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.

[2] A. L. Ternay, Jr., D. W. Chasar, and M. Sax, *J. Org. Chem.*, **32**, 2465 (1967).

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

TABLE I

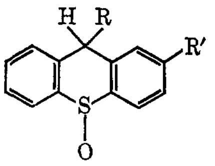
Compound	Ultraviolet spectrum[a-c]	Infrared spectrum[d,e]
cis-Thioxanthen-9-ol 10-oxide (**1**α)[f]	272 (866); 232 (8300); *204* (41,900)	1010, 1098
trans-Thioxanthen-9-ol 10-oxide (**1**β)[f]	285 (558); 273 (1620); *250* (4420); 233 (8060); *214* (42,000)	1002, 1023, 1077
cis-2-Chlorothioxanthen-9-ol 10-oxide (**2**α)	253 (6350); *234* (1290); *205* (44,300)	1028, 1066, 1100
trans-2-Chlorothioxanthen-9-ol 10-oxide (**2**β)	283 (1100); *255* (6690); 235 (11,000); *215* (39,000)	1010, 1031, 1071, 1100
cis-9-Trimethylsiloxythioxanthene 10-oxide (**5**α)	272 (830); 268 (1150); 263 (1760); 234 (8280); 228 (9900); *204* (41,300)	1039
trans-9-Trimethylsiloxythioxanthene 10-oxide (**5**β)	271 (1700); 263 (2700); *250* (4040); *215* (45,800)	1034, 1049, 1079
cis-2-Chloro-9-trimethylsiloxythioxanthene 10-oxide (**6**α)	279 (515); 268 (1880); 261 (3500); 252 (6400); 237 (12,900); *234* (13,100); 209 (41,200); *205* (43,300)	1035
trans-2-Chloro-9-trimethylsiloxythioxanthene 10-oxide (**6**β)	282 (900); 271 (3100); 263 (5000); 253 (6050); 235 (10,700); *216* (42,000)	1035, 1050, 1075, 1095
cis-9-Acetoxythioxanthene 10-oxide (**7**α)	283 (230); 272 (980); 268 (1310); 262 (2010); 233 (9200); 227 (11,100); *203* (41,200)	1032, 1093
trans-9-Acetoxythioxanthene 10-oxide (**7**β)	276 (1110); 269 (1820); 262 (2550); 250 (3900); 231 (9250); *215* (45,800)	1012, 1043, 1095
cis-2-Chloro-9-acetoxythioxanthene 10-oxide (**8**α)	286 (270); 261 (370); 251 (6900); *233* (13,600); 209 (40,200); *204* (44,000)	1036, 1078
trans-2-Chloro-9-acetoxythioxanthene 10-oxide (**8**β)	284 (780); 276 (1690); 269 (2800); 262 (4200), 254 (5620); 234 (12,100); *216* (44,800)	1020, 1043, 1079, 1085

[a] Spectra in 95% ethanol. [b] Wavelengths are in mμ, followed by the molecular extinction coefficient (ϵ) in parentheses; maxima are in italics, and other values refer to shoulders or inflections. [c] Several poorly defined points have been omitted; complete curves are available upon request. [d] Spectra were obtained as Nujol mulls. [e] Only those bands of moderately strong intensity, occurring in the 1000–1100-cm^{-1} region, are listed. Values are in cm^{-1}. [f] See ref 2.

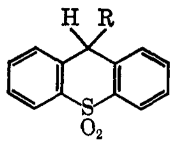
Results and Discussion

Configurational Assignments.—It was found[2] that *cis*- and *trans*-thioxanthenol sulfoxides (**1**α and **1**β) possess strikingly different short-wavelength transitions in the ultraviolet region of the spectrum. Thus, **1**α possesses an intense (ϵ *ca.* 40,000) transition at 204 mμ, whereas **1**β possesses its intense (ϵ *ca.* 40,000) transition, 10 mμ to longer wavelengths, at 214 mμ. A similar pattern was observed for the isomeric 2-chlorothioxanthen-9-ol 10-oxides (**2**α and **2**β).[4]

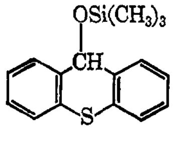
The corresponding acetyl and trimethylsilyl derivatives of **1**α, **1**β, **2**α, and **2**β have now been prepared, starting from the appropriate alcohols. While the acetylation reaction is accompanied by configurational interconversion, the trimethylsilylation proceeds with little or no stereomutation. The derivatives which have been prepared possess the same pattern in their ultraviolet spectra that has been observed in the parent alcohols. Thus, one of each of the isomeric pairs of derivatives (those labeled α) exhibits an intense (ϵ *ca.* 40,000) short-wavelength transition at *ca.* 10 mμ below the intense short-wavelength transitions observed for the other member of each of the isomeric pairs of derivatives (those labeled β). The appropriate data are collected in Table I.



