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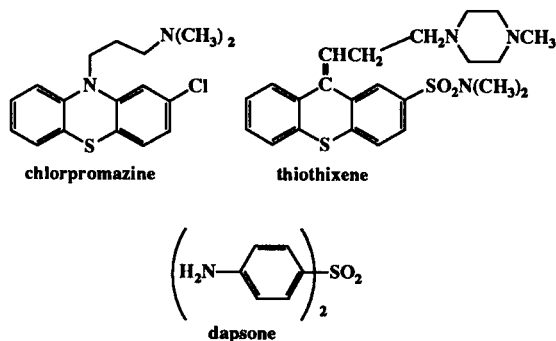
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2-Fluoro-, 2-chloro-, 2-bromo-, 2-methyl-, and 2-methoxythioxanthene have been prepared by borane reduction of the corresponding thioxanthone. The corresponding sulfoxides were prepared by *m*-chloroperoxybenzoic acid oxidation of these sulfides. Proton and carbon chemical shifts have been assigned to these thioxanthene sulfoxides with the aid of LROCSCM and SROCSCM experiments. Carbon chemical shifts in the unsubstituted rings occur at approximately 125 ppm (C5); 128 ppm (C6); 130 ppm (C7); 128 ppm (C8); and 36 ppm (C9). The methylene protons appears as AB doublets at approximately 4.2 and 3.8 ppm. All sulfoxides have the same, pseudo-equatorial geometry.

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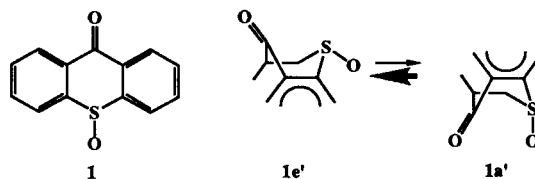
Diaryl sulfur systems are of wide interest as, among other things, pharmaceuticals. This activity encompasses both cyclic and acyclic structures. For example, chlorpromazine is but one of many phenothiazine derivatives affecting the central nervous system while thiothixene is a thioxanthene derivative used as a psychotherapeutic agent. Acyclic diaryl sulfur medicaments are well represented by dapsone, a sulfone used in the treatment of leprosy [1].



The central ring of phenothiazines, thioxanthenes and other so-called 6,6,6-tricyclic systems are folded about an imaginary line containing the two meso positions (*e.g.*, S and N in phenothiazine). Consequently, substituents bonded to sp^3 -hybridized meso atom may occupy either the pseudo-axial (*a'*) or pseudo-equatorial (*e'*) positions. Even when one meso atom is sp^2 -hybridized, as in thioxanthone sulfoxide (1), substituents bonded to the remaining meso position (S in 1) occupy positions with geometries which may be defined as pseudo-equatorial (*e'*) or pseudo-axial (*a'*).

Evidence presented below, and elsewhere [2], suggests that the sulfoxide of a thioxanthone or thioxanthene which

lacks (i) substituents at its peri positions (*e.g.*, C4) and (ii) any other meso substituents, undergoes rapid ring inversion but exists preferentially with an *e'* oxygen. Since



all such sulfoxides exist in similar conformations, they are well suited for studies of electronic effects extending from one aryl ring to another, and other "transannular" phenomena. In this manuscript we present our proton and carbon chemical shifts assignments for a group of sulfoxides of C2-substituted thioxanthenes.

Syntheses.

Thioxanthenes.

Thioxanthenes prepared in this study include 2-trifluoromethylthioxanthene (2), 2-fluorothioxanthene (3), 2-chlorothioxanthene (4), 2-bromothioxanthene (5), thioxanthene (6), 2-methylthioxanthene (7), and 2-methoxythioxanthene (8). They were prepared by the reduction of the corresponding 2-substituted thioxanthenes using borane-tetrahydrofuran complex. As seen from the data in Table 1, the isolated yields in this reaction are quite high, often above 85%.

