Synthesis and Stereochemistry of 10-Alkyl-9-arylthioxanthenium Salts

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10-Alkyl-9-arylthioxanthenium salts were synthesized by the reaction of the corresponding 9-arylthioxanthenes with alkyl iodides in the presence of silver salts. Stereochemistry of the sulfonium salts was determined by detailed investigation of the ^{1}H NMR spectra and by X-ray analysis of *cis*-10-methyl-9-phenylthioxanthenium tetrafluoroborate (1′). We have established a very convenient method using ^{1}H NMR spectroscopy for the determination of the conformation of this class of sulfonium salts.

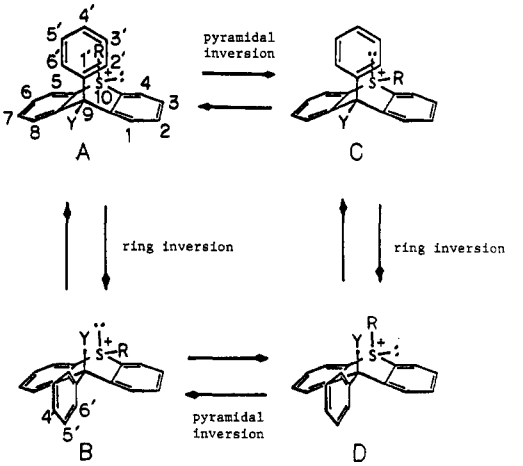
In the course of our studies on the chemistry of thiaanthracene derivatives,[1] we synthesized a large number of 10-substituted 9-arylthioxanthenium salts, precursors of 10-thiaanthracenes. There are four possible stereoisomers for these sulfonium salts. However, systematic studies on the stereochemistry of 9,10-disubstituted thioxanthenium salts are little known.[2] We have investigated the stereochemistry of 10-alkyl-9-arylthioxanthenium salts with the aid of ^{1}H NMR spectra. In the present paper, we describe the details[3] of the synthesis and stereochemistry (conformational analysis) of 10-alkyl-9-arylthioxanthenium salts, including the first success of X-ray crystallographic analysis of one of the thioxanthenium salts, namely *cis*-10-methyl-9-phenylthioxanthenium tetrafluoroborate (1′).

Results and Discussion

Stereochemistry of 10-Alkyl-9-arylthioxanthenium Salts (1–40). Sulfonium salts are pyramidally stable and, in appropriate ring systems, give rise to conformational and configurational isomers. In 10-alkyl-9-arylthioxanthenium salts, there are four possible stereoisomers (A–D) as shown in Scheme I, in analogy with 9-arylthioxanthene 10-oxides whose stereochemistry has been well established by Ternay et al.[4] and our group[1a,5] by ^{1}H NMR methods.

We tried the stereostructure determination of 10-alkyl-9-arylthioxanthenium salts by careful examination of their ^{1}H NMR spectra in trifluoroacetic acid. The ^{1}H NMR spectral data and determined conformers are summarized in Table I. Conformation of the 9-aryl group was determined on the basis of the spectral evidence that anisotropic effects of the 9-aryl group in the pseudoequatorial (e′) position caused the upfield shift of the peri hydrogens at the 1- and 8-positions and that the two benzene rings

Scheme I. Four Possible Stereoisomers of 10-Alkyl-9-arylthioxanthenium Salts



of the thioxanthene molecule shielded the protons and substituents of the 9-aryl group in the pseudoaxial (a′) position. Meanwhile, conformation of the 10-alkyl group was determined by the fact that the 10a′-alkyl group was shielded by the anisotropic effect of the benzene rings of thioxanthene and the signal of the 10a′-alkyl group appeared up field from that of the e′-alkyl group. Particularly, when both of the 9-aryl and 10-alkyl groups occupy that a′-position, the 10-alkyl group was significantly shielded by the anisotropy of the 9a′-aryl group.

In conformers A and C, the 9-aryl group occupies the a′-position. Therefore, protons of the 9-aryl group, particularly $H_{2'}$ and $H_{6'}$ should be shielded by the thioxanthene ring. Compound 1 showed two types of multiplet signals corresponding to $H_{2'}$,$H_{6'}$ and $H_{3'}$,$H_{4'}$,$H_{4'}$,$H_{5'}$ at δ 6.77–7.08 and 7.11–7.42, respectively. The assignment of 9-phenyl protons was achieved by the comparison of the ^{1}H NMR spectrum with that of the corresponding 9-pentadeuteriophenyl derivative 7 which has no signals corresponding to $H_{2'}$,$H_{6'}$ and $H_{3'}$,$H_{4'}$,$H_{5'}$ (see the paragraph at the end of the paper about supplementary material concerning the ^{1}H NMR spectra of the compounds 1 and 7). These two separated multiplet signals of aryl group were observed in compounds 1, 1′, 3, 5, 9–11, 13, 15, 18, and 19. In conformer A, in which the 9-aryl group and 10-alkyl group both occupy the a′-position, the aryl group is expected to shield the 10-alkyl group. In fact, an extremely remarkable upfield shift of the 10-alkyl group was observed in compounds 1, 1′, 3, 5, 7, 9, 11, 13, 15, 18, and 19 as shown in Table I. Compound 1 (conformer A)

(1) (a) Hori, M.; Kataoka, T.; Shimizu, H. *Chem. lett.* **1974**, 1073. (b) Hori, M.; Kataoka, T.; Shimizu, H. *Ibid.* **1974**, 1117. (c) Hori, M.; Kataoka, T.; Shimizu, H.; Ohno, S. *Tetrahedron Lett.* **1978**, 255. (d) Hori, M.; Kataoka, T.; Shimizu, H.; Ohno, S. *J. Org. Chem.*, submitted for publication.