1, R = OH; R′ = H
2, R = OH; R′ = Cl
5, R = OSi(CH$_3$)$_3$; R′ = H
6, R = OSi(CH$_3$)$_3$; R′ = Cl
7, R = OCOCH$_3$; R′ = H
8, R = OCOCH$_3$; R′ = Cl



3, R = OH
4, R = OSi(CH$_3$)$_3$
9, R = OCOCH$_3$



10

The infrared spectra of these derivatives support the assignment of configuration based upon their method of synthesis (for the trimethylsilyl derivatives) and upon their ultraviolet spectra (for trimethylsilyl and acetyl derivatives). It had been established previously[2] that **1**α and **2**α display a simpler infrared absorption pattern in the S–O stretching region than do the corresponding *trans* isomers (**1**β and **2**β). The data collected in Table I reveal that all of the isomers labeled β possess two strong absorptions in the region from 1050 to 1000 cm^{-1} while all of the α isomers exhibit only a single strong absorption in this region.

Thus, as in the case of the isomeric sulfoxide alcohols (**1**α,β and **2**α,β), both infrared and ultraviolet spectra can be employed for configurational assignments. The subsequent discussion indicates that nmr spectra can also be used as an aid in configurational assignments.

Conformational Analysis.—Several properties of the nmr spectra of the compounds under discussion have been employed in order to assign conformational preference.[5,6]

It is instructive to begin with an analysis of the conformational distribution within thioxanthenol sulfone (**3**). This compound displays a moderately intense absorption at 3508 cm^{-1} (1.3×10^{-5} *M*, CCl$_4$), considered to arise from an intramolecular hydrogen bond between the hydroxyl group and the sulfonyl group. The nmr spectrum of **3** offers support for the existence of this hydrogen bond. Thus, even in deuteriochloroform it is possible to observe coupling between the methine proton (C-9) and the hydroxyl proton (Table II). Since rapid exchange would be expected to

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(4) Throughout this paper the designations α and β will be assigned to the *cis* and *trans* configurations, respectively.

(5) It seems unreasonable to assign to these compounds a static conformation. Rather, these results probably represent the preferred conformation in a conformationally mobile system. A similar conclusion has been reached for the thianthrene system.[6]

(6) (a) K. F. Purcell and J. R. Berschied, Jr., *J. Amer. Chem. Soc.*, **89**, 1579 (1967); (b) J. Chickos and K. Mislow, *ibid.*, **89**, 4815 (1967).

TABLE II

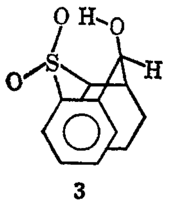
NMR SPECTRA[a,b]

Compd	δ_{C-H}	$\delta_{aromatic}$	$\delta_{Si(CH_3)_3}$	δ_{OCOCH_3}
1$\alpha^{c,d}$	330	442–480		
1$\beta^{c,d}$	359	442–465 474–486		
5α	326	440–484	21	
5β	359	440–460 470–490	6	
6α	325	437–485	22	
6β	360	438–460 469–484	7	
7α	397	440–465 470–492		150
7β	413	437–468 470–490		116
8α	396	437–467 467–488		152
8β	412	440–471 471–492		118
3^{c}	361^{e}	440–490		
4	377	445–491	22	
9	430	440–457 473–490		140
10	317	426–467	16	

[a] Spectra were obtained from deuteriochloroform solutions. Chemical shifts are reported in hertz downfield from internal TMS; values are reported to the nearest hertz. [b] Copies of the spectra are available upon request. [c] The spectrum could only be obtained by the computer averaging of transients. [d] The position of the OH resonance could not be determined under these conditions. [e] This frequency represents the center of a doublet with $J = 8.0$ Hz. The OH proton appears as a doublet ($J = 8.0$ Hz) centered at 197 Hz.

average out this coupling, it is to be concluded that rapid exchange is not occurring and a hydrogen-bonded proton would be consistent with this interpretation.[7] The magnitude of the coupling, moreover, can be readily understood in light of the transoid arrangement of the H-O-C-H bond that would be required for the formation of an intramolecular hydrogen bond.[8]

Thus, both the infrared spectra and the nmr spectra indicate that thioxanthenol sulfone exists in the conformation of structure **3**.