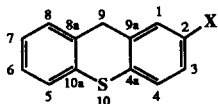
In addition to acceptable elemental analyses and homogeneity on tlc [3], these sulfides all exhibited a characteristic, sharp, methylene proton singlet at approximately 3.9 ppm [4].

Thioxanthene Sulfoxides.

The sulfoxides prepared in this study include 2-trifluoromethylthioxanthene sulfoxide (9), 2-fluorothioxanthene

sulfoxide (10), 2-chlorothioxanthene sulfoxide (11), 2-bromothioxanthene sulfoxide (12), thioxanthene sulfoxide (13), 2-methylthioxanthene sulfoxide (14), and 2-methoxythioxanthene sulfoxide (15) [5]. They were synthesized by the oxidation of the corresponding thioxanthenes using *m*-chloroperoxybenzoic acid at 0° to 5°. Details related to these syntheses are summarized in Table 2.

Table 1
Synthesis of 2-Substituted Thioxanthenes



Compound	2	3	4	5	6	7	8
X	CF ₃	F	Cl	Br	H	CH ₃	OCH ₃
Compound	Yield %	MP [a]	lit MP	Calculated		Observed	
				%C	%H	%C	%H
2	81	92-93	94-95 [b]	---	---	---	---
3	95	129-130	---	72.19	4.19	72.01	4.46
4	90	102-103	102-103 [c,d]	---	---	---	---
5	79	104-105	---	56.28	3.27	56.51	2.93
6	90	127-128	128-129 [e]	---	---	---	---
7	87	81-82	80-82 [f]	---	---	---	---
8	93	132-133	---	73.64	5.29	73.30	4.97

[a] Melting points are uncorrected, from samples recrystallized from 95% ethanol. [b] German Patent 1256238; *Chem. Abstr.*, 68, 105028x (1968). [c] U.S. Patent 2,951,082; *Chem. abstr.*, 55, 4539b (1961). [d] British Patent 863,699; *Chem. Abstr.*, 55 187811 (1961). [e] G. Graebe and G. Schultze, *Liebigs Ann. Chem.*, 263, 1 (1881). [f] M. M. Urberg and E. T. Kaiser, *J. Am. Chem. Soc.*, 89, 5931 (1967).

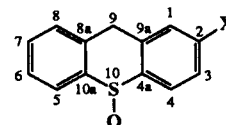
When attempts were made to oxidize thioxanthenes to the corresponding sulfoxides with ceric ammonium nitrate [6] the corresponding thioxanthone was a significant product. Thus, oxidation of 2-methylthioxanthene with ceric ammonium nitrate at 25° in aqueous acetonitrile afforded 73% of 2-methylthioxanthone [7]. Of the oxidants employed, [8] *m*-chloroperoxybenzoic acid generally afforded the highest yields and the lowest number of by-products.

Chemical Shift Assignments.

The aryl portion of the nmr spectra of C2-substituted thioxanthene rings can be divided into two systems. One of these, "A", contains three protonated carbons and is associated with the substituted ring. The other, "B", contains four protonated carbons and is associated with the other aryl ring. The following paragraphs present the assignment of proton and carbon chemical shifts in the "A" ring.

The assignment process begins with thioxanthene sulfoxide (13) which has two identical aryl rings [9]. The only protonated carbon of thioxanthene sulfoxide which shows a *three*-bond correlation to H9 protons in the

Table 2
Synthesis of 2-Substituted Thioxanthene Sulfoxides



Compound	9	10	11	12	13	14	15
X	CF ₃	F	Cl	Br	H	CH ₃	OCH ₃
Compound	Yield % [a]	MP [a] (°C)	lit MP (°C)	Calculated		Observed	
				%C	%H	%C	%H
9	89	147-148	---	59.56	3.21	59.20	3.05
10	69	115-116	---	67.22	3.90	67.09	3.72
11	82	123-124	124-125 [c]	---	---	---	---
12	85	157-158	---	53.25	3.09	53.58	3.20
13	77	117-118	119 [d]	---	---	---	---
14	81	98-99	---	73.60	5.67	73.34	5.19
15	83	128-129	---	68.82	5.30	68.72	4.94

[a] Isolated yields. [b] Melting points are uncorrected, from samples recrystallized from benzene. [c] K. K. Andersen, M. Cinquini and N. P. Papanikolou, *J. Org. Chem.*, 35, 706 (1970). [d] H. J. Shine and L. Hughes, *J. Org. Chem.*, 31, 3142 (1965), A mp of 116-117° also has been reported: A. L. Ternay, Jr. and D. W. Chasar, *J. Org. Chem.*, 32, 3814 (1967).

