

magnesium sulfate the solvent was evaporated, yield 5.5 g (59%), bp 130° (0.7 mm).

Anal. Calcd for C₁₀H₁₃NO₃: C, 61.51; H, 6.85; N, 7.18. Found: C, 61.44; H, 6.80; N, 7.08.

1-Isopropyl- and 1-Benzyl-5-carbethoxy-2-pyridones.—The procedure used for the preparation of 1-ethyl-5-carbethoxy-2-pyridone was used with the exception that the potassium salt of II was used. For 1-isopropyl-5-carbethoxy-2-pyridone, after recrystallization from ligroin (bp 63–75°), the yield was 37%, mp 91–92°.

Anal. Calcd for C₁₁H₁₅NO₃: C, 63.16; H, 7.24; N, 6.69. Found: C, 63.35; H, 7.47; N, 6.48.

For 1-benzyl-5-carbethoxy-2-pyridone, the yield was 47%, mp 60.0–60.5°.

Anal. Calcd for C₁₅H₁₅NO₃: C, 70.01; H, 5.89; N, 5.45. Found: C, 70.03; H, 5.89; N, 5.60.

Sodium Salt of 2-Hydroxy-5-nitropyridine.—The procedure used for the preparation of sodium salt of II was employed. The yield was 86%.

2-Methoxy-5-nitropyridine.—A cold solution of freshly cut sodium (1.45 g, 0.063 mol) in 50 ml of methanol was added slowly to the solution of 2-chloro-5-nitropyridine (10 g, 0.063 mol) in 150 ml of methanol with stirring and continued cooling. After warming to room temperature, the reaction mixture was allowed to stand overnight with stirring. Solvent was removed *in vacuo* and the residue was extracted with 50 ml of chloroform three times. The chloroform was then washed with two 25-ml

portions of water and the solvent was removed under reduced pressure. The product was recrystallized from ethanol, yield 9.4 g (90%), mp 108.0–108.5° (lit.⁸ 108–109°).

2-Ethoxy- and 2-Benzoyloxy-5-nitropyridine.—These compounds were prepared by the method used for 2-methoxy-5-nitropyridine. The 2-ethoxy-5-nitropyridine was obtained in 98% yield, mp 90–91° (lit.⁸ 91–92°). 2-Benzoyloxy-5-nitropyridine was obtained in 95% yield, mp 107–108° (lit.⁸ 107.0–107.5°).

2-Isopropoxy-5-nitropyridine.—Isopropyl iodide (15.3 g, 0.09 mol) was added to the solution of the sodium salt of III (9.2 g, 0.057 mol) in 50 ml of absolute ethanol. The reaction mixture was refluxed until the color of the solution changed to dark brown (about 4 hr). The solvent was removed *in vacuo* and, after steam distillation, the distillate was extracted three times with 30 ml of chloroform. After the chloroform was removed under reduced pressure, the product was recrystallized from ethanol and water, yield 2 g (19%), mp 51.5–52.5°.

Anal. Calcd for C₈H₁₀N₂O₃: C, 52.74; H, 5.53; N, 15.38. Found: C, 52.40; H, 5.76; N, 15.28.

Registry No.—2-Ethoxy-5-carbethoxypyridine, 24903-80-8; 2-benzoyloxy-5-carbethoxypyridine, 24903-81-9; 1-ethyl-5-carbethoxy-2-pyridone, 24903-82-0; 1-isopropyl-5-carbethoxy-2-pyridone, 24903-83-1; 1-benzyl-5-carbethoxy-2-pyridone, 24903-84-2; 2-isopropoxy-5-nitropyridine, 24903-85-3.

Thietanes. Syntheses, Configurations, and Conformations of 2,4-Diphenylthietanes and Their Oxides

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cis- and *trans*-2,4-diphenylthietane (IV and V), their 1-oxides (VI and VII, respectively), and their 1,1-dioxides (VIII and IX, respectively) have been synthesized. Configurations were assigned primarily from the nmr data. The angles of pucker of *cis*-2,4-diphenylthietane *trans*-1-oxide (VI) and of 3-chlorothietane (X) were calculated from their nmr spectra and were in excellent agreement with the angles of pucker of these compounds determined from X-ray crystal analysis (for VI) and from dipole moment data (for X). Pyrolysis of *cis*- or *trans*-2,4-diphenylthietane 1,1-dioxide (VIII or IX) yielded a mixture of *cis*- and *trans*-1,2-diphenylcyclopropanes.

Because of the unusual stereochemistry observed in the formation and decomposition of the intermediate thiirane 1,1-dioxide in the Ramberg-Bäcklund reaction,¹ some years ago we decided to investigate the formation and decomposition, both thermal and catalytic, of substituted thietanes, their monoxides, and dioxides. In this paper, we describe the syntheses and the determinations of configurations and conformations of the 2,4-diphenylthietanes, their monoxides, and dioxides.² In subsequent papers we shall report the rearrangement of either *cis*- or *trans*-2,4-diphenylthietane 1,1-dioxide on treatment with ethylmagnesium bromide to *trans*-1,2-diphenylcyclopropanesulfonic acid,³ the conversion of either *cis*- or *trans*-2,4-diphenylthietane 1-oxide on treatment with potassium *t*-butoxide to *cis*-1,2-diphenylcyclopropanesulfonic acid and *cis*-1,2-diphenylcyclopropanethiol, the rearrangement of 2,4-diphenylthietane 1,1-dioxides with magnesium *t*-butoxide to 3,5-diphenyl-1,2-oxathiolane 2-oxides,⁴ and the conversion of *trans*-2,4-diphenyl-

thietane with potassium *t*-butoxide to 2,3,5-triphenylthiophene and 1,2,4,5-tetraphenylbenzene (low yield).

