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°; ν_{max}^{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°; ν_{max}^{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.

(27) C. A. Reilly and J. D. Swalen, *J. Chem. Phys.*, **34**, 980 (1961).

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

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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.

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

(2) R. M. Dodson, P. D. Hammen, and R. A. Davis, *ibid.*, **36**, 2693 (1971).

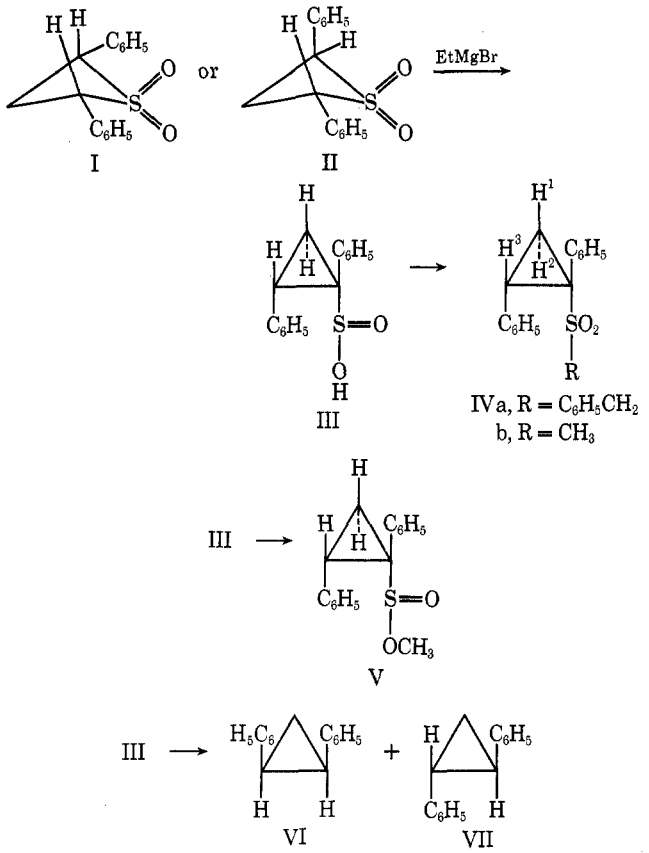
(3) A preliminary account of this work has been published: R. M. Dodson and G. Klose, *Chem. Ind. (London)*, 1203 (1963).

(4) S. Detoni and D. Hadzi, *J. Chem. Soc.*, 3163 (1955).

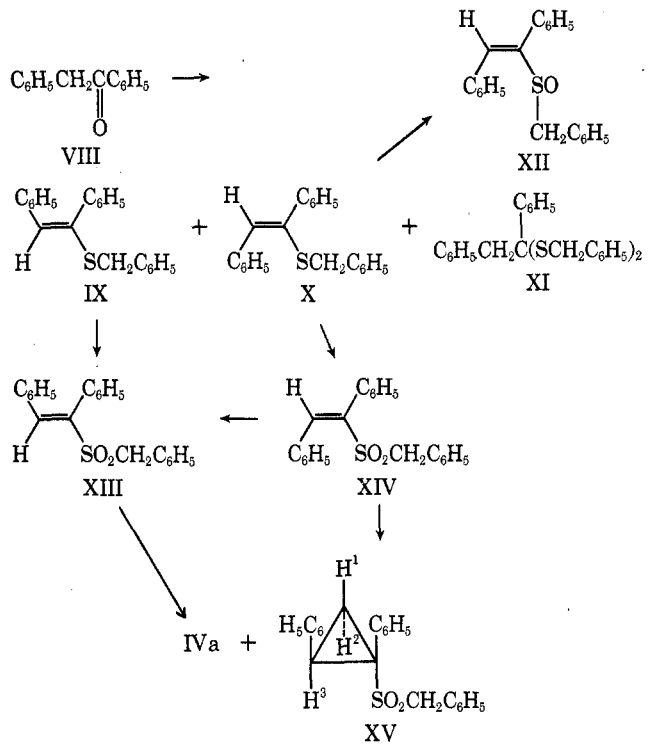
(5) D. Y. Curtin, H. Gruen, Y. G. Hendrickson, and H. E. Knipmeyer, *J. Amer. Chem. Soc.*, **83**, 4838 (1961); B. A. Kazanskii, M. Yu. Lukina, I. L. Safanova, V. T. Aleksanyan, and Kh. E. Sterin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1280 (1958).

(6) T. Okamoto and J. F. Bunnett, *J. Amer. Chem. Soc.*, **78**, 5357 (1956); L. H. Gale, F. R. Jensen, and J. H. Landgrebe, *Chem. Ind. (London)*, 118 (1960); M. M. Kreevoy and R. L. Hansen, *J. Amer. Chem. Soc.*, **83**, 626 (1961).

SCHEME I



SCHEME II



cis- and *trans*-α-benzylthiostilbene (IX and X, 50 and 30.5%, respectively, in the crude product) and deoxybenzoin dibenzylthioketal (XI, 14.5%) were synthesized by an adaptation of the procedure of Campaigne and Leal.[7] The products were separated by chromatography on silica gel. The configurations of IX and X were initially assigned by a comparison of the aromatic region of the nmr spectra of IX and X with those of *cis*- and *trans*-stilbenes.[8] Thus, the nmr spectrum of *cis*-stilbene shows a singlet (430.8 ± 1.8 Hz) for all ten of the aromatic hydrogen atoms; the nmr spectrum of IX shows two singlets, 428 and 435 Hz, probably corresponding to the two cis phenyl groups. The absorption spectrum of the aromatic hydrogen atoms of *trans*-stilbene is very complex (433–458 Hz). Similarly the absorption spectrum of the aromatic hydrogen atoms of X is very complex (412–457 Hz).

