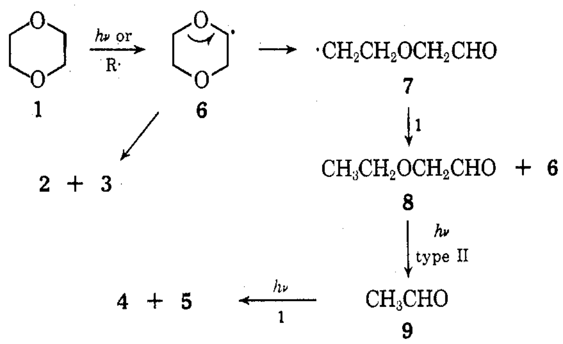

Although the presence of 2–5 does cause some problems during the work-up of preparative photochemical reactions, a major objection to the use of dioxane in quantitative or mechanistic studies is the presence of small steady-state concentrations of 8 and 9, which could cause troublesome sensitization and/or quenching reactions.

Experimental Section

Infrared spectra were obtained on a Beckman IR-8, NMR spectra on a Varian A-60D spectrometer, and gas chromatographic work was carried out on Varian 1200 (flame ionization) and A-90 (thermal conductivity) instruments.

Photolysis of Dioxane. A sample of 200 ml of spectrograde dioxane was purged with nitrogen for 1 hr and then irradiated with a 450-W Hanovia type L lamp for a period of 200 hr. Aliquots were removed during the course of the reaction and analysis on a 6 ft × 0.125 in. 20% Versmid on 60–80 Chromosorb W column at 140° indicated the slow generation of four products with retention times of 8 (A), 12.5 (B), 23, and 31 min. Dioxane was removed by distillation and the residue was distilled to give a fraction, bp 100–120° (17 mm), enriched in the two short retention time peaks. The residue was rich in the two long retention time components and these were separated via preparative GLC on a 6 ft × 0.25 in. 15% DC550 on 80–100 mesh Chromosorb W column at 125°. Melting points and spectral data (ir, NMR, MS) indicated that these were the dimers 2 and 3.[1]

The two early retention time peaks were isolated from the distillation fraction by preparative GLC on a 6 ft × 0.25 in 20% Versmid on 60–80 Chromosorb W column at 110°.

The material corresponding to peak A was identified as 4 (or 5) on the basis of the following data: ν_{max} ($CDCl_3$) 3600, 2870, 2980, and 1120 cm^{-1}; NMR ($CDCl_3$) τ 8.87 (d, J = 6 Hz, 3 H, CH_3), 7.27 (broad s, 1 H, OH), 6.0–6.7 (broad m, 8 H, HCO); MS m/e (rel intensity) 132 (P, 4), 87 (100), 45 (98).

The material corresponding to peak B was identified as 5 (or 4) on the basis of the following data: ν_{max} ($CDCl_3$) 3600, 2865, 2970, 1115 cm^{-1}; NMR ($CDCl_3$) τ 8.83 (d, J = 6.5 Hz, 3 H, CH_3), 7.72 (broad s, 1 H, OH), 5.9–6.6 (broad m, 8 H, HCO); MS m/e (rel intensity) 132 (P, 6), 87 (100), 45 (52).

Acknowledgment. We wish to thank the Center for Materials Research of the University of Maryland for partial support of this work.

Registry No.—1, 123-91-1; 4, 55759-33-6; 5, 55759-34-7.

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(1) K. Pfordte, *Justus Liebigs Ann. Chem.*, **625**, 30 (1959).

(2) Although we would normally expect it to result from hydrogen abstraction processes, in the present case 6 probably arises via excitation of dioxane with 185-nm light. The formation of similar radicals in alcohols has been reported: N. C. Yang, D. P. C. Tang, D. M. Thap, and J. S. Sallo, *J. Am. Chem. Soc.*, **88**, 2851 (1966).

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(4) The photochemistry of methoxyacetone has been studied. This material undergoes efficient Norrish II cleavage (quantum yield = Φ = 0.32) to give acetone and formaldehyde: R. Srinivasan, *J. Am. Chem. Soc.*, **84**, 2475 (1962).

(5) Ketones are known to undergo photoreduction in the presence of dioxane: K. Shima and S. Tsutsumi, *Bull. Chem. Soc. Jpn.*, **36**, 121 (1963); G. O. Schenck, H. D. Becker, K. H. Schutte-Elte, and C. H. Krauch, *Chem. Ber.*, **96**, 510 (1963); W. Droste, H. D. Scharf, and F. Korte, *Justus Liebigs Ann. Chem.*, **724**, 71 (1969).

(6) We have carried out the photoreduction of acetaldehyde in dioxane and it does afford 4 and 5 efficiently.