(2) Andersen, K. K.; Cinquini, H.; Papanikolau, N. E. *J. Org. Chem.* **1970**, *35*, 706.

(3) Preliminary communication of part of this work has been published: Hori, M.; Kataoka, T.; Shimizu, H.; Ohno, S. *Heterocycles* **1979**, *12*, 1555.

(4) (a) Ternay, A. L., Jr.; Hermann, J.; Evans, S. A. *J. Org. Chem.* **1969**, *34*, 940. (b) Ternay, A. L., Jr.; Evans, S. A. *Ibid.* **1974**, 39, 2941. (c) Evans, S. A.; Ternay, A. L., Jr. *Ibid.* **1975**, *40*, 2993.

(5) Hori, M.; Kataoka, T.; Shimizu, H.; Ohno, S. *Heterocycles* **1979**, *12*, 1417.

(6) This chemical shift corresponds to that of the pseudoaxial methyl group at the 10-position.

0022-3263/84/1949-3151$01.50/0

Table I. ^{1}H NMR Spectral Data for 10-Alkyl-9-arylthioxanthenium Salts in CF_3CO_2H[a]

no.	R^1[b]	R^2[c]	R^3	R^4[b]	R^5[c]	$H_{1,8}$	H_9 ($W_{1/2}$, Hz)	10-Me (CH_2)	other absorptions	conformer
1	Ph	H	H	Me	–:	*d*	5.71 (2.4)	2.70	6.77–7.08 ($H_{2',6'}$), 7.11–7.42 ($H_{3',4',5'}$), 7.48–8.13 (ArH)[i]	A
1′	Ph	H	H	Me	–:	*d*	5.88 (2.4)	2.69	6.87–7.20 ($H_{2',6'}$), 7.25–7.45 ($H_{3',4',5'}$), 7.61–8.19 (ArH)[i]	A
2	H	Ph	H	–:	Me	6.99–[e]	5.62 (2.6)	3.39	6.99–7.84 (ArH), 7.84–8.10 ($H_{4,5}$)	D
2′	H	Ph	H	–:	Me	7.19–[e]	5.73 (2.7)	3.39	7.19–7.84 (ArH),[i] 7.93–8.16 ($H_{4,5}$)	D
3	Ph	H	H	Et	–:	*d*	5.79 (2.2)	(2.87) (q, J = 7.4 Hz)	6.68–7.02 ($H_{2',6'}$), 7.10–7.36 ($H_{3',4',5'}$), 7.51–8.07 (ArH)[i]	A
4	H	Ph	H	Et	–:		5.57 (2.8)	(3.67) (q, J = 7.1 Hz)	1.43 (t, J = 7.1 Hz, CH_2CH_3)	D
5	Ph	H	H	Pr	–:	*d*	5.85 (2.4)	(2.78) (t, J = 7.7 Hz)	6.80–7.12 ($H_{2',}$), 7.17–7.48 ($H_{3',4',5'}$), 7.51–8.16 (ArH);[i] 0.80 (t, J = 6.5 Hz, CH_2CH_3), 1.53 (m, 10-$CH_2CH_2CH_3$)	A
6	H	Ph	H	Pr	–:	7.18–[e]	5.63 (2.9)	(3.64) (t, J = 7.5 Hz)	7.18–8.18 (ArH), 1.22 (t, J = 6.6 Hz, CH_2CH_3), 1.85 (m, 10-$CH_2CH_2CH_3$), 8.02 (mc, $H_{4,5}$)	D
7	C_6D_5	H	H	Me	–:	*d*	5.86 (1.2)	2.72	7.59–8.21 (ArH)	A
8	H	C_6D_5	H	Me	–:	7.40 (mc)	5.68 (2.9)	3.40		D
9	Ph	Me	H	Me	–:	*d*		2.51	6.60–6.92 ($H_{2',6'}$), 7.09–7.37 ($H_{3',4',5'}$), 7.45–8.28 (ArH), 2.34 (s, 9-Me)	A
10	Ph	Me	H	–:	Me	*d*		3.51	6.76–7.10 ($H_{2',6'}$), 7.10–7.40 ($H_{3',4',5'}$), 7.40–7.99 (ArH), 2.31 (s, 9-Me)	C
