Thietanes. II. Rearrangement of 2,4-Diphenylthietane Dioxides to 3,5-Diphenyl-1,2-oxathiolane 2-Oxides

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Received August 31, 1970

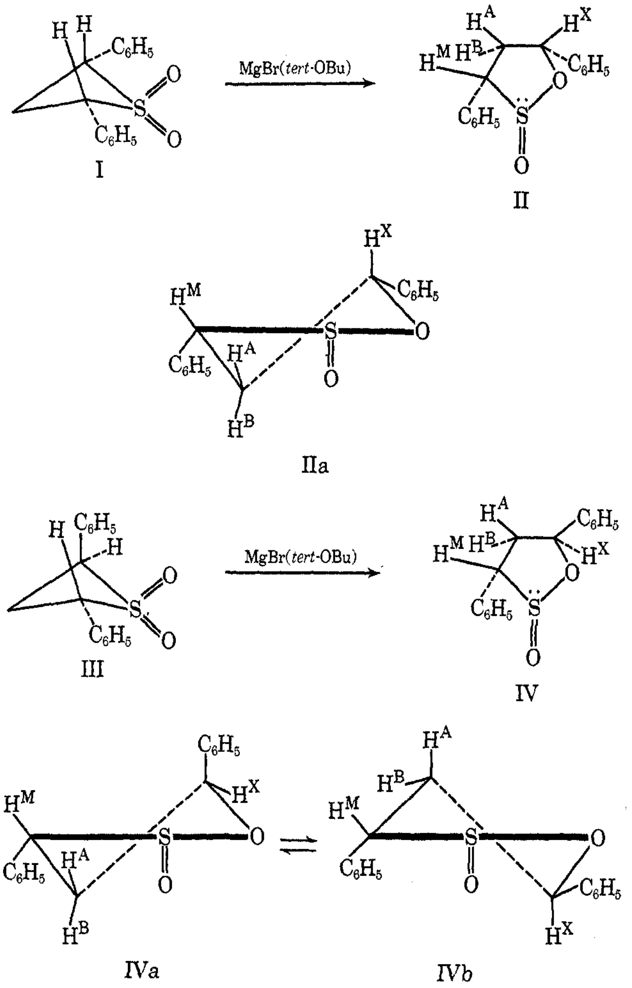
cis- and *trans*-2,4-diphenylthietane 1,1-dioxides (I and III, respectively) when treated with *tert*-butoxymagnesium bromide rearranged to *cis*-3,5-diphenyl-1,2-oxathiolane *cis*-2-oxide (II) and *trans*-3,5-diphenyl-1,2-oxathiolane (2,3)-*cis*-2-oxide (IV), respectively. Configurations for II and IV were assigned from an analysis of their nmr spectra. Probable conformations for II and IV were calculated from the nmr spectra.

Recently we have described the syntheses and the determinations of configurations and conformations of the 2,4-diphenylthietanes, their monoxides, and dioxides.[1] Here, we report the rearrangement of the *cis*- and *trans*-2,4-diphenylthietane 1,1-dioxides (I and III, respectively) by reaction with *tert*-butoxymagnesium bromide to *cis*-3,5-diphenyl-1,2-oxathiolane *cis*-2-oxide (II) and *trans*-3,5-diphenyl-1,2-oxathiolane (2,3)-*cis*-2-oxide (IV),[2] respectively.[3]

Only two examples of the conversion of "thiete dioxides" to cyclic sulfinates[4] had been reported in the literature at the time of our initial report. More recently the conversions of thiete dioxide itself and 2-phenylthiete dioxide to the corresponding 1,2-oxathiol-3-enes have been described.[5] All of the above were pyrolytic transformations; the intermediacy of a vinylsulfene was postulated.[5,6] Related rearrangements of cyclic sulfones to sulfinates have also been postulated to explain the fragmentation patterns of cyclic sulfones in mass spectrometry.[7] However, the rearrangement described here differs from any of those previously reported. This rearrangement is ionic, is catalyzed by base, occurs at moderate temperatures (35°), and is stereospecific.

Syntheses.—Reaction of *cis*-2,4-diphenylthietane 1,1-dioxide (I) with *tert*-butoxymagnesium bromide[8] in ether gave *cis*-3,5-diphenyl-1,2-oxathiolane *cis*-2-oxide (II) in 70% yield (Scheme I). A comparable reaction with *trans*-2,4-diphenylthietane 1,1-dioxide (III) gave *trans*-3,5-diphenyl-1,2-oxathiolane (2,3)-*cis*-2-oxide (IV) in much lower (41%) yield. The constitutions of these sultines,[4c] II and IV, were established by their elementary analyses, by the presence of bands in the ir spectra corresponding to those of sulfinates (1149 and 1138 cm^{-1} for II and IV, respectively), by the presence in their mass spectra of a base peak corresponding to M − SO_2, and by the complete analysis of their nmr spectra. The constitutions of II and IV were confirmed by their independent syntheses from 1,3-diphenyl-3-hydroxypropanethiol[1] (VI) *via* oxidation with chlorine in glacial acetic acid,[9] a method now known to give cyclic sulfinates. *cis*- and *trans*-3,5-diphenyl-5-deuterio-1,2-oxathiolane 2-oxides (5D-II and 5D-IV, respectively) also were synthesized by this same method using 3-deuterio-1,3-diphenyl-3-hydroxypropanethiol (VI), prepared by the reduction of 1,3-diphenyl-3-acetylthio-1-propanone[1] with lithium aluminum deuteride.

SCHEME I



Both II and IV were readily oxidized with *m*-chloroperbenzoic acid to the corresponding diphenyl sultones VII and VIII. Since this oxidation destroyed the asymmetry of the sulfur center, and since distinctly

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[1] R. M. Dodson, E. H. Jancis, and G. Klose, *J. Org. Chem.*, **35**, 2520 (1970).