Synthesis.⁵—The thietanes were synthesized by the sequence of reactions depicted in Scheme I. Ethanthiolic acid was added to benzalacetophenone to give 1,3-diphenyl-3-acetylthio-1-propanone (I) in excellent yield (68–99.5%). Compound I was reduced to 1,3-diphenyl-3-hydroxy-1-propanethiol (II) (97.7% yield) with lithium aluminum hydride in tetrahydrofuran, and II was converted without extensive purification to 1,3-diphenyl-3-chloro-1-propanethiol (III) (90.8% yield) with concentrated hydrochloric acid. Compound III was converted to a mixture of *cis*- and *trans*-2,4-diphenylthietanes (IV and V) (mp 40–85°, 95% yield) with aqueous sodium hydroxide. Fractional crystallization of this mixture from ether and/or petroleum ether gave *trans*-2,4-diphenylthietane (V) (12–15% yield) and a sharp-melting complex of approximately equal amounts of the *cis*- and *trans*-2,4-

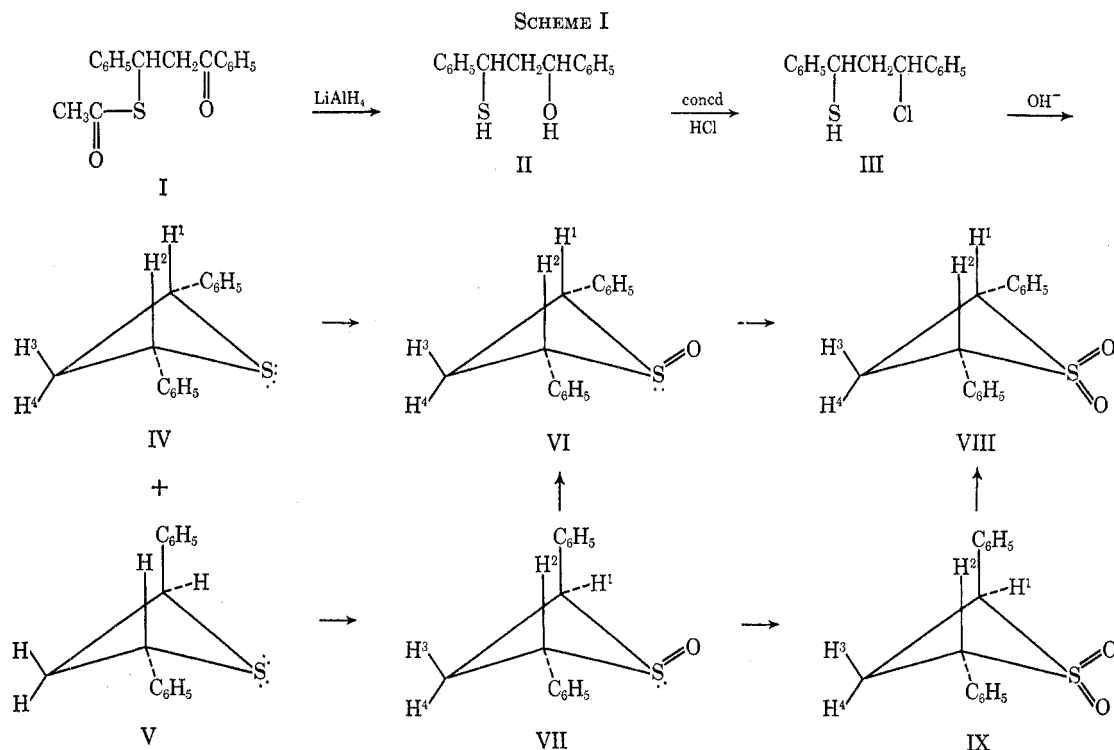
(4) R. M. Dodson, P. D. Hammen, and R. A. Davis, *Chem. Commun.*, 9 (1968); correction, *ibid.*, 535 (1968).

(5) (a) The syntheses of thietanes have recently been reviewed: M. Sander, *Chem. Rev.*, **66**, 341 (1966). (b) For more recent methods and references to more recent methods, see L. A. Paquette and M. Rosen, *J. Amer. Chem. Soc.*, **89**, 4102 (1967); *J. Org. Chem.*, **33**, 3027 (1968); L. A. Paquette, M. Rosen, and H. Stucki, *ibid.*, **33**, 3020 (1968); D. C. Dittmer and E. S. Whitman, *ibid.*, **34**, 2004 (1969); A. Ohno, Y. Ohnishi, and G. Tsuchihashi, *Tetrahedron Lett.*, 161, 283 (1969).

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(2) A preliminary account of this work has been published: R. M. Dodson and G. Klose, *Chem. Ind. (London)*, 450 (1963).

(3) R. M. Dodson and G. Klose, *ibid.*, 1203 (1963).



diphenylthietanes (IV and V) (mp 61–62°, 57–69% yield).⁶ We have not succeeded in isolating pure *cis*-2,4-diphenylthietane (IV). *trans*-2,4-Diphenylthietane (V) was readily oxidized in excellent yields by conventional methods to the corresponding 1-oxide (VII, 89% yield) and 1,1-dioxide (IX, 88% yield). Oxidation of the complex of *cis*- and *trans*-2,4-diphenylthietanes (IV and V) with an equivalent quantity of performic acid yielded a mixture of the 1-oxides which was readily separated by fractional crystallization into *trans*-2,4-diphenylthietane 1-oxide (VII) and *cis*-2,4-diphenylthietane *trans*-1-oxide (VI). We have not succeeded in attempts to prepare *cis*-2,4-diphenylthietane *cis*-1-oxide. Oxidation of compound VI or VII with performic acid yielded the corresponding 1,1-dioxides VIII (94% yield) and IX (94% yield), respectively. Oxidation of the complex of *cis*- and *trans*-2,4-diphenylthietanes (IV and V) with excess performic acid yielded a sharp-melting complex (mp 124–125°) of the corresponding 1,1-dioxides (VIII and IX). This complex could be formed by crystallization of a mixture of equal amounts of *cis*- and *trans*-2,4-diphenylthietane 1,1-dioxides (VIII and IX).

Configurations.—Our first evidence on the configurations of the 2,4-diphenylthietanes and their oxides came from studies on equilibration of the 2,4-diphenylthietane monoxides (VI and VII) and dioxides (VIII and IX) in the presence of base. Thus, isomerization of VII or IX with sodium methoxide in methanol gave 96% or more VI or VIII, respectively. This is easily explained by the assumption that the substituted thietane ring is puckered (not flat) and that the phenyl groups in the more stable molecule occupy pseudo-equatorial conformations⁷ and are, therefore, *cis* to

each other. This evidence established the configuration of the phenyl groups in all of the 2,4-diphenylthietanes and their oxides (IV to IX).

Confirmation of these assignments was obtained from a complete analysis of the nmr spectra of compounds IV to IX (Table I). The spectra of *trans*-2,4-diphenylthietane (V) and *trans*-2,4-diphenylthietane 1,1-dioxide (IX) were deceptively simple AA'BB' spectra.⁸ Each consisted of two triplets at 500-Hz sweepwidth. Spectra of V taken at 50-Hz sweepwidth were still too simple to permit calculation (13 observable transitions out of a possible 28). The spectrum of V was subtracted from the spectrum of the complex of IV and V. This permitted calculation of the spectrum of IV as an A₂BC system, and thus confirmed the assignment of configuration.