11	Ph	Me	H	Et	–:	*d*		(2.66) (q, J = 7.2 Hz)	6.59–6.94 ($H_{2',6'}$), 7.07–7.40 ($H_{3',4',5'}$), 7.45–8.33 (ArH), 1.19 (t, J = 7.2 Hz, CH_2CH_3), 2.37 (s, 9-Me)	A
12	Me	Ph	H	Et	–:	7.27–[f] (mc)		(3.71)	6.97–7.99 (ArH),[i] 1.53 (t, J = 7.3 Hz, CH_2CH_3), 2.26 (s, 9-Me)	D
13	Ph	Me	H	Pr	–:	*d*		(2.45) (t, J = 7.3 Hz)	6.53–6.83 ($H_{2',6'}$), 7.05–7.32 ($H_{2',4',5'}$), 7.50–8.33 (ArH), 0.81 (t, J = 6.4 Hz, CH_2CH_3), 1.50 (m, 10-$CH_2CH_2CH_3$), 2.36 (s, 9-Me)	A
14	Me	Ph	H	Pr	–:	6.90–7.47[f]		(3.63) (t, J = 7.6 Hz)	7.47–7.96 (ArH), 7.83 (mc, $H_{4,5}$), 1.22 (t, J = 6.7 Hz, CH_2CH_3), 1.92 (m, 10-$CH_2CH_2CH_3$), 2.27 (s, 9-Me)	D
15	Ph	Pr	H	Pr	–:	*d*		(2.45) (t, J = 7.5 Hz)	6.78–7.06 ($H_{2',6'}$), 7.12–7.41 ($H_{3',4',5'}$), 7.49–8.09 (ArH), 0.85 (t, J = 6.6 Hz, 10-$CH_2CH_2CH_3$), 0.67–1.76 (m, 9-$CH_2CH_2CH_3$ and 10-$CH_2CH_2CH_3$), 2.50–2.92 (m, 9-$CH_2CH_2CH_3$)	A
16	Pr	Ph	H	Pr	–:			(3.67) (t, J = 7.5 Hz)		
17	*i*-Pr	Ph	H	–:	Me	7.00–[e]		3.62	7.00–7.98 (ArH), 0.85 (d, J = 6.7 Hz, $CH(CH_3)_2$), 2.99 (h, J = 6.7 Hz, $CHMe_2$), 7.37 (s, 9-Ph)	B
18	Ph	H	4-Me	Me	–:	*d*	5.87 (2.8)	2.64	6.80 ($H_{2',6'}$)[e]	A
19	Ph	H	1,4-Me_2	Me	–:	*d*	6.15	2.63	6.80 ($H_{2',6'}$),[e] 6.80–8.30 (ArH), 2.70 (s, 1-Me), 2.81 (s, 4-Me)	A
20	C_6F_5	H	H	–:	Me		6.39 (3.7)	3.63	7.47–8.16 (ArH)	C
21	H	C_6F_5	H	–:	Me	7.32–7.67	6.38 (4.6)	3.48	7.69–8.35 (ArH),[i] 8.18 (mc, $H_{4,5}$)	B
22	H	C_6F_5	H	–:	Pr	7.30–7.63	6.30 (4.8)	(3.69) (t, J = 7.4 Hz)	7.67–8.27 (ArH), 1.19 (t, J = 6.5 Hz, CH_2CH_3), 1.80 (m, 10-$CH_2CH_2CH_3$)	B
23	C_6F_5	H	1-Me	–:	Me		6.50 (2.4)	3.66	7.68–8.14 (ArH), 2.54 (s, 1-Me)	C
24	H	Mes	H	Me	–:	6.96–7.57[g]	6.20 (3.9)	3.29	1.29 (6′-Me),[j] 2.60 (2′-Me),[k] 2.44 (4′-Me), 7.60–8.02 (ArH),[i] 8.02–8.24 ($H_{4,5}$)	D
25	H	Mes	H	Et	–:	7.05–7.50	6.11 (3.6)	(3.62) (q, J = 7.0 Hz)	1.29 (6′-Me), 2.57 (2′-Me), 2.41 (4′-Me), 7.56–8.17 (ArH),[i] 1.48 (t, J = 7 Hz, CH_2CH_3), 7.00 (br s, $H_{5'}$), 7.25 (br s, $H_{3'}$)	D
26	H	Mes	H	Pr	–:	7.20–7.58	6.15 (4.0)	(3.55) (t, J = 7.7 Hz)	1.28 (6′-Me), 2.59 (2′-Me), 2.45 (4′-Me), 7.62–8.19 (ArH),[i] 8.06 (mc, $H_{4,5}$), 1.22 (t, J = 6.3 Hz, CH_2CH_3), 1.86 (m, 10-$CH_2CH_2CH_3$), 7.07 (br s, $H_{5'}$), 7.30 (br s, $H_{3'}$)	D