3

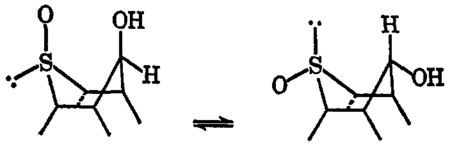
It is suggested that the line position of the methine proton of thioxanthenol sulfone (361 Hz) should be representative of a methine proton in this series that is in the pseudo-equatorial position and *relatively* removed from the magnetic anisotropy of the S-O bond.

The trimethylsilyl derivative of **3** (**4**) might be expected to prefer a conformation in which the 9 substituent exists in the pseudo-equatorial array. Moreover, Carruthers'[9] suggestion that 9-*t*-butyl-9,10-dihydroanthracene exists with the *t*-butyl group in the pseudo-equatorial position supports the availability of this position for the trimethylsiloxy moiety.

If this conformation is favored, one might anticipate a downfield shift of the methine resonance because of the sulfone anisotropy.[10] Indeed, the line position (377 Hz) of this proton occurs 16 Hz downfield from the corresponding alcohol. Johnson–Bovey calculations suggest that a pseudo-axial proton should be more shielded than a pseudo-equatorial proton by virtue of the ring anisotropy.[11] Thus, the 16-Hz downfield shift represents the composite result of the sulfonyl and the aryl anisotropies.

The resonance frequency (359 Hz) of the methine proton of *trans*-thioxanthenol sulfoxide (**1**β) is almost identical with that which is observed for the corresponding sulfone and suggests, therefore, that the preferred conformation of **1**β is that in which the methine proton occupies the pseudo-equatorial geometry. Thus, it appears that the conformation observed for **1**β in the solid state[2] is also the preferred conformation in solution.[12]

cis-Thioxanthen-9-ol 10-oxide (**1**α) can be thought of as existing in two possible conformations. The methine proton would be expected to absorb at *ca.* 360 Hz if conformer a predominates. In reality the resonance frequency is upfield of this value, occurring at 330 Hz. This increased shielding is interpreted as signifying a preponderance of conformer b.



a b

The coupling that was observed in the spectrum of **3** appears to be absent in the spectrum of **1**α (Table II). These results, however, should not be construed as indicating that the hydrogen bond present in **3** is stronger than that which might have been thought to exist in pseudo-diaxial **1**α (*i.e.*, that the sulfonyl is a more powerful hydrogen-bond acceptor than is the sulfoxide group). Whereas it is tempting to draw such a conclusion, the different geometric requirements of the sulfonyl and the sulfinyl moieties may, at least in part, control the preferred conformation of the hydroxyl group.

A similar argument, based upon the line position of the methine proton, also can be applied to the trimethylsilyl derivatives of the corresponding alcohols. To wit, the *cis* isomers (**5**α and **6**α) exhibit this absorption at *ca.* 325 Hz while the corresponding *trans* isomers (**5**β and **6**β) exhibit this absorption at *ca.* 360 Hz (Table II). These frequencies are consistent with the α isomers possessing an axial methine proton and the β isomers possessing an equatorial methine proton.

It is not possible to apply this procedure directly to the corresponding acetates of these alcohols since the methine resonance position has been shifted downfield (see Table II), presumably because of the inductive effect and the anisotropy associated with the acetyl group.

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(7) We have examined the nmr spectra of benzhydrol, xanthydrol, and thioxanthenol, in addition to the derivatives of thioxanthenol presented in this paper. Thioxanthenol sulfone (**3**) is the only compound of those examined which displays this coupling in deuteriochloroform.

(8) J. J. Uebel and H. W. Goodwin, *J. Org. Chem.*, **31**, 2040 (1966), and references cited therein.

(9) W. Carruthers and G. E. Hall, *J. Chem. Soc., Sect. B*, 861 (1966).

(10) E. D. Weil, K. J. Smith, and R. J. Gruber, *J. Org. Chem.*, **31**, 1669 (1966), and references cited therein.

(11) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(12) Strictly speaking, these conclusions are only applicable to chloroform solutions.

However, even in this instance the methine resonance for the two stereoisomers (**7**α,β and **8**α,β) is separated by 16 Hz; the *trans* isomers exhibit a resonance farther downfield than the corresponding *cis* isomers (413 *vs.* 397 Hz). On the bases of these chemical-shift data, it is concluded that the conformational distribution within the various acetates is similar to that which has been observed for the corresponding alcohols and their trimethylsiloxy derivatives.

In the compounds under discussion the C-9–H bonds can assume two extreme arrays relative to the planes of the aromatic rings. In light of the demonstrated dependence of long-range coupling upon geometry,[13] it might be anticipated that the band width of a pseudo-axial proton would be broadened relative to that of a pseudo-equatorial proton.