The assignments of the vicinal coupling constants to the *cis* and *trans* protons in IV could not be made directly, since with small rings ³J_{cis} is sometimes larger than ³J_{trans}.⁹ This problem was readily resolved by consideration of the spectrum of *trans*-2,4-diphenylthietane 1-oxide (VII). Analyzed as an ABCD system, one ³J had a value of 3.16 Hz. Since in any puckering of the thietane ring of VII the dihedral angle between the pseudoequatorial α proton and the β proton *trans* to it approaches 90°, this small coupling constant was assigned to that interaction, J_{1,3} (VII).¹⁰

thietane itself had led to the erroneous conclusion that the ring was planar (C_{2v} symmetry): D. W. Scott, H. L. Finke, W. H. Hubbard, J. P. McCullough, C. Katz, M. E. Gross, J. F. Messerly, R. E. Pennington, and G. Waddington, *J. Amer. Chem. Soc.*, **75**, 2795 (1953); ref 5a.

(8) D. M. Grant and H. S. Gutowsky, *J. Chem. Phys.*, **34**, 699 (1961). B. M. Trost, *et al.*,⁶ report J_{AB} = 6.9 Hz for *trans*-2,4-dimethylthietane but do not indicate how this value was obtained.

(9) (a) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Amer. Chem. Soc.*, **85**, 3218 (1963); H. Weitkamp and F. Korte, *Tetrahedron, Suppl.*, **7**, 75 (1966). (b) Many of our calculations were started before the calculations of W. D. Keller, T. R. Lusebrink, and C. H. Sederholm [*J. Chem. Phys.*, **44**, 782 (1966)] on the nmr spectrum of 3-chlorothietane appeared.

(10) The numbering of the chemical shifts and coupling constants in Table I correspond to the numbering of the protons for IV to IX in Scheme I.

(6) A related sequence of reactions was used by B. M. Trost, W. L. Schinski, and I. B. Mantz [*J. Amer. Chem. Soc.*, **91**, 4321 (1969)] for the synthesis of *cis*- and *trans*-2,4-dimethylthietanes.

(7) This was probably the first reported evidence for a puckered thietane ring (see ref 2). Early thermodynamic and spectroscopic evidence on

TABLE I^a
2,4-DIPHENYLTHIETANES

Compd ^b	ν^1	ν^2	ν^3	ν^4	$J_{1,2}$	$J_{1,3}$	$J_{1,4}$	$J_{2,3}$	$J_{2,4}$	$J_{3,4}$
CDCl ₃ ^c										
IV <i>cis</i> sulfide	290.6	290.6	199.4	190.0	... ^d	7.35	9.95	7.35	9.95	-11.55
V <i>trans</i> sulfide	286	286	199	199	... ^e					
VI <i>cis</i> oxide	257.3	257.3	180.7	141.7	... ^d	9.53	12.62	9.53	12.62	-12.85
VII <i>trans</i> oxide	285.1	269.7	193.5	168.6	-1.12	3.16	8.79	10.24	11.90	-13.81
VIII <i>cis</i> dioxide	321.5	321.5	169.9	157.9	... ^d	9.17	11.12	9.17	11.12	-11.91
IX <i>trans</i> dioxide	335.0	335.0	170.5	170.5	... ^e					
30% CDCl ₃ in C ₆ H ₆ ^f										
VI <i>cis</i> oxide	248	248	150	122	... ^d	9.5	13	9.5	13	-13
VII <i>trans</i> oxide	264	253	162	138	~1	3.0	8.5	10.0	12	-13.5

^a Recorded in hertz downfield from tetramethylsilane; determined at 60 MHz. ^b *cis* and *trans* refer to the relationship of the phenyl groups. ^c These spectra were analyzed by use of the LAOCOON-2 or LAOCOON-3 program of A. A. Bothner-By and S. M. Castellano. The chemical shifts vary slightly with concentration but have not been extrapolated to zero concentration. The coupling constants are reported to three significance figures, since these are the values used to calculate conformations (see below). None of the calculated probable errors of the parameter sets exceeded 0.058 Hz. ^d Coupling constants between A₂ protons in an A₂BC system cannot be directly observed. ^e The simplicity of the spectra made these coupling constants unobservable. $J_{1,3} + J_{1,4} = ca. 15$ Hz for *trans*-2,4-diphenylthietane (V) and *ca.* 17.5 Hz for *trans*-2,4-diphenylthietane dioxide (IX). ^f A mixture of 30% deuteriochloroform in benzene instead of pure benzene was used to increase solubilities. These spectra were not fitted by computer but were analyzed directly by analogy to the spectra in CDCl₃. Accuracy does not exceed ± 0.5 Hz.

This immediately led to assignments of the other three protons in the molecule and to the conclusion that ${}^3J_{trans} > {}^3J_{cis}$ for the pseudoaxial proton. The relative signs of the coupling constants for the protons in VII were determined by the double irradiation technique of Freeman and Anderson.¹¹ From the assignments of chemical shifts and coupling constants for VII, the assignments of chemical shifts and coupling constants for IV, VI, and VIII immediately follow, and the configurations of the phenyl groups are confirmed.

The configuration of the oxygen on sulfur in *cis*-2,4-diphenylthietane *trans*-1-oxide (VI) was assigned on the following bases. (1) Peracids selectively oxidize the sterically less hindered pair of electrons on sulfur in cyclic compounds and yield predominantly equatorial sulfoxides.¹² (2) Compound VII ran faster on thin layer chromatography than VI.¹² (3) The S=O bond shields groups which lie directly behind it (along the axis).^{12b,c,13} Thus, on oxidation of the thietane IV to the 1-oxide VI, H⁴, which lies almost directly behind the S=O bond in a puckered *cis*-2,4-diphenylthietane *trans*-1-oxide, was shielded to a much greater extent than H³ (see Table II).¹⁴ (4) A hydrogen atom (H¹

of electrons (see Table II).¹⁵ This assignment of the configuration of *cis*-2,4-diphenylthietane *trans*-1-oxide (VI) has been confirmed very recently by a crystal analysis of this compound.¹⁶

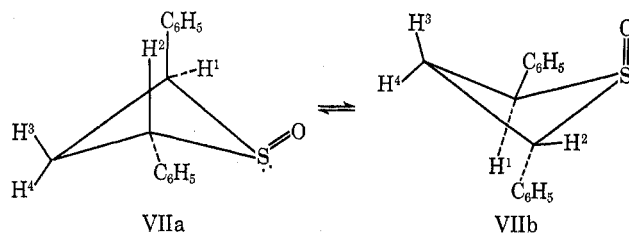
Conformations.—The *cis*-2,4-diphenylthietanes (IV, VI, VIII) should exist almost exclusively in the conformations depicted in Scheme I. The equilibrium studies on VI and VIII support this conclusion.