Table I (Continued)

no.	R^{1b}	R^{2c}	R^3	R^{4b}	R^{5c}	$H_{1,8}$	H_9 ($W_{1/2}$, Hz)	10-Me (CH_2)	other absorptions	conformer
27	H	Mes	3-Me	Me	–:	6.80[e]	6.04 (3.7)	3.23	1.27 (6′-Me),[j] 2.52 (2′-Me),[m] 2.40 (4′-Me), 6.80–7.75 (ArH),[i] 7.88–8.15 ($H_{4,5}$), 2.52 (s, 3-Me)	D
28	H	Mes	3-Me	–:	Me	6.80[e]	5.94 (3.9)	3.60	1.00–2.80 (br, 2′-Me, 6′-Me), 2.36 (4′-Me), 6.80–7.92 (ArH),[i] 2.50 (3-Me)	B
29	H	Mes	3-Me	Et	–:	6.88[e]	6.03 (4.3)	(3.59) (q, J = 7.2 Hz)	1.27 (6′-Me), 2.56 (2′-Me), 2.40 (4′-Me), 6.88–8.10 (ArH),[i] 1.46 (t, J = 7.2 Hz, CH_2CH_3), 2.56 (s, 3′Me), 8.00 (mc, $H_{4,5}$)	D
30	H	Dur	H	Me	–:	7.16–7.45	6.26 (3.7)	3.27	1.19 (6′-Me), 2.18 (2′-Me), 2.49 (3′-, 5′-Me), 7.53–7.87 (ArH),[i] 7.90–8.18 ($H_{4,5}$), 7.27 (br s, $H_{4'}$)	D
31	H	Dur	H	Et	–:	7.18–7.52	6.26 (3.5)	(3.64) (q, J = 7.4 Hz)	1.21 (6′-Me), 2.20 (2′-Me), 2.51 (3′-, 5′-Me), 1.50 (t, J = 7.4 Hz, CH_2CH_3), 7.33 (br s, $H_{4'}$), 7.56–8.25 (ArH),[i] 8.07 (mc, $H_{4,5}$)	D
32	H	Dur	H	Pr	–:	7.17–7.53	6.27 (3.5)	(3.57) (t, J = 7.8 Hz)	1.21 (6′-Me), 2.20 (2′-Me), 2.52 (3′-, 5′-Me), 1.22 (t, J = 7.0 Hz, CH_2CH_3), 1.87 (m, $CH_2CH_2CH_3$), 7.34 (br, $H_{4'}$), 7.60–8.21 (ArH),[i] 8.10 (mc, $H_{4,5}$)	D
33	H	Dur	4-Me	Me	–:	7.01–7.46	6.29 (3.3)	3.27	1,23 (6′-Me), 2.22 (2′-Me), 2.50 3′-, 5′-Me), 2.91 (s, 4-Me), 7.31 (s, $H_{4'}$), 7.52–7.93 (ArH,[i] 7.99–8.26 ($H_{4,5}$)	D
34	H	Dur	4-Me	Et	–:	7.05–7.48	6.23 (3.8)	(3.64) (q, J = 7.1 Hz)	1.22 (6′-Me), 2.22 (2′-Me), 2.51 (3′-, 5′-Me), 1.51 (t, J = 7.1 Hz, CH_2CH_3), 2.92 (s, 4-Me), 7.31 (br s, $H_{4'}$), 7.51–8.20 (ArH),[i] 8.09 (mc, $H_{4,5}$)	D
35	H	Dur	1,4-Me_2	Me	–:	6.99[e]	6.22 (3.6)	3.10	1.09 (6′-Me), 2.06 (2′-Me), 2.43 (5′-Me), 2.63 (3′-Me), 1.75 (s, 1-Me), 2.83 (s, 4′-Me), 7.08 (br s, $H_{4'}$), 7.36 (s, $H_{2,3}$), 6.99–7.76 (ArH),[i] 7.78–8.05) (m, $H_{4,5}$)	D
36[h]	H	2,3,4-$Me_3C_6H_2$	H	Me	–:	7.02–7.45	5.66 (3.0)	3.28	1.53 (2′-Me), 2.44 (4′-Me), 2.26 (3′-Me), 7.18 (br s, $H_{2',3'}$), 7.45–7.80 (ArH),[i] 7.82–8.14 ($H_{4,5}$)	D
37	H	2,3,4-$Me_3C_6H_2$	H	–:	Me		5.91	3.72	2.22 (2′-Me), 2.42 (4′-Me), 2.36 (3′-Me)	B
38	CH_2	H	H	CH_2	–:		5.19	(3.43–3.77) (m)	2.20–2.60 (m, 9-CH_2), 7.37–8.10 (ArH)	
39	CH_2	Ph	H	CH_2	–:	7.26[e]		(3.50–3.84) (m)	2.59–2.92 (m, 9-CH_2), 7.26–7.93 (ArH),[i] 7.96–8.18 ($H_{4,5}$)	D
40	CH_2CH_2	Ph	H	CH_2	–:	6.65[e]		(3.46) (t, J = 5.8 Hz)	1.77-2.30 (m, 9-CH_2CH_2), 2.67 (t, 9-CH_2), 6.84 (mc, $H_{6'}$), 6.65-8.14 (ArH),[i] 7.79 (mc, $H_{4,5}$)	D

[a] Chemical shifts are reported in ppm downfield from tetramethylsilane as an internal standard. mc: The center of the multiplet signals resulting from these protons. [b] Pseudoaxial (a′) substituent. [c] Pseudoequatorial (e′) substituent. [d] The upfield shifts of $H_{1,8}$ were not observed. [e] The absorptions of the downfield side were overlapped with the absorptions of the other aromatic protons. [f] The absorption of 9-phenyl protons is included. [g] The absorption of $H_{3',5'}$ is included. [h] ^1H NMR ($CDCl_3$) δ 1.50 (s, 2′-Me), 2.23 (s, 3′-Me), 2.43 (s, 4′-Me), 3.42 (s, 10-Me), 5.70 (br s, H_9), 7.04–7.42 (m, $H_{5',6'}$ and $H_{1,8}$), 7.51–7.89 (m, ArH), 8.15–8.43 (m, $H_{4,5}$). [i] ArH means all aromatic protons except particularly indicated protons in each compound. [j] $W_{1/2}$ = 0.14 ppm. [k] $W_{1/2}$ = 0.11 ppm. [l] $W_{1/2}$ = 0.11 ppm. [m] Broad signal.

showed the methyl signal at quite a high field (δ 2.70) compared with the corresponding other isomer **2** (conformer D) (δ 3.39). The typical example for the difference of the chemical shifts of 10-methyl groups caused by the 9a′-aryl group between conformer A and conformer C is seen on the ^1H NMR spectra of the compounds **9** and **10** (see the paragraph at the end of the paper about supplementary material concerning the ^1H NMR spectra of the compounds **9** and **10**). The range of upfield shift of the 10-methyl groups goes to 0.59–0.80 ppm higher than the chemical shift (δ 3.31) of the methyl group of 10-methylthioxanthenium perchlorate.[2]