An attempt to add methylene to α-benzylthio-*trans*-stilbene (X) by means of the Simmons–Smith reaction[9] was unsuccessful. Only starting material was recovered. An attempt to add methylene to α-benzylthio-*cis*-stilbene (IX) *via* iodomethylmercuric iodide[10] did not fare any better. Attempts to add methylene from diazomethane[11] to both α-benzylthio-*cis*- and *trans*-stilbenes IX and X using cuprous iodide and cuprous chloride catalysts were equally unsuccessful. Since our initial aim was a stereospecific addition of methylene to the benzylthiostilbenes and since ultraviolet light isomerized the benzylthiostilbenes, the addition of methylene generated by the photochemical decomposition of diazomethane was not attempted.

The α-benzylthiostilbenes IX and X were, therefore, oxidized to the corresponding α-benzylsulfonylstilbenes (XIII and XIV). α-Benzylthio-*cis*-stilbene (IX) was readily oxidized to the corresponding sulfone XIII with hydrogen peroxide in warm acetic acid. An attempt to oxidize α-benzylthio-*trans*-stilbene (X) by this same method gave a mixture of sulfones XIII and XIV (cis/trans ratio 0.25). Cold hydrogen peroxide in cold glacial acetic acid yielded the sulfoxide XII. Pure α-benzylsulfonyl-*trans*-stilbene (XIV) was obtained in 79% yield (94% crude yield) by the oxidation of X with hydrogen peroxide in a cold formic acid–carbon tetrachloride mixture.

α-Benzylsulfonyl-*trans*-stilbene (XIV) was isomerized almost quantitatively to α-benzylsulfonyl-*cis*-stilbene (XIII) by treatment with sodium hydroxide in ethanol. The stereochemistry of the substituted stilbenes (IX, X, XII, XIII, XIV) was confirmed by a detailed comparison of their physical properties (melting points, uv spectra, isomerization of XIV → XIII) with the physical properties of the configurationally defined *p*-tolylthio- and *p*-toluenesulfonylstilbenes prepared by Cristol and Pappas.[12]

The benzyl 1,2-diphenylcyclopropyl sulfones (IVa and XV) were prepared by the method of Truce and Badiger.[13] Reaction of either XIII or XIV with dimethylsulfoxonium methylide yielded a 1:1 mixture of benzyl *cis*- and *trans*-1,2-diphenylcyclopropyl sulfones

(7) E. Campaigne and J. R. Leal, *J. Amer. Chem. Soc.*, **76**, 1272 (1954).
(8) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "Nmr Spectra Catalog," Vol. I, Varian Associates, Palo Alto, Calif., 1962, pp 305, 306.
(9) H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **80**, 5323 (1958).
(10) D. Seyferth, M. A. Eisert, and L. J. Todd, *ibid.*, **86**, 121 (1964).
(11) R. E. Pincock and J. I. Wells, *J. Org. Chem.*, **29**, 965 (1964).
(12) S. J. Cristol and P. Pappas, *ibid.*, **28**, 2066 (1963).
(13) W. E. Truce and V. V. Badiger, *ibid.*, **29**, 3277 (1964).

TABLE I[a]

ALKYL *cis*- AND *trans*-1,2-DIPHENYLCYCLOPROPYL SULFONES

Compd[b]	R	ν_R[c]	ν_1	ν_2	ν_3	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$
IVa trans	$C_6H_5CH_2$	ν_A 217.1, ν_B 237.4, J_{AB} = 12.5 Hz	107.2	155.5	176.95	−5.55[d]	9.50	7.95
IVb trans	CH_3	149	107	160	182	−5.9	10.0	7.9
XV cis	$C_6H_5CH_2$	244	109.0	123.2	197.15	−6.10	7.15	10.25

[a] Recorded in hertz downfield from tetramethylsilane at 60 MHz. [b] Cis and trans refer to the relationship of the phenyl groups. [c] $\nu_{(CH_2)}$ for IVa and XV; ν_{CH_3} for IVb. Spectra for IVa and XV were determined on a Varian A-60 spectrometer in $CDCl_3$ and were analyzed by use of the LAOCOON-2 program of A. A. Bothner-By and S. M. Castellano. Coupling constants should be accurate to ±0.1 Hz. The spectrum of IVb was determined in $CDCl_3$ on a modified Varian Associates Model DP-60 spectrometer at 56.45 MHz and was calculated as an ABX spectrum. The recorded chemical shifts are corrected to 60 MHz. Parameters do not exceed ±0.5 Hz in accuracy. [d] The sign of this coupling constant was determined. The signs of all other negative coupling constants were assigned arbitrarily.

(XV and IVa), which were separated by fractional crystallization. Contrary to the findings of Truce,[13] this reaction was not stereoselective.[14]

Configurations of IVa and XV.—The configurations of the benzyl *cis*- and *trans*-1,2-diphenylcyclopropyl sulfones (XV and IVa) were assigned from the complete analysis of their nmr spectra (Table I). The most conspicuous difference between these spectra was the difference in absorption of the methylene protons of the benzyl groups. The spectrum for IVa showed a well-isolated AB quartet (ν_A 217.1, ν_B 237.4, J_{AB} = 12.5 Hz) while that for XV showed a singlet (244 Hz at 500-Hz sweepwidth). Even though the methylene protons of the benzyl groups of both isomers are "intrinsically nonequivalent," [15] this marked difference in spectra must result from an "unequal conformer population" for these hydrogens in that isomer with the phenyl and α-benzylsulfonyl group cis to each other. Consequently, compound IVa was assigned benzyl *trans*-1,2-diphenylcyclopropyl sulfone.

