The Reduction of Alkyl Aryl Sulfoxides by Iodide Ions in Acid Solution[1]

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The pseudo-first-order rate constants for the reduction of some aryl alkyl sulfoxides in 4 *M* perchloric acid 0.2 *M* in iodide ion were determined and are methyl phenyl (22 × 10^{-5} sec^{-1}), ethyl phenyl (14 × 10^{-5}), isopropyl phenyl (0.46 × 10^{-5}), *t*-butyl phenyl (0.012 × 10^{-5}), methyl *p*-anisyl (27 × 10^{-5}), methyl *p*-tolyl (31 × 10^{-5}), methyl *m*-tolyl (26 × 10^{-5}), methyl *m*-anisyl (15 × 10^{-5}), methyl *p*-chlorophenyl (13 × 10^{-5}), methyl *m*-chlorophenyl (9.4 × 10^{-5}), methyl *m*-nitrophenyl (3.2 × 10^{-5}), and methyl *p*-nitrophenyl (5.1 × 10^{-5}). The kinetics were first order in sulfoxide and first order in iodide ion. An analysis of the substituent effects using the procedure of Taft indicated that the *p*-nitro group was stabilizing the transition state more than the ground state. This argues against the rate-determining decomposition of an intermediate such as $IS(R_2)OH$ or $IS(R_2)OH_2^+$. Assuming that the reaction was second order in acid as indicated by data in the literature a mechanism was proposed involving rate-determining attack of iodide ion on the sulfur of the monoprotonated sulfoxide while a hydronium ion acted as an acid catalyst allowing concerted departure of a water molecule from sulfur as the iodide ion approached.

Sulfoxides can be reduced by numerous reducing agents among which is iodide ion in acid solution[3] (eq 1). To learn more about the mechanism of this

$$R_2SO + 2H^+ + 2I^- \longrightarrow R_2S + H_2O + I_2 \qquad (1)$$

reaction and the influence of structure on reactivity in particular, and substitution at tetravalent tricoordinate sulfur in general, we carried out the work described below. During the course of our work, several articles appeared on this reaction[4-6] as well as some on the reverse reaction, the oxidation of sulfides by iodine,[7] which proved helpful in interpreting our data.

Results

The sulfoxides studied are listed in Tables I and II. Nine of these are *meta*- and *para*-substituted methyl phenyl sulfoxides chosen to study the effect of structure on reactivity while keeping steric effects at the reaction center constant; the remaining three were chosen to study steric effects.

The kinetics were run in aqueous perchloric acid solution under nitrogen with iodide ion in excess so that pseudo-first-order conditions with respect to the disappearance of sulfoxide pertained. The kinetics were followed by titrating the iodine liberated with sodium thiosulfate. The initial sulfoxide concentrations were about 0.005 *M*, the initial iodide concentration was 0.2 *M*, and the perchloric acid was 4 *M*. Generally, the reactions were followed for one half-life, although good first-order plots could be obtained for two half-lives. Beyond this point, the experimental points of first-order plots began to show a lot of scatter. This probably was caused by oxidation of iodide ion by oxygen not completely excluded from the reaction vessels. No organic products other than the sulfide were detected when methyl phenyl sulfoxide was reduced at greater than kinetic concentrations.

Table I

Rate Constants for the Reduction of $XC_6H_4SOCH_3$ (0.005 *M*) by Iodide Ion (0.20 *M*) in Perchloric Acid (4.00 *M*) at 35°

X	$k \times 10^5$, sec^{-1} [a]	X	$k \times 10^5$, sec^{-1}
p-CH_3O[b]	27.3 ± 0.5	*p*-Cl[g]	12.9 ± 0.5
p-CH_3[c]	31.1 ± 1.2	*m*-Cl[h]	9.41 ± 0.50
m-CH_3[d]	25.5 ± 0.1	*m*-NO_2[i]	3.20 ± 0.20
H[e]	22.1 ± 0.6	*p*-NO_2[j]	5.12 ± 0.17
m-CH_3O[f]	14.6 ± 0.3		

[a] Based on three runs each, average deviation given. [b] Registry no.: 3517-99-5; [c] 934-72-5; [d] 13150-71-5; [e] 1193-82-4; [f] 13150-72-6; [g] 934-73-6; [h] 13150-73-7; [i] 3272-42-2; [j] 940-12-5.