LROCSCM [10] occurs at 128.0 ppm and must, therefore, be C1. The proton which correlates with this resonance in the SROCSCM [11] occurs at 7.45 ppm and must, therefore, be H1. The resonance at 124.4 ppm, a doublet in the SROCSCM, is assigned to C4 and the proton (H4) which correlates to it in the SROCSCM occurs at 7.97 ppm. Because the proton signals at 7.44 ppm, 7.45 ppm and 7.47 ppm are crowded together, the proton resonance at 7.97 (H4) was employed for further assignments. The LROCSCM spectrum shows that the carbon resonance at 130.3 ppm is *three*-bond coupled to H4, defining it as C2. The SROCSCM spectrum shows that the resonance at 130.3 ppm is *one*-bond correlated to the proton at 7.44 ppm defining this proton as H2. This leaves C3 to be assigned to a resonance at 127.4 ppm. In turn, the SROCSCM spectrum indicates that the resonance at 7.47 ppm is coupled by *one*-bond to C3 and must, therefore, arise from H3. Compound 13 contains a quaternary carbon at 132.8 ppm which exhibits a *three*-bond coupling to H4 (7.97 ppm) in the LROCSCM spectrum, identifying that carbon as being adjacent to the methylene group. The remaining quaternary carbon (141.7 ppm) must be adjacent to the sulfinyl group, consistent with the electron-withdrawing/anisotropic effect of this group.

For 2-trifluorothioxanthene sulfoxide (9) the assignment sequence begins with C2. Its assignment to the resonance at 132.2 is based upon its coupling to ¹⁹F of the

CF₃ group. That coupling constant is 32.45 Hz, typical of a *two*-bond ¹³C-¹⁹F coupling [12]. In the proton-decoupled spectrum of **9** there are two quartets, centered at 124.8 and 124.3 ppm, with coupling constants of 3.47 and 3.32 Hz, respectively. These values are typical of *three*-bond ¹³C-¹⁹F coupling. Consequently, these two carbons must be C1 and C3, or *vice versa*. The SROCSCM spectrum reveals a singlet for the proton resonance correlated to the carbon at 124.8 ppm, indicating that it lacks a neighboring proton. Consequently, it is assigned to C1. Confirmation of this assignment is seen in its *three*-bond coupling to H9 observed in the LROCSCM spectrum of 2-trifluorothioxanthene sulfoxide. By default, therefore, the resonance at 124.3 ppm is due to C3. The SROCSCM spectrum was used to determine that H1 and H3 resonate at 7.70 and 7.72 ppm, respectively. The LROCSCM spectrum reveals that C2 is *three*-bond coupled to the proton signal at 8.05 ppm, identifying the source of the latter as H4. This proton is directly coupled (SROCSCM) to a carbon resonating at 124.7, identifying the source of the latter as C4. The carbon signal at 133.5 ppm exhibits a *three*-bond coupling to H4 and must, therefore, arise from the carbon adjacent to the methylene group (C9a). The quaternary carbon at 146.4 ppm exhibits a *three*-bond coupling to both H1 (7.70 ppm) and H3 (7.72 ppm) and must, therefore, arise from the aryl carbon adjacent to the sulfinyl group (C4a).