The trimethylsilyl derivatives of the various alcohols were chosen as subjects for *spin-decoupling experiments.* The results of these double irradiation experiments are included in Table III. These data reveal that there are, indeed, differences in the half-band widths of the C-9 protons in these isomers, the *cis* isomer (α) possessing a broader absorption than the corresponding *trans* isomer. This suggests that the C-9 proton of an α isomer is coupled to the aromatic protons to a larger extent than is the C-9 proton of the corresponding β isomer. Confirmation of this hypothesis was obtained by irradiating the region of aromatic absorption; decoupling resulted in a considerable sharpening of the resonance line for the α isomer but minor sharpening for the β isomer.

TABLE III

SPIN DECOUPLING OF TRIMETHYLSILYL DERIVATIVES[a]

Compd	δ_{irr}[b]	w_0[c]	w_{irr}[d]
10	444	5.6	2.5
4	466	6.1	2.3
6α	460	6.0	2.5
6β	457	4.0	2.5

[a] Decoupling experiments were performed on deuteriochloroform solutions using a Varian Model HA-100 in conjunction with an H. P. Model 200CD wide-range oscillator (sweep time, 250 secs; sweep width, 250 Hz). [b] The frequency of irradiation, calculated for 60 MHz. [c] Band width at half-height (mm) before irradiation. [d] Band width at half-height (mm) during irradiation.

These decoupling experiments support the conformational assignment already suggested for **4**, **6**α, and **6**β.

The spin-decoupling technique was also applied to 9-trimethylsiloxythioxanthene (**10**). The decrease in the half-band width of the methine resonance (Table III) is taken as evidence that the methine proton exists to a considerable degree in the pseudo-axial position. This observation suggests that the preferred conformation of **4** may *not* reflect the results of interaction between a sulfonyl oxygen atom and the trimethylsiloxy group but, rather, simply the preferred conformation of the trimethylsiloxy group in this particular ring system. Thus, it may not be correct to assume, *a priori*, that a substituted 9,10-dihydroanthracene, or a heterocyclic analog,[14] bearing a nonpolar substituent on a *meso* position will exist with that substituent in the pseudo-axial conformation.[15]

Purcell[6a] has recently demonstrated that those protons *peri* to the sulfoxide group in thianthrene disulfoxides are deshielded relative to the remainder of the aryl protons. Moreover, although the conformation of the sulfoxide oxygen atom affects the chemical shift of these protons, they are always deshielded relative to the other aryl protons. Examination of the data in Table II reveals that the regions due to aromatic absorptions for the α and β stereoisomers are different, the α possessing a broad multiplet while the β exhibit two distinct regions of absorption. This is quite clear for the isomers of **1**, **5**, and **6**. The inductive effect and/or the anisotropic effect of the acetyl moiety may account for the less clear separation observed in **7** and **8**. However, within a given pair of isomers the low-field limit is essentially the same. Moreover, for all of the compounds that have been examined, this value is fairly constant (*ca.* 485–490 cps). This suggests that, for all of the compounds that have been examined, the hydrogens *peri* to the sulfoxide group are in the same environment and the disappearance of two distinct regions in the nmr is due to a change in the shielding of the hydrogens *peri* to C-9 as the substituent at C-9 changes conformation.

It appears, in summary, that in all of the sulfoxides which have been discussed, *the sulfinyl oxygen occupies the pseudo-equatorial position.*[16]

What the *most* significant factor is in dictating this conformational preference has yet to be determined. However, several considerations may be involved including (a) a preferred conformation for electronic interaction between the sulfinyl group and the aryl π system, (b) hydrogen bonding (or some other attractive interaction) between the aryl *peri* hydrogens and the sulfinyl oxygen atom, or (c) a purely steric (bulk) effect, similar to that which probably dictates the conformation of **10**. A study of the temperature dependence of these and related spectra will be the subject of a future communication.

The nmr spectra of secondary alcohols have been studied in dimethyl sulfoxide (DMSO) because of the coupling that is exhibited between the hydroxylic proton and the corresponding methine proton.[8,17] The magnitude of the coupling constant that is observed for substituted cyclohexanols has been used as a conformational probe.[8] The spectra of *cis*- and *trans*-thioxanthen-9-ol 10-oxides (and the corresponding 2-chloro derivatives) in d_6-DMSO have been determined. The data presented in Table IV clearly reveal that J is dependent upon configuration. Indeed, the magnitude of the difference between the J's observed for the two stereoisomers is much larger than the values observed[8] in the cyclohexanols. It is tempting to construe the large differences in J_{HCOH} to arise because of a favored cisoid rotamer for the β isomer (*trans* configuration, $J \approx 3$ Hz) and a favored transoid rotamer for the α isomer (*cis* configuration, $J \approx 6$ Hz). Such a picture would be consistent with the structure of the β isomer in

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(13) See, for example, P. T. Lansbury, J. F. Bieron, and A. J. Lacher, *J. Amer. Chem. Soc.*, **88**, 1482 (1966), and references cited therein.