Table II

Rate Constants for the Reduction of C_6H_5SOR (0.005 *M*) by Iodide Ion (0.20 *M*) in Perchloric Acid (4.0 *M*) at 35°, for the Reaction of Alkylthiosulfates with Sulfite Ion, and for the Reaction of Alkyl Bromides with Bromide Ion

	C_6H_5SOR		$RSSO_3^-$ [a]	RCH_2Br[b]
R	$k \times 10^5$, sec^{-1}	$100k_R/k_{CH_3}$	$100k_R/k_{CH_3}$	$100k_R/k_{HC_3}$
CH_3	22.1 ± 0.6	100 (100)[c]	100	100
CH_3CH_2[d]	13.7 ± 0.2	62 (81)	50	65
$(CH_3)_2CH$[e]	0.455 ± 0.024	2.1 (1.8)	0.7	3.3
$(CH_3)_3C$[f]	0.012[g]	0.05 (0.07)	0.0006	0.0015

[a] Reference 10. [b] Reference 11. [c] Values in parentheses are from ref 5. [d] Registry no.: 4170-80-3; [e] 4170-69-8; [f] 4170-71-2. [g] Estimated from an initial and final point after correcting, by means of a blank, for iodine formation due to oxygen.

Several runs were carried out using methyl phenyl sulfoxide in which the hydrogen and iodide ions were kept in excess while the initial sulfoxide concentration was varied. The results presented in Table III indicate that the reaction is first order in sulfoxide in agreement with the results obtained by others.[4,5]

Table III lists the first-order rate constants which increased with increasing acid concentration indicating that the reaction is acid catalyzed. A plot of log *k vs.* H_0 gave a straight line of slope 1.82. Montanari, *et al.*, obtained a slope of 1.22 for the reduction of dimethyl sulfoxide.[5b] These values were obtained using the H_0 values of Paul and Long.[8] Using the values of Yates and Wai,[9] the slopes are 2.1 and 1.3, respectively. The effect of the sodium iodide on the H_0 values is not known.

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[2] This article is based on the Ph.D. Thesis of R. A. S., University of New Hampshire, 1966.

[3] E. N. Karaulova and G. D. Gal'pern, *Zh. Obsch. Khim.*, **29**, 3033 (1959); *Chem. Abstr.*, **54**, 12096*d* (1960).

[4] (a) S. Allenmark, *Ark. Kemi*, **26**, 37 (1966); *Chem. Abstr.*, **66**, 10354*t* (1967); (b) S. Allenmark and H. Johnsson, *Acta Chem. Scand.*, **21**, 1672 (1967); (c) *ibid.*, **19**, 1 (1965), and other papers in this series.

[5] (a) D. Landini, F. Montanari, H. Hogeveen, and G. Maccagnani, *Tetrahedron Lett.*, 2691 (1964); (b) G. Modena, G. Scorrano, D. Landini, and F. Montanari, *ibid.*, 3309 (1966).

[6] J. H. Krueger, *Inorg. Chem.*, **5**, 132 (1966).

[7] (a) T. Higuchi and K. H. Gensch, *J. Amer. Chem. Soc.*, **88**, 5486 (1966); (b) T. Higuchi, I. H. Pitman, and K. H. Gensch, *ibid.*, **88**, 5676 (1966).

[8] M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

[9] K. Yates and H. Wai, *J. Amer. Chem. Soc.*, **86**, 5408 (1964).

