Because of the greater stability of the arylsulfonyl iodides (which usually permits their isolation) the preparation of various arylsulfonyl iodides containing an electronegative substituent on the aromatic ring should be possible. We have indeed found that *p*-nitrobenzenesulfonyl iodide can be prepared in the same manner as *p*-toluenesulfonyl iodide,[1,8] by combining an aqueous solution of the sulfinate with an ethanolic solution of iodine. This sulfonyl iodide was found to slowly evolve iodine vapors at room temperature and appeared to be about as stable as *p*-toluenesulfonyl iodide.

Experimental Section

All melting points are uncorrected. Nmr spectra were recorded on a Varian A-60A and ir spectra were recorded on a Beckman IR-33. The nmr spectral data are reported in chemical shift from TMS (δ 0), with s, d, t, q, and m referring to singlet, doublet, triplet, quartet, and multiplet, respectively. Microanalyses were performed by Dr. C. S. Yeh and staff of this department. The α toluenesulfonyl chloride was purchased from Eastman and the 3-methyl-1,2-butadiene was obtained from Chemical Samples Co.

Preparation of Sodium Trichloromethanesulfinate. Trichloromethanesulfonyl chloride (20.5 g, 0.10 mol) was treated with sodium sulfite (25.2 g, 0.20 mol) and sodium bicarbonate (16.8 g, 0.20 mol) in water at 40–45° to give 20.5 g (85.4%) of the sulfinate, ir strong absorption at 790, 1040, and 1085 cm^{-1}. *Anal.* Calcd for CCl_3NaO_2S: Cl, 51.77; Na, 11.19. Found: Cl, 51.63; Na, 11.30. The sulfinate was found to decompose slowly in air. If the reaction temperature was raised to 90°, the yield and purity were greatly reduced.

Preparation of Sodium *p*-Nitrobenzenesulfinate. *p*-Nitrobenzenesulfonyl chloride (22.16 g, 0.10 mol) was treated with sodium sulfite (25.2 g, 0.20 mol) and sodium bicarbonate (16.8 g, 0.20 mol) in approximately 100 ml of water at 75–95° to give 5.0 g (24%) of sodium *p*-nitrobenzenesulfinate: mp 232–233° dec; ir 1510 and 1350 cm^{-1} ($-NO_2$); nmr (D_2O, TMS external standard) δ 7.83 (q).

Preparation of α-Toluenesulfonyl Iodide and Attempted Addition to 3-Methyl-1,2-butadiene. Treatment of α-toluenesulfonyl chloride (38.13 g, 0.20 mol) with sodium sulfite (50.4 g, 0.40 mol) and sodium bicarbonate (33.6 g, 0.40 mol) in 200 ml of water afforded 25.1 g (70.5%) of white solid sulfinate which after a few minutes of exposure to air began to fume and to liberate heat. The material was quickly transferred to a vacuum desiccator and subsequently protected from the air. The nmr spectrum of this product (D_2O, TMS external standard) showed that purity of this material was now not greater than 50%. Because of the apparent instability of the sodium α-toluenesulfinate, the salt was not isolated, but was used as a freshly prepared aqueous solution. Thus, α-toluenesulfonyl chloride was treated with 1 equiv of sodium sulfite and sodium bicarbonate in water at 70–75° and the resulting crude aqueous solution was used without further purification in the following preparation of α-toluenesulfonyl iodide. The α-toluenesulfonyl iodide was generated by vigorously mixing the freshly prepared aqueous solution of sodium α-toluenesulfinate (0.025 mol) with a benzene solution of iodine (5.08 g, 0.02 mol, in *ca.* 200 ml of benzene). The bright yellow benzene solution was separated and dried, then used immediately in the following reaction.

The benzene solution of α-toluenesulfonyl iodide (0.02 mol in *ca.* 200 ml of benzene) was treated with 3-methyl-1,2-butadiene (1.5 g, 0.221 mol). Upon illumination from a 250-W General Electric sun lamp, the bright yellow color rapidly faded and the solution became colorless. Evaporation of the solvent under vacuum gave 3.9 g (89.4%) of benzyl iodide, nmr ($CDCl_3$) δ 4.23 (s, 2), 7.0–7.33 (m, 5). The infrared spectrum of this material contained no sulfone bands, and the nmr spectrum of this material showed only the presence of benzyl iodide; no adducts between 3-methyl-1,2-butadiene and α-toluenesulfonyl iodide could be detected. Further proof of the product identification was obtained as follows.

