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).

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the National Aeronautics and Space Administration, and to the National Institutes of Health (Grant No. AM 12954) for the support of this research. We are indebted to Dr. William Schwabacher for aid on our initial nmr analyses.

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

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Received November 3, 1970

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

(1) R. M. Dodson, P. D. Hammen, E. H. Jancis, and G. Klose, *J. Org. Chem.*, **36**, 2698 (1971).

(2) R. M. Dodson, E. H. Jancis, and G. Klose, *ibid.*, **35**, 2520 (1970).

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

(4) 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).

(5) Cyclopropanethiol has been prepared by the photolysis of carbonyl sulfide in the presence of cyclopropane: A. R. Knight, O. P. Strausz, and H. E. Gunning, *ibid.*, **85**, 1207 (1963).

(6) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, pp 54, 220.

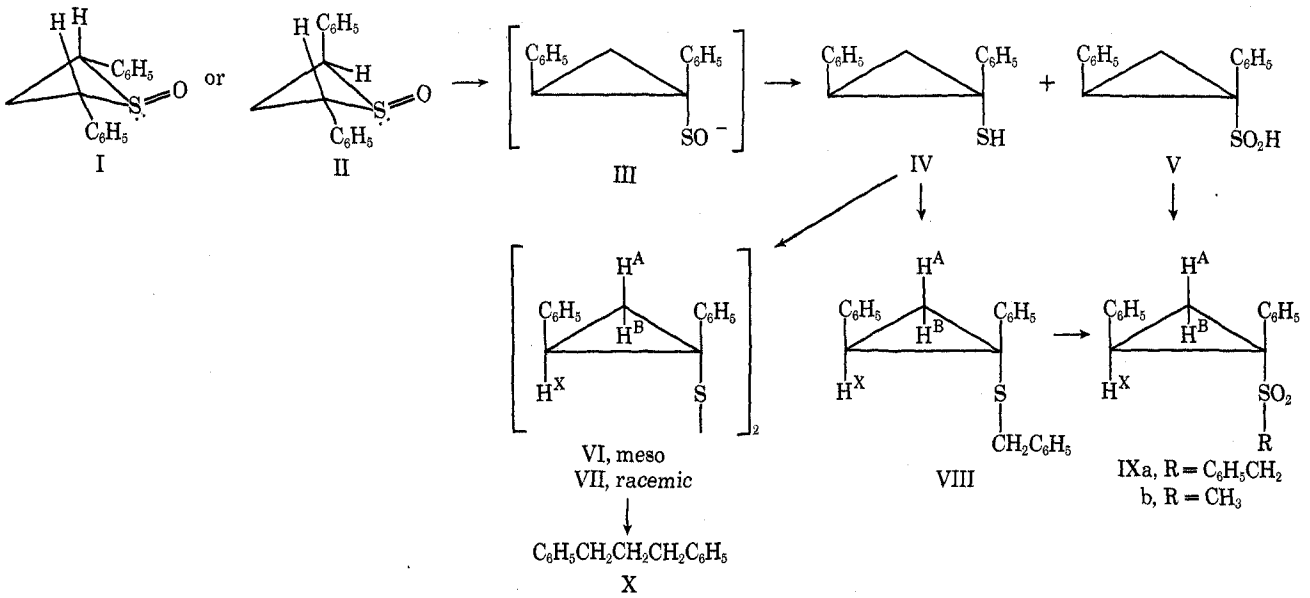
TABLE I[a]

DERIVATIVES OF *cis*-1,2-DIPHENYLCYCLOPROPANETHIOL

	ν_A	ν_B	ν_X	J_{AB}[d]	J_{AX}	J_{BX}
IXb methyl sulfone ($CDCl_3$)[b]	114.3	133.9	204.1	−5.85	7.18	9.90
IXa benzyl sulfone ($CDCl_3$)[b]	109.0	123.2	197.2	−6.10	7.15	10.25
VIII benzyl sulfide (CCl_4)[c]	99.0	85.6	152.4	−5.8	6.3	9.3
VI meso disulfide ($CDCl_3$)[c]	103.5	98.7	160.4	−5.9	6.0	9.9

[a] Recorded in hertz downfield from tetramethylsilane at 60 MHz. The lettering of the protons correspond to that given in the formulas. [b] Determined at 50-Hz sweepwidth and calculated by the LAOCOON-2 program of A. A. Bothner-By and S. M. Castellano. Coupling constants should be accurate to ±0.1 Hz. [c] Determined at 500-Hz sweepwidth and calculated as ABX spectra. Coupling constants should be accurate to ±0.5 Hz. [d] The sign of this coupling constant was not independently determined but follows from our previous determination (ref 1).