TABLE III

DEPENDENCE OF RATE CONSTANTS FOR THE REDUCTION OF METHYL PHENYL SULFOXIDE BY IODIDE ION (0.20 *M*) ON PERCHLORIC ACID CONCENTRATION AND ON SULFOXIDE CONCENTRATION AT 35°

Sulfoxide, *M*	$HClO_4$, *M*	$k \times 10^5$, sec^{-1}
0.010	4.0	21.7
0.005	4.0	22.1
0.001	4.0	19.0
0.005	3.0	2.64 ± 0.28[a]
0.005	3.5	7.50 ± 0.10[a]
0.005	4.5	58.8 ± 1.1[a]

[a] These runs in triplicate.

The effect of iodide ion concentration was also studied. Since the reaction appears to be reversible when the iodide ion concentration approaches the sulfoxide concentration,[4c,5] we varied the initial iodide ion concentration from 0.025 to 0.3 *M* while keeping the initial methyl phenyl sulfoxide concentration at 0.005 *M*. The first-order rate constant was then calculated assuming that the reaction was first order in sulfoxide and zero order in iodide ion. Then the second-order rate constants were determined assuming that the reaction was first order in both sulfoxide and iodide ion. The results are listed in Table IV. Although both the first- and second-order rate constants increase with increasing iodide ion concentration, the first-order constants increase 20-fold while the second-order constants increase only by a factor of two over the 0.025–0.3 *M* range of iodide ion concentration. We conclude that the reaction is first order in iodide ion with the slight increase in second-order rate constants being a salt effect.

TABLE IV

DEPENDENCE OF RATE CONSTANTS FOR THE REDUCTION OF METHYL PHENYL SULFOXIDE (0.005 *M*) ON IODIDE ION CONCENTRATION IN PERCHLORIC ACID (4.0 *M*) AT 35°

I^-, *M*	$k^a \times 10^5$, sec^{-1}	$k^a \times 10^4$ l. mol^{-1} sec^{-1}
0.025	1.78 ± 0.00	5.79 ± 0.02
0.050	4.21 ± 0.00	7.62 ± 0.05
0.100	8.68 ± 0.25	9.18 ± 0.00
0.200	22.1 ± 0.6	10.73 ± 0.10
0.300	37.1 ± 0.4	12.49 ± 0.14

[a] All runs in duplicate except for 0.2 *M* in triplicate.

Discussion

Several mechanisms seem consistent with the kinetic evidence which requires involvement of one sulfoxide molecule, one iodide ion, and an unknown number of protons or hydronium ions in the transition state. These mechanisms all presuppose a preequilibrium protonation of the sulfoxide (eq 2). Thereafter, they

$$R_2SO + H_3O^+ \rightleftharpoons R_2SOH^+ + H_2O \qquad (2)$$

differ in certain details of one or more intermediate steps, but, with the exception of one, finally converge in agreeing to the formation of R_2SI^+ which reacts rapidly with iodide ion in one or more steps to give the products (eq 3). The iodine reacts further to give triodide ion.

$$R_2SI^+ + I^- \longrightarrow R_2S + I_2 \qquad (3)$$

One possible mechanism, quite reminiscent of an SN2 displacement on carbon, involves the formation of a sulfur to iodine bond with the synchronous breakage of the sulfur to oxygen bond. This is depicted by eq 4 where the transition state, with charges omitted, has partially formed and broken bonds are indicated by dotted lines.

$$I^- + R_2SOH^+ \longrightarrow I \cdots S(R_2) \cdots OH \longrightarrow ISR_2^+ + OH^- \qquad (4)$$

The mechanism may be modified by the inclusion of a hydronium ion with consequent displacement of a water molecule rather than a hydroxide ion (eq 5).

$$I^- + R_2SOH^+ + H_3O^+ \longrightarrow I \cdots S(R_2) \cdots OH \cdots H \cdots OH_2 \longrightarrow ISR_2^+ + 2H_2O \qquad (5)$$

Diprotonation of the sulfoxide prior to iodide ion attack seems unlikely since a dication involving adjacent positive charges on sulfur and oxygen would be formed.