In conformers B and D, in which the aryl group adopts the e′ array, H_1 and H_8 of the thioxanthene ring are considered to be shielded by the anisotropic effect of the aryl group. Compound **21** showed the upfield shift signals of H_1 and H_8 at δ 7.32–7.62 which were clearly separated from other aryl protons. This upfield shift of H_1 and H_8 was similarly observed in compounds **2**, **2′**, **8**, **12**, **14**, **17**, **21**, **22**, **24–36**, **39**, and **40**. In the compounds having a phenyl group and another group at the 9-position, the bulkier group is considered to take an a′ array because of the steric repulsion with the peri hydrogens (H_1 and H_8). In compound **17**, since a bulkier isopropyl group occupies the 9a′-conformation and the 9-phenyl group is forced to exist in the e′-conformation, the upfield shift of H_1 and H_8 was

observed. The 9-aryl group possessing the methyl groups at the 2′- and/or 6′-positions as in the compounds **24–37** takes the e′ array, because of the great steric hindrance of the methyl group with the thioxanthene ring, which was easily confirmed by studying a Dreiding model. Moreover, in these compounds, since the rotation about the C_9–$C_{1'}$ bond is hindered and the 2′- or 6′-methyl group is fixed just under the thioxanthene ring and hence affected by the anisotropic effect of the thioxanthene ring, the methyl signal is shifted to very high field (δ 1.00–1.29).

Compound **39** or **40** has a bridged 9,10-alkano group, so it takes the 9a′,10a′-conformation.

In their investigation of the stereochemistry of thioxanthene 10-oxides, Ternay et al.[4] and we[5] observed that the half-height width ($w_{1/2}$) of the axial H_9 signal is broader than that of the equatorial H_9 because of the allylic coupling with peri hydrogens (H_1 and H_8) of the thioxanthene ring, and furthermore, observed that the chemical shift of the axial H_9 appears at higher field than that of the equatorial H_9 since the former proton is shielded and the latter is deshielded by the anisotropic effect of the thioxanthene ring. These observations were obtained in the ^{1}H NMR spectra of thioxanthenium salts, but are limited to the comparison between a pair of the conformational isomers possessing the same substituents at the 9- and 10(*S*)-positions, respectively, as shown in Table I. Compounds such as **18**, **19**, and **33–35** having a methyl group at the 4-position took the 10a′-conformation because of steric repulsion between the 10-alkyl group and a methyl group peri to the sulfur atom. This conformational assignment is similar to that of the sulfinyl oxygen atom of thioxanthene 10-oxides.[4,5] Similarly, compounds such as **19** and **23** having a methyl group at the 1-position take the 9a′-conformation of the aryl group except in the case of the compound **35** in which the bulkiness of the 2′- or 6′-methyl substituent prevents the aryl group from occupying a a′-conformation according to the reason mentioned before. In compound **35**, the methyl group at the 1-position was shielded by the 9e′-aryl group, and hence the methyl signal appeared at very high field (δ 1.75). On the contrary, the 1-methyl signal of compounds **19** and **23** appeared at δ 2.54 and 2.70, respectively.

In general, the absorptions of the 10a′-methyl groups appeared at higher field than δ 3.39 (δ 3.39–3.10) and those of 10e′-methyl groups appeared at lower than δ 3.48 (δ 3.48–3.66). However, in the case of the 9a′-aryl compounds, 10a′-methyl signals appeared at exceptionally higher field than δ 2.70 (δ 2.51–2.70).

The stereoisomers isolated here were not conformers by ring inversion (conformational isomers) but by pyramidal inversion (configurational isomers).

As described above, the stereostructures (conformers) of all 9,10-disubstituted thioxanthenium salts we synthesized could be determined by the detailed investigation of the ^{1}H NMR spectral data.

Next, in order to confirm the structure of the conformers determined only by ^{1}H NMR spectral data, we carried out the X-ray crystal analysis of a typical 10-alkyl-9-arylthioxanthenium salt, 10-methyl-9-phenylthioxanthenium tetrafluoroborate (**1′**) which has a nice crystal form for the X-ray analysis and was determined as conformer A by ^{1}H NMR as presented above.

Figure 1 is an ORTEP drawing of the *cis*-10-methyl-9-phenylthioxanthenium tetrafluoroborate (**1′**). The X-ray analysis reveals that both the 9-phenyl and 10-methyl groups occupy axial positions, which is the absolutely identical conformer with that determined on the basis of ^{1}H NMR spectral data. The six-membered heterocyclic ring has a boat conformation, namely the deviations of the sulfur atom and C_9 atom from planarity of the best plane were 0.384 (2) and 0.469 (7) Å, respectively. The dihedral angle between the planes of the two benzene rings is 139.5°. This is the first example of the X-ray analysis of the thioxanthenium salts.

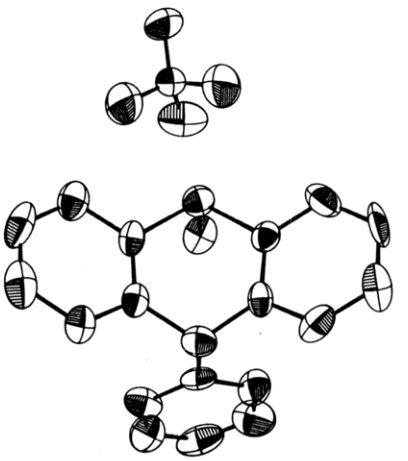


Figure 1. Perspective ORTEP drawing of *cis*-10-methyl-9-phenylthioxanthenium tetrafluoroborate (**1′**).