SCHEME I



Raney Ni to 1,2- and 1,3-diphenylpropane,[7] and by analyses of their nmr spectra. The nmr spectrum of one of the isomeric disulfides could be analyzed as a simple ABX system (Table I). That of the second disulfide could be analyzed as two similar but superimposed ABX systems (see Table I and Experimental Section). This more complex spectrum could result from the partial association of the (+) and (−) isomers of the racemic compound in solution. The structures were assigned accordingly: the meso disulfide VI to that compound, mp 142–143°, with the simpler nmr spectrum; the racemic disulfide VII to that compound, mp 121–122°, with the more complex nmr spectrum.[8] It is realized that these assignments are highly speculative.

The deshielding effect of the sulfone group on cis-vicinal protons (compared to its effect on trans-vicinal protons and to the effect of S) is immediately apparent from Table I. Thus, with the sulfide or disulfides, H^B is farthest upfield while with the sulfones (see also ref 1) H^A appears at highest field (see Scheme I).

The mass spectrum of VI was also consistent with its constitution. The molecular ion peak (450) was very weak (0.1% of base peaks at 223 and 121). Base peaks corresponded to M/2 − 2H (223) and $C_6H_5CS^+$ (121). A very strong peak (66% of base peaks) corresponded to M/2 − S (193). The ir spectra of the stereoisomeric disulfides VI and VII were almost identical.

Mechanisms.—In this series of papers, four different base-catalyzed reactions have been presented. (1) The isomerization[2] of *trans*-2,4-diphenylthietane mono- and dioxides (II and XII) to the corresponding cis isomers I and XI, respectively, was accomplished with a relatively weak base (sodium methoxide) in the presence of an abundance of available protons (methanol). Concentrations of the intermediate anions should be very low. (2) The stereoselective rearrangements[1] of the *cis*- and *trans*-2,4-diphenylthietane 1,1-dioxides (XI and XII) to the *trans*-1,2-diphenylcyclopropanesulfinate anion (XIV) occurred on treatment of XI or XII with ethylmagnesium bromide. Here, the α-sulfonyl carbanion formed rapidly, and protons were not available. Consequently, the intermediate carbanion was stabilized by rearrangement to the *trans*-1,2-diphenylcyclopropanesulfinate anion (XIV). (3) In a related manner, the stereoselective rearrangement of *cis*- and *trans*-2,4-diphenylthietane 1-oxides (I and II) to the *cis*-1,2-diphenylcyclopropanesulfenate anion (III) occurred in the presence of strong base (potassium *tert*-butoxide) and low availability of protons (dimethylformamide as solvent). It is probable that the potassium salt of the sulfenic acid III formed first and that

(7) Since dimers connected by a C–C bond had previously been isolated from rearrangements of thietanes [(R. M. Dodson and J. Yu Fan, *J. Org. Chem.*, **36**, 2708 (1971)], we felt it necessary to prove that these dimers were not of this type.

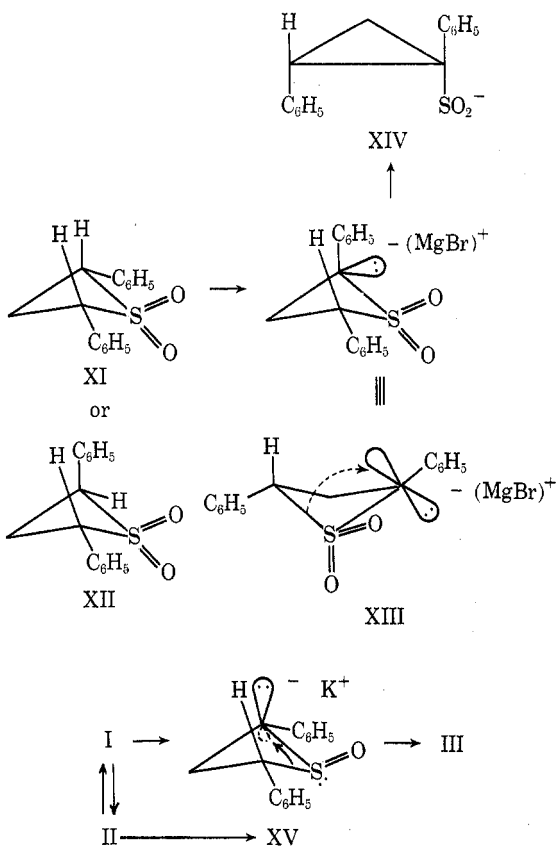
(8) For a simpler study which distinguished between meso and *dl* symmetrically substituted 1,2-diols and 1,3-dioxalanes, see M. Gianni, J. Saavedra, R. Myhalyk, and K. Wursthorn, *J. Phys. Chem.*, **74**, 210 (1970).

this then disproportionated to the potassium salts of the sulfinic acid V and the mercaptan IV.[9]

We consider these latter two reactions as modified Stevens rearrangements.[10] Any mechanism for them should explain their high stereoselectivity. We believe that the stereoselectivity of these reactions is controlled by the configurational stability of the intermediate anions XIII and XV.