Alternatively, mechanisms involving tetravalent tetracoordinate sulfur intermediates, analogous to SF_4 in structure, may be formulated. The first is given by eq 6 and 7. Either the formation or decomposition of the intermediate could be rate determining.

$$I^- + R_2SOH^+ \longrightarrow IS(R)_2OH \qquad (6)$$

$$IS(R_2)OH \longrightarrow ISR_2^+ + OH^- \qquad (7)$$

Again the mechanism may be modified by the inclusion of additional acid (eq 8–10) to avoid expulsion of a hydroxide ion.

$$I^- + R_2SOH^+ \longrightarrow IS(R)_2OH \qquad (8)$$

$$IS(R)_2OH + H_3O^+ \longrightarrow IS(R)_2OH_2^+ + H_2O \qquad (9)$$

$$IS(R)_2OH_2^+ \longrightarrow ISR_2^+ + H_2O \qquad (10)$$

Another possible mechanism involving a monoprotonated sulfoxide is rate-determining attack by iodide ion on the sulfinyl oxygen rather than on sulfur (eq 11 and 12).[4c,6]

$$R_2SOH^+ + I^- \longrightarrow R_2S + HOI \qquad (11)$$

$$HOI + HO_3^+ + I^- \longrightarrow I_2 + 2H_2O \qquad (12)$$

Some evidence against this possibility has been given.[5,6] We carried out the reduction of the methyl, ethyl, isopropyl, and *t*-butyl phenyl sulfoxides hoping to shed some more light on this point. Our thought was to plot our rate constants *vs.* those of Fava and Iliceto[10] for the reaction of alkylthiosulfates with radioactive sulfite ion (eq 13). Our results, those of

$$RSSO_3^- + S^*O_3^{2-} \longrightarrow RSS^*O_3^- + SO_3^{2-} \qquad (13)$$

Fava and Iliceto, and those of de la Mare[11] for the exchange of radiobromide in a series of alkyl bromides are listed in Table II. The radiobromide exchange follows an SN2 pathway. Fava and Iliceto argued that their data supported a similar pathway for nucleophilic substitution on divalent sulfur; *i.e.*, the sulfite ion attacked the divalent sulfur of the thiosulfate from a direction backside to the departing sulfite ion. In order to make this comparison, a methylene group in de la Mare's work was taken to equal the divalent sulfur atom in Fava and Iliceto's work. A similar assumption must be made in order to compare the influence of steric factors on the sulfoxide reduction with the other two sets of data (Table II). The general trend in data suggests that steric effects parallel one another in these three reaction series. One might say that this is

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[10] A. Fava and A. Iliceto, *J. Amer. Chem. Soc.*, **80**, 3478 (1958).

[11] P. B. D. de la Mare, *J. Chem. Soc.*, 3180 (1955).

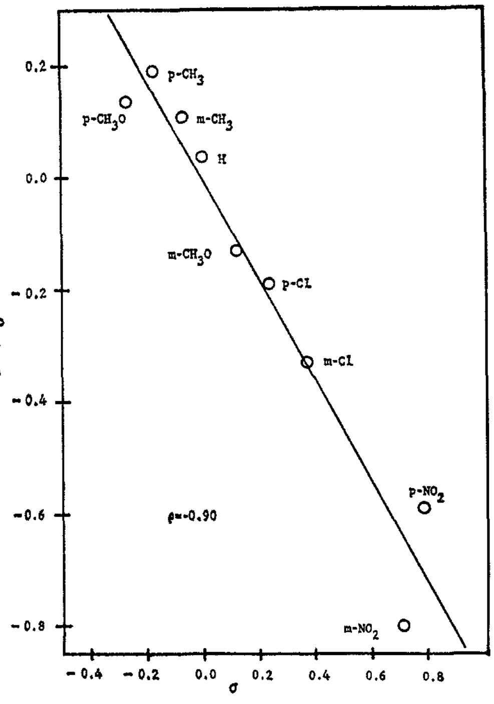

Figure 1.—Hammett plot of pseudo-first-order rate constants.