(14) The geometries of the folded analogs, while not identical with that of 9,10-dihydroanthracene, are, nonetheless, quite similar. For pertinent reports, see ref 2 and citations therein.

(15) A. H. Beckett and B. A. Mulley, *Chem. Ind.* (London), 146 (1955), and subsequent papers in this series.

(16) Thioxanthene sulfoxide also appears to prefer that conformation in which the sulfinyl oxygen atom is pseudo-equatorial (unpublished results, with L. Ens).

(17) O. L. Chapman and R. W. King, *J. Amer. Chem. Soc.*, **86**, 1256 (1964).

TABLE IV

NMR SPECTRA IN d_6-DMSO[a]

Compd	$\delta_{\text{C-H}}{}^b$	$\delta_{\text{OH}}{}^{b,c}$	J_{CHOH}
1α	328	418	6.5
1β	360	378	3.1
2α	329	426	6.3
2β	360	387	3.4

[a] Values are reported in hertz downfield from internal TMS. [b] The center of the doublet. [c] The resonance position of the hydroxyl proton was found to be independent of concentration over the range examined. Identification of the hydroxyl absorption was achieved by observing the disappearance of the signal upon addition of D_2O.

the solid state, the H-C-O-H having been shown[2] to be 34°.

Experimental Section[18]

The preparation of the following compounds has already been described:[2,3] *cis*- and *trans*-thioxanthen-9-ol 10-oxide (**1**α,β); *cis*- and *trans*-2-chlorothioxanthen-9-ol 10-oxide (**2**α,β); and thioxanthen-9-ol 10,10-dioxide (**3**).

9-Trimethylsiloxythioxanthene 10,10-Dioxide (**4**).—Thioxanthen-9-ol 10,10-dioxide (**3**) (0.50 g, 0.0020 mol) was dissolved, with shaking, in a mixture of pyridine (10 ml), hexamethyldisilazane (2 ml), and trimethylchlorosilane (1 ml).[19] After 5 min, water (40 ml) was added and the upper layer was evaporated with nitrogen. Water (*ca.* 300 ml) was then added and the resultant solid was removed by filtration. A chloroform solution of this solid was dried (magnesium sulfate) and the solvent was removed (stream of nitrogen) to afford 0.53 g (0.0017 mol) (85% yield) of **4**, mp 122–124°. This solid was homogeneous on tlc[20] and the infrared spectrum exhibited intense absorptions at 1305, 1250, 1200, 1163, 1135, 1108, 1052, 884, 845, and 750 cm^{-1}.

Anal. Calcd for $C_{16}H_{18}O_3SSi$: C, 60.34; H, 5.70; S, 10.07; Si, 8.82. Found: C, 60.15; H, 5.68; H, 10.07; Si, 8.55.

cis-**9-Trimethylsiloxythioxanthene 10-Oxide** (**5**α).—The general method described for **4** was used for **5**α. Thus, 1.0 g (0.0044 mol) of **1**α was treated with a mixture of 20 ml of pyridine, 4 ml of hexamethyldisilazane, and 2 ml of trimethylchlorosilane to afford 0.86 g (0.0029 mol) (66% yield) of a white solid, mp 118–119.5°. Purification by vacuum sublimation afforded a material which was homogeneous on tlc, mp 119–120.6°.

Anal. Calcd for $C_{16}H_{18}O_2SSi$: C, 63.54; H, 6.00; S, 10.60; Si, 9.28. Found: C, 63.32; H, 5.87; S, 10.58; Si, 9.06.

trans-**9-Trimethylsiloxythioxanthene 10-oxide** (**5**β) was prepared in the same manner, starting with **1**β. The product, mp 99–101°, was obtained in an 80% yield and was homogeneous on tlc.

Anal. Found: C, 63.29; H, 5.92; S, 10.35; Si, 8.94.

cis-**2-Chloro-9-trimethylsiloxythioxanthene 10-Oxide** (**6**α).—The general method described above was used to convert 0.89 g (0.0034 mol) of **2**α into crude **6**α (1.12 g, 0.0033 mol, 99%), mp 169–170.5°. Recrystallization from ethyl acetate afforded 0.72 g of **6**α, mp 170.5–171.5°. This material was homogeneous on tlc.