[2] By (2,3)-*cis*-2-oxide we designate that the oxygen on the sulfur atom at 2 is cis to the phenyl group at C-3

[3] A preliminary account of this work has been published: R. M. Dodson, P. D. Hammen, and R. A. Davis, *Chem. Commun.*, 9 (1968); 535 (1968) (correction).

[4] (a) R. W. Hoffmann and W. Sieber, *Justus Liebigs Ann. Chem.*, **703**, 96 (1967); (b) D. C. Dittmer, R. S. Henion, and N. Takashina, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Abstract O-101; (c) D. C. Dittmer, R. S. Henion, and N. Takashina, *J. Org. Chem.*, **34**, 1310 (1969).

[5] J. F. King, K. Piers, D. J. H. Smith, C. L. McIntosh, and P. de Mayo, *Chem. Commun.*, 31 (1969); C. L. McIntosh and P. de Mayo, *ibid.*, 32 (1969).

[6] J. F. King, A Hawson, D. M. Deaken, and J. Komery, *ibid.*, 33 (1969).

[7] E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **88**, 2836 (1966), plus additional references given in ref 4c.

[8] The structure of *tert*-butoxymagnesium bromide has been determined by X-ray diffraction: P. T. Moseley and H. M. M. Shearer, *Chem. Commun.*, 279 (1968).

[9] P. D. Hammen, Ph.D. Thesis, University of Minnesota, April 1967; E. N. Givens and L. A. Hamilton, *J. Org. Chem.*, **32**, 2857 (1967).

Table I[a]

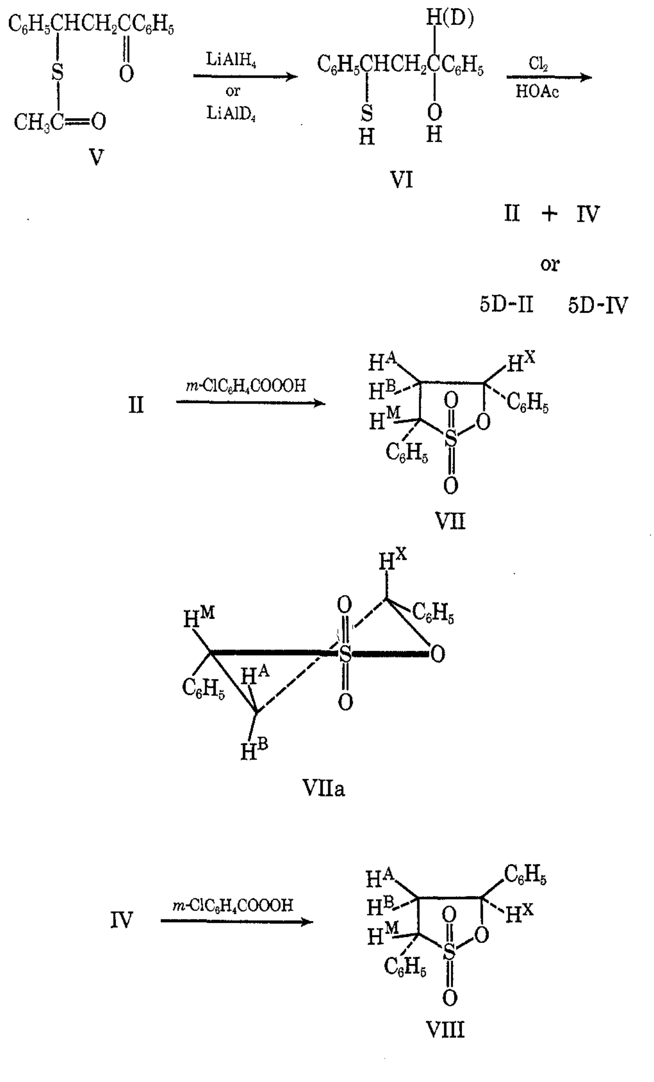
3,5-Diphenyl-1,2-oxathiolanes

Compd[b]	ν_A	ν_B	ν_M	ν_X	J_{AB}	J_{AM}	J_{AX}	J_{BM}	J_{BX}	J_{MX}
				$CDCl_3$						
II cis sultine	163.7	172.0	257.5	334.8	−13.30	5.73	5.54	14.01	11.00	−0.12
IV trans sultine	154.7	197.7	260.8	370.4	−13.04	7.36	2.53	12.59	8.56	−0.10
VII cis sultone	180.9	177.9	283.2	338.2	−13.57	6.44	5.80	13.66	11.03	−0.22
VIII trans sultone	171.4	198.5	273.9	345.9	−13.43	8.05	4.36	10.51	7.93	−0.05
				C_6H_6						
II cis sultine	125.4	160.4	224.7	311.3	−13.15	5.76	5.60	13.84	10.95	−0.15
IV trans sultine	119.4	176.6	233.5	355.1	−12.93	7.40	2.48	12.69	8.67	−0.12
VII cis sultone	120.3	148.2	252.6	301.6	−13.32	6.44	5.73	13.54	11.00	−0.07
VIII trans sultone	126.1	161.2	252.5	316.6	−13.54	8.08	4.33	10.49	7.96	−0.04

[a] Recorded in hertz downfield from tetramethylsilane; determined at 60 MHz. [b] Cis and trans refer to the relationship of the phenyl groups.

different diphenylsultones, VII and VIII, were obtained, it followed that one of these must have *cis*-phenyl groups while the other must have *trans*-phenyl groups (Scheme II).