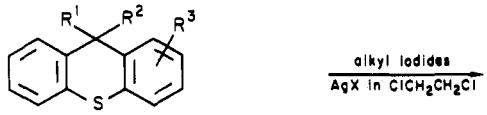
Thus, it was finally established that the ^{1}H NMR data can be a strong tool for the determination of the conformers of thioxanthenium salts. Moreover, it is expected that the ^{1}H NMR method is applicable for the conformational studies of analogous skeletons having other heteroatoms.

Synthesis of 10-Alkyl-9-arylthioxanthenium Salts (1–40). 10-Alkyl-9-arylthioxanthenium perchlorates **1–37** or tetrafluoroborates **1′** and **2′** were synthesized in high yield by the treatment of the corresponding 9-arylthioxanthenes **41–55** with alkyl iodides in the presence of silver perchlorate or silver tetrafluoroborate in 1,2-dichloroethane, respectively (Scheme II). Bridged thioxanthenium salts **38–40** were prepared by the intramolecular cyclization of the corresponding 9-aryl-9-halogenoalkylthioxanthenes **56–59** with silver perchlorate in 1,2-dichloroethane as shown in Scheme II. The melting points and yields of the thioxanthenium salts prepared are listed in Table II (Experimental Section). Some new thioxanthenes were prepared as shown in Scheme III. Thioxanthenes **43** and **44** were synthesized by the reaction of 9-phenylthioxanthylium perchlorate (**60**) with methyl- or propylmagnesium iodide, respectively. Thioxanthene **54** was prepared from the reaction of 1,4-dimethylthioxanthylium perchlorate (**61**) and 2,3,5,6-tetramethylphenyl (duryl)-magnesium bromide. Thioxanthene **56** was obtained by chlorination of 2-(thioxanthen-9-yl)ethanol (**62**)[7] with thionyl chloride. Thioxanthene **56** was easily converted to the corresponding iodide **57** by treatment with sodium iodide. Thioxanthene **58** was synthesized the following way. Condensation of **60** with diethyl malonate afforded **63**[8] which was hydrolyzed and then decarboxylated to give **64**. Esterification of **64** gave **65** which was reduced with

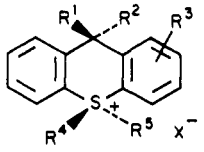
(7) Okabayashi, I.; Miyoshi, F.; Arimoto, M. *Yakugaku Zasshi* **1972**, *92*, 1390.

(8) Hori, M.; Kataoka, T.; Asahi, Y.; Mizuta, E. *Chem. Pharm. Bull.* **1973**, *21*, 1415.

Scheme II[a]

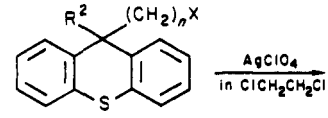


41, R^1 = Ph; R^2 = R^3 = H
42, R^1 = C_6D_5; R^2 = R^3 = H
43, R^1 = Ph; R^2 = Me; R^3 = H
44, R^1 = Ph; R^2 = Pr; R^3 = H
45, R^1 = Ph; R^2 = *i*-Pr; R^3 = H
46, R^1 = Ph; R^2 = H; R^3 = 4-Me
47, R^1 = Ph; R^2 = H; R^3 = 1,4-Me_2
48, R^1 = C_6F_5; R^2 = R^3 = H
49, R^1 = C_6F_5; R^2 = H; R^3 = 1-Me
50, R^1 = Mes;[a] R^2 = R^3 = H
51, R^1 = Mes; R^2 = H; R^3 = 3-Me
52, R^1 = Dur;[b] R^2 = R^3 = H
53, R^1 = Dur; R^2 = H; R^3 = 4-Me
54, R^1 = Dur; R^2 = H; R^3 = 1,4-Me_2
55, R^1 = 2,3,4-$Me_3C_6H_2$; R^2 = R^3 = H

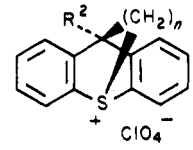


X = ClO_4, BF_4

1-37



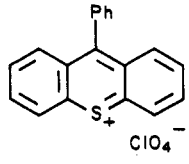
56, R^2 = H; X = Cl; *n* = 2
57, R^2 = H; X = I; *n* = 2
58, R^2 = Ph; X = Cl; *n* = 2
59, R^2 = Ph; X = I; *n* = 3



38-40

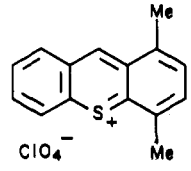
[a] Mes = 2,4,6-trimethylphenyl(mesityl). [b] Dur = 2,3,5,6-tetramethylphenyl(duryl).

Scheme III



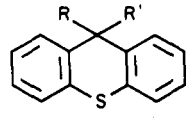
60

R^2MgI → 43 or 44



61

DurMgBr → 54



62, R = H; R′ = $(CH_2)_2OH$
63, R = Ph; R′ = $CH(CO_2Et)_2$
64, R = Ph; R′ = CH_2CO_2H
65, R = Ph; R′ = CH_2CO_2Et
66, R = Ph; R′ = $(CH_2)_2OH$
67, R = Ph; R′ = $(CH_2)_3SPh$

$LiAlH_4$ to lead to **66**. Chlorination of **66** with thionyl chloride afforded **58** in good yield. Thioxanthene **59** was synthesized from the reaction of **60** and (3-(phenylthio)-propyl)magnesium bromide[9] (yielding **67**) followed by treatment of **67** with a mixture of methyl iodide and sodium iodide in DMF.