The assignment of the nuclei in the C2 substituted aryl ring in 2-fluorothioxanthene (**10**), like that of **9**, uses the fluorine to make the initial assignment. The simple, proton-decoupled ¹³C spectrum of **10** contains a doublet centered at 163.7 ppm with *J* = 251.3 Hz. This coupling is indicative [13] of a *one*-bond ¹³C-¹⁹F coupling and, therefore, the carbon giving rise to this must be C2. Its rather atypical chemical shift supports this assignment. Carbon resonances at 115.6 and 114.5 ppm have the next smaller couplings to ¹⁹F. The values of *J*, 22.74 and 22.34 Hz, indicate a *two*-bond ¹³C-¹⁹F coupling and require that these two carbons be C1 and C3 or *vice versa*. The SROCSCM reveals that a carbon resonance at 115.6 ppm correlates with a "singlet" proton at 7.17 ppm. Because of its multiplicity, this carbon must be C1 and the proton H1. (This assignment is confirmed by the LROCSCM which shows that the resonance at 115.6 ppm correlates with H9 through a *three*-bond coupling.) Consequently, the carbon resonance at 114.5 ppm must be assigned to C3. The SROCSCM shows that C3 is coupled directly to the proton giving rise to signal at 7.15 ppm, identifying it as H3.

A quaternary carbon at 135.9 ppm and a methine carbon at 127.0 ppm are *three*-bond coupled to fluorine (8.25 and 9.36 Hz, respectively). As a result of this, the resonance at 135.9 ppm is assigned to the carbon adjacent to the methylene group while the protonated carbon signal at 127.0 ppm is assigned to C4. A carbon resonance at 137.3 ppm shows *three*-bond couplings to the protons at 7.15 and 7.17 ppm and must, therefore, be the arise from the carbon adjacent to sulfur.

By this stage in these analyses it is clear that C1 and H1 are readily identified in all C-2 substituted thioxanthene sulfoxides [14] since they, alone, give rise to a "singlet" proton correlation in the SROCSCM spectrum. Using this method, C1 and H1 of 2-methoxythioxanthene sulfoxide (**15**) were identified as resonating at 114.5 and 6.98 ppm, respectively. The signal at 114.5 ppm shows a *three*-bond correlation in the LROCSCM spectrum with a proton resonance at 6.94 ppm as well as to the H9 protons. Consequently, the signal at 6.94 ppm must arise from H3. Using the SROCSCM identifies the resonance at 112.3 as arising from C3. (The LROCSCM spectrum shows that the signal at 112.3 ppm correlates to the proton response at 6.98 ppm, confirming this proton signal as being due to H1.)

The quaternary carbon at 161.4 is assigned to C2 since, in addition to its atypical chemical shift, it did not exhibit any correlation to H9. (Indeed, this is observed for all C2 atoms. Furthermore, C2 is the only quaternary carbon which does not correlate to H9 in the LROCSCM spectrum.) A quaternary carbon at 132.6 ppm correlates (LROCSCM) with both H1 and H3 and must, therefore, be due to the aryl carbon adjacent to sulfur. The protonated carbon at 127.2 was assigned to C4 and, using the SROCSCM, the corresponding H4 was found at 7.80 ppm. The aryl quaternary carbon adjacent to the methylene group in the "A" ring was ascribed to the resonance at 135.7 ppm by, among other things, its *three*-bond correlation to H4. Indeed, this carbon occurs over a narrow (3 ppm) range throughout this series.

Similar analyses were used to assign the C2-substituted rings of 2-chlorothioxanthene sulfoxide (**11**), 2-bromothioxanthene sulfoxide (**12**) and 2-methylthioxanthene sulfoxide (**14**). It is noteworthy that these assignments are independent of any chemical shift/substituent additivity arguments.

