This substance was unaffected on refluxing with potassium carbonate in toluene. Sodium methoxide in refluxing methanol yielded starting material and three transformation products (thin-layer chromatogram); the mixture could not be separated by column chromatography.

A solution of 0.1 g. of V in 10 ml. of tetralin was refluxed with 100 mg. of freshly heated anhydrous potassium carbonate for 4 hr., allowed to stand at room temperature, and filtered. The potassium carbonate was washed with benzene, and the combined organic solvents evaporated *in vacuo.* The residue gave two spots on thin-layer chromatography (silica gel–anhydrous ether), one of which corresponded to starting material.

The crude product was dissolved in benzene and chromatographed over acid-washed alumina. Benzene eluted nothing. Benzene–anhydrous ether (2:1, 25-ml. fractions) eluted an oil in the first 50 ml. (fraction A) and a solid in the subsequent 75 ml. (fraction B). Fraction B on crystallization from ethyl acetate–petroleum ether yielded 0.04 g. of starting material, m.p. and m.m.p. 200°.

Fraction A on crystallization from ether–petroleum ether gave an epimer, wt. 0.03, which was homogeneous in thin-layer chromatography but had m.p. 97–107°. The m.p. did not improve even after four crystallizations. The infrared spectrum exhibited bands at 1770 and 1715 cm.$^{-1}$ and differed significantly from that of V in the fingerprint region. Optical rotatory dispersion curve in methanol, $(\phi)_{310}$ 2000°, $(\phi)_{270}$ −1100°, a + 31.

Anal. Calcd. for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53; O, 20.31. Found: C, 71.35; H, 8.58; O, 20.18.

The optical rotatory dispersion curve of VII[2] in methanol exhibited $(\phi)_{305}$ +800°, $(\phi)_{282.5}$ +110°, a + 7°. However, the weak intensities make it doubtful whether these values represent true peaks and troughs.

Acknowledgment.—We wish to express our thanks to Professor W. Klyne for the optical rotatory dispersion curves.

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cis- and *trans-*Stilbene Sulfides

ROGER KETCHAM AND VINOD P. SHAH

Department of Pharmaceutical Chemistry, School of Pharmacy, University of California Medical Center, San Francisco, California

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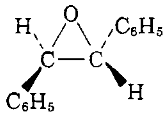
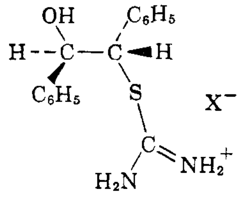
The preparation and reactions of a wide variety of stilbene oxides have been reported in the literature.[1] However, the sulfur analogues have not been previously described. Culvenor, Davies, and Health[2] attempted to convert stilbene oxide, presumably the *trans* isomer, to an episulfide by the use of thiourea. The only products isolated were stilbene, urea, and sulfur. This observation led them to conclude that stilbene episulfide was too unstable to exist. That both styrene sulfide[3] and tetraphenylethylene sulfide[4] have been reported suggested that the intermediate diphenyl and triphenylethylene sulfides should also be capable of existence.

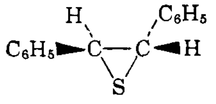
Bordwell[5] reported the preparation of a variety of episulfides by treatment of epoxides with thiourea and acid to afford thiuronium salts, which when treated with alkali yielded episulfides. Application of Bordwell's procedure has afforded both *cis-* and *trans-*stilbene sulfides from the corresponding *cis-* and *trans-*stilbene oxides. The analytically pure thiuronium sulfates [*erythro-S-*(1,2-diphenyl-2-hydroxyethyl)thiuronium sulfate (IIa) from *trans-*stilbene oxide (I) and *threo-S-*(1,2-diphenyl-2-hydroxyethyl)thiuronium sulfate (V) from *cis-*stilbene oxide (IV)] were obtained in high yield without purification. When treated with base, the thiuronium salts afforded the expected sulfides (III from II and VI from V) in nearly quantitative yield. When stored at room temperature, unprotected from light, *cis-*stilbene sulfide (VI), m.p. 77–78°, is stable, but *trans-*stilbene sulfide (III), m.p. 53–54°, slowly deteriorates to what appears to be a polymer. When protected from light and stored at 5°, *trans-*stilbene sulfide is quite stable.