Treatment of benzyl chloride (1.26 g, 0.01 mol) with sodium iodide (6.0 g, 0.04 mol) in acetone according to the procedure of Coleman and Hauser[9] yielded 1.75 g (80.3%) of benzyl iodide. The benzyl iodide prepared in this manner was compared by ir and nmr and found to be identical with the material produced in the above reaction from α-toluenesulfonyl iodide.

Treatment of the product (1.09 g, 0.005 mol) with sodium benzenesulfinate (1.64 g, 0.01 mol) in methanol at room temperature yielded 1.1 g (94.8%) of the known[10] benzyl phenyl sulfone: mp 149–150° (lit.[5] mp 148°); nmr ($CDCl_3$) δ 4.28 (s, 2), 6.90–7.77 (m, 10).

Preparation of *p*-Nitrobenzenesulfonyl Iodide. When an aqueous solution of sodium *p*-nitrobenzenesulfinate (0.52 g, 0.0025 mol) was treated with a solution of iodine (0.635 g, 0.0025 mol) in ethanol, a yellow solid rapidly precipitated from solution. The solid was collected and recrystallized from CCl_4 to give 0.4 g (51.1%) of *p*-nitrobenzenesulfonyl iodide: mp 96–100° dec; nmr ($CDCl_3$) δ 8.28 (q). The product was found to slowly evolve iodine at room temperature, but was more stable at −10°. The sulfonyl iodide was particularly unstable in chloroform solution.

Attempted Preparation of Trichloromethanesulfonyl Iodide. Treatment of a benzene solution of iodine (0.254 g, 0.001 mol) with an aqueous solution of sodium trichloromethanesulfinate (0.41 g, 0.002 mol) produced no visible reaction. Use of iodine monochloride in place of iodine in the above procedure also failed to produce the sulfonyl iodide (as evidenced by no visible color change) even when a large excess of the sulfinate was employed.

Attempted Preparation of Chloromethanesulfonyl Iodide. Treatment of chloromethanesulfonyl chloride (7.45 g, 0.05 mol) with sodium sulfite (6.3 g, 0.05 mol) and sodium bicarbonate (8.4 g, 0.10 mol) in water at 50–55° yielded 4.1 g (60.2%) of crude sulfinate of approximately 88% purity (by nmr), nmr (D_2O, TMS external standard) δ 4.10 (s), impurity δ 6.07 (s). The impurity is believed to be sodium dichloromethanesulfinate derived from dichloromethanesulfonyl chloride believed to be present in the starting material. Repeated distillation, however, was ineffective in purifying the starting chloromethanesulfonyl chloride. Recrystallization from ethanol was ineffective in purifying the sodium chloromethanesulfinate, thus the sulfinate was used in this purity in the following attempts to prepare chloromethanesulfonyl iodide. The sulfonyl iodide could not be produced by treating an aqueous solution of excess sulfinate with either a solution of iodine in benzene or a solution of iodine monochloride in benzene. In neither case was the dark color (of the iodine or iodine monochloride) discharged.

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Registry No. Sodium trichloromethanesulfinate, 42521-49-3; trichloromethanesulfonyl chloride, 2547-61-7; sodium p-nitrobenzenesulfinate, 15959-31-6; *p*-nitrobenzenesulfonyl chloride, 98-74-8; α-toluenesulfonyl iodide, 42880-77-3; 3-methyl-1,2-butadiene, 598-25-4; benzyl iodide, 620-05-3; *p*-nitrobenzenesulfonyl iodide, 42880-78-4; chloromethanesulfonyl chloride, 3518-65-8; sodium chloromethanesulfinate, 42880-79-5.