The other, "B", rings of these sulfoxides were analyzed in a similar manner. Because of its uniqueness, identification of *three*-bond correlation to the methylene protons often was the first step in the assignment. This unequivocally assigned C8 in all of these structures. Consider, for example, 2-bromothioxanthene sulfoxide (**12**). A protonated carbon resonating at 128.2 exhibits *three*-bond coupling to H9 in the LROCSCM spectrum. Since C1 already has been assigned (131.0 ppm), the signal at 128.2 must arise from C8. In turn, C8 correlates in the SROCSCM spectrum to a proton resonance at 7.42, identifying the source of the latter as H8. The remaining proton doublet (7.91 ppm) in the SROCSCM spectrum must be assigned to H5. A carbon resonance at 124.4 ppm shows a *one*-bond correlation to H5, identifying its source as C5. The LROCSCM spectrum shows a carbon resonance at 130.3 which *three*-bond couples to H5, in turn requiring its source to be C7. A proton resonance at 7.43 in the SROCSCM correlates with H7 and must arise from H7. The quaternary carbon resonance at 131.9 ppm exhibits *three*-bond couplings to H5 (7.91 ppm) and H7 (7.43 ppm), labelling its source as C8a (adjacent to the methylene group). Consequently, the remaining unassigned qua-

ternary carbon (141.4 ppm) must be due to the carbon adjacent to sulfur (C10a) while the remaining protonated carbon (127.7 ppm) must be due to C6.

2-Fluorothioxanthene sulfoxide (10) provides an additional illustration of the methods used to assign resonances to the unsubstituted ("B") aryl ring. The protonated carbon at 128.2 ppm exhibits a *three*-bond coupling to the methylene protons (LROCSCM) and must, therefore, arise from C8. A proton signal shows a *one*-bond correlation in the SROCSCM spectrum, identifying its source as H8. The remaining unassigned doublet (124.8 ppm) in the SROCSCM spectrum is due, therefore, to C5. The proton resonating at 7.91 ppm is directly bonded to C5 (SROCSCM) and must, therefore, be due to H5. C7 is assigned to a resonance at 130.3 ppm since that protonated carbon shows a *three*-bond correlation to H5 (7.91 ppm) in the LROCSCM. C8a is assigned to a quaternary carbon resonance at 132.4 ppm since it exhibits *three*-bond correlations (LROCSCM) to proton resonances at 7.91 ppm (H5) and 7.43 ppm (H7). The remaining quaternary carbon at 141.6 ppm is assigned to C10a. The remaining protonated carbon/proton pair, C6/H6, occur at 127.7 and 7.47 ppm, respectively.

Similar methods were used to assign all carbons and protons in the unsubstituted ring of these sulfoxides. For example, C2 is separated from the methylene protons (H9) by *four*-bonds, while the other quaternary carbons are separated from them by three or less. Therefore, as noted above, C2 does not show any coupling to H9 in the LROCSCM experiments. This lack of coupling was used to assign the source of the quaternary carbon resonance at 140.5 ppm in the spectrum of 2-methylthioxanthene sulfoxide as C2. In the LROCSCM spectrum C2 showed a *three*-bond coupling to a proton resonance at 7.80 ppm, identifying the source of the latter as H4. The carbon signal at 124.7 ppm (SROCSCM) is *one*-bond correlated to H4, identifying this as C4. The singlet at 128.9 ppm in the SROCSCM defines the C1 resonance. This is confirmed by, among other things, the coupling between C1 and both H9 and the methyl protons (2.38 ppm) in the LROCSCM spectrum. C1 also shows a *three*-bond coupling to the pro-

ton signal at 7.25 ppm, identifying the source of the latter as H3. In the SROCSCM spectrum C1 shows a *one*-bond correlation to a proton signal at 7.25 ppm, identifying it as due to H1. Thus, both H1 and H3 have essentially the same chemical shift.

The carbon resonances at 128.07 and 128.03 ppm are quite close in the SROCSCM spectrum. However, these signals are seen in different slices in the SROCSCM spectrum. For example, one slice shows a *one*-bond coupling between the carbon resonance at 128.03 ppm and the proton resonance at 7.25 ppm in the SROCSCM spectrum, identifying that carbon as C3. (This was confirmed by the observation of coupling between C3 and the methyl protons in the LROCSCM spectrum.) The remaining nuclei in this and the other sulfoxides were assigned using these general methods and the assignments met all tests for self-consistency. The resulting assignments are presented in Tables 3 and 4. Among other things, it is clear from these data that the quaternary carbon proximal to sulfur in the B ring is essentially insensitive to the C2 substituent.