Scheme II



Studies on the course of the rearrangements of I and III to II and IV, respectively, using nmr spectroscopy as the diagnostic method, showed that the cis sulfone I rearranged to the *cis*-3,5-diphenyl-1,2-oxathiolane *cis*-2-oxide (II) which persisted through the total time of the reaction. The trans sulfone III, however, initially rearranged to *trans*-3,5-diphenyl-1,2-oxathiolane (2,3)-*cis*-2-oxide (IV) which then slowly rearranged to the cis sultine II. After 76 hr only the cis sultine II could be isolated from the reaction of the trans sulfone III with *tert*-butoxymagnesium bromide. The nmr spectral studies of the course of this reaction also showed absorption bands at intermediate times (6.5 to 24 hr) that could have belonged to a third isomeric sultine. The relative stabilies of II and IV in the presence of *tert*-butoxymagnesium bromide provided evidence for the relative configurations of the phenyl groups. Five-membered rings with large groups at the 1 and 3 positions are usually more stable in the cis than in the trans configuration.[10] Thus, from these data, a cis configuration was assigned to the phenyl groups in II and a trans configuration to the phenyl groups in IV.

Configurations.—The relative configurations of the phenyl groups in II and IV were confirmed by a complete analysis of the nmr spectra of the cis sultine II and the trans sultine IV (Table I). If the sultines exist in half-chair conformations corresponding to IIa, and IVa and/or IVb, the nmr spectrum of the cis sultine IIa with both phenyl groups occupying pseudoequatorial conformations should show two vicinal coupling constants of moderate size (J_{AM} and J_{AX}) and two vicinal coupling constants of large size (J_{BM} and J_{BX}). This is exactly what is found for that isomer assigned the *cis*-diphenyl configuration from stability studies. If either conformer IVa or IVb predominates for the trans sultine IV, then the nmr spectrum of IV should show one large, one small, and two moderately sized vicinal coupling constants. The experimental results indicate the predominance of one conformer.

The nmr spectra of the isomeric 5-deuterio-3,5-diphenyl-1,2-oxathiolane 2-oxides (5D-II and 5D-IV) lacked those absorption bands at lowest field [334.8 and 370.4 Hz ($CDCl_3$) for II and IV, respectively]. Consequently, these chemical shifts (ν_X) were assigned to the C-5 hydrogen atoms of II and IV. This immediately led to a complete assignment of the chemical shifts (ν) and coupling constants (J) to the protons of the isomeric sultines II and IV.[11] It also indicated that

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(10) For discussion of the relative stabilities of the *cis*- and *trans*-1,3-dimethylcyclopentanes, see E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, p 202.

(11) The labeling of the hydrogen atoms in the formulas (Scheme I and Scheme II) corresponds to the labeling of the atoms in Table I. In all cases except that of the cis sultone VII, the protons are labeled from high to low field by the sequence ABMX. For the cis sultone VII the order from high to low field becomes BAMX (in $CDCl_3$ only).

trans-3,5-diphenyl-1,2-oxathiolane (2,3)-*cis*-2-oxide existed largely in conformation IVa or one closely resembling this.

The configurations of the oxygen atoms at S-2 in the isomeric sultines were determined by comparison of chemical shifts in the sultines II and IV and sultones VII and VIII and by change of chemical shifts with change of solvent. The effect of the 3- and 5-phenyl groups on the chemical shifts of H_A and H_B in the trans sultine IVa should be comparable. The difference in chemical shifts between H_A and H_B should result largely from the orientation of the oxygen on sulfur. Since it is known that the sulfoxide group shields those protons which lie more directly behind the S=O bond (along the axis) and deshields groups which lie 1,3 diaxially to the S=O bond,[1,12] the oxygen at S-2 in the trans sultine IVa should lie trans to H_A and cis to H_B (cis to the C-3 phenyl group). By application of a similar argument to the H_X protons of the cis sultine II and trans sultine IV, the marked shielding of H_X in II [ν_X(IV) − ν_X(II) = 35.6 Hz ($CDCl_3$)] can best be explained by assignment of the S=O configuration in II trans to H_X (cis to the phenyl groups).

The above configurational assignments were confirmed by a study of the change of chemical shifts of the various protons with change of solvent (Table II).

TABLE II[a]

Δν = [ν(C_6H_5) − ν($CDCl_3$)] Hz

	H_A	H_B	H_M	H_X
II cis sultine	−38.3	−11.6	−32.8	−23.5
IV trans sultine	−35.3	−21.1	−27.3	−15.3
VII cis sultone	−60.6	−29.7	−30.6	−36.6
VIII trans sultone	−45.3	−37.3	−21.4	−29.3

[a] Negative values indicate upfield shifts.

It has been shown that those protons lying more directly behind the group dipole[13] of a sulfoxide are shifted to higher field with change of $CDCl_3$ to C_6H_6 than those protons lying farther from the dipole–vector.[12c,d,14] If configurations of the oxygen on sulfur and conformations of the rings of both cis and trans sultines IIa and IVa are similar, then (in both instances) H_A lies more directly behind the group dipole than H_B, and ν_A should be shifted to higher fields (in both instances) by change of solvent from $CDCl_3$ to C_6H_6 than ν_B. Similar predictions would be made from the postulated structures of the benzene complexes.[12d,15] Experimental results (Table II) confirm these expectations. The large upfield shift of ν_M (for both isomers) and the larger upfield shift for ν_X (cis sultine II) than for ν_X (trans sultine IV) are also in agreement with expectations but internal standards are not available for ν_M. The very large upfield shift of ν_A (−60.6 Hz) compared to ν_B (−29.7 Hz) with change of solvent ($CDCl_3$ to C_6H_6) indicates that the cis sultone VII possesses conformation VIIa as expected. Related data ($\Delta\nu_A$ = −45.3; $\Delta\nu_B$ = −37.3 Hz) indicate considerable conformational mobility for the trans sultone VIII.