Anal. Calcd for $C_{16}H_{17}O_2ClSSi$: C, 57.04; H, 5.09; Cl, 10.52; S, 9.52; Si, 8.34. Found: C, 56.90; H, 5.12; Cl, 10.23; S, 9.66; Si, 8.12.

trans-**2-Chloro-9-trimethylsiloxythioxanthene 10-oxide** (**6**β) was prepared in the same manner. The crude product, mp 148–150°, was obtained in a 92% yield. Recrystallization from ethyl acetate afforded a material, mp 151–152° (74% yield), which was homogeneous on tlc.

Anal. Found: C, 57.18; H, 5.07; Cl, 10.46; S, 9.49; Si, 8.15.

9-Acetoxythioxanthene 10,10-Dioxide (**9**).—Thioxanthenol sulfone (**3**) was acetylated according to the procedure described by Fehnel.[21] Thus, 0.24 g (0.00098 mol) of **3** afforded 0.28 g (0.00097 mol) (98%) of **9**, mp 156–157.5° (lit.[21] mp 155.5–56°). The infrared spectrum (Nujol) possessed absorptions at 1755, 1300, 1160, and 1200 cm^{-1}.

trans-**9-Acetoxythioxanthene 10-Oxide** (**7**β).—A mixture (*ca.* 1:1) of **1**α and **1**β (3.00 g, 0.013 mol) was dissolved in acetic anhydride (15 ml) containing 2 drops of 96% sulfuric acid. The resultant solution was shaken for 5 min. After an additional 5 min, the solution was diluted with water (30 ml) and then allowed to stand for 1 hr. The resulting solid was removed by filtration, washed with water, and dried under vacuum (sodium hydroxide) to afford 3.37 g (0.012 mol, 95% yield) of crude product, mp 127–141°. The nmr indicated that this product consisted of *ca.* 80% *trans* isomer and 20% *cis* isomer.[22]

Several recrystallizations from ethyl acetate afforded 1.8 g (0.0066 mol, 51% yield) of **7**β, mp 149–150°.

Anal. Calcd for $C_{15}H_{12}O_3S$: C, 66.16; H, 4.44; S, 11.74. Found: C, 65.92; H, 4.45; S, 11.79.

cis-**9-Acetoxythioxanthene 10-Oxide** (**7**α).—The ethyl acetate mother liquors from the recrystallizations described above were combined and concentrated to *ca.* one-third the initial volume (steam bath). Upon cooling, two different types of crystals were deposited. The yellow crystalline material (the other material was colorless) was found to be **7**β contaminated with thioxanthone. The colorless crystals were found (ir, nmr) to be **7**α contaminated with **7**β. These colorless crystals were removed mechanically. This operation was repeated on several batches of mother liquors to afford *ca.* 0.5 g of crude **7**α. Recrystallization (ethyl acetate) afforded 0.38 g (0.0014 mol, 13%) of **7**α, mp 149.5–151°. Although **7**α and **7**β have similar melting points, their spectral behavior (Tables I and II) clearly indicates that these are stereoisomers.

Anal. Found: C, 66.05; H, 4.49; S, 11.81.

cis- **and** *trans*-**2-Chloro-9-acetoxythioxanthene 10-Oxide** (**8**α,β).—A mixture of **3**α and **3**β (2.00 g, 0.0076 mol) was dissolved in acetic anhydride (8 ml) with 1 drop of 96% sulfuric acid and then worked up as described for **7**β to afford 2.13 g (0.0070 mol, 92%) of a light yellow solid, mp 133–142°. (The nmr indicated that this mixture contained both stereoisomers.)

Slow crystallization of this solid from ethyl acetate afforded two types of crystals. Mechanical separation afforded 0.12 g of a yellow solid (mp 169–180°) and 1.51 g of a white, crystalline solid, mp 139–148°.

Recrystallization of the yellow solid from ethyl acetate afforded 0.07 g (0.0002 mol, 3.0% yield) of a feathery, white solid, **8**α, mp 183–184°.

Anal. Calcd for $C_{15}H_{11}O_3ClS$: C, 58.73; H, 3.61; S, 10.45; Cl, 11.56. Found: C, 58.55; H, 3.81; S, 10.60; Cl, 11.67.

The white, crystalline solid, mp 139–148°, was recrystallized from ethyl acetate to afford 1.13 g (0.0037 mol, 49%) of **8**β, mp 147–148.5°.

Anal. Found: C, 58.56; H, 3.64; S, 10.63; Cl, 11.78.