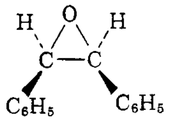

I. (*d, l* pair)

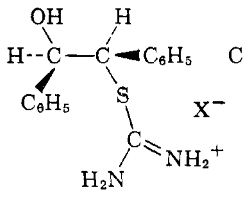

erythro

IIa. $X^- = 1/2\ SO_4^{-2}$

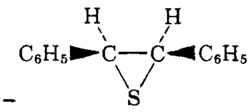
b. X^- = *d*-camphorsulfonate


III. (*d, l* pair)


IV. (*meso*)


threo

V. $X^- = 1/2\ SO_4^{-2}$


VI. (*meso*)

The fact that *trans-*stilbene oxide (I) afforded a lower melting sulfide than that derived from *cis-*stilbene oxide (IV) suggested that the reaction may not have proceeded through the generally accepted two-inversion path for conversion of simpler oxides to episulfides by thiourea[6] or thiocyanate,[7] but that perhaps the *trans* oxide had yielded the *cis* sulfide. The greater stability of the *cis* sulfide was also consistent with this possibility.

Evidence bearing on this question was obtained from ultraviolet and n.m.r. spectra, and stereochemical studies. The ultraviolet absorption maxima of *trans-*stilbene oxide (I) appear at longer wave lengths than those of *cis-*stilbene oxide (IV).[8] It has been shown that the red shifts in *trans-*stilbene oxide arise from conjugation of the three-membered ring with the two phenyl groups.[8] In the *trans* oxide the phenyl groups may assume that geometry which gives the most favorable orbital overlap. In the *cis* isomer, however, the steric hindrance of the two eclipsed phenyl groups is so great that its ultraviolet spectrum is almost identical to that of bibenzyl. The geometries of the sulfides cannot be much different from the oxides, so that, if the sulfur-containing three-membered ring is also

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[1] S. Winstein and R. B. Henderson, "Heterocyclic Compounds," Vol. I, edited by R. C. Elderfield, John Wiley and Sons, Inc., New York, N. Y., 1950, chap. 1, pp. 1–60.

[2] C. C. J. Culvenor, W. Davies, and N. S. Health, *J. Chem. Soc.*, 278 (1949).

[3] C. O. Guess and D. L. Chamberlain, *J. Am. Chem. Soc.*, **74**, 1342 (1952).

[4] A. Schonberg and M. Z. Barakat, *J. Chem. Soc.*, 1074 (1939).

[5] F. G. Bordwell and H. M. Andersen, *J. Am. Chem. Soc.*, **75**, 4959 (1953).

[6] C. C. J. Culvenor, W. Davies, and N. E. Savige, *J. Chem. Soc.*, 4480 (1952).

[7] E. E. Van Tamelen, *J. Am. Chem. Soc.*, **73**, 3444 (1951).

[8] L. A. Strait, D. Jambotkar, R. Ketcham, and M. Hrenoff, Intern. Conf. Spect. 9, Lyons, France, 1961, Trans., Vol. 1-3, G.M.A.S., Paris-15^e, France, 1962, in press. *Cf.* also M. Rogers, *J. Am. Chem. Soc.*, **69**, 2544 (1947) and N. H. Cromwell, F. H. Sumacher, and J. L. Adelfang, *ibid.*, **83**, 974 (1961).

capable of conjugation with the phenyl groups, similar red shifts should be observed for *trans*- relative to *cis*-stilbene sulfide. In the absence of such interaction the spectra of the *cis* and *trans* isomers should be identical. In any event the *cis* isomer should not absorb at longer wave lengths than the *trans*. The sulfide obtained from *trans*-stilbene oxide absorbs at a longer wave length than the isomeric sulfide thus indicating that configuration is retained. Davis has shown[9] that the sulfur analogue of ethylene oxide absorbs at a higher wave length than the oxide itself; the same relationship between oxides and sulfides is observed in this case. The data are given in Table I.