Corey and coworkers[11] have shown that, on base-catalyzed exchange of an α-hydrogen atom of a sulfone for deuterium, the hydrogen atom lying conformationally between the oxygen atoms of the sulfone is preferentially exchanged and rotation of the intermediate anion is restricted. Since the energy of the transition state for ionization should be similar to the energy of the anion, the anion so produced should be the conformationally most stable one. This conclusion is in agreement with the conclusions of Lipscomb and coworkers[11b] from a crystal structure determination of tetramethylsulfamide and an LCAO–MO calculation on tetrafluorosulfamide. From this, one can conclude that the most stable structure for the anion of the sulfones XI or XII should be XIII (Scheme II). In this rearrangement the sulfones XI and XII are converted entirely and irreversibly to the anion (Grignard reagent). If this now rearranges with migration of the C–S bond (*via* an intermediate diradical pair[10]) to the back lobe (near lobe) of the partially p orbital of the anion, the anion of *trans*-1,2-diphenylcyclopropanesulfinic acid (XIV) results.

SCHEME II



Recent experiments by Baldwin and coworkers,[12] however, on the base-catalyzed exchange of α hydrogens for deuterium in benzyl methyl sulfoxide, have contradicted the previous experiments of Wolfe and Rauk[13] and have indicated that the α hydrogen lying conformationally between the oxygen of the sulfoxide and the methyl group is preferentially exchanged. This would lead to the prediction that XV should be the configurationally most stable anion from the sulfoxides I and II. This configuration has both phenyl groups in pseudoequatorial conformations and has the oxygen of the S=O dipole in close vicinity to the positive ion. Rearrangement of this anion with migration of the C–S bond to the back lobe (near lobe) of the partially p orbital of the anion would yield the anion of *cis*-1,2-diphenylcyclopropanesulfenic acid (III). This mechanism assumes that the activation energy for rearrangement to cis or trans isomers is similar.

It should be realized that there is the possibility of some equilibration of I and II in this system. Similar experiments on *trans*-2,4-diphenylthietane 1,1-dioxide (XII) using potassium *tert*-butoxide in dimethylformamide yielded some *cis*-2,4-diphenylthietane 1,1-dioxide (XI).

(4) The rearrangement of *cis*- and *trans*-2,4-diphenylthietane dioxides (XI and XII) to *cis*- and *trans*-3,5-diphenyl-1,2-oxathiolane (2,3)-*cis*-2-oxides (XVI and XVII, respectively) on treatment with *tert*-butoxymagnesium bromide is stereospecific with respect to the phenyl groups but stereoselective with respect to the oxygen atoms on sulfur. We believe that the differences between this rearrangement and the rearrangements of the thietane monoxides and dioxides to the cyclopropanesulfenate and sulfinate respectively result from the unique structure of the dimeric *tert*-butoxymagnesium bromide–ether complex.[14] In the interaction of the sulfone with this basic catalyst both the anion and the *tert*-butyl alcohol so formed are held in close proximity to each other permitting the rapid reprotonation of the anion, either before or after rearrangement. Since the sultine should be far less acidic than the sulfone, the products of the rearrangement XVI and XVII should be moderately stable to further interaction with the catalyst. If the proton (from the complexed *tert*-butyl alcohol) were not immediately available, the anion should be stabilized by rearrangement to the cyclopropanesulfinate.

The intermediates for this rearrangement can be formulated as anion diradicals in a solvent cage[10] and thus the stereospecificity can be explained. Rear-

(9) N. Kharasch and T. C. Bruice, *J. Amer. Chem. Soc.*, **73**, 3240 (1951); N. Kharasch, Ed., "Organic Sulfur Compounds," Vol. 1, Pergamon Press, Elmsford, N. Y., 1961, p 392.

(10) U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, **9**, 763 (1970); R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 131.

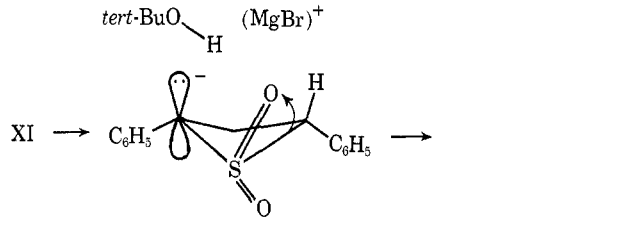
(11) (a) E. J. Corey, H. Konig, and T. H. Lowry, *Tetrahedron Lett.*, 515 (1962); E. J. Corey and T. H. Lowry, *ibid.*, 793, 803 (1965). (b) T. H. Jordan, H. W. Smith, L. L. Lohr, Jr., and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **85**, 846 (1963).