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The Crystal Structure of *cis*-2,4-Diphenylthietane *trans*-1-Monoxide[1]

George L. Hardgrove, Jr.,* J. Stuart Bratholdt, and Mary M. Lein

Department of Chemistry, St. Olaf College, Northfield, Minnesota 55057

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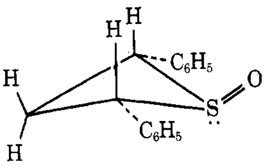
Dodson, Jancis, and Klose have studied the unusual stereochemistry of small heterocyclic rings containing sulfur in various substituted thietanes and their monoxides and dioxides.[2] The crystal structure analysis of *cis*-2,4-diphenylthietane *trans*-1-monoxide was initially begun to confirm the stereochemical arrangement of the phenyl groups and the oxygen atom about the four-membered thietane ring. This work also confirms the estimate of ring puckering from planar conformation made by Dodson, Jancis, and Klose[2] from an analysis of proton spin–spin coupling constants of both the *cis*- and *trans*-2,4-diphenylthietane monoxides determined from nuclear magnetic resonance spectra. Using four coupling constants $J_{HH'}$ between protons on adjacent carbon atoms in the trans and two from the cis derivative, they determined values of the three constants *A, B,* and *C* in the Barfield–Karplus equation[3]

$$J_{HH'} = A\cos^2\phi + B\cos\phi + C$$

and three dihedral angles ϕ. Assuming the H–C–H angle at C-2 as the value found in trimethylene oxide of 112°,[4] and assuming bond distances C–C = 1.54 Å and C–S = 1.83 Å, they determined the pucker angle of the ring to be 39.7°, which is the angle between the plane of C-1, C-2, and C-3, and that of the plane determined by C-1, S, and C-3.



Experimental Section

Crystal Data. The crystals were kindly supplied by Dr. Dodson, who had characterized the compound by elemental analysis, infrared and nmr spectra, and thin layer chromatography.[2] The sample was slowly recrystallized from a 3:1 mixture of chloroform and petroleum ether (bp 30–60°). Large, flat, colorless crystals was obtained, and these were cut to obtain suitable crystals for diffraction. Cell dimensions of a = 11.756 (11) Å, b = 10.302 (14) Å, c = 10.721 (10) Å, and β = 98° 49′ (15) were obtained from Si calibrated Weissenberg photographs taken at room temperature with Cu Kα radiation, λ = 1.5418 Å. The density measured by flotation methods of 1.255 g/ml is in agreement with that of 1.255 g/ml calculated for four $C_{15}H_{14}SO$ molecules per cell. Systematic absences for the $h0l$ reflections of $l = 2n + 1$ and for the $0k0$ reflections of $k = 2n + 1$ are consistent with the space group $P2_1/c$. The intensities of 1800 reflections above the detection limit were estimated by visual comparison of multifilm Weissenberg photographs with an intensity standard. The zones photographed include $h0l$ through $h8l$, and these were placed on a common scale by comparisons with measurements on the $hk0$ and $hk1$ photographs. There were 498 reflections below the detection limit.

Determination and Refinement of the Structure. Lorentz and polarization corrections were applied and Fourier synthesis and isotropic diagonal-matrix least-squares calculations were performed on the IBM 1130 computer using programs kindly supplied by Cooper.[5] The structure was resolved by straightforward application of the Patterson function and heavy atom techniques. Least-squares refinement with the program described above gave convergence at R = 0.208. Analysis of a difference synthesis indicated anisotropic thermal motion, and it contained maxima at positions expected for hydrogen atoms. Further least-squares refinements were carried out on the CDC 6600 computer using the program UMLSTSQ.[6] One cycle of block-diagonal refinement and three cycles of full-matrix anisotropic temperature factor refinement reduced R to 0.129. Hydrogen atom scattering was included in the F_c calculations, but the hydrogen positions were not refined.[7]

Discussion

The general shape of the molecule (Figure 1) is flattened as the benzene rings extend in an equatorial direction from the puckered thietane ring. The molecules pack together with their S–O bonds nearly parallel with the b axis. As no intramolecular bond distances involving O and H are less than 2.3 Å, hydrogen bonds between molecules are not found. The bond distances and angles are shown in Figures 2 and 3. The bond distances and angles found are compared to those reported by Abrahamsson and Rehnberg for *trans*-1-thiacyclobutane-3-carboxylic acid 1-oxide[8] (Table I).