An analysis of the changes of chemical shifts of the various protons on oxidation of the sultines to sultones also confirmed the above assignments (Table III).

TABLE III[a]

Δν = [ν(sultone) − ν(sultine)] Hz

	H_A	H_B	H_M	H_X
	$CDCl_3$			
VII–II, cis	17.2	5.9	25.7	3.4
VIII–IV, trans	16.7	0.8	13.1	−24.5
	C_6H_6			
VII–II, cis	−5.1	−12.2	27.9	−9.7
VIII–IV, trans	6.7	−15.4	19.0	−38.5

[a] Positive values indicate downfield shifts; negative values upfield shifts.

Replacement of the lone pair of electrons on sulfur with an oxygen atom (S=O) should lead to greater shielding (less deshielding) of those protons lying more directly behind (along the axis of) the new S=O group.[12d] Thus, on oxidation of either the cis or trans sultine II or IV H_B should be shielded to a greater extent (deshielded to a lesser extent) than H_A. Again, experimental results confirm these expectations (Table III). The fact that H_X in the cis sultine II occupies a different configuration with respect to the incoming oxygen than H_X in the trans sultine IV is also apparent from the changes of chemical shift on oxidation (Δν = +3.4 and −24.5 Hz).

Conformations.—Because of the large size of the phenyl groups, the conformation of the cis sultine II should be that (IIa) with pseudoequatorial phenyl groups. The isomerization of the trans sultine IV to the cis sultine II tends to confirm this conclusion.

Because of the very small size of J_{AX} (2.48 Hz)[16] compared to the size of J_{BM} (12.69), one can conclude that the *trans*-diphenylsultine exists largely in conformation IVa. However, both conformations IVa and IVb possess a pseudoaxial and a pseudoequatorial phenyl group. In order to obtain an estimate of the position of the equilibrium IVa ⇄ IVb, the following assumptions were made. (1) The *cis*-diphenylsultine II exists entirely in the conformation IIa. (2) J_{BM} (IVa) ≈ J_{BM} (IIa) ≈ 13.84; J_{AX} (IVb) ≈ J_{BX} (IIa) ≈ 10.95; J_{AX} (IVa) ≈ J_{BM} (IVb) ≈ J. Because the dihedral angles $\angle H_ACCH_X$ (IVa) and $\angle H_BCCH_M$ (IVb) both approximate 90°, J will have a relatively small value. From these assumptions and from the values of J_{AX} and J_{BM} for IV, one can obtain two simultaneous equations

$$\begin{array}{llll} & & \text{IVa} & \text{IVb} \\ J_{BM}\ (\text{IV}) = & 12.69 = & x(13.84) & +\ (1-x)J \\ J_{AX}\ (\text{IV}) = & 2.48 = & xJ & +\ (1-x)(10.95) \end{array}$$

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(12) (a) K. W. Buck, A. B. Foster, W. D. Pardoe, M. H. Qadir, and J. M. Webber, *Chem. Commun.*, 759 (1966); A. B. Foster, J. M. Duxbury, T. D. Inch, and J. M. Webber, *ibid.*, 881 (1967); (b) R. Nagarajan, B. H. Chollar, and R. M. Dodson, *ibid.*, 550 (1967); (c) P. B. Sollman, R. Nagarajan, and R. M. Dodson, *ibid.*, 552 (1967); (d) R. D. G. Cooper, P. V. DeMarco, J. C. Cheng, and N. D. Jones, *J. Amer. Chem. Soc.*, **91**, 1408 (1969); (e) C. R. Johnson and Walter O. Siegl, *Tetrahedron Lett.*, 1879 (1969).

(13) The group dipole of a sulfoxide lies *ca.* 21.5° from the S–O bond in the direction of the lone pair of electrons: N. J. Leonard and C. R. Johnson, *J. Amer. Chem. Soc.*, **84**, 3701 (1962).

(14) (a) R. A. Archer and P. V. De Marco, *ibid.*, **91**, 1530 (1969); (b) R. D. G. Cooper, P. V. De Marco, and D. O. Spry, *ibid.*, **91**, 1528 (1969); (c) D. H. R. Barton, F. Comer, and P. G. Sammes, *ibid.*, **91**, 1529 (1969); (d) E. T. Stom, B. S. Snowden, Jr., and P. A. Toldan, *Chem. Commun.*, 50 (1969); (e) M. Nishio, *ibid.*, 51 (1969).

(15) T. Ledaal, *Tetrahedron Lett.*, 1683 (1968).

(16) If conformers IVa and IVb were of equal importance both J_{AX} (*ca.* 4.2) and J_{BM} (*ca.* 7.5) would be of moderate size. Because of the greater accuracy of the data (see Experimental Section), all of the following calculations are done with coupling constants from spectra determined in benzene.

From these one can calculate that, in benzene solution, *trans*-1,3-diphenylsultine IV consists of *ca.* 91% IVa and 9% IVb and that J_{AX} (IVa) ≈ 1.60. These calculations are made on the assumption that the puckering of IVa and IVb is equal to that of IIa. The 1,3-pseudodiaxial interaction of H_M and the 5-phenyl group should tend to flatten IVa and a similar interaction of H_X and the 3-phenyl group would tend to flatten IVb. Any less puckering of these conformers [lowering the values of J_{BM} (IVa) and J_{AX} (IVb)] will give calculations showing >91% IVa. Similar calculations for the trans sultone VIII indicated considerable conformational mobility (74% of conformer corresponding to IVa and 26% of conformer corresponding to IVb).

