88%) of 3-carbomethoxy-2,6-dimethyltetrahydro-1,4-thiapyrone 1,1-dioxide: mp 185–186°; ir (KBr) 1736, 1712, 1305, 1143, and 1129 cm^{-1}; NMR ($CDCl_3$) δ 1.47 (d, 6, J = 6 Hz), 2.5–4 (m, 5), 3.8 ppm (s, 3).

Anal. Calcd for $C_6H_{14}O_5S$: C, 46.15; H, 6.03. Found: C, 46.34; H, 6.05.

This oxidation under different conditions has been described as yielding a sulfone, mp 174–175°.[19b] We obtained by the latter procedure a mixture, mp ca. 173°, of two components: the sulfone and a corresponding sulfoxide (which could be further oxidized to the sulfone). The mixture could not be resolved by crystallization, but column chromatography on silicic acid readily gave 3-carbomethoxy-2,6-dimethyltetrahydro-1,4-thiapyrone 1-oxide: mp 163° dec; mmp with the sulfone 173° dec; ir (KBr) 1736, 1712, and 1042 cm^{-1}; NMR ($CDCl_3$) δ 1.47 (d, 6, J = 6.5 Hz), 2.3–3.6 (m, 5), 3.8 ppm (s, 3).

Anal. Calcd for $C_9H_{14}O_4S$: C, 49.54; H, 6.47. Found: C, 49.69; H, 6.18.

2,6-Dimethyltetrahydro-1,4-thiapyrone 1,1-Dioxide. A mixture of 15.0 g (0.064 mol) of 3-carbomethoxy-2,6-dimethyltetrahydro-1,4-thiapyrone 1,1-dioxide, 200 ml of concentrated hydrochloric acid, 150 ml of distilled water, and 25 ml of ethanol was heated at 100° for 24 hr. The solvent was removed under reduced pressure, and the residue was dried by repeatedly treating with benzene and evaporating to dryness. Finally, recrystallization from benzene–hexane gave 11.0 g (97.5%) of 2,6-dimethyltetrahydro-1,4-thiapyrone 1,1-dioxide: mp 143–146°; ir (KBr) 1724, 1319, 1266, 1145, and 1120 cm^{-1}; NMR ($CDCl_3$) δ 1.46 (d, 6, J = 6 Hz), 2.5–3.6 ppm (m, 6).

Anal. Calcd for $C_7H_{12}O_3S$: C, 47.72; H, 6.87. Found: C, 47.19; H, 6.98.

4-Acetoxy-*cis*-2,6-dimethyl-2,5-dihydrothiapyran 1,1-Dioxide. To a solution of 5.82 g (0.033 mol) of the ketosulfone in 50 ml of chloroform were added 15 ml of acetic anhydride and 3 drops of 70% perchloric acid. After 20 hr at 25° the dark solution was treated with excess solid anhydrous sodium acetate; upon neutralization, the solution became less dark. Solvent was removed under reduced pressure, and the residue was extracted with carbon tetrachloride. The concentrated extracts were submitted to column chromatography under standard conditions.[20]

The first substance obtained from the chromatography was recrystallized from benzene–hexane to give 2.83 g (30.8%) of 4,4-diacetoxy-*cis*-2,6-dimethyltetrahydrothiapyran 1,1-dioxide: mp 155–156°; NMR ($CDCl_3$) δ 1.33 (d, 6, J = 7 Hz), 2.03 (s, 3), 2.12 (s, 3), 2.2–3.4 ppm (m, 6). It should be noted that nonequivalent acetoxyl groups in conjunction with equivalent ring methyl groups define the relative stereochemistry of the latter as cis.

Anal. Calcd for $C_{11}H_{18}O_6S$: C, 47.48; H, 6.52. Found: C, 47.97; H, 6.23.

The second substance eluted was recrystallized from benzene–hexane to give 2.11 g (29.3%) of 4-acetoxy-*cis*-2,6-dimethyl-2,5-dihydrothiapyran 1,1-dioxide: mp 97–98°; NMR ($CDCl_3$) δ 1.39 (d, 3, J = 6.5 Hz), 1.44 (d, 3, J = 7 Hz), 2.12 (s, 3), 2.64 (m, 2), 3.33 (quin, 1, J = 7 Hz), 3.85 (m, 1), and 5.21 ppm (m, 1).

Anal. Calcd for $C_9H_{14}O_4S$: C, 49.54; H, 6.47. Found: C, 49.90; H, 6.31.