The ^{13}C chemical shift additivity method was used by Rauckman to assign chemical shifts of thioxanthene sulfoxide, using benzene, phenyl sulfoxide and benzyl groups as the basis for his calculation [15]. The results obtained in the present study generally support his conclusions. However, the use of chemical shift additivities fails to give unequivocal chemical shift assignments for some 2-substituted thioxanthene sulfoxides [16]. One phenomenon commonly observed in these substituted systems is that ^{13}C signals of some aromatic nuclei may be very close to one another. Consequently, a 1 ppm difference in calculated and observed chemical shifts is some-times too large to permit unequivocal assignments. An illustration of this problem is found in the spectrum of 2-chlorothioxanthene sulfoxide, which contains four resonances between 128.2 and 127.6 ppm. Furthermore, C4a and C10a of 2-chlorothioxanthene sulfoxide differ in chemical shift by 1.1 ppm yet the calculated difference is approximately 4 ppm [17].

One aspect which is essential to any meaningful comparison of these data is the assumption that all of these

Table 3

^1H and ^{13}C Chemical Shift Assignments for Protonated Carbons of 2-Substituted Thioxanthene Sulfoxides [a]

Compound	Chemical Shifts							
	C1 (H1)	C3 (H3)	C4 (H4)	C5 (H5)	C6 (H6)	C7 (H7)	C8 (H8)	C9 (H9, H'9)
9	124.82 (7.70)	124.30 (7.72)	124.73 (8.05)	124.16 (7.93)	127.85 (7.51)	130.36 (7.45)	128.16 (7.46)	35.66 (4.21, 3.82)
10	115.60 (7.17)	114.52 (7.15)	127.01 (7.89)	124.83 (7.91)	127.66 (7.74)	130.32 (7.43)	128.20 (3.81)	35.61 (4.19, 3.81)
11	128.17 (7.43)	127.56 (7.43)	125.90 (7.84)	124.51 (7.92)	127.65 (7.48)	130.26 (7.44)	128.17 (3.77)	35.38 (4.13, 3.77)
12	131.03 (7.60)	130.51 (7.59)	126.05 (7.77)	124.50 (7.91)	127.67 (7.49)	130.27 (7.43)	128.15 (3.78)	35.35 (4.13, 3.78)
13 [b]	128.04 (7.45)	127.37 (7.47)	124.44 (7.97)	-----	-----	-----	-----	35.61 (4.17, 3.79)
14	128.90 (7.25)	128.03 (7.25)	124.70 (7.80)	124.70 (7.92)	127.29 (7.43)	130.01 (7.40)	128.07 (7.41)	35.56 (4.15, 3.76)
15	114.46 (6.98)	112.33 (6.94)	127.15 (7.80)	125.36 (7.92)	127.36 (7.42)	130.21 (7.40)	128.26 (7.41)	35.77 (4.24, 3.80)

[a] One dimensional spectra were acquired in deuteriochloroform at 25° and are referenced either to residual protiochloroform (7.26 ppm) or to the center peak of the deuteriochloroform (77.00 ppm). [b] C2/H2: 130.25/7.44 ppm.

structures exist with a common preferred conformation, *i.e.*, with the sulfinyl oxygen in either the a' or the e' conformation. The fact that all of the "AB quartets" of these sulfoxides arising from their respective methylene groups exhibit the (broader) a' proton upfield of the (sharper) e' indicates that they all exist with a predominantly e' sulfinyl group. Furthermore, it can be seen from data in Table 3 that the chemical shifts of the a' and e' protons (approximately 3.8 and 4.2 ppm, respectively) are rather constant throughout this series, supporting a similar geometry for all members of the group.