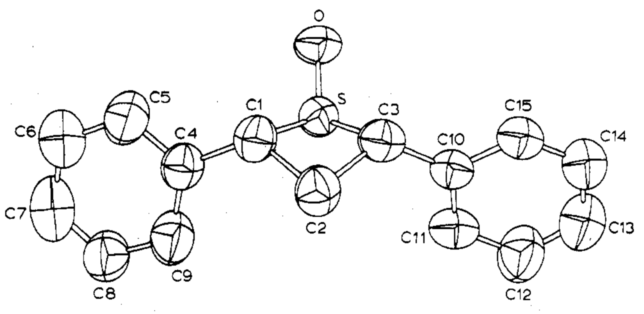


Figure 1. ORTEP drawing of the molecule.

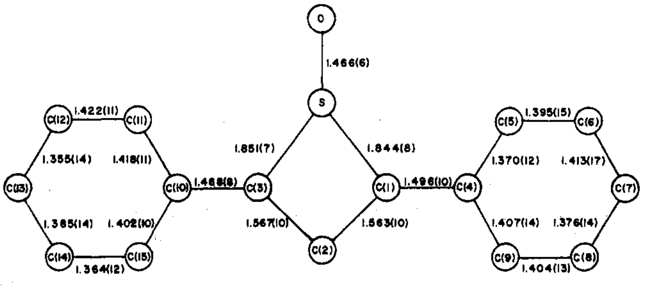


Figure 2. Bond distances.

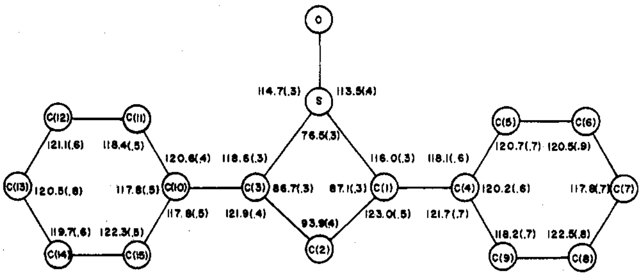


Figure 3. Bond angles.

Table I

	Ref 8	This work
S–O	1.526 (10) Å	1.466 (6) Å
S–C	1.842 (8) Å	1.847 (4) Å
C–C	1.529 (11) Å	1.565 (7) Å
C–S–C	76.6 (5) °	76.5 (3) °
O–S–C	112.0 (4) °	114.1 (3) °
S–C–C	90.2 (4) °	86.9 (3) °
C–C–C	96.6 (9) °	93.9 (4) °
Pucker angle	27°	41.9

The degree of twist of the thietane ring is evident from the pucker angle of 41.9°, which is the angle between the plane of S, C-1, and C-3, and the plane of C-1, C-2, and C-3. This compares with the estimate of 39.7° made from nmr measurements described above.[2] The probable error in our determination is 0.6°, but the difference is probably not significant considering the approximations in the Barfield–Karplus treatment. Pucker angles in other thietanes are 27° for *trans*-1-thiacyclobutane-3-carboxylic acid 1-oxide[8] and unsubstituted thietane which exhibits a symmetrical double-minimum potential function for ring puckering with minima 32° from a planar structure.[9] The pucker angle in this study of 41.9° may be larger than that of the other compounds cited because of the bulky phenyl groups tending toward equatorial conformation. The measured torsional angles of this study are O–S–C-1–C-4 = 95.7° and O–S–C-3–C-10 = 98.8° indicating the twist of C-1 and C-3. The atoms in the benzene ring C-4–C-9 have a maximum deviation from planarity of 0.04 Å and those in the ring C-10–C-15 have a maximum deviation of a 0.02 Å.

Acknowledgment. We are especially indebted to Dr. Dodson for supplying the crystals, for his continuing encouragement, and for his generous support for the final least-squares calculations on the CDC 6600. We also thank Dr. G. J. Palenik for providing the ORTEP drawing.

Registry No. *cis*-2,4-Diphenylthietane *trans*-1-monoxide, 24605-73-0.

Supplementary Material Available. The atomic coordinates, anisotropic temperature factors, and a packing diagram will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-246.

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Photochemistry of 4-Cyclooctenone[1a]

Jack K. Crandall,*[1b] Charles F. Mayer, Jack P. Arrington,[1c] and Richard J. Watkins[1d]

Contribution No. 2318 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401

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In a preliminary communication we reported on the photochemistry of *cis*-4-cyclooctenone (**1**), emphasizing the unusual nature of its transformation to 3-vinylcyclohexanone (**2**).[2] The present report reveals that **1** is reversibly isomerized to the trans isomer **3** upon n–π^* irradiation, whereas higher energy light is required for the formation of **2**.