The third substance obtained from the chromatography was recrystallized from benzene–hexane to give 1.42 g (24.5%) of recovered ketosulfone. This could be combined with the *gem*-diacetate and recycled to afford more enol acetate. It seems that the acetylation procedure yields an equilibrium mixture in the above proportions.

4-Acetoxy-*trans*-2,*trans*-6-dimethyl-*cis*-3,4-(dichloromethano)tetrahydrothiapyran 1,1-Dioxide. A mixture of 2.66 g (12.2 mmol) of the enol acetate from the above procedure and 22.75 g (51.7 mmol) of phenyl(bromodichloromethyl)mercury in 80 ml of benzene was stirred magnetically at 80° for 14 hr. The solution was cooled, and 16.4 g of phenylmercuric bromide was collected. The filtrate was evaporated to dryness under reduced pressure. The residue was taken up in carbon tetrachloride and submitted to column chromatography by the standard procedure.[20] Some oily, mercury containing material was eluted first, followed in subsequent fractions by the desired product and then by additional substances as described below.

Fractions containing the first solid material were combined and recrystallized from benzene–hexane to give 2.14 g (58%) of 4-acetoxy-*trans*-2,*trans*-6-dimethyl-*cis*-3,4-(dichloromethano)tetrahydrothiapyran 1,1-dioxide: mp 131.5–132°; ir (KBr) 1761, 1307, 1143, 1130 cm^{-1}; NMR ($CDCl_3$) δ 1.34 (d, 3, J = 6.5 Hz) 1.67 (d, 3, J = 7 Hz), 1.90 (d, 1, J = 4.5 Hz), 2.08 (s, 3), 2.2–3.6 ppm (m, 4).

Anal. Calcd for $C_{10}H_{14}Cl_2O_4S$: C, 39.89; H, 4.69. Found: C, 40.05; H, 4.77.

In subsequent chromatographic fractions was found 0.095 g of a stereoisomer, formulated as 4-acetoxy-*cis*-2,*cis*-6-dimethyl-*cis*-3,4-(dichloromethano)tetrahydrothiapyran 1,1-dioxide: mp 198–199°; NMR ($CDCl_3$) δ 1.35 (d, 3, J = 6.5 Hz), 1.70 (d, 3, J = 7 Hz), 2.08 (s, 3), 2.1–4.3 ppm (m, 5).

Anal. Calcd for $C_{10}H_{14}Cl_2O_4S$: C, 39.89; H, 4.69. Found: C, 40.24; H, 4.75.

Finally, from the chromatography, there was obtained 0.30 g (11%) of recovered enol acetate and a small amount of the corresponding ketosulfone.

4-Acetoxy-*trans*-2,*trans*-6-dimethyl-*cis*-3,4-(*syn*-chloromethano)tetrahydrothiapyran 1,1-Dioxide. A mixture of 3.45 g (11.45 mmol) of the major dichlorocarbene adduct in 6.54 g (22.5 mmol) of freshly distilled tributylstannane was flushed with argon and then was heated with magnetic stirring at 130°.[21a] Stirring was continued until the mixture became homogeneous, and the solution was maintained at 130° under an argon atmosphere for 10 hr. The solution was cooled and diluted with 10 ml of chloroform and 10 ml of carbon tetrachloride. The resulting solution was filtered and submitted to column chromatography by the standard procedure.[20] The early fractions eluted contained as oils the organotin products. Subsequent fractions were observed to solidify upon removal of solvent. The first of these (containing the major reaction product) was combined and recrystallized from benzene–hexane to give 1.76 g (58.6%) of 4-acetoxy-*trans*-2,*trans*-6-dimethyl-*cis*-3,4-(*syn*-chloromethano)tetrahydrothiapyran 1,1-dioxide:[21] mp 161–163°; NMR ($CDCl_3$) δ 1.34 (d, 3, J = 6.5 Hz), 1.63 (d, 3, J = 7 Hz), ca. 1.64 (q?, 1, coupling obscured by methyl resonance), 2.00 (s, 3), 2.2–3.6 ppm (m, 6).

Anal. Calcd for $C_{10}H_{15}ClO_4S$: C, 45.04; H, 5.67. Found: C, 45.63; H, 5.77.