Calculation of Dihedral Angles.[17]—The average dihedral angles ∠HCCH of the cis and trans sultines II and IV were calculated from their nmr spectra in the following way. (1) The vicinal coupling constants were fitted to an equation of the form $^3J_{H,H'} = A \cos^2 \phi + B \cos \phi + C$.[18] (2) The geminal angle $\angle H_ACH_B$ of the sultines II and IV and of the sultones VII and VIII was assigned the value 109° 28′, and the angle $\angle H_ACH_B$ projected along the C_3–C_4 and C_4–C_5 bonds was assigned a value of 120° (ω). (3) The coupling constants of the trans sultine IV were assigned to the principle conformer IVa. Since we have estimated that a maximum of 9% of IV could exist as IVb, a comparable error in these calculations may result. (4) That portion of the equation determining the angular dependence of the coupling constants (A and B) was assumed to be identical for vicinal coupling between hydrogen atoms on C_3 and C_4 and on C_4 and C_5. Differences, because of the inductive or hybridization effects of the –SO– attached to C-3 or the –O– attached to C-5, were absorbed in the constants C and C', respectively.

By use of the above and the coupling constants from the nmr spectra of II and IV, the following eight nonlinear equations in eight unknowns were written.

cis sultine II

$$J_{AM} \quad 5.76 = A \cos^2 \phi + B \cos \phi + C$$

$$J_{BM} \quad 13.84 = A \cos^2 (\omega + \phi) + B \cos (\omega + \phi) + C$$

$$J_{AX} \quad 5.60 = A \cos^2 \phi' + B \cos \phi' + C'$$

$$J_{BX} \quad 10.95 = A \cos^2 (\omega + \phi') + B \cos (\omega + \phi') + C'$$

trans sultine IV

$$J_{AM} \quad 7.40 = A \cos^2 \phi'' + B \cos \phi'' + C$$

$$J_{BM} \quad 12.69 = A \cos^2 (\omega + \phi'') + B \cos (\omega + \phi'') + C$$

$$J_{AX} \quad 2.48 = A \cos^2 (\omega - \phi''') + B \cos (\omega - \phi''') + C'$$

$$J_{BX} \quad 8.67 = A \cos^2 \phi''' + B \cos \phi''' + C'$$

Solution of these equations, gave the equations

$$^3J_{H,H'} = 10.2 \cos^2 \phi - 1.9 \cos \phi + 2.35 \quad HC_3C_4H \tag{1}$$

$$^3J_{H,H'} = 10.2 \cos^2 \phi - 1.9 \cos \phi + 0.60 \quad HC_4C_5H \tag{2}$$

and the following dihedral angles.[19]

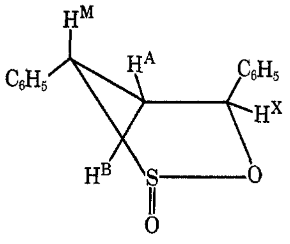
	$\angle H_ACCH_M$	$\angle H_BCCH_M$	$\angle H_ACCH_X$	$\angle H_BCCH_X$
cis sultine IIa	47.2°	167.2°	36.9°	156.9°
trans sultine IVa	36.6°	156.6°	110.3°	9.7°

The validity of these equations and of the previous assumptions on conformation can be tested by the application of the equations to the cis sultone VII. If VII consists largely of conformer VIIa and if eq 1 and 2 are valid,[20] then the value (120°) of the projected geminal angle $\angle H_ACH_B$ should be calculable from the coupling constants.

	$\angle H_ACCH_M$	$\angle H_BCCH_M$	$\angle H_ACCH_X$	$\angle H_BCCH_X$
cis sultone VIIa	42.9°	163.4°	36.1°	157.0°

ω (calcd) = 120.5 and 120.9°, in excellent agreement with the expected value and with each other. Application of these same equations to the trans sultone VIII (not conformationally pure) gives ridiculous values for the projected geminal angle; ω = 111.6 and 139.9°.

From the angles calculated above it can be seen that, as expected, the trans sultine IV is far less puckered than the cis sultine II. In fact, the ratio of the angles $\angle H_ACCH_M$ and $\angle H_BCCH_X$ is such that the conformation of the trans sultine IV more closely resembles an envelope IVc than the half-chair originally postulated. The stability of this conformation IVc is probably accounted for by the pseudoequatorial conformation of the C-3 phenyl group, by the lack of strong steric interactions between the C-5 phenyl group, the pseudoaxial H_M, and the nonbonding electrons on sulfur,



IVc

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[17] The use of the following method of analysis on the nmr spectra of *cis*- and *trans*-2,4-diphenylthietane 1-oxides gave an average angle of pucker for *cis*-2,4-diphenylthietane *trans*-1-oxide of 39.7°. A crystal structure analysis of this same compound gave a value of 41.9° for this same angle (see ref 1). Our nmr analyses are done on molecules of high conformational purity and on molecules with similarly oriented bond dipoles. Thus, we hope we have avoided the usual errors in the application of Karplus type equations to conformations. It should be realized that, in axially hydroxy-substituted steroids (in which the C–O bond dipole is syn to the adjacent C–C bond), any difference between H,H′ J_{ee} and J_{ea} was <0.5 Hz [D. H. Williams and N. S. Bhacca, *J. Amer. Chem. Soc.*, **86**, 2742 (1964)].

[18] (a) M. Barfield and M. Karplus, *ibid.*, **91**, 1 (1969); (b) M. Barfield and D. M. Grant, *Advan. Magn. Resonance*, **1**, 187 (1965).

[19] The values of the dihedral angles given above are the solutions of the equations. Since we have estimated that 9% of IV could exist as conformer IVb, a comparable error in these calculations may result.