The *trans*-2,4-diphenylthietane 1-oxide (VII) can exist as a mixture of the conformers VIIa and VIIb. That VII exists largely as one conformer can be seen immediately from the analysis of its nmr spectrum. If VIIa and VIIb were of comparable importance, $J_{1,3}$ should be approximately equal to $J_{2,4}$. However $J_{1,3}$ (3.16) is the smallest vicinal coupling constant, while $J_{2,4}$ (11.90) is the largest vicinal coupling constant. The preferred conformation of *trans*-2,4-diphenylthietane 1-oxide (VII) followed from the data presented in Table II. Thus on oxidation of the sulfide to the sulfoxide, H⁴ was shielded to a greater extent than H³, and H² was shielded to a greater extent

TABLE II
 $\Delta\nu$ (SULFOXIDE - SULFIDE)

	$\Delta\nu$, Hz			
	H ¹	H ²	H ³	H ⁴
(VI - IV) <i>cis</i>	-33.3	-33.3	-18.7	-48.3
(VII - V) <i>trans</i>	-0.9	-16.3	-5.5	-30.4

and H²) in the conformational relationship to a vicinal sulfoxide group depicted in VI should be markedly shielded by the S=O bond and/or the unshared pair



than H¹. In the preferred conformation, therefore, the oxygen on sulfur was pseudo-equatorial (VIIa). Further evidence for this was obtained from the changes of the chemical shifts of H¹ and H² with change of solvent;^{12c,15,17} $\Delta\nu$ (C₆H₆-CDCl₃) for H¹ = -21.1

- (11) R. Freeman and W. A. Anderson, *J. Chem. Phys.*, **37**, 2053 (1962).
 (12) (a) C. R. Johnson and D. McCants, Jr., *J. Amer. Chem. Soc.*, **87**, 1109 (1965); (b) R. Nagarajan, B. H. Chollar, and R. M. Dodson, *Chem. Commun.*, 550 (1967); (c) P. B. Sollman, R. Nagarajan, and R. M. Dodson, *ibid.*, 552 (1967).
 (13) K. W. Buck, A. B. Foster, W. D. Pardoe, M. H. Qadir, and J. M. Webber, *ibid.*, 759 (1966); C. R. Johnson and W. O. Siegl, *Tetrahedron Lett.*, 1879 (1969).
 (14) An analysis of the shielding contributions from the ring currents of the 2- and 4-phenyl groups in various conformations indicated high improbability that the relative shielding of H³ and H⁴ resulted from this source: C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

- (15) R. A. Archer and P. V. DeMarco, *J. Amer. Chem. Soc.*, **91**, 1530 (1969); D. H. R. Barton, F. Comer, and P. G. Sammes, *ibid.*, **91**, 1529 (1969); R. M. Dodson and R. F. Sauers, unpublished work on the stereochemistry of substituted 2,5-dihydrothiophene 1-oxides.
 (16) Private communication: G. L. Hardgrove, J. S. Bratholdt, and M. M. Lien, Department of Chemistry, St. Olaf College, Northfield, Minn.
 (17) E. T. Strom, B. S. Snowden, Jr., and P. A. Toldan, *Chem. Commun.*, 50 (1969); M. Nishio, *ibid.*, 51 (1969); P. V. DeMarco, J. C. Cheng, and N. D. Jones, *J. Amer. Chem. Soc.*, **91**, 1408 (1969); R. D. G. Copper, P. V. DeMarco, and D. O. Spry, *ibid.*, **91**, 1528 (1969).

and for $H^2 = -16.7$ Hz. Although the difference between these values is small "the values are consistent with the conclusion that H^2 is *cis* and H^1 is *trans* to the oxygen attached to sulfur."

An estimate of the position of the equilibrium VIIa \rightleftharpoons VIIb can be obtained as follows. Since a 1,3-diaxial phenyl-hydrogen interaction occurs in VII but not in VI, the angle of pucker of *cis*-2,4-diphenylthietane *trans*-1-oxide (VI) should be at least as large as the angle of pucker of VIIa or VIIb. If it is assumed that the angle of pucker of VIIa and VIIb are equal and are also equal to the angle of pucker of VI then $J_{1,4}(VI) \cong J_{2,4}(VIIa) \cong J_{1,3}(VIIb) \cong 12.6$ Hz. From these assumptions and from $J_{1,3}$ and $J_{2,3}$ for VII, one can calculate that VII consists of *ca.* 93% VIIa and 7% VIIb and that $J_{1,3}(VIIa) = 2.44$. Any decrease in the angle of pucker of VIIa and VIIb compared with VI would lead to calculations showing an increased quantity of VIIa. Any moderate decrease of the angle of pucker of VIIb compared with VIIa will have little effect on the calculations. The above conclusions are consistent with the recent observations of Johnson and Siegel.¹⁸ They found that the "sulfinyl oxygen in a four-membered ring exerts a pseudoequatorial preference," and that equilibration of *cis*- and *trans*-3-*p*-chlorophenylthietane 1-oxide gives largely the *cis* isomer (*cis/trans* ratio of *ca.* 87:13).

Calculation of Dihedral Angles.—The dihedral angles HCCH of *cis*- and *trans*-2,4-diphenylthietane 1-oxides (VI and VII) were calculated from their nmr spectra in the following way. (1) The vicinal coupling constants were fitted to an equation of the form ${}^3J_{H,H'} = A \cos^2 \phi + B \cos \phi + C$.¹⁹ (2) The geminal angle H^3CH^4 of all of the thietanes was assigned the same value, 112° , the geminal angle HCH found in trimethylene oxide.²⁰ The internal angle $C^2C^3C^4$ of all of the thietanes was also assigned the same value, 94° , the value published by Allenmark²¹ for this same angle in *trans*-3-carboxythietane 1-oxide. The use of these angles gave a value of $\omega = 127.49^\circ$, for the projection of the geminal angle H^3CH^4 perpendicular to the C^2-C^3 bond. (3) The coupling constants determined for *trans*-2,4-diphenylthietane 1-oxide (VII) were assigned entirely to the principle conformer (VIIa). Since we have estimated that 7% of VII could exist as the conformer VIIb, a comparable error in these calculations may result.