The coupling constants and chemical shifts of the protons of the cyclopropyl rings are in agreement with the above configurational assignments. In both cases the proton at lowest field is H^3, that on the carbon atom of the cyclopropane ring holding the phenyl group. The proton at highest field, H^1, is that trans to the α-benzylsulfonyl group. The α-benzylsulfonyl group deshields H^2 in both isomers. In cyclopropanes, cis coupling constants are invariably larger than trans coupling constants for the same molecule.[16] Thus, for IVa, H^1 is trans to the α-benzylsulfonyl group and cis to H^3; H^2 and H^3 are trans to each other. The assignments of chemical shifts, coupling constants, and configurations of the protons of XV follow accordingly.

The size of the vicinal coupling constants ($J_{1,3}$ and $J_{2,3}$) also reflect the steric effects in the isomers IVa and XV. The steric interaction between cis sulfonyl and phenyl groups must be greater than the steric interaction between two cis phenyl groups (see the isomerization of XIV to XIII above). Thus steric effects in IVa should lead to a greater distortion of the molecule (an increase of the dihedral angles H^1CCH^3 and H^2CCH^3) than steric effects in XV. Consequently, $J_{1,3}$ (IVa) should be smaller than $J_{2,3}$ (XV) (9.50 < 10.25), and $J_{2,3}$ (IVa) should be larger than $J_{1,3}$ (XV) (7.95 > 7.15), in good agreement with experiment.

The chemical shifts and coupling constants determined from the spectrum of methyl *trans*-1,2-diphenylcyclopropyl sulfone (IVb), while less accurate than those of the benzyl isomers IVa and XV, are in excellent agreement with those of IVa.

As further confirmation of the above assignments, the relative signs of the coupling constants in IVa were investigated. A comparison of line intensities (calculated with experimental) showed that $J_{1,2}$ (IVa) must be opposite in sign from $J_{1,3}$ (IVa).[17] A double irradiation study[18] showed that $J_{1,3}$ and $J_{2,3}$ have the same sign, but that $J_{1,2}$ has a sign opposite to that of $J_{1,3}$ and $J_{2,3}$.

Stereoselectivity of the Rearrangement.—The ir spectrum of the *trans*-1,2-diphenylcyclopropanesulfinic acid (III) obtained from I was virtually identical with that obtained from II. Comparison of these spectra with the ir spectrum of *cis*-1,2-diphenylcyclopropanesulfinic acid[19] showed that little, if any, of the *cis*-1,2-diphenylcyclopropanesulfinic acid could be present in the trans isomer III. Since the sulfinic acids were rather unstable, samples of III from both *cis*- and *trans*-2,4-diphenylthietane 1,1-dioxide (I and II) were converted to methyl *trans*-1,2-diphenylcyclopropanesulfinate (V) with diazomethane. The ir spectra of both samples of V were virtually identical, were characteristic of a sulfinate ester[4] (690–714, 980–1010, 1130–1149 cm^{-1}), and differed entirely from that of the methyl *trans*-1,2-diphenylcyclopropyl sulfone (IVb). To obtain quantitative data on the stereoselectivity of the reaction, *trans*-1,2-diphenylcyclopropanesulfinic acid (III) from I and from II was converted to benzyl *trans*-1,2-diphenylcyclopropyl sulfone (IVa) under conditions that would have given comparable yields of benzyl *cis*-1,2-diphenylcyclopropyl sulfone (XV) from the *cis*-1,2-diphenylcyclopropanesulfinic acid. Examination of the nmr spectra of these materials around 240 Hz ($C_6H_5CH_2SO_2$) indicated the absence of the cis isomer XV (<2% XV).

We believe that this rearrangement proceeded

(14) The reaction of either *cis*- or *trans*-1-benzylsulfonyl-1-phenyl-1-propene with dimethylsulfoxonium methylide also yielded both 1-benzylsulfonyl-*cis*- and *trans*-1-phenyl-2-methylcyclopropanes: R. M. Dodson and J. E. Burcsu, unpublished results.

(15) L. M. Jackman and S. Sternhell, "Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Elmsford, N. Y., 1969, p 368.

(16) Reference 15, p 286.

(17) This is an unusual ABX spectrum, one in which X(H^1) is geminal to A(H^2).

(18) R. Freeman and D. H. Whiffen, *J. Mol. Phys.*, **4**, 321 (1961); E. F. Friedman and H. S. Gutowsky, *J. Chem. Phys.*, **45**, 3158 (1966).

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

through a mechanism resembling that of the Stevens rearrangement,[20] as discussed in the following paper.

Experimental Section[21]

trans-1,2-Diphenylcyclopropanesulfinic Acid (III).—To a solution of ethylmagnesium bromide prepared from 1.20 g (0.0492 g-atom) of magnesium and 5.40 g (0.0495 mol) of ethyl bromide in ether (25 ml) and benzene (75 ml) was added with stirring 4.25 g (0.0164 mol) of *trans*-2,4-diphenylthietane 1,1-dioxide (II) in solid form. The reaction mixture was stirred and heated under reflux for 2 hr.[22] After being cooled to room temperature the reaction mixture was treated with dilute hydrochloric acid. The aqueous layer was separated, and the organic layer was extracted with a concentrated aqueous sodium bicarbonate solution. The sodium bicarbonate solution, when acidified with concentrated hydrochloric acid, yielded 3.26 g (0.0126 mol, 77%) of *trans*-1,2-diphenylcyclopropanesulfinic acid (III): mp 134–136°; $\lambda_{max}^{ethanol}$ 218.6 nm (ϵ 16,880), shoulders at 253.3 (1885), 259 (1700), 266 (1330), and 270 (1065); ν_{max}^{Nujol} 695, 740, 772, 833 (broad), 853, 1033 (broad), and 2400 cm^{-1} (w, broad).[4] Attempted recrystallization of this material from acetone–petroleum ether mixture led to decomposition of the product.