evidence for the backside attack of iodide ion on the sulfoxide sulfur presumably with inversion of configuration.[12] Unfortunately, the analogy is not so straightforward for sulfoxides. The effect of the alkyl groups on the basicity of the sulfoxides has been neglected. If one knew the pK_a's of these sulfoxides, a more valid comparison of steric factors might be possible. Nevertheless, the effects of differences in basicity should exert a minor influence on the rate constants compared with the steric effects. This reason taken together with the work in the literature makes us exclude the mechanism illustrated by eq 11 and 12 from further consideration in this article.

The remaining mechanistic possibilities differ in two essential points: (1) the presence or absence of a tetracoordinate intermediate, and (2) the number of protons or hydronium ions involved in the transition state. Krueger[6] found the reduction of dimethyl sulfoxide in dimethyl sulfoxide–water mixtures to be first order in iodide ion and second order in acid. Deviation from third-order kinetics occurred when the sulfoxide ion concentration dropped to 62.5%. Montanari and coworkers found the reduction of methyl phenyl sulfoxide and dimethyl sulfoxide in 77.4% acetic acid to be second order in hydriodic acid.[5a] If we consider the hydriodic acid concentration to be equal to the acid concentration (H^+) and to the iodide concentration, then the rate equation is first order in acid and first order in iodide ion. If the acetic acid is functioning as a general acid catalyst, then we can reconcile the difference in acid dependence found by Krueger and by Montanari and coworkers. The mechanisms involving either eq 5 or eq 8–10 are consistent with Krueger's data and our interpretation of Montanari's results.

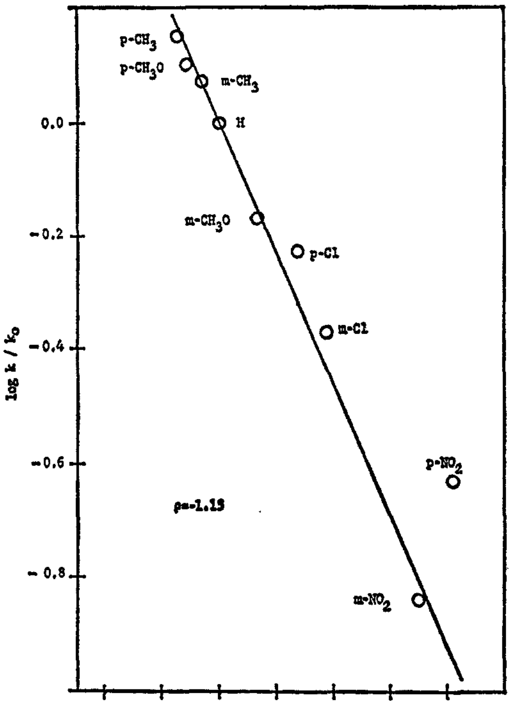

Figure 2.—Taft–Hammett plot of pseudo-first-order rate constants.

The effects of substituent changes on the phenyl group on the observed rate constants, *k*, were also measured. A Hammett plot of log (k/k_0) *vs.* σ had a ρ of -0.90, a correlation coefficient of 0.971, and a standard derivation of 0.08 (Figure 1).

In addition, a search for specific resonance effects was made using the procedure of Taft.[13] The first-order rate constants, *k*, listed in Table I were used. The four *meta*-substituted and the unsubstituted phenyl methyl sulfoxide were used to define the slope of a Hammett plot according to Taft's procedure (Figure 2). The resulting equation was log $(k/k_0) = -1.15$ with a correlation coefficient of 0.998 and a standard deviation of 0.04. Next, the log (k/k_0) values were placed on the plot using the *para* σ^0 values. These σ values are based on several reaction series in which direct resonance interaction between the reaction center and the substituted benzene ring were excluded. A deviation of a *para* value from the straight line is a measure of the greater resonance stabilization of the ground state, R_2SO, relative to the transition state, or *vice versa*, in the reaction. It should be pointed out that we can neglect resonance effects on any intermediates.