A similar calculation using the value J_{AX} (IVa) = 1.60, calculated above for the principle conformer of IV, gave $^3J_{H,H'} = 11.1 \cos^2 \phi - 1.9 \cos \phi + 1.65$ HC_3C_4H; $^3J_{H,H'} = 11.1 \cos^2 \phi - 1.9 \cos \phi - 0.1$ HC_4C_5H. Note that by making some allowance for the distribution of conformers of IV the constant C' used to account for the inductive or hybridization effects of oxygen is reduced to a very small value (for discussion of this point see ref 1). The values calculated from these equations differed slightly from those given above: IIa, $\angle H_ACCH_M = 45.5°$; $\angle H_ACCH_X = 36.2°$. IVa, $\angle H_ACCH_M = 35.9°$; $\angle H_BCCH_X = 11.6°$. The validity of the assumption, J_{AX} (IVa) ≈ J_{BM} (IVb) ≈ J used to estimate the position of the equilibrium IVa $\rightleftarrows$ IVb can also be checked from these equations. Thus, for IVa, $\angle H_ACCH_X = 108.4°$; $J_{AX} = 1.61$. If IVb is puckered to the same extent as IVa, then for IVb, $\angle H_BCCH_M = 84.1°$; $J_{BM} = 1.57$.

[20] Application of eq 2 should be valid since change in the oxidation state of sulfur should not markedly effect either the inductive or hybridization effects at C_4 and C_5.

and by the relatively strong anomeric effect[21] of the pseudoaxial S=O bond.

From the time and equilibrium studies performed, it appears that the *cis*-3,5-diphenyl-1,2-oxathiolane (2,3)-*cis*-2-oxide (IIa) is the most stable of the four possible racemic modifications. If so, the cis configuration of the 2-oxygen and the 3-phenyl group must be explainable either on the basis of the anomeric effect[21] of the pseudoaxial S=O group or by the increased stability of a gauche 2-oxa-3-phenyl interaction.[22] This point will be examined in greater detail in the future.

Oxidation of the cis sultine II to the cis sultone VII resulted in a small reduction (−4.3°) of the dihedral angles at C_3–C_4 with very little change (−0.8°) of the dihedral angles at C_4–C_5, the "oxygen side" of the molecule. A similar flattening (−3.9°) was observed on the oxidation of *cis*-2,4-diphenylthietane *trans*-1-oxide to the corresponding 1,1-dioxide.[1] This small reduction in the puckering of the molecule probably results from the slight increase in the C–S–C or 1-O-S–C angle on oxidation from the sulfoxide (or sulfinate) to the sulfone (or sulfonate).[23]

Mechanism.—We believe this rearrangement proceeds by a mechanism closely resembling that of the Stevens rearrangement.[24] Detailed discussion of the mechanism is presented in the accompanying part IV of this series[25] together with consideration of some related reactions.

Experimental Section[26]

***trans*-3,5-Diphenyl-1,2-oxathiolane (2,3)-*cis*-2-Oxide (IV).**—A solution of ethylmagnesium bromide prepared from 3.54 g (0.0324 mol) of ethyl bromide and 1.60 g (0.066 g-atom) of magnesium in 25 ml of ether was treated with 2.46 g (0.033 mol) of *tert*-butyl alcohol (dried by distillation from sodium) in 20 ml of anhydrous ether. The reaction was stirred at room temperature for 1 hr. *trans*-2,4-Diphenylthietane 1,1-dioxide (III) (1.00 g, 0.00387 mol) was added, and the reaction was heated under reflux with stirring for 44 hr. The magnesium complex was decomposed with 3.6% aqueous hydrochloric acid. The organic products were isolated by extraction with ether. Thin layer chromatography of the organic material showed that it contained some starting material plus one other component.

This material was chromatographed on silica gel (25 g, 100–200 mesh) using mixtures of petroleum ether (bp 30–60°) and benzene. *trans*-2,4-Diphenylthietane 1,1-dioxide (0.131 g, 13% recovery) was eluted with 30% petroleum ether (bp 30–60°)–70% benzene and was identified by a mixture melting point determination with an authentic sample. *trans*-3,5-Diphenyl-1,2-oxathiolane (2,3)-*cis*-2-oxide (IV) (0.356 g, 0.00138 mol, 41% yield allowing for recovered starting material) was eluted with 10% petroleum ether (bp 30–60°)–90% benzene. Crystallization from petroleum ether (bp 60–68°)–chloroform mixture yielded white crystals of IV (0.314 g, 0.00122 mol, 36% yield): mp 73–74.5°; $\nu_{\max}^{\mathrm{KBr}}$ 689, 738, 760, 780, 830, 890, 950, 1108 (S(=O)O), 1138, 1452, and 1492 cm^{-1}; mass spectrum, base peak *m/e* 194 (M − SO_2); uv spectrum in ethanol showed only phenyl group absorption.

Anal. Calcd for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46. Found: C, 69.70; H, 5.65.

One preparation of this material [crystallized from CCl_4 and petroleum ether (bp 60–68°)] gave *trans*-3,5-diphenyl-1,2-oxathiolane (2,3)-*cis*-2-oxide (IV), mp 60–61°; ir and nmr spectra were identical with the above preparation.

***cis*-3,5-Diphenyl-1,2-oxathiolane *cis*-2-Oxide (II).**—A solution of ethylmagnesium bromide prepared from 10.62 g (0.0976 mol) of ethyl bromide and 1.60 g (0.066 g-atom) of magnesium in 50 ml of ether was treated with 4.92 g (0.066 mol) of anhydrous *tert*-butyl alcohol in 50 ml of ether. The reaction was stirred at room temperature for 1 hr. *cis*-2,4-Diphenylthietane 1,1-dioxide (2.00 g, 0.00775 mol) was added and the resulting mixture was heated under reflux with stirring for 23 hr.