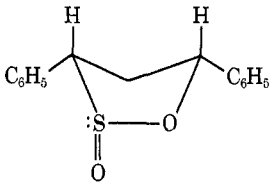
(12) J. E. Baldwin, R. E. Hackler, and R. M. Scott, *Chem. Commun.*, 1415 (1969). See also, M. Nishio, *ibid.*, 562 (1968); 51 (1969). The results of B. J. Hutchinson, K. K. Andersen, and A. R. Katritzky [*J. Amer. Chem. Soc.*, **91**, 3839 (1969)] from the exchange of the α-hydrogen atoms of *trans*-4-phenyltetrahydrothiopyran 1-oxide in dimethyl sulfoxide, although tending to support our conclusions, were not stereoselective to within experimental error.

(13) S. Wolfe and A. Rauk, *Chem. Commun.*, 778 (1966). See also the quantum mechanical calculations on the conformation of this anion: A. Rauk, S. Wolfe, and I. G. Csizmadia, *Can. J. Chem.*, **47**, 113 (1969).

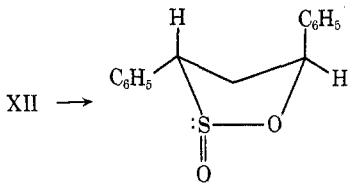
(14) The structure of *tert*-butoxymagnesium bromide has been determined by X-ray diffraction: P. T. Moseley and H. M. M. Shearer, *Chem. Commun.*, 279 (1968).

rangement to upper oxygen (that on the same side of the molecule as the catalyst) leads to the conformationally more favorable transition state and thus helps explain the stereoselectivity of the rearrangement with respect to the oxygen atoms on sulfur.

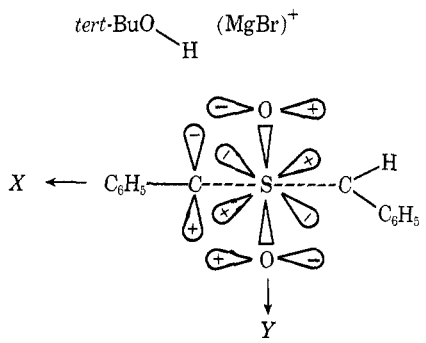




XVI



XVII



However, it should be realized that rearrangement of XI → XVI, unlike most 1,2-anionic rearrangements, is a symmetry-allowed rearrangement.[15] In order to formulate it, the molecular orbital picture of the sulfone and of its conjugation with adjacent unsaturation as formulated by Moffitt was used.[16] Attack of *tert*-butoxymagnesium bromide on an α proton will remove the proton and generate a p orbital on carbon. This p orbital (pictured p_y) will perturb the va_2 π orbital of the sulfone. The va_2 orbital is composed of $S_{d_{xy}}$ and $(O_{p_z} - O_{p_z})$ (pictured). Conjugation is that of case Ia of Moffitt[16] and partially resembles spiroconjugation.[17] The result should be an increase in energy of the perturbed va_2 orbital with an increase in electron concentration in that oxygen on the same side of the molecule as $(MgBr)^+$. The antibonding rb_1 orbital of the alkyl groups, composed of $S_{p_x} - S_{p_{xx}}$, and $-(R_\sigma - R_\sigma')$, already lowered in energy because of the high positive charge on sulfur, can now interact with the perturbed va_2 orbital, the alkyl group (to the right in the picture) rearranging without its electrons to oxygen (upper), with the electrons occupying the S_{p_x} orbital and becoming the nonbonding electrons of the sultine. The nonbonding electrons should be trans to the newly formed C–O bond; thus the stereochemistry of the sulfinate group is explained. Finally, with rearrangement, the electrons in the p_y orbital on carbon become more basic, the proton is returned (from the same side), and the catalyst is regenerated. The energy for the reaction comes from the relief of strain of the four-membered ring and from substitution of a C–O bond for a C–S bond. No firm decision between an anion-diradical mechanism and a concerted mechanism can be made from the presently available evidence.

Experimental Section[18]

Benzyl *cis*-1,2-Diphenylcyclopropyl Sulfide (VIII) and Benzyl *cis*-1,2-Diphenylcyclopropyl Sulfone (IXa) from *trans*-2,4-Diphenylthietane 1-Oxide (II).—*trans*-2,4-Diphenylthietane 1-oxide[2] (II) (0.811 g, 3.35 mmol, mp 152–155°) in dimethylformamide (30 ml, dried by distillation over calcium hydride) was stirred for 1.25 hr under nitrogen at room temperature with potassium *tert*-butoxide (2.00 g, 0.0178 mol). Benzyl chloride (2.30 g, 0.0182 mol) was then added and the reaction was stirred under nitrogen for 24 hr. The reaction contents were poured into water and extracted repeatedly with ether. The combined ether extracts were washed with water and dried over sodium sulfate. Evaporation of the solvent left a crystalline solid, which was thoroughly washed with petroleum ether. The nmr spectrum of the solid indicated a mixture of 94% benzyl *cis*-1,2-diphenylcyclopropyl sulfone (IXa) and 6% benzyl *trans*-1,2-diphenylcyclopropyl sulfone. Crystallization from petroleum ether–chloroform yielded 0.210 g (18%) of benzyl *cis*-1,2-diphenylcyclopropyl sulfone (IXa), mp 173–174°, identical (mixture melting point and ir spectrum) with material synthesized from α-benzylsulfonylstilbene.[1]