By use of the above and the coupling constants from the nmr spectra of VII and VI, the following six nonlinear equations in six unknowns were written.

trans-Oxide (VII)

$$\begin{aligned} J_{1,4} &= 8.79 = A \cos^2 \Phi + B \cos \Phi + C \\ J_{1,3} &= 3.16 = A \cos^2 (\omega - \Phi) + B \cos (\omega - \Phi) + C \\ J_{2,3} &= 10.24 = A \cos^2 \Phi' + B \cos \Phi' + C \\ J_{2,4} &= 11.90 = A \cos^2 (\omega + \Phi') + B \cos (\omega + \Phi') + C \end{aligned}$$

cis-Oxide (VI)

$$\begin{aligned} J_{1,3} &= 9.53 = A \cos^2 \Phi'' + B \cos \Phi'' + C \\ J_{1,4} &= 12.62 = A \cos^2 (\omega + \Phi'') + B \cos (\omega + \Phi'') + C \end{aligned}$$

(18) C. R. Johnson and W. O. Siegel, *J. Amer. Chem. Soc.*, **91**, 2796 (1969).

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

(20) J. Fernandez, R. J. Myers, and W. D. Gwinn, *J. Chem. Phys.*, **23**, 758 (1955). It should be realized that the potential energy function for the ring-puckering vibration of trimethylene oxide also has a double minimum: S. I. Chan, T. R. Borgers, J. W. Russell, H. L. Strauss, and W. D. Gwinn, *ibid.*, **44**, 1103 (1966).

(21) S. Allenmark, *Ark. Kemi*, **26**, 73 (1967).

Solution of these equations, gave the equation

$${}^3J_{H,H'} = 9.9 \cos^2 \phi - 0.9 \cos \phi + 3.12 \quad (1)$$

and the following dihedral angles²² (degrees)

	$\angle H^1CCH^3$	$\angle H^1CCH^4$	$\angle H^2CCH^3$	$\angle H^2CCH^4$
VII <i>trans</i> -oxide	91.0	36.5	26.5	154.0
VI <i>cis</i> -oxide	31.6	159.1		

From the above it is immediately apparent that the *trans*-2,4-diphenylthietane 1-oxide (VII) is a badly distorted molecule. The C^2 atom is rotated to a greater degree (37°) than the C^4 atom (27°). This can be readily understood if the C_6H_5 group on C^2 is *cis* to the oxygen on sulfur. Thus, these calculations also confirm the conformation (S=O pseudoequatorial) previously assigned to VII.

Calculation of Angles of Pucker.—To calculate the shape of the thietane molecule, it is necessary to have two adjacent angles and the lengths of the sides. The bond lengths used in this calculation were those used by Gwinn²³ and coworkers [S-C = 1.833 Å; C-C = 1.54 Å] in their detailed analysis of the microwave spectrum of thietane. These bond lengths are in excellent agreement with those listed by Sutton.²⁴ From the dihedral angle H^1CCH^3 of *cis*-2,4-diphenylthietane *trans*-1-oxide (VI), the angles given in (2) of the preceding section, an assignment of 112° to the geminal angle $H^1C^2-C_6H_5$, and the bond lengths given above, the dihedral angle between the C^2-S-C^4 and the $C^2-C^3-C^4$ planes of VI can be calculated to be 140.3° (angle of pucker 39.7°).²⁵ A crystal structure analysis¹⁶ still in progress gave a value of 138.8° (angle of pucker 41.2°) for the angle between these planes.^{25a} The angle of pucker of thietane itself, determined from its microwave spectrum,²³ is 32° . We calculated an angle of pucker of 29.7° for *trans*-3-carboxythietane 1-oxide from the unrefined data given by Allenmark.²¹

Unfortunately, sufficient data were not available to fit completely the Barfield-Karplus¹⁹ equation to *cis*-2,4-diphenylthietane (IV) and *cis*-2,4-diphenylthietane dioxide (VIII). However, if it is assumed that that portion of eq 1 determining the angular dependence of the coupling constants remains unchanged and that changes in oxidation state (inductive effects) largely affect the value of the constant C , two simultaneous equations in two unknowns can be written and solved for the dihedral angle H^1CCH^3 and C . For *cis*-2,4-diphenylthietane dioxide (VIII) this procedure gave $C = 2.2$ and ϕ ($\angle H^1CCH^3$) = 27.7° . This corresponds to a dihedral angles between the C^2-S-C^4 and the

(22) A similar calculation using the value $J_{1,3}(VIIa) = 2.44$, calculated above for the principle conformer of VII, gave a slightly different equation

$${}^3J_{H,H'} = 10.75 \cos^2 \phi - 0.9 \cos \phi + 2.43$$

but gave dihedral angles practically identical with those calculated above (maximum difference $\pm 0.8^\circ$).

(23) D. O. Harris, H. W. Harrington, A. C. Luntz, and W. D. Gwinn, *J. Chem. Phys.*, **44**, 3467 (1966); private communication from Dr. D. O. Harris.

(24) "Tables of Interatomic Distances and Configurations in Molecules and Ions," L. E. Sutton, Ed., Special Publications No. 11 and No. 18, The Chemical Society, London, 1958 and 1965.

(25) Allowance was made for the projection of the geminal angles $H^3C^3H^4$ and $H^1C^2-C_6H_5$ (both assigned values of 112°) perpendicular to the C^2-C^3 bond. Since the projected angle of $H^1C^2-C_6H_5$ will change with change of the angle $S-C^2-C^3$, an iterative calculation was used.

(25a) NOTE ADDED IN PROOF.—Refinement of calculations gave a value of 41.9° for this angle.¹⁶

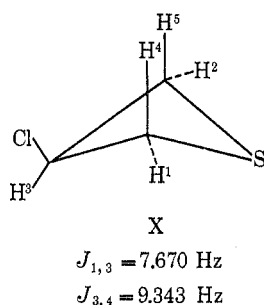
$C^2-C^3-C^4$ planes of 145° and an angle of pucker of 35° .