9-Trimethylsiloxythioxanthene (**10**).—Thioxanthen-9-ol[2] (5.0 g, 0.023 mol) was refluxed 15 hr in 50 ml of hexamethyldisilazane in the presence of 0.5 g of sea sand (Fisher ignited). Upon cooling, thioxanthenol precipitated out. The supernatant was concentrated to one-third the initial volume to afford more solid. The remaining solution was concentrated to dryness (stream of nitrogen) to afford 4.1 g of an off-white solid, mp 69–100°. Vacuum sublimation of this material yielded 1.5 g of a white solid, mp 67–80°. Four recrystallizations (95% ethanol) afforded 0.89 g (0.0031 mol, 13%) of **10**, a white, crystalline solid, mp 82–84. The infrared spectrum of **10** exhibited intense absorptions at 1254, 1200, 1105, 1060, 885, 845, and 745 cm^{-1}.

Anal. Calcd for $C_{16}H_{18}OSSi$: C, 67.09; H, 6.33; S, 11.19; Si, 9.80. Found: C, 67.30; H, 6.09; S, 11.38; Si, 9.55.

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(18) Melting points were obtained in a Mel-Temp apparatus and are corrected. Infrared spectra were recorded on either a Beckman Model IR-8 or a Perkin-Elmer Model 521. Ultraviolet spectra (320-200 mμ) were recorded on a Cary Model 15. Nmr spectra were recorded on a Varian Model A-60 or a Varian Model HA-60A equipped with a Varian Model C-1024 time-averaging computer except where indicated. Microanalyses were performed by the Galbraith Laboratories, Knoxville, Tenn. Thin layer chromatographies were performed employing glass plates coated with silica containing a fluorescent indicator. Development was achieved with ethyl acetate, chloroform or chloroform-ethyl acetate mixtures (9:1 v/v). Ultraviolet light and/or iodine vapor were used for visualization.

(19) The procedure is that of C. C. Sweeley, R. Bentley, M. Makita, and W. W. Wells, *J. Amer. Chem. Soc.*, **85**, 2497 (1963).

(20) Several preparations afforded small amounts of **3**. Vacuum sublimation readily purified these samples.

(21) E. A. Fehnel, *ibid.*, **71**, 1063 (1949).

(22) Preparation of all of the isomeric acetates described herein, starting with *isomerically pure* sulfoxide alcohol, inevitably led to mixtures consisting of approximately 80% *trans* isomer and 20% *cis* isomer. Indeed, we have observed that the isomeric acetates do equilibrate under the reaction conditions (acetic anhydride and traces of concentrated sulfuric acid). The mechanism of the equilibration is under investigation.

Registry No.—**1**α, 13096-56-5; **1**β, 13096-57-6; **2**α, 10396-60-1; **2**β, 13096-61-2; **3**, 16354-75-9; **4**, 16354-76-0; **5**α, 16354-77-1; **5**β, 16354-78-2; **6**α, 16354-79-3; **6**β, 16354-80-6; **7**α, 16354-81-7; **7**β, 16354-82-8; **8**α, 16354-83-9; **8**β, 16354-84-0; **9**, 3353-98-8; **10**, 16354-86-2.

Reactions of Mercuric Salts with Bis(diethylthiocarbamoyl) Disulfide and Benzenesulfenyl Chloride

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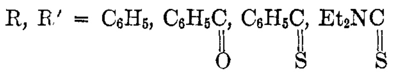
When mercuric carboxylates were treated with bis(diethylthiocarbamoyl) disulfide (1), acid anhydrides were obtained in good yields along with mercuric diethyldithiocarbamate and an unidentified oxygenated product. Further, it was found that treatment of mercuric carboxylates with 2 equiv of benzenesulfenyl chloride (5) gave acid anhydrides, diphenyl disulfide, and mercuric chloride in high yields. A transient intermediate of this reaction, sulfenyl carboxylate, was trapped by treating a mercuric carboxylate with 5 in the presence of an olefin. Reactions of mercuric thiolates with these organic sulfur compounds were also studied.

As part of a continuing study on the behavior of organic sulfur compounds in redox reaction systems, reactions of lead thiolates with disulfides were examined in our laboratory[1] (eq 1). It was concluded that the

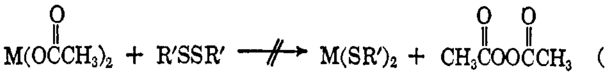
$$\mathrm{Pb(SR)_2} + \mathrm{R'SSR'} \longrightarrow \mathrm{Pb(SR')_2} + \mathrm{RSSR} \qquad (1)$$



$$\mathrm{R,\ R'} = \mathrm{C_6H_5},\ \mathrm{C_6H_5}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}},\ \mathrm{C_6H_5}\underset{\overset{\|}{\mathrm{S}}}{\mathrm{C}},\ \mathrm{Et_2N}\underset{\overset{\|}{\mathrm{S}}}{\mathrm{C}}$$

oxidizing power of the disulfides increases in the following order: diphenyl disulfide < dibenzoyl disulfide < bis(thiobenzoyl) disulfide < bis(diethylthiocarbamoyl) disulfide. The present paper deals with the reactions of some mercuric salts, such as mercuric carboxylates and mercuric thiolates, with some sulfides or benzenesulfenyl chloride.