The mother liquors from the crystallization and from the original washing were chromatographed on a silica gel column (30 g, 100–200 mesh). Elution with 4:1 petroleum ether (bp 40–60°)–benzene yielded, as a viscous liquid, 0.351 g (33%) of benzyl *cis*-1,2-diphenylcyclopropyl sulfide (VIII): ν_{max}^{neat} 700, 753, 773, 1028, 1075, 1455, 1500 and 1547 cm^{-1}; nmr (CCl_4) 427.5 (s, 5.8 H, C_6H_5), 419 (s, 4.8 H, C_6H_5), 384.5–415 (complex multiplet, 4.8 H, C_6H_5), 214 Hz (s, 2 H, $CH_2C_6H_5$), ABX system of cyclopropyl protons (see Table I).

Anal. Calcd for $C_{22}H_{20}S$ (316.47): C, 83.50; H, 6.37. Found: C, 82.90, 83.89; H, 6.51, 6.96.

Additional benzyl *cis*-1,2-diphenylcyclopropyl sulfone (IXa) (0.054 g, 0.17 mmol, total yield 23%) was obtained by elution of the column with 4:6 chloroform–petroleum ether (bp 40–60°).

Benzyl *cis*-1,2-Diphenylcyclopropyl Sulfone (IXa) from Benzyl *cis*-1,2-Diphenylcyclopropyl Sulfide (VIII).—The benzyl *cis*-1,2-

(15) E. G. Miller, D. R. Rayner, H. T. Thomas, and K. Mislow (*J. Amer. Chem. Soc.*, **90**, 4861 (1968)] have proposed an intramolecular, concerted mechanism for the rearrangement of benzyl *p*-toluenesulfenate to benzyl *p*-tolyl sulfoxide. J. Jacobus [*Chem. Commun.*, 709 (1970)] has shown that the CIDNP observed in the nmr spectrum of that rearrangement may result from secondary reactions not on the direct rearrangement path.

(16) (a) W. Moffitt, *Proc. Roy. Soc., Ser. A*, **200**, 409 (1950); (b) H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951). To facilitate reading, orbitals are named using the same coordinate system, the same symmetry designations, and similar symbolism to that used by Moffitt.

(17) H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, **89**, 5208 (1967); R. Hoffmann, A. Imamura, and G. D. Zeiss, *ibid.*, **89**, 5215 (1967).

(18) Melting points were taken on a Fisher-Johns melting point apparatus, calibrated against a set of standard compounds. Nmr spectra were determined on a Varian A-60 spectrometer at concentrations of 10–20% and using tetramethylsilane as an internal standard. Mass spectra were determined on a Hitachi Perkin-Elmer Model RMU-6D mass spectrometer. The vapor phase chromatograms were run on an Aerograph manual temperature programmer gas chromatograph, Model A-90P, using a 20% Apiezon L, 60–80 firebrick (5 ft × 0.25 in.) column and using helium at 386 ml/min as the carrier gas. The following temperatures were used: column 220°, injector 240°, detector 250°. The chart speed was 1.7 cm/min. Petroleum ether, unless otherwise specified, refers to that fraction, bp 60–68°.

diphenylcyclopropyl sulfide (VIII) (0.136 g, 0.430 mmol), obtained from the reaction immediately above, was oxidized with 30% hydrogen peroxide in carbon tetrachloride–formic acid as previously described.[1] The benzyl *cis*-1,2-diphenylcyclopropyl sulfone (IXa) (0.15 g, 0.431 mmol, 100%) was obtained as a white crystalline solid, mp 166–170°. The nmr spectrum of this sulfone showed the presence of *ca.* 10% of the trans isomer. Crystallization from petroleum ether–chloroform raised the melting point of IXa to 174–175°; the sulfone IXa was identical (mixture melting point and ir spectrum) with the benzyl *cis*-1,2-diphenylcyclopropyl sulfone[1] previously prepared.

Benzyl *cis*-1,2-Diphenylcyclopropyl Sulfide (VIII) and Benzyl *cis*-1,2-Diphenylcyclopropyl Sulfone (IXa) from *cis*-2,4-Diphenylthietane *trans*-1-Oxide (I).—*cis*-2,4-Diphenylthietane *trans*-1-oxide[2] (I) (0.811 g, 3.35 mmol) was allowed to react with potassium *tert*-butoxide and the benzyl chloride in the manner described above. The benzyl *cis*-1,2-diphenylcyclopropyl sulfone (0.253 g, 0.725 mmol, 22% yield), mp 163–167°, obtained by thoroughly washing the crystals with petroleum ether, was virtually free of the trans isomer (<1%, from nmr spectrum), and after crystallization from petroleum ether–chloroform was identical (mp 173–174°, mixture melting point, ir spectrum) with IXa previously prepared.[1] Benzyl *cis*-1,2-diphenylcyclopropyl sulfide (VIII) (0.236 g, 0.746 mmol, 22%) was isolated by chromatography and identified by comparison of its ir spectrum and R_f value on thin layer chromatography with that of VIII obtained above.