Anal. Calcd for $C_{15}H_{14}O_2S$ (258.34): C, 69.74; H, 5.46. Found: C, 69.56; H, 5.59.

Reaction of *cis*-2,4-diphenylthietane 1,1-dioxide (I) with ethylmagnesium bromide under comparable conditions (15 min reaction time) yielded *trans*-1,2-diphenylcyclopropanesulfinic acid, mp 129–133°, 74% yield. The ir spectra of the *trans*-1,2-diphenylcyclopropanesulfinic acids from *cis*- and *trans*-2,4-diphenylthietane 1,1-dioxide (I and II) were identical and differed markedly from the ir spectrum of *cis*-1,2-diphenylcyclopropanesulfinic acid.[19] Comparison of these spectra showed that little if any of the *cis*-1,2-diphenylcyclopropanesulfinic acid could be present in the *trans*-1,2-diphenylcyclopropanesulfinic acid (III) prepared above.

On reaction of *cis*-2,4-diphenylthietane 1,1-dioxide (I) with excess (16 molar equiv) ethylmagnesium bromide, 1.12 equiv of ethane was evolved (theoretical 98 ml; found 110 ml).

cis- and *trans*-1,2-Diphenylcyclopropanes (VI and VII) from *trans*-1,2-Diphenylcyclopropanesulfinic Acid (III). A.—*trans*-1,2-Diphenylcyclopropanesulfinic acid (2.00 g, 7.7 mmol, mp 134–136°) was dissolved in 200 ml of 10% aqueous sodium hydroxide, and the solution was acidified with glacial acetic acid. The resulting solution was warmed on the steam bath for 10 min and mercury(II) chloride (30 g) was added. The reaction mixture was heated for 1 hr on the steam bath; during this time a white crystalline material separated. This mercuric salt (10.50 g) was separated by filtration, then suspended in concentrated hydrochloric acid (150 ml) and ethanol (150 ml), and heated on the steam bath for 1 hr. Extraction with ether gave a mobile light yellow liquid (1.10 g, 5.67 mmol, 74%, $n^{26}D$ 1.5947) which had the characteristic odor of 1,2-diphenylcyclopropane. The product was purified by distillation and the cis and trans isomers separated by gas chromatography.[1] The *cis*-1,2-diphenylcyclopropane was identified by its mp 35–36° (reported[5] 36.7, 38–38.5°) and by its time of elution on gas chromatography (direct comparison with an authentic sample). The *trans*-1,2-diphenylcyclopropane was identified by $n^{26}D$ 1.5961 (reported[5] $n^{20}D$ 1.5997), by its time of elution on gas chromatography (direct comparison), and by the identity of its nmr spectrum with that of an authentic sample.

A sample of *cis*- and *trans*-1,2-diphenylcyclopropane prepared by this desulfination but not distilled had cis/trans = 4.25. This ratio had been reported[8] previously as 0.125 on a distilled (atmospheric pressure) and probably equilibrated sample.

B.—A solution of *trans*-1,2-diphenylcyclopropanesulfinic acid (III) (0.492 g, 1.9 mmol, mp 134–138°) in ether was added over a 1-min period to a solution of ethylmagnesium bromide (0.0192 mol) in 50 ml of benzene and 10 ml of ether. The reaction mixture was vigorously stirred and heated under reflux for 8.75 hr. The magnesium complex was decomposed by addition of 3.6% aqueous hydrochloride acid, the reaction mixture was extracted with ether, and the combined ether extracts were, in turn, extracted with sodium bicarbonate solution. Acidification of the bicarbonate solution gave no precipitate. The ether extracts were washed with water and dried over sodium sulfate. Evaporation of the ether yielded a yellow oil (0.367 g). Thin layer chromatography indicated the presence of at least nine compounds, the predominant one being a mixture of *cis*- and *trans*-1,2-diphenylcyclopropane (VI and VII). This oil was chromatographed on silica gel (12 g, 100–200 mesh) and the diphenylcyclopropanes were eluted with 20% petroleum ether–80% benzene. The *cis*- and *trans*-1,2-diphenylcyclopropanes (0.143 g, 39%, cis/trans = 0.22) were separated and collected by preparative vapor phase chromatography and identified by comparison of their ir specta with those of authentic samples.[1,23]

Benzyl *trans*-1,2-Diphenylcyclopropyl Sulfone (IVa).—*trans*-1,2-Diphenylcyclopropanesulfinic acid (III) (0.50 g, 1.93 mmol, mp 131–135°) was dissolved in concentrated sodium bicarbonate solution (75 ml), and the resulting solution was neutralized with hydrochloric acid. Benzyl chloride (0.550 g, 4.35 mmol) dissolved in ethanol (50 ml) was added with stirring. After being stirred for 48 hr at room temperature, the reaction mixture was extracted with ether, and the ether extracts were washed with 10% aqueous sodium hydroxide and with water. The ether extracts were dried over sodium sulfate, and the solvent was removed under reduced pressure. Petroleum ether (25 ml) was added to the residue. On being cooled the solution deposited 0.60 g (89%) of benzyl *trans*-1,2-diphenylcyclopropyl sulfone (IVa), mp 164–165°. The analytical sample was crystallized from acetone–petroleum ether: mp 165–166°; $\lambda_{max}^{ethanol}$ 202.3 nm (ϵ 26,300), 211 (24,300), 219.1 (26,000), shoulders 253.7 (585), 259.6 (718), 263.3 (668), 264.9 (635), 270.2 (451); ν_{max}^{Nujol} 664, 698, 717, 741, 771, 826, 917, 935, 967, 1031 (cyclopropane), 1082, 1121, 1142 (SO_2), 1181, 1250, 1287, 1309 cm^{-1} (SO_2).