Eluted immediately following, in the chromatography, was a stereoisomer. After ca. 100 mg of mixed fractions, there was obtained, after recrystallization from benzene–hexane, 0.35 g (11.5%) of material assigned the structure 4-acetoxy-*trans*-2,*trans*-6-dimethyl-*cis*-3,4-(*anti*-chloromethano)tetrahydrothiapyran 1,1-dioxide: mp 159–160° (mmp with syn isomer ca. 130°); NMR ($CDCl_3$) δ (d, 3, J = 6.5 Hz), 1.60 (d, 3, J = 7 Hz), ca. 1.40 (q?, 1, coupling obscured by methyl resonance), 2.07 (s, 3), 2.3–3.4 ppm (m, 6).

Anal. Calcd for $C_{10}H_{15}ClO_4S$: C, 45.05; H, 5.67. Found: C, 45.31; H, 5.70.

Finally there was obtained from the chromatography (following

an additional 100 mg of mixed fractions) 0.25 g of material, mp 138–140° after recrystallization from benzene–hexane, which was formulated as the bishydrodechlorination product, but which was not further investigated.

Anal. Calcd for $C_{10}H_{16}O_4S$: C, 51.72; H, 6.94. Found: C, 51.65; H, 6.94.

***trans*-2,7-Dimethyl-5-oxo-2,5,6,7-tetrahydrothiepin 1,1-Dioxide.**[22] To a magnetically stirred solution of 267 mg (1.0 mmol) of the major chlorocyclopropane from the above procedure in 50 ml of ether under an argon atmosphere at 0° was added, over a period of 5 min, a standardized ether solution of 10 mequiv (hydride) of lithium aluminum hydride. The mixture was then immediately quenched at 0° with 5 ml of 10% sulfuric acid, and the mixture was stirred until a clear (two phase) solution resulted. The ether was removed under reduced pressure, and the residue was extracted seven times with chloroform. The combined extracts were concentrated and submitted to column chromatography on 15 g of neutral silicic acid with chloroform elution. The first material eluted contained unreacted starting material (ca. 6 mg) plus other substances. This was followed by several fractions containing a total of 140 mg of the crude cyclopropanol from reductive deacetylation. This was taken up in 25 ml of benzene, and 120 mg of triethylamine was added. After 1 hr at 25°, 67 mg of triethylamine hydrochloride was collected. The filtrate was evaporated to dryness, and the residue was submitted to column chromatography as before. The fractions which solidified upon removal of solvent amounted to 94 mg. Two recrystallizations from benzene–hexane followed by sublimation at 100° (0.1 mm), and an additional recrystallization finally gave 61 mg (31%) of *trans*-2,7-dimethyl-5-oxo-2,5,6,7-tetrahydrothiepin 1,1-dioxide: mp 157–158.5° dec (darken 145°); ir (KBr) 1692, 1307, and 1130 cm^{-1}; NMR (CCl_4) δ 1.46 (d, 3, J = 7 Hz), 1.67 (d, 3, J = 7 Hz), 2.75 (d-m, 1, $|J|$ = 18 Hz), 3.2 (d, 1, $|J|$ = 18 Hz), 3.65 (m, 1), 4.32 (d-q, 1, J = 7, 2.5 Hz), and 6.19 ppm (m, 2).

Anal. Calcd for $C_8H_{12}O_3S$: C, 51.06; H, 6.43. Found: C, 51.15; H, 6.48.

As subsequently shown,[10] an epimerization of one methyl group must have occurred in the latter step. The mother liquors from the recrystallization contained the cis isomer and were reserved for the preparation of **3.**

***trans*-2,7-Dimethyl-2,7-dihydrothiepin 1,1-Dioxide (4).** To a solution of 103.5 mg (0.57 mmol) the above unsaturated ketosulfone was added portionwise 50 mg of sodium borohydride. After gas evolution had subsided, 0.5 g of silicic acid was added, and the solvent was removed at reduced pressure. The residue was repeatedly extracted with hot chloroform, and the combined extracts were evaporated to dryness. The new residue was taken up in 2 ml of cold 93% sulfuric acid and allowed to stand for 10 min at 0°. The mixture was diluted with ice, saturated with potassium bisulfate, and extracted repeatedly with chloroform. The combined extracts were dried, and the solvent was removed under reduced pressure. The residual oil was submitted to column chromatography on 4 g of silicic acid with chloroform elution. Early fractions found to contain solid material upon removal of solvent were combined and gave, after recrystallization from hexane at 0°, a total of 21 mg (21.5%) of *trans*-2,7-dimethyl-2,7-dihydrothiepin 1,1-dioxide (**4**): mp 83–83.5°; NMR (CCl_4) δ 1.57 (d, 6, J = 7.1 Hz), 3.29 (d-q, 2, J = ca. 7 Hz), 5.70 (d-d-m, 2, J = 9.6, 5.9 Hz), and 6.42 ppm (d-m, 2, J = 9.6 Hz).