***cis*-1,2-Diphenylcyclopropanesulfinic Acid (V)** was isolated from the reaction of *trans*-2,4-diphenylthietane 1-oxide with potassium *tert*-butoxide in dimethylformamide at 80° by pouring the initial reaction into ice water, extracting this thoroughly with ether, and then acidifying the aqueous layer with hydrochloric acid. The liberated sulfinic acid V was then extracted into ether, the ether solution washed with water, and the sulfinic acid extracted with dilute sodium bicarbonate solution. Acidification with dilute hydrochloric acid yielded *cis*-1,2-diphenylcyclopropanesulfinic acid (V, 10% yield): mp 125–127°; $\lambda_{max}^{ethanol}$ shoulder 223 nm (ϵ 17,119); ν_{max}^{Nujol} 699, 741, 755, 769, 807 (s), 843 (s), (SO_2H), 886, 911, 923, 944, 957, 1022 (s) (SO_2H), 1034 1064, 1087 (s) (SO_2H), 1096, 1111, 2314 (w, broad), 2387–2513 cm^{-1} (w, broad) (SO_2H).

Anal. Calcd for $C_{15}H_{14}O_2S$ (258.34): C, 69.74; H, 5.46. Found: C, 69.45; H, 5.75.

The best melting sample of *cis*-1,2-diphenylcyclopropanesulfinic acid (V), mp 133–135° (20% yield), was obtained from a rearrangement of *trans*-2,4-diphenylthietane 1-oxide (II) with potassium *tert*-butoxide in anhydrous ether under nitrogen at room temperature for 5 hr. This reaction also gave, after benzylation, a 39% yield of benzyl *cis*-1,2-diphenylcyclopropyl sulfide (VIII). The rearrangement also occurred when II was treated with sodium methoxide in dimethylformamide but did not occur when II was treated with sodium hydride in anhydrous ether.

Benzyl *cis*-1,2-Diphenylcyclopropyl Sulfone (IXa), mp 174–175° (71% yield), was obtained by the reaction of the sodium salt of the sulfinic acid V with benzyl chloride by the procedure previously described[1] and was identical (mixture melting point and ir spectrum) with previously prepared IXa.[1]

***cis*-1,2-Diphenylcyclopropyl Methyl Sulfone (IXb).**—*cis*-1,2-Diphenylcyclopropanesulfinic acid (V) (0.612 g, 2.37 mmol, mp 130–136°) was dissolved in saturated sodium bicarbonate solution (50 ml) and the solution was neutralized with hydrochloric acid. Methyl iodide (2.00 g, 0.0141 mol) in ethanol (50 ml) was added, and the slurry was stirred for 19 hr at room temperature. Water was added and the resulting suspension was repeatedly extracted with ether. The ether extracts were dried over anhydrous sodium sulfate and then evaporated. The resulting white crystalline residue on crystallization from chloroform–petroleum ether yielded 0.224 g (35%) of *cis*-1,2-diphenylcyclopropyl methyl sulfone (IXb): mp 144–148°; recrystallized from the same solvent, mp 147–148°; ν_{max}^{KBr} 693, 770, multiplets at 1133 and 1300 (SO_2), 1380, 1450, 1500, 1603 cm^{-1}; nmr ($CDCl_3$) 432.5 (s, C_6H_5), 402.5–428.5 (m, C_6H_5) 163 Hz (s, CH_3), ABX system of cyclopropyl protons (see Table I).

Anal. Calcd for $C_{16}H_{16}O_2S$ (272.37): C, 70.56; H, 5.92. Found: C, 70.51; H, 5.83.

***cis*- and *trans*-1,2-diphenylcyclopropanes** were obtained from *cis*-1,2-diphenylcyclopropanesulfinic acid (V) by desulfination of V with mercury(II) chloride as previously described.[1] The isomeric 1,2-diphenylcyclopropanes were separated by gas chromatography, cis/trans ratio 3.8. The infrared spectrum of *cis*-1,2-diphenylcyclopropane was identical with that of an authentic sample.[1,2,19]

***cis*-1,2-Diphenylcyclopropanethiol (IV).**—A mixture of *cis*- and *trans*-2,4-diphenylthietane 1-oxides[2] (2.00 g, 8.28 mmol, mp 122–126°) was dissolved in dry dimethylformamide (40 ml) and treated with 4.2 g (0.0375 mol) of potassium *tert*-butoxide. The reaction was stirred at room temperature under nitrogen for 3.5 hr. The reaction mixture was poured into water (100 ml) and extracted with ether. The ether extracts were washed thoroughly with water, dried over sodium sulfate overnight, and then evaporated. A yellow foul-smelling oil (1.05 g) was obtained whose infrared spectrum showed the presence of the SH stretching absorption (2600 cm^{-1}). This oil was chromatographed on 50 g of silica gel (100–200 mesh). Elution with 9:1 petroleum ether–benzene yielded *cis*-1,2-diphenylcyclopropanethiol (IV) (0.532 g, 2.38 mmol, 28% yield): ν_{max}^{neat} 695, 760 doublet, 800, 1030, 1075, 1453 doublet, 1503, 1603, 2600 cm^{-1} (SH). This material IV showed only one spot when examined with thin layer chromatography.