Conformational Aspects of 1,4-Oxathiane S-Oxide by Carbon Magnetic Resonance Spectroscopy

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Recently, considerable discussion has focused on the conformational preferences of the sulfinyl oxygen atom (S–O) in a variety of six-membered rings. For example, *trans*-1,4-dithiane 1,4-dioxide, possessing a diaxial oxygen conformation in the solid state,[1] appears to exist preferentially in the same conformation in solution.[2] This axial preference of the S–O group has been established for thiane *S*-oxide (1) by low-temperature ^1H NMR techniques[3] while an equilibrium mixture of anancomeric *cis*- and *trans*-4-*tert*-butylthiane *S*-oxides (2 and 3) exhibits a predominance of the cis isomer bearing the axial oxygen.[4] In contrast, the sulfinyl oxygen atom of 3,3-dimethylthiane *S*-oxide prefers the equatorial conformation (>95%).[5] The equatorial preference in the 3,3-dimethyl derivative is undoubtedly due to the repulsive 1,3-syn–axial methyl–sulfinyl oxygen atom interaction while the axial preference in 1 has been ascribed to an attractive interaction between the axial sulfinyl oxygen atom and the syn-axial C–H atoms.[6] In 1,3-dithiane *S*-oxide[7] and 1,3-oxathiane *S*-oxide[8] the sulfur oxygen atom favors the equatorial conformation in the former and the axial position in the latter. In view of the growing concern for those factors which influence (and possibly control) the conformations of sulfoxides in cyclic systems, we wish to report our results and conclusions regarding the conformations of 1,4-oxathiane *S*-oxide (4).

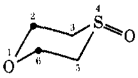
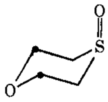
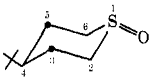
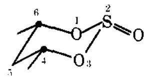
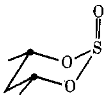
We have examined the conformational equilibria of 1,4-oxathiane *S*-oxide and the corresponding 3,3,5,5-tetradeuterio derivative 5 using ^{13}C NMR spectroscopy.

At −80° in CD_2Cl_2, two absorptions are observed for 5 while in a separate experiment four absorptions were visible for 4. The carbons α to the ring oxygen and the ones α to the sulfinyl group were easily assigned since deuteration served to "mask"[9] only carbons adjacent to the sulfinyl group. Inspection of the low-temperature spectrum of 4 revealed two low-field absorptions of unequal intensity (δ 57.66 and 64.68 ppm) which exhibited a chemical shift difference of 7.02 ppm. A similar result was obtained for the high-field carbons α to the S–O group ($\Delta\delta$ = 7.42 ppm = 51.67 − 44.25). The conformer assignments for the two forms were made by comparison with the appropriate carbon shifts of other systems with established conformations as shown in Table I.

In all cases, it is apparent that the axial (sc) sulfinyl oxygen atom in a *chair conformation* engenders an upfield shift on the β carbons as compared to the equatorial (ap) sulfinyl oxygen atom.[10,11] From these data we conclude that the high-intensity absorptions (most populous conformer) correspond to the one with the *axial sulfinyl oxygen* atom (4a). This conclusion is in harmony with the one arrived at by Szarek et al.[15] from an examination of the ^1H NMR couplings and proton chemical shifts of 4 at ambient temperature. Calculation of the corresponding conformational free energy ($\Delta G°$) gave the data in Chart I.[16] The data on the conformational equilibrium of thiane *S*-oxide[3] are included for comparison.

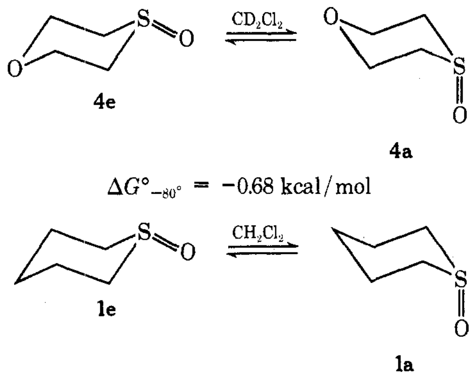
It is especially noteworthy that the $\Delta G°$ for 4 is more than three times that observed for thiane *S*-oxide under similar conditions ($\Delta G°_{-80°}$ = 0.68 ± 0.07 kcal/mol for 4 and $\Delta G°_{-90°}$ = 0.17 ± 0.03 kcal/mol[3] for 1). Dreiding mo-

Table I
^{13}C NMR Shifts of β-Antiperiplanar (ap) and β-Synclinal (sc) Carbons in Six-Membered Ring Sulfoxides[a]

Conformer or diastereoisomer		Carbon chemical shift difference (Δδ), ppm[b]
ap	sc	
		7.02[c,d]
		7.45[e]
		9.10[f]

[a] The ap and sc carbons relative to the sulfinyl oxygen atom are identified as darkened circles. [b] $\Delta\delta = \delta_{\mathrm{ap}} - \delta_{\mathrm{sc}}$. [c] Carbon shift difference measured at −80° in CD_2Cl_2 solution. [d] The shift difference for the appropriate carbons in **5** is identical with that observed for **4**; however, the deuterium isotope effect caused a slight upfield shift for C-2 and C-6 relative to internal Me_4Si. Cf. D. Lauer, E. L. Motell, D. Traficants, and G. E. Maciel, *J. Am. Chem. Soc.*, 94, 5335 (1972). [e] Data obtained from $CDCl_3$ solutions at ambient temperature. [f] G. W. Buchanan, J. B. Stothers, and G. Wood, *Can. J. Chem.*, 51, 3746 (1973).