Table 4

¹³C Chemical Shift Assignments for Quaternary Carbons of 2-Substituted Thioxanthene Sulfoxides [a]

Compound	Chemical Shifts				
	C2	C4a	C8a	C9a	C10a
9	132.15	146.36	131.51	133.54	141.10
10	163.74	137.26	132.42	135.88	141.57
11	136.28	140.40	132.01	134.63	141.45
12	124.50	141.09	131.94	134.78	141.43
13	-----	141.73	132.76	132.76	141.73
14	140.50	138.44	133.14	132.93	141.90
15	161.35	132.64	133.71	135.74	141.79

[a] One dimensional spectra were acquired in deuteriochloroform at 25° and are referenced either to residual protiochloroform (7.26 ppm) or to the center peak of the deuteriochloroform signal (77.00 ppm).

EXPERIMENTAL

Thioxanthenes 2-8.

To a suspension of 0.02 mole of the appropriate 2-substituted thioxanthone in tetrahydrofuran (50 ml) there was added, dropwise and with stirring, 40 ml (0.04 mole) of a 1 M solution of borane in tetrahydrofuran at 0° to -5°. Stirring was continued for 0.5 hours at 0° to -5° and then for 1 hour at room temperature. Excess reductant was decomposed by the careful addition of acetone (10 ml) at 0° to -5°. Removal of all volatiles using a rotary evaporator afforded an oily residue. Addition of approximately 200 ml of water resulted in a solid which was removed by filtration and then dried, *in vacuo*, over potassium hydroxide. The resulting crude product was recrystallized from ethanol to afford the desired thioxanthene. All products were shown to be homogeneous on tlc and to have ¹H and ¹³C spectra as well as elemental analyses consistent with the assigned structures.

Results are summarized in Table 1.

Thioxanthene Sulfoxides 9-15.

To the solution of a 2-substituted thioxanthene (0.010 mole) in methylene chloride (100 ml) there was added, dropwise and with stirring, a solution of *m*-chloroperoxybenzoic acid (0.010 mole of 83.2% purity) in methylene chloride (50 ml) at -10° to -5°. After stirring for 15 to 20 hours at -10° to -5°, the reaction mixture was allowed to reach room temperature. The reaction mixture was washed with the saturated aqueous sodium bicarbonate

and then with saturated sodium chloride solution. The organic layer was separated, dried (sodium sulfate) and the drying agent removed by filtration. The solvent was removed on a rotary evaporator and the resulting crude solid washed with hexane to remove any unreacted starting material.

The homogeneity of the product was checked by tlc [18]. Any product which remained impure [19] was purified by flash chromatography on 200-325 mesh silica gel [20]. Compounds were eluted by mixtures of benzene-chloroform of gradually increasing polarity (from 4:1 to 1:1 v/v). Final purification was achieved by recrystallization from benzene.

Results are summarized in Table 2.

NMR.

All spectra were recorded using 100-300 mg of sample dissolved in 4 ml of deuteriochloroform with a Nicolet NT-200 spectrometer equipped with a Nicolet 1280 data processor and a Model 293A' programmable pulser. The 12 mm probe was maintained at 25° ± 1° throughout. Proton chemical shifts are reported in ppm relative to residual chloroform (7.26 ppm). Carbon chemical shifts are referenced to the center peak of the deuteriochloroform peak. The 90° proton and carbon widths were 41.4 and 21.5 μs. The 90° decoupler pulse was 19 μs.

Typical parameters for proton spectra were as follows: 30° tip angle, 8k data points, 2400 Hz sweep width, quadrature detection, 20-32 transients, 1 s interpulse delay and digital resolution of 0.6 Hz. Typical parameters for carbon spectra are as follows: 45° tip angle, 16k data points, 12048 Hz spectral width, quadrature detection, broadband, bi-level decoupling, 3 s interpulse delay, 1.5 Hz line broadening and a digital resolution of 1.5 Hz.