For positive identification this compound was benzylated with benzyl chloride and potassium *tert*-butoxide in dimethylformamide. The benzyl *cis*-1,2-diphenylcyclopropyl sulfide (VIII) after purification by chromatography had an ir spectrum identical with VIII previously prepared.

***meso*- and *rac*-Bis(*cis*-1,2-Diphenylcyclopropyl) Disulfides (VI and VII).**—A solution of *cis*-2,4-diphenylthietane *trans*-1-oxide (2.50 g, 0.0103 mol, mp 134–137°) in dry dimethylformamide (50 ml) was stirred for 2 hr at 0° with potassium *tert*-butoxide (4.10 g, 0.0366 mol). The reaction mixture was then poured into water (100 ml) and extracted thoroughly with ether. From the aqueous layer, 0.642 g (24% yield) of *cis*-1,2-diphenylcyclopropanesulfinic acid (V), mp 130–134°, was isolated. The ether extracts were dried briefly over sodium sulfate and then filtered. A slow stream of air was blown over the ether solution until it had been reduced to 30 ml in volume. It was then allowed to stand in a partially covered 125-ml erlenmeyer flask with occasional shaking for 4 days. The crystals which formed during this time were separated from the oil and washed with a small amount of ether. Crystallization from chloroform–petroleum ether yielded 0.176 g (0.39 mmol, 8%) of *meso*-bis(*cis*-1,2-diphenylcyclopropyl) disulfide (VI), mp 123–143°. Recrystallization from chloroform–petroleum ether gave 0.122 g of pure VI: mp 142–143°; $\lambda_{max}^{ethanol}$ 227.5 nm (ϵ 37,300); ν_{max}^{KBr} 643, 691, 735, 743, 761, 789, 872, 900, 915, 928, 949, 1025 (CH_2 of cyclopropane), 1040, 1072, 1081, 1092, 1149, 1159, 1445, 1455, 1497, 1578, 1599, 2985, 3000, 3035, 3062, 3090 cm^{-1}; nmr ($CDCl_3$) 425.5 (s, 10 H, C_6H_5), 394–422 Hz (complex multiplet, 10 H, C_6H_5), ABX system of cyclopropane ring (see Table I); mass spectrum, molecular ion 450 (0.1% of B), base peak 223, 193 (66% of B) (M/2 − S), 121 (100% of B) $C_6H_5CS^+$.

Anal. Calcd for $C_{30}H_{26}S_2$ (450.67): C, 79.96; H, 5.82. Found: C, 79.91; H, 5.85.

The ether washings were combined with the residual oil and the ether was evaporated. The residual oil was chromatographed on silica gel (30 g, 100–200 mesh). Fractions eluted with 9:1 and 8:2 petroleum ether (bp 30–60°)–benzene were combined and crystallized from petroleum ether. The *rac*-bis(*cis*-1,2-diphenylcyclopropyl) disulfide (VII) (0.336 g, 15%, mp 110–117°) after recrystallization from petroleum ether gave analytically pure VII: mp 121–122°; $\lambda_{max}^{ethanol}$ 227.5 nm (ϵ 36,800); ν_{max}^{KBr} 642, 689, 732, 761, 788, 872, 898, 911, 928, 946, 1023, 1039, 1070, 1079, 1090, 1442, 1452, 1495, 1576, 1598, 2998, 3033, 3065, 3090 cm^{-1}; nmr ($CDCl_3$) 424 (s, 10 H, C_6H_5), 392.8–422.3 (complex multiplet 10 H, C_6H_5), two superimposed ABX systems, one corresponding to that of the meso isomer (see Table I), a second ν_A 99.5, ν_B 8.80, ν_X 160.2, J_{AB} = −6.0, J_{AX} = 6.1, J_{BX} = 9.7 Hz (±0.5 Hz).

Anal. Calcd for $C_{30}H_{26}S_2$ (450.67): C, 79.96; H, 5.82; S, 14.23. Found: C, 79.60; H, 5.20; S, 14.28.