Chart I
Conformational Free Energy of 1,4-Oxathiane S-Oxide and Thiane S-Oxide



$\Delta G°_{-80°}$ = −0.68 kcal/mol

$\Delta G°_{-90°}$ = −0.17 kcal/mol[a]

[a] J. B. Lambert and R. G. Keske, *J. Org. Chem.*, **31**, 3429 (1966).

lecular models indicate that the distances between an axial sulfinyl oxygen atom and the 2,6-CH positions in **4** (2.75 Å) and the 3,5-CH positions in **1** (2.70 Å) are not significantly different. This, therefore, might suggest that spatial differences between these groups are only marginally reponsible for the disparity in conformational energy between **1** and **4**. It would seem likely that an electrostatic interaction of the type described for the axial preference in 4-chlorocyclohexanone may, in part, be responsible for this additional stabilization of the axial conformer **4a** (as compared to **1a**).[17]

Experimental Section

The carbon FT NMR spectra were recorded on a Varian Model XL-100-12 NMR spectrometer controlled by a 620/f computer. Noise-decoupled and gated decoupled spectra[18] were obtained at ambient (30°) and low temperature (−80°) and the Fourier transforms were based upon 8K data points. The low temperature was measured by insertion of a thermometer directly into the 10-mm tube. Chemical shifts (δ) are reported in parts per million and measured as CD_2Cl_2 solutions downfield from internal tetramethylsilane (Me_4Si). Both ambient- and low-temperature spectra were obtained with pulse widths of $^{6}/_{14}$–$^{10}/_{14}$ μsec, acquisition time of 1.6 sec, and 400–1000 transients. Gated decoupled low-temperature spectra were obtained at PD + AD + AT = 30 sec and the number of transients was 400–600. The gated decoupling experiments gave averaged area ratios (K = 6.06 at −80°) consonant with those obtained by planimeterization and electronic integration (K = 5.82 at −80°) of the appropriate carbon signals.

1,4-Oxathiane *S*-oxide (**4**) was prepared by oxidizing 1,4-oxathiane with sodium metaperiodate in 50% aqueous methanol solution as previously described.[19]

3,3,5,5-Tetradeuterio-1,4-oxathiane *S*-Oxide (5). A solution of **4** (4.0 g, 32.5 mmol) in 20 ml of D_2O was added to a solution of NaOD (0.033 g-atom of Na) in 10 ml of D_2O and heated to reflux for 48 hr. The solution was cooled and extracted with CH_2Cl_2 (2 × 75 ml) and the organic layer was dried ($MgSO_4$) and concentrated to give an oil. Sublimation gave 500 mg of the desired sulfoxide (55°, 0.1 Torr). The proton and carbon spectra were consistent with the desired structure.

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Registry No.—**2**, 937-08-6; **3**, 769-94-8; **4**, 109-03-5; **5**, 55758-73-1; NaOD, 14014-06-3.

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(2) C. Y. Chen and R. J. W. Le Fevre, *Aust. J. Chem.*, **16**, 917 (1963).
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(4) C. R. Johnson and D. McCants, Jr., *J. Am. Chem. Soc.*, **87**, 1109 (1965); **86**, 2935 (1964). See also J. C. Martin and J. J. Uebel, *ibid.*, **86**, 2936 (1964). This also appears to be the case in acidic media; see R. Curci, F. D. Furia, A. Levi, V. Lucchini, and G. Scorrano, *J. Chem. Soc., Perkin Trans. 2*, 341 (1975).
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(9) The carbon absorptions (CD_2) α to the sulfinyl group are surpressed from loss of the nuclear Overhauser effect, by being split into a pentet, and less efficient spin-lattice relaxation.
(10) G. W. Buchanan, J. B. Stothers, and G. Wood, *Can. J. Chem.*, **51**, 3746 (1973); N. K. Wilson and J. B. Stothers, *Top. Stereochem.*, **8**, 1 (1974).
(11) Although the γ-gauche effect is well documented[12] (particularly in six-membered rings[13]), we exercise some caution in defining this effect as purely steric[14] with regard to the sc CH/SO array.
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(16) See the Experimental Section.
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(19) N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962); C. R. Johnson and J. E. Keiser, "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., 1973, p 791.
(20) Note Added in Proof. After this manuscript was submitted for publication a report appeared [G. W. Buchanan and T. Durst, *Tetrahedron Lett.*, 1683 (1975)] which corroborated our findings on the chemical shift difference (7.5 ppm) of the 3,5 carbons in **2** and **3**. In addition, the low temperature (−93°) ^{13}C NMR spectrum of **1** gave chemical shift results compatible with those observed for **4**.