Table II. Preparation of 10-Alkyl-9-arylthioxanthenium Salts (1-40)[a,r]

no.	appearance	recrystallization solvent	mp, °C, dec	yield, %
1	leaflets	CH_2Cl_2–ether	160–162	99[c]
2	needles	CH_2Cl_2–ether	156–159	
1′	needles	CH_2Cl_2–ether	158–159	97[d]
2′	plates	EtOH–ether	147–149	
3	leaflets	CH_2Cl_2–ether	164–166	88[e]
4[b]				
5	needles	CH_2Cl_2–ether	163–165	86[f]
6	prisms	CH_2Cl_2–ether	160–162	
7	needles	CH_2Cl_2–ether	155–158	93[g]
8[b]				
9	rhombs	Me_2CO–AcOH–ether	191–193	97[h]
10	needles	Me_2CO–AcOH–ether	189–191	
11	needles	CH_2Cl_2–ether	144–147	90[i]
12	prisms	CH_2Cl_2–ether	175–177	
13	prisms	CH_2Cl_2–ether	138–140	36[j]
14	needles	CH_2Cl_2–ether	140–141	
15	needles	CH_2Cl_2–ether	141–143	66[k]
16[b]				
17	prisms	CH_2Cl_2–ether	188–192	91
18	needles	CH_2Cl_2–ether	178–179	63
19	needles	CH_2Cl_2–ether	179–181	72
20	needles	Me_2CO–ether	178[l]	87[m]
21	prisms	Me_2CO	216–218	
22	needles	Me_2CO–ether	176–178	30
23	plates	CH_2Cl_2–ether	172–176	95
24[n]	needles	CH_2Cl_2–ether	209–216	94
25[n]	prisms	CH_2Cl_2–ether	181–183	93
26[n]	needles	CH_2Cl_2–ether	170–174	93
27	scales	CH_2Cl_2–MeOH	189–193	93[o]
28	needles	CH_2Cl_2–MeOH	172–176	
29	needles	CH_2Cl_2–ether	151–153	89
30[n]	needles	CH_2Cl_2–ether	215–217	97
31[n]	scales	CH_2Cl_2–ether	191–192	93
32[n]	needles	CH_2Cl_2–ether	185–187	91
33	plates	CH_2Cl_2–ether	211–217	98
34	needles	CH_2Cl_2–ether	171–176	63
35	scales	MeOH	202–207	71
36	needles	CH_2Cl_2–ether	191–192	90
37[b]				
38	needles	CH_2Cl_2–ether	210–213	94[p], 95[q]
39	needles	Me_2CO–ether	220–224	93
40	rhombs	CH_2Cl_2–ether	193–195	59

[a] All compounds are perchlorate salts except 1′ and 2′ which are tetrafluoroborate salts. See Table I on the substituents at the 9- and 10-positions and on the benzene rings of the thioxanthene skeleton. [b] Not separated. [c] The ratio of 1 and 2 (1/2) = 3.9 (by NMR). [d] 1′/2′ = 4 (by NMR). [e] 3/4 = 3.4 (by NMR). [f] 5/6 = 3.9 (by NMR). [g] 7/8 = 3.6 (by NMR). [h] 9/10 = 3.6 (by NMR). [i] 11/12 = 6.1 (by NMR). [j] Trace amounts of **14**. [k] Trace amounts of **16**. [l] After melting, it changed to another isomer **21**. [m] These two isomers are mutually interconverted during recrystallization (**20**/**21** = 0.83). [n] References 1c and 1d. [o] **27**/**28** = 7 (by NMR). [p] The yield from **56**. [q] The yield from **57**. [r] Satisfactory combustion analytical data (±0.3%) for CH were obtained for these compounds.

Experimental Section

Melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. Microanalyses were performed at the Microanalytical Laboratory of our college. ^1H nuclear magnetic resonance (^1H NMR) spectra were recorded on a Hitachi R-20B spectrometer with tetramethylsilane as an in-

(9) This Grignard reagent was prepared from 3-(phenylthio)propyl bromide[10] and magnesium in ether.
(10) Yano, Y.; Oae, S. *Tetrahedron* **1970**, *29*, 67.
(11) Corey, E. J.; Jautelat, M. *Tetrahedron Lett.* **1968**, 5787.

ternal standard. Infrared (IR) spectra were determined on a JASCO Model IRA-1.

Materials. The following thioxanthenes were prepared by the reported methods: 9-phenylthioxanthene (**41**),[12] 9-(pentadeuteriophenyl)thioxanthene (**42**),[13] 9-isopropyl-9-phenylthioxanthene (**45**),[13] 4-methyl-9-phenylthioxanthene (**46**),[13] 1,4-dimethyl-9-phenylthioxanthene (**47**),[13] 9-(pentafluorophenyl)thioxanthene (**48**),[13] 1-methyl-9-(pentadeuteriophenyl)thioxanthene (**49**),[13] 9-mesitylthioxanthene (**50**),[1d] 3-methyl-9-mesitylthioxanthene (**51**),[1d] 9-durylthioxanthene (**52**),[1d,14] 4-methyl-9-durylthioxanthene (**53**),[13] (2,3,4-trimethylphenyl)thioxanthene (**55**).[1d] Some of 10-alkyl-9-arylthioxanthenium perchlorates were prepared by the reported procedures: 9-mesityl-10-methylthioxanthenium perchlorate (**24**),[1d] 10-ethyl-9-mesitylthioxanthenium perchlorate (**25**),[1d] 9-mesityl-10-propylthioxanthenium perchlorate (**26**),[1d] *cis*- and *trans*-3,10-dimethyl-9-mesitylthioxanthenium perchlorates (**27**, **28**),[1d] 9-duryl-10-methylthioxanthenium perchlorate (**30**),[1d] 9-duryl-10-ethylthioxanthenium perchlorate (**31**),[1d] 9-duryl-10-propylthioxanthenium perchlorate (**32**),[1d] *cis*- and *trans*-10-methyl-9-(2,3,4-trimethylphenyl)thioxanthenium perchlorates (**36**, **37**).[1d]