Desulfurization of *meso*-Bis(*cis*-1,2-Diphenylcyclopropyl) Disulfide (VI).—Raney nickel (W-2, 1/2 tsp) was added to a mixture of 0.091 g of VI, mp 140–142°, in 95% ethanol (50 ml). The reaction was stirred at the reflux temperature for 5.5 hr. The nickel was separated by filtration and washed with boiling 95% ethanol. Evaporation of the ethanol left a colorless oil. This was dissolved in ether and the ether solution was dried over sodium sulfate. Evaporation of the ether left 0.056 g (71%) of a pale

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yellow, pleasant-smelling oil. Vapor phase chromatography indicated the presence of two products in a ratio of 0.89 to 1. The first product eluted (10.0 cm from the air peak) had a retention time identical with that of the minor component obtained by catalytic reduction of *trans*-1,2-diphenylcyclopropane:[20] ν_{max}^{neat} 693, 730, 755, 1011, 1027, 1066, 1374, 1451, 1494, 1600, 2930, 2965, 3032, 3063, 3093 cm^{-1}. It was tentatively identified as 1,2-diphenylpropane.

The second product eluted (15.3 cm from the air peak) was identified as 1,3-diphenylpropane (X): ν_{max}^{neat} 693, 740, 901, 1028, 1081, 1452, 1495, 1602, 2862, 2940, 3035, 3070, 3092 cm^{-1}. Its retention time and its infrared spectrum were identical with that of an authentic sample of 1,3-diphenylpropane (X) prepared by the hydrogenation of *trans*-diphenylcyclopropane.[15,16] Similar results were obtained on desulfurization of *rac*-bis(*cis*-1,2-diphenylcyclopropyl) disulfide (VII).

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Registry No.—I, 24605-73-0; II, 22601-50-9; IV, 30256-27-0; V, 30256-28-1; VI, 30256-29-2; VII, 30256-30-5; VIII, 30256-31-6; IXb, 30256-32-7.

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

Notes

Thietanes. V. Products Formed *via* Dimerization of *trans*-2,4-Diphenylthietane

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Received November 3, 1970

In our previous publications on 2,4-diphenylthietanes, their monoxides, and dioxides,[1] we have described rearrangements that could be formulated readily as modified Stevens rearrangements. Here, we describe the preparation, isolation, and proof of structure of products whose formation can only be explained by complex and multiple reactions.

Treatment of *trans*-2,4-diphenylthietane (I) with potassium *tert*-butoxide in dimethylformamide yielded a dark brown viscous oil that showed bands in its ir spectrum corresponding to carbonyl (1682 cm^{-1}) and thiol (2535 cm^{-1}) groups. Thin layer chromatography of this material indicated the presence of nine different products. By chromatography on silica gel, four of these products have been separated and identified. An additional three products have been isolated but, because of the very small quantity obtained, have not as yet been identified.

The first product obtained from this reaction was easily identified as 2,3,5-triphenylthiophene (II), mp 141–142°. The structure of the compound was established (1) from its analysis, (2) from the presence in its ir spectrum of bands characteristic of phenylthiophenes (694, 754, 844, 913, 1071, 3070, and 3090 cm^{-1}),[2] and (3) from its mass spectrum which indicated a molecular weight of 312 and a molecular formula of $C_{22}H_{16}S$ However, previous reports on 2,3,5-triphenylthiophene gave melting points of 127[3] and 198°.[4] The synthesis of Smith[3] was repeated. Reaction of 1,2,4-triphenylbutane-1,4-dione with phosphorus pentasulfide yielded, after chromatography and repeated crystallizations, 2,3,5-triphenylthiophene (II), mp 143.5–144°, identical with that obtained above.

Next 1,2,4,5-tetraphenylbenzene (III), mp 267–267.5°, was isolated. Its structure was established by direct comparison (mixture melting point and ir spectra) with a sample of 1,2,4,5-tetraphenylbenzene prepared by the reaction of diphenylacetylene with 3,4-diphenyl-4-hydroxycyclopent-2-enone.[5]

The fourth product eluted was benzylacetophenone (V) (1,3-diphenyl-1-propanone). This was identified by direct comparison with an authentic sample[6] prepared by the hydrogenation of benzalacetophenone.

The third product isolated was most unusual. Its analysis, molecular weight, and mp 143–145° corresponded with that of one of the bis(*cis*-1,2-diphenylcyclopropyl) disulfides previously reported.[1d] However, its ir, uv, and mass spectra differed entirely from that of the bis(*cis*-1,2-diphenylcyclopropyl) disulfide. The ir spectrum of the cyclopropyl disulfides showed no appreciable C–H stretching bands below 3000 cm^{-1}; the new compound showed absorption bands at 2920 and 2985 cm^{-1}. The uv spectrum of the cyclopropyl disulfides showed a maximum at 227.5 nm (ϵ 37,700); the uv spectrum of the new compound showed a maximum at 212 nm (ϵ 32,200). The most definitive comparison came from the mass spectra. The mass spectrum of the new compound showed a relatively intense molecular ion peak, 3.0% of the *m/e* 91 peak. It also showed strong peaks at *m/e* 382–386; *m/e* 386 corresponds to M − S_2. Strong

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