Anal. Calcd for $C_{22}H_{20}O_2S$ (348.46): C, 75.83; H, 5.79; S, 9.20. Found: C, 76.04; H, 6.04; S, 9.41.

In our hands, probably because of the instability of the diphenylcyclopropanesulfinic acid or because of varying reaction times, the yields on this benzylation reaction were erratic. Nevertheless, its was used to estimate the extent of stereoselectivity of this rearrangement.

A sample of the diphenylcyclopropanesulfinic acid, mp 126–134°, obtained in 73% yield from *trans*-2,4-diphenylthietane 1,1-dioxide (II), was converted to benzyl *trans*-1,2-diphenylcyclopropyl sulfone (IVa) (mp 160–162°, 32% yield) by the above procedure (reaction time, 24 hr). An nmr spectrum of the entire crude sulfone was taken. Only the trans isomer was present; the maximum amount of benzyl *cis*-1,2-diphenylcyclopropyl sulfone (XV) which could have been present without detection was 1%.[24]

A sample of the diphenylcyclopropanesulfinic acid, mp 121–127°, obtained in 65% yield from *cis*-2,4-diphenylthietane 1,1-dioxide (I), was converted to benzyl *trans*-1,2-diphenylcyclopropyl sulfone (IVa) (13% yield) by the above procedure (reaction time 5 hr). The nmr spectrum of the crude sulfone showed only the trans isomer to be present. The maximum amount of *cis*-1,2-diphenylcyclopropyl sulfone (XV) which could have been present without detection was 2%.

Methyl *trans*-1,2-Diphenylcyclopropyl Sulfone (IVb).—*trans*-1,2-Diphenylcyclopropanesulfinic acid (III) (0.25 g, 0.97 mmol, mp 134–136°) was dissolved in 10% aqueous sodium hydroxide (25 ml) and the excess base was neutralized with hydrochloric acid. The solution was cooled to 0°, and then 5.0 g (0.035 mol) of methyl iodide was added. The reaction mixture was stirred for 60 hr in the cold. It was then freed of excess methyl iodide by heating on a steam bath. The product was extracted with ether, and the ether extracts were washed with dilute sodium hydroxide solution and water and then dried (Na_2SO_4). Evaporation of the solvent and crystallization of the residue from acetone–

(20) For leading references on the Stevens rearrangement and a brief discussion of the problems involved, see R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 131, and U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, **9**, 763 (1970).

(21) Melting points were taken on a Fisher-Johns melting point apparatus, calibrated against a set of standard compounds, or on a calibrated Mel-Temp apparatus. Petroleum ether refers to that fraction, bp 60–68°, unless otherwise stated. All nmr data in this section were measured at 60 MHz and are recorded in hertz downfield from tetramethylsilane.

(22) Comparable yields can be obtained on heating for 15 min.

(23) S. G. Beech, J. H. Turnbull, and W. Wilson, *J. Chem. Soc.*, 4686 (1952).

(24) Reaction of *cis*-1,2-diphenylcyclopropanesulfinic acid, mp 133–135°, with benzyl chloride for 24 hr under the above conditions gave a 35% yield of benzyl *cis*-1,2-diphenylcyclopropyl sulfone.

petroleum ether yielded 0.20 g (76%) of methyl *trans*-1,2-diphenylcyclopropyl sulfone (IVb), mp 105–111°. Repeated crystallizations from acetone–petroleum ether were necessary to obtain the analytic sample of IVb: mp 114–115°; ν_{max}^{Nujol} 702 (s), 777 (s), (C_6H_5), 1116, 1145 (s), 1186, 1300 (s), 1311 cm^{-1} (s) (SO_2).

Anal. Calcd for $C_{16}H_{16}O_2S$ (272.37): C, 70.56; H, 5.92. Found: C, 70.30; H, 6.08.

Methyl *trans*-1,2-diphenylcyclopropanesulfinate (V) was prepared by the reaction of the diphenylsulfinic acids from both *cis*- and *trans*-2,4-diphenylthietane 1,1-dioxides (I and II) with diazomethane. The ir spectra of the crude products obtained from both samples of sulfinic acid were virtually identical. Since they were prepared in very small quantity and since they failed to crystallize, they were not further characterized: ν_{max}^{neat} 650, 690–714, 739, 772, 806, 929, 962, 980–1010, 1032, 1059, 1081, 1130–1149, 1178, 1449, 1495, 1603, 2924, 3021, and 3049 cm^{-1}.[4]