The pulse sequence employed for SROCSCM and LROCSCM experiments are as described by Bax [21]. Phase cycling was employed to achieve quadrature detection in both dimensions and the coherence transfer echo was detected. The data were displayed as contour plots in the absolute value mode. Typical parameters are as follows: carbon spectral widths were between 400-1000 Hz for SROCSCM and 1200-1600 Hz for LROCSCM; proton spectral widths were between 200-400 Hz for SROCSCM and 900-1200 Hz for LROCSCM. Between 100-256 blocks of 1K or 2K data points were acquired. Processing was done using exponential and/or double exponential multiplication for the t2 dimension. Processing of the t1 dimension included zero-filling to 256-512 data points followed by appropriate signal conditioning. Corresponding delays of 50 μs and 30 μs (J = 10 Hz) were used for LROCSCM experiments.

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REFERENCES AND NOTES

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[1] S. G. Browne, *Advan. Pharmacol. Chemother.*, **7**, 211 (1969).

[2a] See, for example, A. L. Ternay, Jr., J. Herrmann, B. Hayes and P. Joseph-Nathan, *J. Org. Chem.*, **45**, 189 (1980); [b] In a study of the oxygen-17 nmr spectra of a series of substituted thioxanthene sulfoxides, we have found that the sulfoxides described in this manuscript

have approximately the same chemical shift (acetonitrile solvent; 75°) and that the minor differences which are observed can be related to substituent electronic effects rather than to alterations in a' vs e' preferences. Furthermore, a' oxygen resonates downfield of e' oxygen in these sulfoxides (W. W. Lam, B. Mlotkowska and A. L. Ternay, Jr., manuscript in preparation).

[3] Benzene eluent, Eastman silica gel plates, iodine and/or uv visualization.

[4] The presence of a singlet demands that these rings undergo rapid ring inversion; a "frozen" ring would have given rise to a pair of AB doublets.

[5] Attempts to prepare the sulfoxide of 2-nitrothioxanthene have thus far been unsuccessful due, in part, to the low solubility of this substance.

[6] T. L. Ho and C. M. Wong, *Synthesis*, 561 (1972).

[7] This behavior is to be contrasted to the ceric ammonium nitrate oxidation of a series of 2-substituted thioxanthenes, which usually produced the corresponding sulfoxide in at least 50% yield. One outstanding exception is 2-nitrothioxanthone which was unoxidized after being refluxed with a mixture of ceric ammonium nitrate, acetonitrile and water for 72 hours (Unpublished results with C. P. Yu).

[8] The oxidation of 2-chlorothioxanthene with sodium metaperiodate in aqueous dioxane at 0° afforded a mixture of 2-chlorothioxanthone (32%), 2-chlorothioxanthene sulfoxide (16%) and starting material. This behavior was typical of that of several thioxanthenes.

[9] The effect of acidity upon the nmr of 13 has been discussed [ref. 2a].

[10] Long Range Optimized Chemical Shift Correlation Map

[11] Short Range Optimized Chemical Shift Correlation Map

[12a] K. Takahashi, A. Yoshino and H. Muramatsu, *Bull. Chem. Soc. Japan.*, **58**, 755 (1985); [b] N. Muller and D. T. Carr, *J. Phys. Chem.*, **67**, 112 (1963).

[13] F. J. Weigert and J. D. Roberts, *J. Am. Chem. Soc.*, **93**, 2361 (1971).

[14] This is equally valid for sulfones, sulfilimines, and so forth, as well as for the parent sulfides.

[15] E. J. Rauckman, Ph.D. Dissertation, Duke University, 1976.

[16] The method also fails for some corresponding thioxanthenes (unpublished results).

[17] Calculations employed the method proposed by Ewing: D. F. Ewing, *Org. Magn. Reson.*, **12**, 499 (1979). The necessary parameters were found in entries 121, 663 and 679 in this reference.

[18] Eastman silica gel plates; benzene-chloroform (3:2 v/v) eluent; iodine visualization.

[19] The contaminants, if any, corresponded to the thioxanthone and/or thioxanthene sulfone.

[20] Compounds were eluted by mixtures of benzene-chloroform of increasing polarity (from 4:1 to 1:1 v/v).

[21] A. Bax, *Two-Dimensional Nuclear Magnetic Resonance in Liquids*, Delft University Press, D. Reidel Publishing Co., Boston, 1984, pp 50-64.