Application of this same procedure to the nmr data for *cis*-2,4-diphenylthietane (IV) gave the equation²⁶

$$^3J = 9.9 \cos^2 \phi - 0.9 \cos \phi + 0.7 \quad (2)$$

and a calculated dihedral $\phi(H^1CCH^3) = 30.0^\circ$. This gave a dihedral angle (angle between the planes C^2-S-C^4 and $C^2-C^3-C^4$) of 142.3° (angle of pucker 37.7°) for IV.

The reliability of this eq 2, when applied to thietanes, can be checked in two ways. Keller and coworkers^{2b} have analyzed in detail the nmr spectrum of 3-chlorothietane (X). If it is assumed that X exists largely in the conformation depicted [this same assumption was made by Arbuzov (see ref 27 below)] then from $J_{1,3}$ and $J_{3,4}$ and the above equation one can calculate the dihedral angles $H^1CCH^3 = 27.6^\circ$ and $H^4CCH^3 =$



152.9° . By the method used above, the dihedral angle between the C^2-S-C^4 and $C^2-C^3-C^4$ planes can be calculated to be 142.4° (angle of pucker 37.6°). This is in excellent agreement with the dihedral angle of 143° calculated for 3-chlorothietane by Arbuzov and coworkers²⁷ from dipole moment data. Finally, from the calculated dihedral angles, $\angle H^1CCH^3 = 27.6^\circ$ and $\angle H^4CCH^3 = 152.9^\circ$, the projection of the geminal angle $H^4C^2H^1$ perpendicular to the C^2-C^3 bond is equal to 125.3° . From the usual assignment of a value of 112° to the geminal angle $H^4C^2H^1$ and from the calculated angle of pucker, the projected geminal angle $\omega = 129.5^\circ$ is determined, in fair agreement with value of 125.3° found above.

Pyrolysis^{2,28} of either *cis*- or *trans*-2,4-diphenylthietane 1,1-dioxide (VIII or IX) at 250° led to the evolution of sulfur dioxide and yielded a mixture of *cis*- and *trans*-1,2-diphenylcyclopropanes that approximated in composition the equilibrium mixture expected at that temperature.²⁹

Experimental Section³⁰

1,3-Diphenyl-3-acetylthio-1-propanone (I).—Benzalacetophenone (317.6 g, 1.525 mol) was dissolved in a mixture of benzene

(26) Use of the equation given in footnote 22, yielded $\phi = 29.6^\circ$ and $C = 0.0$. It is known that C approximates zero for compounds free of strongly electronegative substituents (see ref 19b).

(27) B. A. Arbuzov, O. N. Nuretdinova, and A. N. Vereschagin, *Dokl. Akad. Nauk SSSR*, **172** (3), 591 (1967); *Chem. Abstr.*, **66**, 89337y (1967).

(28) For recent examples of the pyrolysis of cyclic sulfones, see E. J. Moriconi, R. E. Misner, and T. E. Brady, *J. Org. Chem.*, **34**, 1651 (1969), and many references contained therein.

(29) L. B. Rodewald and C. H. de Puy, *Tetrahedron Lett.*, 2951 (1964); R. J. Crawford and T. R. Lynch, *Can. J. Chem.*, **46**, 1457 (1968).

(30) Melting points were taken on a Fisher-Johns melting point apparatus, calibrated against a set of standard compounds. Petroleum ether refers to that fraction of bp $60-68^\circ$. The nmr spectra were determined on a Varian A-60 spectrometer in solutions of approximately 20%. Spectra on com-

pounds VI, VII, and VIII and the complex (IV and V) were determined at 50-Hz sweepwidth and calibrated using a Hewlett-Packard Model 202A low-frequency function generator. The nmr data on compounds VI, VII, and VIII are the average of at least four spectra.

(300 ml) and petroleum ether (600 ml). The resulting solution was heated to reflux. While it was stirred, ethanethioic acid (200 g, 2.633 mol) was added from a dropping funnel over a 1-hr period. Stirring and heating were continued for 1 hr more. When the reaction was cooled, 1,3-diphenyl-3-acetylthio-1-propanone (431.5 g, 1.517 mol, 99.5%, mp $76.5-77.5^\circ$, $\nu_{\max}^{\text{Nujol}}$ 1675 cm^{-1}) separated as a pale yellow crystalline solid. Crystallization from petroleum ether removed the color and raised the melting point to $77-78^\circ$. In one instance mp $85-86^\circ$ was obtained by crystallization from methanol.

Anal. Calcd for $C_{17}H_{16}O_2S$: C, 71.80; H, 5.67. Found: C, 71.62; H, 5.83.

1,3-Diphenyl-3-hydroxy-1-propanethiol (II).—1,3-Diphenyl-3-acetylthio-1-propanone (I) (100.00 g, 0.352 mol) was dissolved in purified, anhydrous tetrahydrofuran (300 ml) and added with stirring over 1 hr to lithium aluminum hydride (30 g, 0.786 mol) suspended in tetrahydrofuran (400 ml). After the addition was complete, the reaction mixture was heated under reflux for 2 hr and was then cooled to room temperature. The excess lithium aluminum hydride was decomposed by the slow addition of ethyl acetate, followed by the addition of a few milliliters of water. The reaction mixture was poured onto concentrated hydrochloric acid (800 ml) and ice, and the product was extracted with several portions of ether. The ether solution was washed thoroughly with water. To further purify II, it was extracted from the ether with several portions of 10% aqueous sodium hydroxide. The product was immediately liberated from the basic solution with concentrated hydrochloric acid and was extracted with ether. The ether solution was washed thoroughly with water, dried (magnesium sulfate), and evaporated. The 1,3-diphenyl-3-hydroxy-1-propanethiol [84.04 g, 0.344 mol, 97.7%; ν_{\max}^{neat} 3350 (s) , 2992 (w) , 2940 (w) , 2840 (w) , $2520 \text{ cm}^{-1} \text{ (w)}$, (SH)] was obtained as a viscous, golden-yellow oil, which did not solidify upon being cooled and which was used directly in the next step.