The deviations from the line, $\bar{\sigma} - \sigma^0$, where $\bar{\sigma} = -\log (k/k_0)/1.15$, are small except for the case of *p*-nitrophenyl methyl sulfoxide where it is equal to -0.27 σ units.[14] The value of *k* is larger than one would expect. This is due to resonance stabilization of the transition state relative to the ground state; the nitro group is accepting electrons to a greater extent in the transition state than in the ground state.

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(12) Inversion of configuration at a tricoordinate sulfur atom undergoing a nucleophilic displacement reaction has been established for several reactions: exchange of alkoxy groups in sulfinate esters [H. Phillips, *J. Chem. Soc.*, **127**, 2552 (1925)]; sulfinate esters to sulfoxides [P. Bickart, M. Axelrod, J. Jacobus, and K. Mislow, *J. Amer. Chem. Soc.*, **89**, 697 (1967)]; alkoxysulfonium salts to sulfoxides [C. R. Johnson and D. McCants, Jr., *ibid.*, **87**, 5404 (1965)]; and sulfoxides to sulfilimines [J. Day and D. J. Cram, *ibid.*, **87**, 4398 (1965)].

(13) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960). For a similar approach, see H. Van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. Trav. Chim. Pays-Bas*, **78**, 815 (1959).

(14) The other specific resonance effects are *p*-CH_3O, 0.04; *p*-CH_3, 0.02; and *p*-Cl, -0.07.

If an intermediate is formed in the reaction, its rate-determining decomposition by expulsion of a hydroxide ion (eq 7) or a water molecule (eq 10) is not to be expected. Neither of these processes is consistent with the specific resonance effect observed for the *p*-nitro group. Election withdrawal should not favor bond breakage with loss of either a hydroxide ion or a water molecule.

If the reaction (eq 1) is second order in acid as the literature evidence strongly suggests, we can narrow down the mechanistic possibilities to two. The first involves eq 5 as the rate-determining step; the second involves eq 8–10 with either 9 or 10 being rate determining. However, the analysis of our substituent effects argues against eq 10 as the rate-determining step. Equation 9 is also an unlikely rate-determining step. Transfer of a proton from one oxygen atom to another is usually very fast;[15] thus eq 8 is also unacceptable as it involves only one proton.

We are left with one possibility (eq 5), which satisfies the criteria of being first order in sulfoxide and first order in iodide, of involving two protons, and of not being inconsistent with the substituent effect analysis. The over-all process (eq 1) would then involve a series of steps given by eq 2, 5, and 3 in that order.[16]

Experimental Section

Sulfoxides.—All of the sulfoxides used in this work were known compounds. The melting points and boiling points of the aryl methyl sulfoxides used in this study were reported earlier.[17] The melting point (or boiling point where pressures are given) of the other sulfoxides are phenyl ethyl sulfoxide, 91–92° (0.5 mm) [lit.[18] 101–102 (1 mm)]; phenyl isopropyl sulfoxide, 85–86° (0.25 mm) [lit.[18] 127° (7 mm)]; phenyl *t*-butyl sulfoxide, 56.5–57.5° (lit.[18] 58–59°).

Procedure for Kinetic Runs.—Baker and Adamson reagent grade 70% perchloric acid and Mallinkrodt analytical reagent grade sodium iodide dried at 125° were used to prepare the acid and iodide ion stock solutions, respectively. Oxygen-free, distilled water was prepared by refluxing the water while passing a stream of prepurified nitrogen through it. All solutions were prepared under nitrogen. Transferral of stock solutions to the reaction flasks was done by syringe. All flasks were sealed by rubber serum caps.