***cis*- and *trans*-α-Benzylthiostilbene (IX and X).**—A solution of 9.8 g (0.050 mol) of deoxybenzoin (VIII) and 9.3 g (0.075 mol) of benzylmercaptan in 100 ml of absolute ethanol was saturated with anhydrous hydrogen chloride and then was allowed to stand for 2.5 hr. The reaction mixture was poured into 400 ml of ice water. The products were isolated by ether extraction. The organic residue (14 g) consisted of *ca.* 50% α-benzylthio-*cis*-stilbene (IX), 30.5% α-benzylthio-*trans*-stilbene (X), 14.5% desoxybenzoin dibenzylthioketal (XI), and 4.5% deoxybenzoin (analysis by nmr spectroscopy). The residue on being allowed to stand with 25 ml of petroleum ether formed crystals, mp 74–85°. Crystallization of this solid from methanol gave 4.7 g (31%) of α-benzylthio-*cis*-stilbene (IX), mp 88–91°. Repeated crystallizations from methanol yielded analytically pure IX: mp 90.5–91°; $\lambda_{max}^{ethanol}$ 308 nm (ε 13,700); ν_{max}^{KBr} 690, 751, 763, 781, 833, 943, 1025, 1065, 1160, 1440, 1495, 1600, 3000 cm^{-1}; nmr (CCl_4) 218 (CH_2), 402.5 (>C=C<$_H$), 413, 415, and 418 (5 H), 428 and 435 Hz (10 H).

Anal. Calcd for $C_{21}H_{18}S$ (302.44): C, 83.40; H, 6.00; S, 10.60. Found: C, 83.35; H, 6.06; S, 10.55.

The residue from the combined mother liquors from the above crystallizations was chromatographed on 230 g of silica gel. α-Benzylthio-*trans*-stilbene (X) was eluted with 5% benzene in petroleum ether. Crystallization of the various fractions from methanol gave 1.05 g of X, mp 52–53°, and 1.21 g of X, mp 46–51° (total yield 15%). Recrystallization of an aliquot of the purer material from methanol yielded analytically pure α-benzylthio-*trans*-stilbene (X): mp 53–53.5°; $\lambda_{max}^{ethanol}$ 309 nm (ε 13,100); ν_{max}^{KBr} 680, 695, 753, 856, 873, 912, 940, 1028, 1070, 1440, 1490, 1600, 3000 cm^{-1}; nmr (CCl_4) 213 (CH_2), 403 (>C=C<$_H$), 412 to 457 Hz (very complex C_6H_5).

Anal. Calcd for $C_{21}H_{18}S$ (302.44): C, 83.40; H, 6.00; S, 10.60. Found: C, 83.17; H, 6.06; S, 10.39.

Further elution with 5% benzene in petroleum ether yielded, after crystallization from methanol, 0.54 g of pure α-benzylthio-*cis*-stilbene (IX), mp 90–91°; total isolated yield 35%.

Deoxybenzoin dibenzylthioketal (XI) (3.24 g) was eluted from the column with 15% benzene in petroleum ether. Crystallization from methanol gave 2.78 g (13%) of material, mp 65–66°. An aliquot crystallized twice more from methanol yielded pure deoxybenzoin dibenzylthioketal: mp 66.8–67.2°; ν_{max}^{KBr} 635, 690–730, 733, 750, 770–790, 860, 958, 1030, 1070, 1085, 1230, 1420, 1600, 2930, 3000 cm^{-1}; nmr (CCl_4) 198.5 (2 H), 226.5 Hz (4 H).

Anal. Calcd for $C_{28}H_{26}S_2$ (426.64): C, 78.83; H, 6.14; S, 15.03. Found: C, 78.68; H, 6.33; S, 15.09.

Finally deoxybenzoin (0.47 g, 4.8%, mp 52–53°; 2,4-dinitrophenylhydrazone, mp 200–204°) was eluted with 50% benzene in petroleum ether.

α-Benzylsulfonyl-*cis*-stilbene (XIII).—To a hot solution of 0.20 g (0.66 mmol) of α-benzylthio-*cis*-stilbene in 6 ml of glacial acetic acid was added 1 ml of 30% hydrogen peroxide. After being heated on the steam bath for 5 min the solution was allowed to stand at room temperature for 1 hr and was then poured into 20 ml of ice water. The crude product (0.20 g, mp 130–150°) was crystallized from ethanol and yielded 0.15 g (68%) of α-benzylsulfonyl-*cis*-stilbene (XIII): mp 157.5–158°; $\lambda_{max}^{ethanol}$ 271 nm (ε 16,600); ν_{max}^{Nujol} 640, 690, 710, 725, 760, 775, 827, 912, 950, 1125, 1310 cm^{-1}; nmr ($CDCl_3$) 247 (CH_2), 455 (>C=C<$_H$), 449 and 441.5 (singlet aromatic absorptions, 10 H), 415–438 Hz (complex, 5 H).

Anal. Calcd for $C_{21}H_{18}O_2S$ (334.44): C, 75.42; H, 5.43; S, 9.59. Found: C, 75.68; H, 5.58; S, 9.65.

For the preparation of larger quantities of α-benzylsulfonyl-*cis*-stilbene (XIII), the two procedures given above were combined, all chromatography was omitted, and XIII, mp 156.5–158° (22%), was purified by repeated crystallizations from ethanol containing a small amount of sodium methoxide.

When α-benzylthio-*trans*-stilbene (X) was oxidized to the sulfone by the above procedure, a mixture of *cis*- and *trans*-α-benzylsulfonylstilbenes (XIII and XIV, respectively) was obtained; cis/trans ratio 0.25 from nmr spectroscopy.