Anal. Calcd for $C_8H_{12}O_2S$: C, 55.80; H, 7.03. Found: C, 55.77; H, 7.23.

***cis*-2,7-Dimethyl-2,7-dihydrothiepin 1,1-Dioxide (3).** The combined mother liquors from the recrystallizations of the precursor to **4** were evaporated under reduced pressure, and the residue was submitted to the borohydride reduction–dehydration procedure. Column chromatography as before gave a quantity of the trans isomer **4** eluted first, followed closely by a small amount of the cis isomer. Fractions rich in the latter were combined and recrystallized from pentane at low temperatures to give a few milligrams of *cis*-2,7-dimethyl-2,7-dihydrothiepin 1,1-dioxide (**3**): mp 53–54°; NMR (CCl_4) δ 1.45 (d, 6, J = 7 Hz), 3.77 (d-q, 2, J = ca. 7 Hz), 5.7 (m, 2), and 6.3 ppm (m, 2). There was insufficient material for elemental analysis; the purified sulfone was committed to thermolysis. It was confirmed by NMR analysis of crude reaction mixture that no **3** was formed from purified (recrystallized) precursor ketone of **4.** It follows that further methyl group epimerization under the acid-catalyzed dehydration had not occurred.

***cis*-2,7-Dimethyl-4-oxo-2,7-dihydrothiepin 1,1-Dioxide.** For the purpose of confirmation of the assigned stereochemistry of **4**, an alternative ring expansion was performed upon the ketosulfone, *cis*-2,6-dimethyltetrahydro-1,4-thiapyrone 1,1-dioxide, produced earlier in the sequence and shown unambiguously to have cis-methyl groups. A recently developed technique[23] which avoids the possibility of base-induced epimerization was employed. To a solution of 6.79 g (38.5 mmol) of the ketosulfone in 100 ml of methylene chloride was added 8.0 g (42.0 mmol) of triethyloxonium fluoborate in 20 ml of methylene chloride. To the resulting solution at 0° was added 5.05 g (44.3 mmol) of ethyl diazoacetate, and the mixture was allowed to come slowly to 25° over night (gas evolution). The solution was then treated with 5 g of calcium carbonate and 5 g of silicic acid, and the mixture was stirred until gas evolution had subsided. The filtered solution was then concentrated under reduced pressure, and the residue was submitted to column chromatography under standard conditions.[20] There were several components in the product mixture; the major substance, which was the first eluted (and which gave a positive ferric chloride test for enol content), proved to be the desired material, 2.8 g of 5-carbethoxy-*cis*-2,7-dimethyl-4-oxothiapane 1,1-dioxide, mp ca. 80°, contaminated with a small amount of the glycidic ester derived also from the ketosulfone and ethyl diazoacetate. The keto ester was decarbethoxylated directly. A mixture of 2.16 g (8.2 mmol) of the ester, 50 ml of concentrated hydrochloric acid, and 50 ml of distilled water was heated at 100° for 3 hr. The solution was cooled and extracted repeatedly with chloroform. Upon drying and evaporation, the extracts yielded a residue which upon recrystallization from benzene–hexane gave 1.35 g (18% overall) of *cis*-2,7-dimethyl-4-oxothiapane 1,1-dioxide; mp 103–104° (2,4-DNP derivative, mp 213–214°); NMR ($CDCl_3$) δ 1.43 (d, 6, J = 6.8 Hz), ca. 2.0 (m, 2), ca. 2.7 (m, 4), and ca. 3.3 ppm (m, 2).

Anal. Calcd for $C_8H_{14}O_3S$: C, 50.52; H, 7.42. Found: C, 50.31; H, 7.46.

Comparison of *cis*- and *trans*-2,7-Dimethyl-4-oxothiapane 1,1-Dioxide. Catalytic hydrogenation (palladium on carbon) of 15 mg of the unsaturated ketone precursor to **4** in a few milliliters of ethyl acetate results in the rapid uptake of 1 equiv of hydrogen. Removal of the catalyst and solvent gave *trans*-2,7-dimethyl-4-oxothiapane 1,1-dioxide as an oil which failed to crystallize at 0°, even when seeded with the cis isomer from the preceding experiment. Comparison of NMR spectra confirmed the nonidentity of the new material with the cis isomer; all resonances were confined to the same region (δ 1.5–4 ppm), but there were no congruencies of individual lines in the spectra (2,4-DNP derivative, mp 236–237°; 2,4-DNP derivative with 2,4-DNP derivative of cis isomer mmp 202–212°). It follows that **4** does not have cis-methyl groups. (The possibility that a gross rearrangement had occurred is excluded by the following experiment.)