The magnesium complex was decomposed with 3.6% aqueous hydrochloric acid, and the organic product was isolated by ether extraction. Crystallization of the material so obtained from chloroform–petroleum ether (bp 60–68°) gave 1.4 g (0.0054 mol, 70% yield) of *cis*-3,5-diphenyl-1,2-oxathiolane *cis*-2-oxide (II): mp 121–122.5°; $\nu_{\max}^{\mathrm{KBr}}$ 643, 690, 716, 777, 790, 826, 880, 950, 1030, 1115 (S(=O)O), 1149, 1157, 1218, 1369, 1451, and 1491 cm^{-1}; mass spectrum, base peak *m/e* 194 (M − SO_2); uv spectrum in ethanol showed only phenyl absorption.

Anal. Calcd for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46. Found: C, 69.73; H, 5.77.

***cis*-3,5-Diphenyl-1,2-oxathiolane *cis*-2-Oxide (II) from *trans*-2,4-Diphenylthietane 1,1-Dioxide (III).**—Studies on the course of the above rearrangements with time, using nmr spectra as the analytical tool, indicated that *cis*-3,5-diphenylthietane 1,1-dioxide (I) rearranged initially to *cis*-3,5-diphenyl-1,2-oxathiolane *cis*-2-oxide (II) which persisted through the course of the reaction. *trans*-3,5-Diphenylthietane 1,1-dioxide (III) rearranged initially to *trans*-3,5-diphenyl-1,2-oxathiolane (2,3)-*cis*-2-oxide (IV). This was slowly converted, possibly *via* an intermediate with absorption in the nmr spectrum in the 347–356 Hz ($CDCl_3$) range, to *cis*-3,5-diphenyl-1,2-oxathiolane *cis*-2-oxide (II). Thus, after reaction of *trans*-2,4-diphenylthietane 1,1-dioxide (III) with *tert*-butoxymagnesium bromide for 76 hr only *cis*-3,5-diphenyl-1,2-oxathiolane *cis*-2-oxide (II) was present in the reaction mixture. This was confirmed by the isolation of II, mp and mmp 121–123°.

Independent Synthesis of II and IV.—1,3-Diphenyl-3-hydroxypropanethiol[1] (VI) (2.00 g, 0.00820 mol) dissolved in glacial acetic acid (10 ml) was treated with 1.18 g (0.017 mol) of chlorine in 50 ml of glacial acetic acid. The solution was closed to the atmosphere and stirred vigorously for 10 min. The solvent was removed under vacuum at 60° (water bath temperature). The residue was dissolved in ether and then washed with water, 10% sodium bicarbonate solution, and water. The ether solution was dried and evaporated. The remaining oil was dissolved in 70% petroleum ether (bp 30–60°)–30% benzene and chromatographed on silica gel (50 g, 100–200 mesh). Elution with 50% petroleum ether (bp 30–60°)–50% benzene and a 30:70 mixture of these two solvents yielded 0.386 g (1.50 mmol, 18% yield) of *cis*-3,5-diphenyl-1,2-oxathiolane *cis*-2-oxide (II), mp 121–123°. Identity was confirmed by comparison of the nmr and ir spectra with those of the previously obtained samples.

Further elution with a 30:70 and a 10:90 mixture of the same solvents yielded 0.435 g (1.69 mmol, 21%) of *trans*-3,5-diphenyl-1,2-oxathiolane (2,3)-*cis*-2-oxide, mp 65–68°. Identity was confirmed by comparison of the nmr and ir spectra with those of the previously obtained samples.

In our first independent synthesis of these compounds, 10 mg of material, mp 97–100° [$\nu_{\max}^{\mathrm{KBr}}$ 687, 705, 725, 751, 764, 796, 880, 1106 (CO), and 1130 cm^{-1} (S(=O)O)], was isolated. The mass spectrum of this material suggested that it was a third isomeric 3,5-diphenyl-1,2-oxathiolane 2-oxide.

***cis*-3,5-Diphenyl-5-deuterio-1,2-oxathiolane *cis*-2-Oxide and *trans*-3,5-Diphenyl-5-deuterio-1,2-oxathiolane (2,3)-*cis*-2-Oxide.**—1,3-Diphenyl-3-acetylthio-1-propanone[1] (V) was reduced with lithium aluminum deuteride to 1,3-diphenyl-3-deuterio-3-hydroxypropanethiol (VI) by the method previously described. This was converted to 5-deuterio-II, mp 117–118°, and 5-deuterio-IV, mp 60–61°, by the procedure given above.

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[25] R. M. Dodson, P. D. Hammen, and J. Yu Fan, *J. Org. Chem.*, **36**, 2703 (1971).

[26] Melting points were taken on a Fisher-Johns melting point apparatus, calibrated against a set of standard compounds.

***cis*-3,5-Diphenyl-1,2-oxathiolane 2,2-Dioxide** (VII).—A solution of 0.50 g (0.0019 mol) of *cis*-3,5-diphenyl-1,2-oxathiolane *cis*-2-oxide (II) in 50 ml of benzene was treated with 0.30 g (85%, 0.0015 mol) of *m*-chloroperbenzoic acid in benzene solution. The reaction was stirred at room temperature for 24 hr. It was then washed with water, 10% aqueous sodium bicarbonate solution, and then finally with water. The benzene solution was dried and the solvent was evaporated. Crystallization of the solid so obtained from carbon tetrachloride–petroleum ether (bp 60–68°) yielded 0.308 g (58%) of *cis*-3,5-diphenyl-1,2-oxathiolane 2,2-dioxide (VII): mp 120–121°; $\nu_{\max}^{\text{KBr}}$ 1172, 1344 cm^{-1} (SO_2O). A mixture of this material with the starting material showed a large melting point depression.