α-Benzylsulfinyl-*trans*-stilbene (XII) was obtained on attempted oxidation of α-benzylthio-*trans*-stilbene (X) by the above procedure on mixing the reagents at room temperature, then allowing the reaction to stand overnight in the refrigerator. Crystallization of the product from diisopropyl ether yielded analytically pure α-benzylsulfinyl-*trans*-stilbene: mp 124–125° (53% yield); $\lambda_{max}^{ethanol}$ 264 nm (ε 12,900); ν_{max}^{KBr} 690, 748, 754, 762, 880, 1020 (s) (SO), 1067, 1440, and 1488 cm^{-1}; nmr ($CDCl_3$) 237.5 (CH_2), 451 (>C=C<$_H$?), 417–472 Hz (15 H, C_6H_5).

Anal. Calcd for $C_{21}H_{18}OS$ (318.44): C, 79.21; H, 5.70; S, 10.07. Found: C, 78.91; H, 5.67; S, 10.11.

α-Benzylsulfonyl-*trans*-stilbene (XIV).—To a solution of 0.30 g (1.0 mmol) of α-benzylthio-*trans*-stilbene in 5 ml of carbon tetrachloride and 2.5 ml of 88% formic acid was added 2.5 ml of 30% hydrogen peroxide in the course of 10 min. The mixture was stirred at room temperature for 4 hr and was then poured into dilute aqueous potassium hydroxide. The layers were separated and the aqueous layer was washed with two 20-ml portions of carbon tetrachloride. The carbon tetrachloride extracts were combined, washed with water, and then evaporated. The crude residue (0.315 g, 94%, mp 108–115°) on crystallization from diisopropyl ether yielded 0.263 g (79%) of pure α-benzylsulfonyl-*trans*-stilbene (XIV): mp 114.8–115.5°; $\lambda_{max}^{ethanol}$ 277 nm (ε 13,700); ν_{max}^{KBr} 690, 720, 750, 780, 880, 885, 930, 1030, 1075, 1120 (s) (SO_2), 1140 (s) (SO_2), 1195, 1245, 1300 (s) (SO_2), 1450, 1460, 1500, and 1610 cm^{-1}; nmr ($CDCl_3$) 242 (CH_2), 438 (>C=C<$_H$?), 435, 444, 420–470 (C_6H_5).

Anal. Calcd for $C_{21}H_{18}O_2S$ (334.44): C, 75.42; H, 5.43; S, 9.59. Found: C, 75.41; H, 5.72; S, 9.61.

α-Benzylsulfonyl-*cis*-stilbene (XIII) from α-Benzylsulfonyl-*trans*-stilbene (XIV).—A solution of 76.5 mg (0.229 mmol) of α-benzylsulfonyl-*cis*-stilbene in 10 ml of ethanol and 5 ml of 0.2 *N* sodium hydroxide in ethanol was heated under reflux for 12 hr. The reaction mixture was cooled and then poured into 25 ml of water. The product (69 mg, 90%, mp 137–164°) was removed by filtration and washed well with water. Its nmr spectrum ($CDCl_3$) was identical with that of α-benzylsulfonyl-*cis*-stilbene with the exception of two very small singlets at 95 and 203.5 Hz. No α-benzylsulfonyl-*trans*-stilbene could be detected by nmr spectroscopy.

Benzyl *cis*- and *trans*-1,2-Diphenylcyclopropyl Sulfones (XV and IVa).—Solid trimethylsulfoxonium iodide (2.20 g, 0.01 mol) was added in small increments to a solution of 0.24 g (0.01 mol) of sodium hydride in 8 ml of dimethyl sulfoxide. Hydrogen was evolved. To the above solution was added 1.8 g (5.4 mmol) of α-benzylsulfonyl-*cis*-stilbene in 10 ml of dimethyl sulfoxide. A yellow solution formed, then turned red for about 5 min, and then became light yellow again. The reaction mixture was allowed to stand for 1 hr at room temperature and was then poured into 100 ml of cold water. The white precipitate was separated by filtration, washed well with water, washed with a small quantity of ethanol, and was then dried. The product (1.82 g, 97%, mp 130–150°) was a 52:48 mixture of benzyl *cis*- and *trans*-1,2-diphenylcyclopropyl sulfones (XV and IVa). Analysis was effected by integrating the methylene absorptions in the nmr spectrum. Fractional crystallization from ethanol gave both products. The less soluble benzyl *cis*-1,2-diphenylcyclopropyl sulfone (XV), (0.43 g, 23%, mp 171–173°) was identical in all respects (melting point, mixture melting point, ir, nmr) with a sample of XV, prepared by the benzylation of *cis*-1,2-diphenylcyclopropanesulfinic acid[19] and crystallized from petroleum ether (bp 30–60°)–benzene. Benzyl *cis*-1,2-diphenylcyclopropyl sulfone: mp 174–175.5°; ν_{max}^{KBr} 481, 511 (s), 532 (s), 566, 580, 618 (s), 670, 690 (vs), 741, 762 (s), 770 (s), 809, 821 (s), 875, 913, 944, 1025, 1049, 1084, 1125 (vs) (SO_2), 1140, 1155, 1170, 1256, 1298 (vs) (SO_2), 1443, 1452, 1491 (s), 1602 cm^{-1}.

Anal. Calcd for $C_{22}H_{20}O_2S$ (348.46): C, 75.83; H, 5.79. Found: C, 76.01; H, 6.09.

The more soluble benzyl *trans*-1,2-diphenylcyclopropyl sulfone (IVa) (mp 161–163°, 5.3%) was identical in all respects (mixture melting point, ir, nmr) with the benzyl *trans*-1,2-diphenylcyclopropyl sulfone (IVa) prepared from *trans*-1,2-diphenylcyclopropanesulfinic acid (III, above).