Stereochemical Confirmation of Structure for 3 and 4. Comparison of *cis*- and *trans*-2,7-Dimethylthiapane 1,1-Dioxide. Authentic *cis*-2,7-dimethylthiapane 1,1-dioxide was prepared as follows. A tosylhydrazone of the crystalline saturated 4-ketone (above) was prepared in ethanol in 97% yield, mp 199–200° dec. This was treated in methanol solution with a large excess of sodium borohydride,[24] and the resulting solution was refluxed overnight. Evaporation and extraction with carbon tetrachloride followed by column chromatography on silicic acid gave a low yield of a noncrystalline sulfone, *cis*-2,7-dimethylthiapane 1,1-dioxide.

Catalytic hydrogenation (palladium on carbon) of 8 mg of **4** in a few milliliters of ethyl acetate resulted in the rapid uptake of 2 equiv of hydrogen. Removal of the catalyst and solvent gave *trans*-2,7-dimethylthiapane 1,1-dioxide as an oil which failed to crystallize.

The stereoisomers of the saturated sulfones were separable by GLC on a neopentylglycol succinate column at 200°. The cis isomer had a retention time 0.96 times that of the trans isomer. Equilibration, starting with either stereoisomer, was achieved in dimethyl sulfoxide solution in the presence of a trace of potassium *tert*-butylate. The reaction was followed by NMR; each isomer gave after several hours at 40° a cis:trans ratio of 60:40 ± 5% as estimated from the intensity of the overlapping but distinguishable methyl resonances of the individual isomers (in DMSO). The NMR spectral resolution was superior to that of GLC. Other spectral properties of the individual isomers were very similar: NMR (CCl_4) δ 1.36 (d, 6, J = 7 Hz), ca. 1.75 (m, 8), and ca. 2.8 ppm

(m, 2), essentially identical for both isomers. Interconversion of stereoisomers establishes that the thiapane ring was indeed produced by both ring expansion techniques[21,22] and rigorously proves the assigned stereochemistry of **3** (cis) and **4** (trans).

Pyrolyses of 1 and 2. As described under Results, thermal decomposition of the dimethylsulfolenes was conducted by heating a quantity of the sulfone in an enclosed vessel connected to a cold trap from which the hydrocarbon was subsequently collected. Analysis[14a] by GLC (tris(2-cyanoethoxy)propane column) gave the results described in Table I. Resolution was sufficiently clean (no overlap of peaks) that an upper limit of 0.1% crossover product could be set. The stereochemical integrity of the sulfone samples submitted to pyrolysis cannot be guaranteed to greater than this limit.

Pyrolyses of 3 and 4. As described under Results, thermal decomposition of the dimethyldihydrothiepin dioxides was conducted by injecting small quantities in (ca. 5%) chloroform solution into the heated inlet of a gas chromatograph (nominal temperatures: 195° for **3**, 240° for **4**). Subsequent analysis (column: 85°, packing 20 ft of 5% tris(2-cyanoethoxy)propane gave the results listed in Table II. The relative retention times for the various octatrienes were as follows: trans,trans,trans, 1.0; trans,cis,trans, 1.16; cis,-cis,trans, 1.25; cis,cis,cis, 1.33. As noted under Results, at higher injection port temperatures (260°), the last two products interconvert.[13] This was of assistance in establishing an upper limit for the amount of *cis,cis,trans*-2,4-6-octatriene produced from **4**. Since the latter triene appeared only as a shoulder on the tail of the very intense trans,cis,trans peak, it was an advantage to be able to measure the intensity of the well-resolved peak of the all-cis isomer at 260° and thereby independently check the estimate of the amount of *cis,cis,trans*-2,4-6-octatriene present. At the higher temperatures (~260°), a small peak of near relative retention time 1.12 appeared also. We tentatively suggest that this may be the cis,-trans,trans isomer since retention time appears to be proportional to cis content. Spectral data for the trienes were structurally uninformative. The assignments in the chromatographic data just given correlate with information kindly supplied by Professor E. N. Marvell regarding the trans,cis,trans and cis,cis,trans isomers, which have been prepared in his laboratory.[13]

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