TABLE I

ULTRAVIOLET SPECTRAL DATA FOR *cis*- AND *trans*-STILBENE OXIDES AND *cis*- AND *trans*-STILBENE SULFIDES[a]

	λ_1 max	ϵ	λ_2 max	ϵ
		trans		
Oxide (I)[b]	228	(23,500)	267	(902)
Sulfide (III)	238	(17,300)	269.5	(1400)
		cis		
Oxide (IV)[b]	218	(12,250)	261	(470)
Sulfide (VI)	226	(10,600)	268	(800)

[a] Recorded on a Carey Model 11 spectrophotometer in 95% ethanol. [b] Ref. 8.

The n.m.r. spectra of *cis*- and *trans*-stilbene oxides are significantly different, and the spectrum of each sulfide is almost identical with that of the oxide from which it was derived. Although the lack of model compounds makes difficult a rigorous interpretation of these spectra in terms of structure, the downfield shift of the ethylenic CH resonance in *cis*-stilbene oxide relative to *trans*-stilbene oxide should be paralleled in the sulfur analogs. The demonstration of this relationship is taken as evidence for retention of configuration. The data are in Table II.

TABLE II

N.M.R. SPECTRAL DATA FOR *cis*- AND *trans*-STILBENE OXIDES AND *cis*- AND *trans*-STILBENE SULFIDES[a]

	trans		*cis*	
	(δ p.p.m.[b]) phenyl	(δ p.p.m.[b]) ethylene	(δ p.p.m.[b]) phenyl	(δ p.p.m.[b]) ethylene
Stilbene oxide	7.392	3.884	7.192	4.367
Stilbene sulfide	7.358	3.982	7.15	4.40

[a] Recorded on a Varian A-60 n.m.r. spectrophotometer at room temperature in deuteriochloroform. [b] Chemical shifts, in parts per million downfield from tetramethylsilane.

Absolute proof of the correctness of the stereochemical assignments was obtained by partial asymmetric synthesis of optically active *trans*-stilbene sulfide (III). *cis*-Stilbene sulfide (VI) has a plane of symmetry perpendicular to the central C—C bond and is therefore a *meso* compound. The *trans* isomer on the other hand does not have any of the elements of symmetry, and is therefore normally obtained as a racemate. The preparation of optically active *trans*-stilbene sulfide was achieved *via* the *erythro*-thiuronium *d*-camphorsulfonate (IIb) obtained from *trans*-stilbene oxide (I), thiourea and *d*-camphorsulfonic acid.

Repeated crystallization of the *d*-camphorsulfonate afforded a product (m.p. 209°, $[\alpha]^{20}\text{D}$ +29.7°) which when treated with sodium carbonate gave inactive *trans*-stilbene sulfide. The mother liquor from the first crystallization was evaporated and the residue treated with base to afford optically active *trans*-stilbene sulfide ($[\alpha]^{20}\text{D}$ +13.6° in hexane). At present we cannot estimate, but it is unlikely that a high degree of optical purity has been attained.

Experimental[10]

erythro-*S*-**(1,2-Diphenyl-2-hydroxyethyl)thiuronium Sulfate (IIa).**—Following Bordwell's procedure[5] 5 g. (0.026 mole) of *trans*-stilbenze oxide (I)[11] was added gradually over 30 min. to a stirred solution of 15 ml. of water, 1.6 g. (0.85 ml., 0.032 equiv.) of concentrated sulfuric acid, and 2.5 g. (0.032 mole) of thiourea at room temperature. The resulting suspension was stirred for 20 hr. and the *erythro*-*S*-(1,2-diphenyl-2-hydroxyethyl)thiuronium sulfate was filtered and washed with ether. There was obtained 7.8 g. (95%) of analytically pure salt, m.p. 169–170°.