In the first place, the reaction of a metal salt having the metal–oxygen bond, such as lead, silver, zinc, and mercuric acetates, was tried with the assumption that an oxidative coupling product, organic diacyl peroxide, and a metal salt of a thiol would result by the following redox reaction (eq 2). Among various metal acetates



$$\mathrm{M(O}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH_3)_2} + \mathrm{R'SSR'} \not\longrightarrow \mathrm{M(SR')_2} + \mathrm{CH_3}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OO}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH_3} \qquad (2)$$

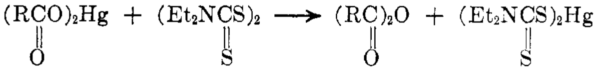
examined, mercuric and silver[2] acetates were found to react with bis(diethylthiocarbamoyl) disulfide (**1**) at room temperature, while cadmium, lead, and zinc acetates did not react in boiling chloroform. In addition, it was established that diphenyl disulfide and dibenzoyl disulfide did not react with mercuric acetate in boiling chloroform, and the starting materials were recovered quantitatively. This result suggests that the reactivities of the disulfides in this reaction depend on the oxidizing power of the disulfides.

Next, the reactions of various mercuric carboxylates with disulfide **1** were studied in detail. Contrary to our expectations, diacyl peroxides could not be obtained when mercuric carboxylates were treated with **1** at room temperature. Instead, acid anhydrides and mercuric diethyldithiocarbamate (**2**) were obtained in good yields together with a substantial amount of a yellow precipitate. Similarly, the anhydride of carbobenzyloxyglycine was also obtained from the corresponding mercuric salt in 72% yield as shown in Table I. However, when mercuric propionate or benzoate was allowed to react with **1** in the presence of water under the same conditions, 66 or 95% of the corresponding acid and 86 or 96% of **2** were obtained. Gas evolution was not observed in the reaction (eq 3).

TABLE I

REACTIONS OF MERCURIC CARBOXYLATES WITH BIS(DIETHYLTHIOCARBAMOYL) DISULFIDE

Mercuric carboxylate	Solvent	Yield, % Anhydride	$(\mathrm{Et_2N}\underset{\overset{\|}{\mathrm{S}}}{\mathrm{C}}\mathrm{S})_2\mathrm{Hg}$
Acetate	Benzene	68	75
Propionate	CH_2Cl_2	84	50
Butyrate	CH_2Cl_2	86	54
Benzoate	CH_2Cl_2	67	53
Succinate	CH_2Cl_2	88	76
Phthalate	Benzene	57	76
Cbo-Gly	Dioxane	72	68



$$(\mathrm{R}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\mathrm{O})_2\mathrm{Hg} + (\mathrm{Et_2N}\underset{\overset{\|}{\mathrm{S}}}{\mathrm{C}}\mathrm{S})_2 \longrightarrow (\mathrm{R}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}})_2\mathrm{O} + (\mathrm{Et_2N}\underset{\overset{\|}{\mathrm{S}}}{\mathrm{C}}\mathrm{S})_2\mathrm{Hg} \qquad (3)$$

1 **2**

The structure of **2** was confirmed by elemental analysis and the infrared spectrum. In the case of mercuric acetate, propionate, and butyrate, the yellow precipitate decomposed in the reaction mixture at room temperature in about 20 min into a black solid. This may be mercuric sulfide. With mercuric succinate and phthalate, the yellow precipitate (**3**) was rather stable and could be isolated. Compound **3** might be an oxygenated product. The infrared spectrum of **3** showed a strong band at 1700 cm^{-1}. Recrystallization of **3** from acetonitrile gave pale yellow crystals (**4**) whose infrared spectrum differed from that of **3**. The infrared spectrum of **4** was almost identical with that of **2**, but showed no band at 1700 cm^{-1}. Elemental analysis and the infrared spectrum of **4** indicated a molecular formula of $C_{10}H_{20}N_2O_6S_4Hg$ or $C_{10}H_{20}N_2O_4S_5Hg$, which corresponds formally to a combination of **2** and O_6 or of **2**, SO_2, and O_2, but its structure

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[1] T. Mukaiyama and T. Endo, *Bull. Chem. Soc. Jap.*, **40**, 2388 (1967).

[2] In this case, only silver diethyldithiocarbamate could be isolated in 94% yield.