1,3-Diphenyl-3-chloro-1-propanethiol (III).—1,3-Diphenyl-3-hydroxy-1-propanethiol (84.04 g, 0.344 mol) was dissolved in ether (400 ml) and added during 1 hr at room temperature with stirring to concentrated hydrochloric acid. After being stirred vigorously for an additional hour, the reaction was quenched with water (2 l.), separated, and extracted with several portions of ether. The ether extracts were washed with water, dried over magnesium sulfate, and then evaporated. The 1,3-diphenyl-3-chloropropanethiol [82.0 g, 0.313 mol, 90.8%; ν_{\max}^{neat} 2910 (w) , $2520 \text{ cm}^{-1} \text{ (w)}$ (SH)] was obtained as a dark yellow oil which did not solidify upon being cooled and which was used directly in the next step.

cis- and *trans*-2,4-Diphenylthietanes.—1,3-Diphenyl-3-chloropropanethiol (III) (82.0 g, 0.313 mol) was dissolved in ether (300 ml) and was added slowly with stirring over a 1-hr period to cold (ice bath) 10% aqueous sodium hydroxide (800 ml). Stirring was continued for an additional 2 hr in the cold. The ether layer was separated and the sodium hydroxide solution was extracted with several portions of ether. The combined extracts were washed thoroughly with water, dried over magnesium sulfate, and then reduced to a low volume. When the solution was cooled, *trans*-2,4-diphenylthietane (V) (10.60 g, 0.0469 mol, 15%), mp $96-97^\circ$, separated first in the form of long needles. Crystallization from petroleum ether, gave *trans*-2,4-diphenylthietane: mp $102-103^\circ$; $\lambda_{\max}^{\text{ethanol}}$ 217 nm (ϵ 21,470); $\nu_{\max}^{\text{Nujol}}$ 699 (s) , 730 (m) , 763 (s) , 1081 (m) , 1490 (m) , $1600 \text{ cm}^{-1} \text{ (m)}$.

Anal. Calcd for $C_{15}H_{14}S$ (226.34): C, 79.60; H, 6.23. Found: C, 79.49; H, 6.20; mol wt (Rast) 233.

The ether mother liquors from the above isolation were evaporated. White crystals (51.2 g, 0.227 mol, 72%), mp $50-60^\circ$, were obtained. Further crystallization of this material from petroleum ether gave a sharp-melting complex of approximately equal quantities of *cis*- and *trans*-2,4-diphenylthietane, mp $61-62^\circ$ (40.11 g, 0.1774 mol, 56.7%).

Anal. Calcd for $C_{15}H_{14}S$ (226.34): C, 79.60; H, 6.23. Found: C, 79.41; H, 6.34; mol wt (Rast) 233.

***trans*-2,4-Diphenylthietane 1-Oxide (VII).**—To *trans*-2,4-diphenylthietane (1.00 g, 0.0044 mol, mp $96-97^\circ$) dissolved in methanol (35 ml) and 96% formic acid (3 ml) was added 30% hydrogen peroxide (0.50 g, 0.0044 mol). The mixture was

warmed on the steam bath just below reflux temperature for 12 hr. Partial evaporation of the solvent and cooling led to precipitation of *trans*-2,4-diphenylthietane 1-oxide (0.70 g, mp 152–153°). Further condensation and cooling of the mother liquors yielded a second crop (0.25 g, mp 152–153°; total yield 0.95 g, 88.8%). Recrystallization from methanol–water yielded pure *trans*-2,4-diphenylthietane 1-oxide (VII), mp 154–155°, $\nu_{\max}^{\text{Nujol}}$ 1064 cm^{-1} .

Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{OS}$: C, 74.34; H, 5.82. Found: C, 74.21; H, 5.88.

***cis*-2,4-Diphenylthietane *trans*-1-Oxide (VI).**—Oxidation of the molecular complex of *cis*- and *trans*-2,4-diphenylthietanes (16.0 g, 0.070 mol, mp 59–61°) by the method described above yielded a mixture of *cis*- and *trans*-2,4-diphenylthietane 1-oxides (15.7 g, 0.065 mol, 93%), mp 100–120°. Fractional crystallization of this material from benzene yielded *trans*-2,4-diphenylthietane 1-oxide (2.13 g, 0.0089 mol, 14%), mp 153–154°, and *cis*-2,4-diphenylthietane *trans*-1-oxide (8.78 g, 0.0362 mol, 55.7%), mp 127–129°. Thin layer chromatography showed that the *cis* isomer still contained a small amount of the *trans* isomer. Two crystallizations from benzene yielded pure *cis*-2,4-diphenylthietane *trans*-1-oxide, mp 135.5–136.5°.

In an alternate preparation, the molecular complex of *cis*- and *trans*-2,4-diphenylthietanes (10.0 g) was oxidized by the method described above, and the *trans*-2,4-diphenylthietane 1-oxide (1.20 g, 11% yield, mp 152–155°) was isolated by crystallization from petroleum ether–chloroform. The material remaining in the mother liquors was then isomerized with sodium methoxide in methanol (see below). Crystallization of the product from petroleum ether–chloroform yielded pure *cis*-2,4-diphenylthietane *trans*-1-oxide (3.86 g, 0.016 mol, 36%), mp 135–137°, $\nu_{\max}^{\text{Nujol}}$ 1069 cm^{-1} .

Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{OS}$: C, 74.34; H, 5.82. Found: C, 74.20; H, 6.11.

Isomerization of *trans*-2,4-Diphenylthietane 1-Oxide.—A solution of pure *trans*-2,4-diphenylthietane 1-oxide (VII) (0.70 g, mp 153–154°) in methanol (125 ml) containing sodium methoxide (2.8 g) was heated under reflux for 48 hr. The volume of the solution was reduced to 20 ml by distillation, water was added, and the solution was cooled. Light yellow crystals (0.641 g, 0.00265 mol, 91.6%), mp 123–127°, separated. Thin layer chromatography [silica gel G, ethyl acetate–benzene (1:4); product was detected with 2% aqueous potassium permanganate solution] showed the presence of two products, a very small quantity of the faster running product corresponding in position to *trans*-2,4-diphenylthietane 1-oxide and a much larger quantity of a slower running product corresponding in position to *cis*-2,4-diphenylthietane *trans*-1-oxide.

An nmr analysis on a similarly prepared mixture indicated the presence of approximately 96% *cis*- and 4% *trans*-2,4-diphenylthietane 1-oxides. Isomerization of *cis*-2,4-diphenylthietane *trans*-1-oxide under similar conditions gave similar results.