The above reaction was repeated on 1.17 g (3.5 mmol) of α-benzylsulfonyl-*trans*-stilbene (XIV). The product (1.05 g, 86%, mp 124–164°) was a 49:51 mixture of benzyl *cis*- and *trans*-1,2-diphenylcyclopropyl sulfones (XV and IVa); analysis from the nmr spectrum.

Registry No.—I, 18744-27-9; II, 24609-91-4; III, 30256-16-7; IVa, 30256-17-8; IVb, 30256-18-9; IX, 30256-19-0; X, 30256-20-3; XI, 29055-91-2; XII, 30256-21-4; XIII, 30256-22-5; XIV, 30256-23-6; XV, 30256-24-7; deoxybenzoin, 451-40-1, 5637-51-4 (2,4-DNP).

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Thietanes. IV. Rearrangement of 2,4-Diphenylthietane Oxides

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Reaction of either *cis*- or *trans*-2,4-diphenylthietane 1-oxide (I or II) with potassium *tert*-butoxide in dimethylformamide yielded a mixture of *cis*-1,2-diphenylcyclopropanethiol (IV) and *cis*-1,2-diphenylcyclopropanesulfinic acid (V). The structure of the sulfinic acid V was established by conversion to the known benzyl *cis*-1,2-diphenylcyclopropyl sulfone (IXa). The structure of the mercaptan IV was established by conversion to benzyl *cis*-1,2-diphenylcyclopropyl sulfide (VIII) which was oxidized to the known sulfone IXa. The mercaptan IV was also oxidized to *meso*- and *rac*-bis(1,2-diphenylcyclopropyl) disulfides (VI and VII). The rearrangements of the *cis*- and *trans*-2,4-diphenylthietane oxides (I and II) to *cis*-1,2-diphenylcyclopropanethiol (IV) and *cis*-1,2-diphenylcyclopropanesulfinic acid (V) are highly stereoselective. Mechanisms are postulated for the stereoselective rearrangements of 2,4-diphenylthietane mono- and dioxides to cyclopropane derivatives and for the stereospecific rearrangements 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.

Recently we have described the stereoselective rearrangement of *cis*- and *trans*-2,4-diphenylthietane 1,1-dioxides to *trans*-1,2-diphenylcyclopropanesulfinic acid.[1] Here, we report the stereoselective rearrangement of *cis*-2,4-diphenylthietane *trans*-1-oxide[2] (I) and *trans*-2,4-diphenylthietane 1-oxide[2] (II) to a mixture of *cis*-1,2-diphenylcyclopropanethiol (IV) and *cis*-1,2-diphenylcyclopropanesulfinic acid (V).

Treatment of *trans*-2,4-diphenylthietane 1-oxide (II) with potassium *tert*-butoxide in dimethylformamide yielded *cis*-1,2-diphenylcyclopropanesulfinic acid (V) (10–20% yield). Initial information on the constitution of this acid was obtained from its ir spectrum which was typical of that of a sulfinic acid[3] and from its conversion with mercury(II) chloride[1,4] and acid hydrolysis to a mixture of *cis*- and *trans*-1,2-diphenylcyclopropanes (cis/trans ratio 3.8). Benzylation of the *cis*-1,2-diphenylcyclopropanesulfinic acid (V) yielded the previously described benzyl *cis*-1,2-diphenylcyclopropyl sulfone (IXa).[1] Methylation of V gave *cis*-1,2-diphenylcyclopropyl methyl sulfone (IXb).

To obtain greater insight into the course of the reaction, *trans*-2,4-diphenylthietane 1-oxide (II) was treated with potassium *tert*-butoxide in dimethylformamide followed, after 1.25 hr, by the addition of benzyl chloride to the reaction mixture. From the reaction benzyl *cis*-1,2-diphenylcyclopropyl sulfone (IXa, 23%) and benzyl *cis*-1,2-diphenylcyclopropyl sulfide (VIII, 33%) were isolated. The nmr spectrum ($C_6H_5CH_2$ region)[1] of the crude IXa indicated the presence of 6% benzyl *trans*-1,2-diphenylcyclopropyl sulfone. The benzyl *cis*-1,2-diphenylcyclopropyl sulfide (VIII) was identified by its analysis, by its ir and nmr (Table I) spectra, and by its oxidation to benzyl *cis*-1,2-diphenylcyclopropyl sulfone (IXa). Similar rearrangement of *cis*-2,4-diphenylthietane *trans*-1-oxide (I) followed by benzylation yielded the same sulfone IXa (22% yield) and sulfide VIII (22% yield). In this case the sulfone IXa was virtually free (<1%) of benzyl *trans*-1,2-diphenylcyclopropyl sulfone.[1]

The intermediacy of the *cis*-1,2-diphenylcyclopropanethiol[5] (IV) was established by its isolation by chromatography, by evidence of purity from thin layer chromatography, by the presence in its ir spectrum of an absorption band at 2600 cm^{-1} characteristic of the –SH group,[6] and by its conversion to benzyl *cis*-1,2-diphenylcyclopropyl sulfide (VIII). Further evidence for the intermediacy of the mercaptan IV was obtained by the air oxidation of the mercaptan from the rearrangement of *cis*-2,4-diphenylthietane *trans*-1-oxide (I) (>99% stereoselective) to the corresponding disulfides VI and VII. Since *cis*-1,2-diphenylcyclopropanethiol (IV) exists as a racemic modification (*d* and *l* forms), two different inactive disulfides (a meso,*dl* compound and a racemic, *dd* plus *ll* modification) should be obtained. Both of these were isolated.

The constitutions of these disulfides VI and VII were established by their analyses, by their conversion with

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