Three stock solutions were prepared: one of perchloric acid, one of sulfoxide dissolved in the perchloric acid, and one of sodium iodide.

The reaction vessels were 125-ml erlenmeyer flasks. Sodium iodide solution (10 ml) was added to each of the flasks followed by 14 ml of perchloric acid solution. After reaching constant temperature (35.00 ± 0.02°), 1 ml of sulfoxide solution was added. At the end of the appropriate time, each flask was cooled and crushed ice was added to quench the reaction. The iodine liberated was titrated with standard sodium thiosulfate solution. The acid concentration of the runs was determined by titration with standardized sodium hydroxide.

The amount of iodine formed by dissolved oxygen was corrected for by running a blank and assuming that the iodine formation was proportional to time.

The pseudo-first-order rate constants were obtained from the slope of log $[R_2SO]$ *vs.* time plots. An IBM 360 digital computer was used.[20] Generally seven points were included in these plots excluding the initial concentration. All of the data were also plotted graphically in order to see if any deviation from linearity was present. Second-order rate constants were determined graphically.

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(15) M. Eigen, *Angew. Chem. Intern. Ed. Engl.*, **3**, 1 (1964).

(16) Note Added in Proof.—See D. Landini, F. Montanari, G. Modena, and G. Scorrano, *Chem. Commun.*, 86 (1968), for the results of a study on the acid dependence of the reduction of sulfoxides by halide ions which complements the investigation described above.

(17) K. K. Andersen, W. H. Edmonds, J. B. Biasotti, and R. A. Strecker, *J. Org. Chem.*, **31**, 2859 (1966).

(18) A. Cerniani, G. Modena, and P. Todesco, *Gazz. Chim. Ital.*, **90**, 3 (1960).

(19) I. V. Baliah and R. Varadachari, *J. Indian Chem. Soc.*, **37**, 321 (1960).

(20) The authors wish to thank Professor J. J. Uebel for supplying the least-squares plot computer program.

A Nuclear Magnetic Resonance Investigation of the Conformational Preferences of Isomeric Thioxanthenol Sulfoxides and Related Compounds

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The trimethylsilyl and acetyl derivatives of isomeric thioxanthenol sulfoxides and 2-chlorothioxanthenol sulfoxides have been prepared. Configurations have been assigned to these compounds on the basis of their ultraviolet spectra. The parent alcohols, these derivatives, and related compounds have been assigned preferred conformations on the basis of their nmr spectra. The sulfinyl group has been found to prefer the pseudo-equatorial conformation. *trans*-Thioxanthenol sulfoxide appears to exist in the same conformation in solution as in the solid state. 9-Trimethylsiloxythioxanthene prefers that conformation in which the substituent occupies the pseudo-equatorial position.

The thioxanthene ring system serves as an excellent model for stereochemical studies of diaryl sulfur compounds because of the conformational restrictions inherent in this heterocyclic ring system. The initial report of our studies in this area presented the results of the single crystal X-ray analysis of *trans*-thioxanthen-9-ol 10-oxide (1β).[2] As part of a general study of the stereochemistry of this system we have investigated the conformational preferences in solution of a number of *cis*- and *trans*-9-substituted thioxanthene sulfoxides. The purpose of this report is to present the results of an nmr study of the conformational preferences of some of these compounds. Furthermore, the surprising differences[2,3] in the ultraviolet spectra of 1β and 1α (the corresponding *cis* isomer) suggested[3] that ultraviolet spectroscopy could serve as a simple criterion for assigning configuration to other pairs of thioxanthene sulfoxides which possess a dipolar functional group in the 9 position. This report broadens the application of ultraviolet spectroscopy in assigning configurations to heterocyclic sulfoxides.

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(1) To whom inquiries should be directed. Support of this research by U. S. Public Health Service Research Grant No. CA-10139 from the National Cancer Institute is gratefully acknowledged.

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(3) A. L. Ternay, Jr., and D. W. Chasar, *ibid.*, **32**, 3814 (1967).