Irradiation of a cyclohexane solution of **1** with a 450-W Hanovia source through a Pyrex filter for 20 hr gave a mixture of **1** and its trans isomer **3** as the only products. Similar results were also obtained with a benzene solution irradiated through a Vycor filter. The identical 60:40 mixture of **1**:**3** was achieved starting from either isomer in small-scale photolyses conducted in a Rayonet reactor using 3100-Å lamps. Under these conditions prolonged irradiation of an acetone solution of **1** did not result in appreciable reaction. On the other hand, 30 min of irradiation with the Hanovia source directly through a *quartz* probe converted **1** predominantly into cyclohexanone **2**. A minor product (6%) in this photolysis had the same glpc characteristics as **3**. Irradiation of identical samples of **1** and **3** through quartz test tubes in the Rayonet reactor with 2537-Å bulbs for 15 min resulted in 17% conversion of **3** to **2** but only 3% of **1** to **2**. The **3** to **1** isomerization was also more rapid than the conversion of **1** to **3**. Cyclohexanone **2** gave only photoreduction to a mixture of isomeric cyclohexanols upon irradiation of a cyclohexane solution with the Pyrex-filtered Hanovia source.

Isolation of a 95% pure sample of **3** was effected by selective extraction into 5% aqueous $AgNO_3$ and preparative glpc at <130°. The assignment of structure **3** follows from the photoequilibration studies and its spectral properties: ir 5.88, 6.09, and 10.1 μ;[3] nmr δ 5.9 (1, m), 5.1 (1, m), and 3.0–1.8 (10, m). A spin-decoupling experiment indicated a 16-Hz coupling constant between the two olefinic hydrogens, consonant only with a trans double bond.[4] The mass spectra of **1** and **3** were similar but not identical. The uv spectrum of **3** was unusual in that exceptional low-wavelength absorption was observed in addition to normal n–π^* absorption: λ_{max} 222 nm (ϵ 1000) and 280 nm (24) in ethanol and λ_{max} 287 (11), ϵ_{220} 1120 in cyclohexane. The cis isomer shows λ_{max} 285 nm (ϵ 16) and ϵ_{222} 268 in ethanol and λ_{max} 287 (11), ϵ_{220} 206 in cyclohexane. This feature of **3** is probably attributable to its structural rigidity, which holds the two π systems in close proximity to each other. Many β,γ-unsaturated ketones show such abnormality in their uv spectra.[5]

There was a slow disappearance of **3** upon refluxing in xylene leading to both **1** and uncharacterized higher molecular weight materials, but no **2** was thus produced. Exposure to *p*-toluenesulfonic acid in benzene solution for 4 days did not appreciably transform **3** to either **1** or **2**.

This photochemical system presents several noteworthy aspects. Irradiation into the n–π^* band of the carbonyl group promotes clean cis-trans isomerization of the transannular double bond at the expense of the normally expected photochemistry of a nonconjugated, medium-ring ketone (Norrish type I and type II cleavages, reductions, etc.).[6] Nor is there any evidence for intramolecular photocycloaddition leading to oxetane formation.[7] More exacting physical studies will be required to demonstrate the mechanism for this conversion, but several potential pathways can be imagined. The photoequilibration of **1** and **3** could involve n–π^* excitation, intersystem crossing, triplet-energy transfer from carbonyl to the double bond (either intra- or intermolecularly), and subsequent collapse of the triplet olefin to the isomeric cyclooctenones. This is a well-precedented mechanistic possibility.[6] However, intermolecular energy transfer (and possibly the intramolecular counterpart) is contradicted by the lack of reaction upon photolysis in acetone solution, since the triplet acetone generated under these conditions should also be effective at energy transfer and thus promote the **1** to **3** conversion. A detailed study[8] of the photobehavior of 5-hepten-2-one, an acyclic γ,δ-unsaturated ketone, has led to the conclusion that intramolecular singlet exciplex formation accounts for the nonquenchable oxetane formation and geometrical isomerization, exceptionally short-lived excited singlet, and lack of the normally expected Norrish type II reaction that have been found for this system.[9] A similar intermediate can be invoked for the interconversion of **1** and **3** in the present system, although there is some question regarding the compatibility of the severely restricted geometries of these medium-ring compounds