Anal. Calcd for $C_{15}H_{14}O_3S$: C, 65.67; H, 5.14. Found: C, 65.87; H, 5.12.

***trans*-3,5-Diphenyl-1,2-oxathiolane 2,2-Dioxide** (VIII).—Oxidation of 0.50 g of *trans*-3,5-diphenyl-1,2-oxathiolane (2,3)-*cis*-2-oxide (IV), mp 60–61°, by the method described above, yielded 0.258 g (49%) of *trans*-3,5-diphenyl-1,2-oxathiolane 2,2-dioxide (VIII): mp 84–84.5°; $\nu_{\max}^{\text{KBr}}$ 1170, 1348 cm^{-1} (SO_2O).

Anal. Calcd for $C_{15}H_{14}O_3S$: C, 65.67; H, 5.14. Found: C, 65.85; H, 5.29.

Nmr spectra were determined on a Varian A-60 spectrometer. A Hewlett-Packard Model 202A low-frequency function generator was used to calibrate the spectra at 50- and 100-Hz sweep-width. Tetramethylsilane was used as an internal standard. Spectra were determined at high concentrations (52 ± 3% w/w) in order to observe the low intensity absorption bands in the spectra of the cis sultine II and the cis sultone VII. The spectra were initially calculated as ABMX systems using the energy levels given by Reilly and Swalen.[27] The parameters so obtained were then used in the LAOCOON-3 program of A. A. Bothner-By and S. M. Castellano, and the data reported herein are from the latter calculations. The sign of the geminal coupling constants was not experimentally determined. The chemical shifts (ν) vary with concentration but have not been extrapolated to zero concentration. The calculated probable errors in the coupling constants were ±0.05 Hz or less for those spectra determined in benzene and ±0.07 Hz or less for those determined in $CDCl_3$ with the exception of the cis sultone VII in $CDCl_3$. In the latter case, because of the very small difference in chemical shift between H_A and H_B low intensity lines were very difficult to locate and the maximum calculated probable error is ±0.15 Hz. Small deviations between the data reported here and that previously reported[3] result from differences in concentrations, more accurate calculations, and a small numerical error in the previous calculation of ν_A and ν_B for the cis sultine II.

Registry No.—I, 18744-27-9; II, 30237-95-7; III, 24609-91-4; IV, 30237-97-9; VII, 30237-98-0; VIII, 30237-99-1.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to Archer Daniels Midland Co., and to the National Institutes of Health (Grant No. AM 12954) for the support of this research.

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Thietanes. III. Rearrangement of 2,4-Diphenylthietane Dioxides to *trans*-1,2-Diphenylcyclopropanesulfinic Acid

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Received August 31, 1970

cis- and *trans*-2,4-diphenylthietane 1,1-dioxides (I and II) when treated with ethylmagnesium bromide are rearranged to *trans*-1,2-diphenylcyclopropanesulfinic acid (III) in a highly stereoselective manner. The sulfinic acid III was converted to the benzyl and methyl *trans*-1,2-diphenylcyclopropyl sulfones (IVa and IVb, respectively) and to a mixture of *cis*- and *trans*-1,2-diphenylcyclopropanes (VI and VII). Benzyl *cis*- and *trans*-1,2-diphenylcyclopropyl sulfones (XV and IVa, respectively; *ca.* 50:50 mixture) were synthesized independently by the reaction of either α-benzylsulfonyl-*cis*- or -*trans*-stilbene (XIII or XIV) with dimethylsulfoxonium methylide. The configurations of the benzyl 1,2-diphenylcyclopropyl sulfones (IVa and XV) were definitively established by a complete analysis of their nmr spectra.

Recently we have described the syntheses and the determinations of configurations and conformations of the 2,4-diphenylthietanes, their monoxides, and dioxides.[1] We have also described the rearrangement of *cis*- and *trans*-2,4-diphenylthietane 1,1-dioxides to *cis*- and *trans*-3,5-diphenyl-1,2-oxathiolane (2,3)-*cis*-2-oxides, respectively,[2] a stereospecific rearrangement. Here, we report the conversion of *cis*- and *trans*-2,4-diphenylthietane 1,1-dioxides (I and II) to *trans*-1,2-diphenylcyclopropanesulfinic acid (III),[3] a highly stereoselective rearrangement.

Treatment of either *cis*- or *trans*-2,4-diphenylthietane 1,1-dioxide (I or II) with ethylmagnesium bromide yielded *trans*-1,2-diphenylcyclopropanesulfinic acid (III) (75% yield) and liberated 1 equiv of ethane. The constitution of III was established by (1) its analysis, (2) by the presence in its ir spectrum of bands at 833, 1033, and 2400 cm^{-1} typical of those of sulfinic acids,[4] and (3) by its conversion to a mixture of *cis*- and *trans*-1,2-diphenylcyclopropanes[1,5] (VI and VII) by heating with an excess of ethylmagnesium bromide (VI/VII, *cis*/*trans* ratio 0.22) or *via* an intermediate alkylmercuric chloride[6] followed by acid hydrolysis (VI/VII, *cis*/*trans* ratio 4.25). The *trans*-1,2-diphenylcyclopropanesulfinic acid (III) was rather unstable but was easily converted to the stable benzyl and methyl *trans*-1,2-diphenylcyclopropyl sulfones (IVa and IVb, respectively) by reaction of its sodium salt with benzyl chloride or methyl iodide (Scheme I).

Independent Synthesis of IVa.—The benzyl *trans*-1,2-diphenylcyclopropyl sulfone (IVa) was synthesized by the sequence of reactions shown in Scheme II.

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