Anal. Calcd. for $C_{30}H_{34}N_4O_6S_3$: S, 14.95. Found: S, 14.72.

Attempts to recrystallize the salt from water, acetone, alcohol, or acetonitrile resulted in partial conversion to *trans*-stilbene sulfide (infrared spectrum and m.p.).

trans-**Stilbene Sulfide (III).**—The intermediate thiuronium salt (IIa, 20 g.) was suspended in 40 ml. of water and made alkaline (pH 9) with 10% sodium carbonate. The mixture was stirred for 20 min. and the crude *trans*-stilbene sulfide (12 g., 90%, m.p. 49–50°) collected. Crystallization from methanol gave white, silky flakes, m.p. 53–54°.

Anal. Calcd. for $C_{14}H_{12}S$: C, 79.20; H, 5.70; S, 15.10. Found: C, 78.86; H, 5.70; S, 14.87.

threo-*S*-**(1,2-Diphenyl-2-hydroxyethyl)thiuronium Sulfate (V).**—The above procedure was repeated with *cis*-stilbene oxide (IV).[11] The *cis*-stilbene thiuronium sulfate, m.p. 136–137°, was obtained in 73% yield.

Anal. Calcd. for $C_{30}N_{34}N_4O_6S_3$: S, 14.95. Found: S, 14.74.

cis-**Stilbene Sulfide (VI).**—Neutralization of *threo*-*S*-(1,2-diphenyl-2-hydroxyethyl)thiuronium sulfate (V) afforded *cis*-stilbene sulfide in 90% yield, m.p. 71–72°. Crystallization from methanol gave white needles, m.p. 77–78°.

Anal. Calcd. for $C_{14}H_{12}S$: C, 79.20; H, 5.70; S, 15.10. Found: C, 79.00; H, 5.71; S, 14.90.

erythro-*S*-**(1,2-Diphenyl-2-hydroxyethyl)thiuronium *d*-Camphorsulfonate (IIb) and Optically Active *trans*-Stilbene Sulfide.**—Treatment of *trans*-stilbene oxide (I) with thiourea, water, and *d*-camphorsulfonic acid afforded *erythro*-*S*-(1,2-diphenyl-2-hydroxyethyl)thiuronium *d*-camphorsulfonate, m.p. 176–180°, in 88% yield. The salt was repeatedly crystallized from absolute alcohol until the m.p. (209°) and rotation ($[\alpha]^{20}\text{D}$ = 29.7°) remained unchanged.

Anal. Calcd. for $C_{25}H_{32}O_5S_2N_2$: S, 12.70. Found: S, 12.56.

After each crystallization of the *d*-camphorsulfonate the mother liquor and a sample of the crystallized product were neutralized with sodium carbonate. The optical rotation of the *trans*-stilbene sulfide obtained in each case was measured in methanol. Only the sulfide obtained from the mother liquor of the first crystallization gave optically active sulfide (m.p. 49–51°). To avoid the possibility that some optically active starting material or intermediate salt might be present, the optical rotation was also measured in hexane. The optically active *trans*-stilbene sulfide in hexane had a specific rotation of 13.6° at 20°. *trans*-Stilbene sulfide recovered from the hexane had physical properties (ultraviolet and infrared spectra, and m.p.) identical with those of purified *trans*-stilbene sulfide. Optical rotations were measured on a Rudolph photoelectric polarimeter, Model 200As-8003.

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R. E. Davis, *J. Org. Chem.*, **23**, 216 (1958).

(10) Melting points are not corrected. Analyses are by the Microanalytical Laboratory, Department of Chemistry, University of California, Berkeley, Calif.

(11) A. C. Cope, P. A. Trambull, and E. R. Trumbull, *J. Am. Chem. Soc.*, **80**, 2844 (1958).