***trans*-2,4-Diphenylthietane 1,1-Dioxide (IX).** A.—To a solution of *trans*-2,4-diphenylthietane (6.00 g, 0.0264 mol, mp 96–97°) in carbon tetrachloride (75 ml) and 96% formic acid (60 ml) was added slowly, with stirring, hydrogen peroxide (30%, 60 ml) over a 0.5-hr period. During this addition the temperature rose to about 50°. Stirring at this temperature was continued for 4 hr. The reaction mixture was poured into brine, the carbon tetrachloride layer was separated, and the aqueous layer was extracted with several portions of carbon tetrachloride. The combined extracts were washed with water and dried over sodium sulfate. After distillation to a volume of approximately 100 ml, *trans*-2,4-diphenylthietane 1,1-dioxide (5.50 g, 0.0213 mol, 80.3%), mp 166–167°, was obtained in the form of fine white crystals. An additional 0.60 g of IX, mp 164–166°, was obtained from the mother liquors, total yield 89.1%. An analytical sample showed the following properties: mp 166–167°; $\lambda_{\max}^{\text{ethanol}}$ 226.0 nm (ϵ 28,533); $\nu_{\max}^{\text{Nujol}}$ 1117 (s), 1159 (s), 1183 (s), 1193 (m), 1312 (s), cm^{-1} ($-\text{SO}_2-$).

Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{O}_2\text{S}$: C, 69.74; H, 5.46. Found: C, 69.47; H, 5.71.

B.—Oxidation of *trans*-2,4-diphenylthietane 1-oxide (VII) (0.20 g, mp 152–153°) by the above method yielded *trans*-2,4-diphenylthietane 1,1-dioxide (0.20 g, 93.9%), mp 165–167°, identical in all respects (mixture melting point, ir spectrum) with that prepared above.

***cis*-2,4-Diphenylthietane 1,1-Dioxide (VIII).**—Oxidation of *cis*-2,4-diphenylthietane *trans*-1-oxide (VI) (0.20 g, mp 135–136°) by the method described above (20 hr) yielded *cis*-2,4-diphenyl-

thietane 1,1-dioxide (0.20 g, 93.9%), mp 162.5–163.5°, identical with that from the isomerization of the *cis*- and *trans*-2,4-diphenylthietane 1,1-dioxide complex (below).

Complex of *cis*- and *trans*-2,4-Diphenylthietane 1,1-Dioxides.—Oxidation of the sharp-melting complex of *cis*- and *trans*-2,4-diphenylthietanes (25.0 g, mp 59–60°) by the method described above yielded 25.5 g (92.1%) of the complex of *cis*- and *trans*-2,4-diphenylthietane 1,1-dioxides, mp 121–124°. Crystallization from acetone–petroleum ether raised the melting point to 124–125°.

This same complex was obtained by mixing equal amounts of *cis*-2,4-diphenylthietane 1,1-dioxide (0.50 g, mp 165–166°) and *trans*-2,4-diphenylthietane 1,1-dioxide (0.50 g, mp 166–167°) (mixture had mp 125–150°) and crystallizing the mixture from methanol–water (complex, mp and mmp 124–125°).

***cis*-2,4-Diphenylthietane 1,1-Dioxide (VIII) from Isomerization of the Above Complex.**—A solution of the 2,4-diphenylthietane 1,1-dioxide complex (10.00 g, 0.039 mol, mp 123–124°) and sodium methoxide (20.00 g, 0.11 mol) in methanol (300 ml) was heated under reflux for 45 hr. Isolation of the product followed by its crystallization from petroleum ether yielded *cis*-2,4-diphenylthietane 1,1-dioxide (VIII) (8.70 g, 87%): mp 165–166°; $\lambda_{\max}^{\text{ethanol}}$ 225.2 nm (ϵ 27,050); $\nu_{\max}^{\text{Nujol}}$ 1139, 1178, 1309 cm^{-1} ($-\text{SO}_2-$).

Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{O}_2\text{S}$ (258.3): C, 69.74; H, 5.46. Found: C, 69.56; H, 5.49; mol wt (Rast) 253.2.

Isomerization of *trans*-2,4-diphenylthietane 1,1-dioxide (IX) using the above method gave similar results. A nmr analysis of the product of isomerization (97% yield) of the *cis*- and *trans*-2,4-diphenylthietane 1,1-dioxide complex indicated that it consisted of at least 96% *cis* isomer.

Pyrolysis of *cis*-2,4-Diphenylthietane 1,1-Dioxide.—*cis*-2,4-Diphenylthietane 1,1-dioxide (1.00 g, 0.0039 mol, mp 165–166°) was pyrolyzed in a small distilling flask heated in a metal bath. With a bath temperature of 250°, sulfur dioxide was vigorously evolved. Heating at 250° was continued for 15 min. 1,2-Diphenylcyclopropane (0.70 g, 0.0037 mol, 93%, n_D^{25} 1.5952) was distilled (70 min) as a light yellow liquid.

The mixtures of *cis*- and *trans*-1,2-diphenylcyclopropanes were analyzed by gas chromatography using a column (0.25 in. \times 10 ft) of Dow silicone high-vacuum grease (20%) absorbed on Johns-Manville Chromosorb W (60–80 mesh) at temperatures of 180 and 220°. The ratios of *cis/trans*-diphenylcyclopropanes from *cis*-2,4-diphenylthietane dioxide (VII) and *trans*-2,4-diphenylthietane dioxide (VIII) were 0.131 and 0.134, respectively. To determine whether extensive isomerization was occurring during analysis, a sample of 1,2-diphenylcyclopropane consisting largely of the *cis* isomer was analyzed at both 180 and 220° with comparable results (*cis/trans* = 3.7 (180°); 3.8 (220°)).

For identification, pure samples of *cis*- and *trans*-1,2-diphenylcyclopropanes were prepared by vapor phase chromatography. *cis*-1,2-Diphenylcyclopropane: mp 37.5–38°, n_D^{25} 1.5870; lit.³¹ mp 36.7°, 38–38.5°, n_D^{25} 1.5892. *trans*-1,2-Diphenylcyclopropane: n_D^{25} 1.5965; lit.³¹ n_D^{25} 1.5995.

Anal. Calcd for $\text{C}_{15}\text{H}_{14}$: C, 92.74; H, 7.26. Found: C, 92.66; H, 7.56.

The nmr spectra of the pure samples of the *cis*- and *trans*-1,2-diphenylcyclopropanes, while not analyzed in detail, were consistent with the assigned structures.

Registry No.—I, 24621-54-3; II, 24621-55-4; III, 24621-56-5; IV, 24609-87-8; V, 24609-88-9; VI, 24605-73-0; VIIa, 24609-89-0; VIII, 18744-27-9; IX, 24609-91-4.

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