10-Methyl-9-phenylthioxanthenium Tetrafluoroborates (1′ and 2′). To a solution of 9-phenylthioxanthene (**41**, 1 g) and methyl iodide (5.2 g) in 1,2-dichloroethane (20 mL) was added silver tetrafluoroborate (713 mg) in limited amounts with stirring and the mixture was stirred at room temperature for 30 h. The reaction mixture was filtered and the filtrate was diluted with ether to precipitate 1.15 g (97%) of crystals as a mixture of 1′ and 2′, which were separated by fractional recrystallization from CH_2Cl_2–ether. The results are shown in Tables I and II.

10-Alkyl-9-arylthioxanthenium Perchlorates (1–40). 1 and 2. To a solution of 9-phenylthioxanthene (**41**, 1 g) and methyl iodide (5 g) in 1,2-dichloroethane (20 mL) was added silver perchlorate ($AgClO_4$) (900 mg) in limited amounts with stirring and the mixture was stirred overnight. The precipitate was filtered off and washed with hot acetone. The filtrate was concentrated to ca. 10 mL in vacuo and diluted with ether to afford a mixture of **1** and **2**. Fractional recrystallization from CH_2Cl_2–ether gave colorless leaflets **1** and colorless needles **2**.

In a similar manner as above, the thioxanthenium perchlorates (**3–26**, **29–37**) were prepared from the corresponding thioxanthenes and alkyl iodides in the presence of $AgClO_4$. The results are shown in Tables I and II.

39. To a solution of **58** (660 mg) in 1,2-dichloroethane (40 mL) was added $AgClO_4$ (550 mg) in limited amounts with stirring and the mixture was stirred for 3 h. The precipitate was filtered off and washed with hot acetone. The filtrate was concentrated to ca. 10 mL in vacuo and diluted with ether to afford **39**. Recrystallization from acetone–ether gave colorless needles.

In a similar manner as above, bridged thioxanthenium perchlorates (**38** and **40**) were prepared. The results are shown in Tables I and II.

9-Methyl-9-phenylthioxanthene (43). To an ethereal solution of methylmagnesium iodide prepared from methyl iodide (6 g), Mg (1.4 g), and ether (60 mL) was added 9-phenylthioxanthylium perchlorate (**60**,[12b] 5 g) in limited amounts with stirring and the mixture was refluxed for 1 h. After treatment with an NH_4Cl solution, the organic layer was separated, washed with water, and then dried over anhydrous $MgSO_4$. Removal of the solvent gave solids which were recrystallized from CH_2Cl_2–MeOH to afford 2.8 g (72%) of **43** as colorless needles: mp 138–140 °C; ^1H NMR ($CDCl_3$) δ 2.02 (s, 9-Me), 6.57–6.91 (m, ArH), 6.92–7.54 (m, ArH).

9-Phenyl-9-propylthioxanthene (44). In a similar manner as with **43**, the crude oil of **44** was obtained from the reaction of **60** with propylmagnesium bromide. The oil was purified by column chromatography on silica gel with petroleum ether to afford 56% of **44** and 14% of reduction product, **41**, of **60**. **44**: colorless needles (ether–MeOH); mp 98–100 °C; ^1H NMR ($CDCl_3$) δ 0.53–1.43 (m, $CH_2CH_2CH_3$), 2.08–2.46 (m, $CH_2CH_2CH_3$), 6.60–7.50 (m, ArH).

1,4-Dimethyl-9-durylthioxanthene (54). To a solution of durylmagnesium bromide prepared from duryl bromide (6.3 g), Mg (720 mg), THF (20 mL), and catalytic amounts of I_2 was added ether (30 mL) and then 1,4-dimethylthioxanthylium perchlorate (**61**,[13] 3.2 g) in limited amounts with stirring and the mixture was refluxed for 30 min. After treatment with an NH_4Cl solution, the reaction mixture was extracted with CH_2Cl_2 and the organic layer was separated, washed with water, and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was recrystallized from chloroform–MeOH and afforded 2.2 g (62%) of **54** as colorless needles: mp 210–212 °C; ^1H NMR ($CDCl_3$) δ 1.75 (s, 1-Me), 1.85 (br, 6′-Me), 2.16 (br, 3′- and 5′-Me), 2.34 (br, 2′-Me), 6.10 (s, H_9), 6.51–7.25 (m, ArH). Anal. Calcd for $C_{25}H_{26}S$: C, 83.75; H, 7.31. Found: C, 83.83; H, 7.31.

9-(2-Chloroethyl)thioxanthene (56). To a solution of 2-(thioxanthen-9-yl)ethanol (**62**,[7] 7.5 g) in chloroform (40 mL) was added dropwise thionyl chloride (8 mL) and the mixture was refluxed for 2 h. Removal of the solvent and excess thionyl chloride gave an oil which soon solidified. Recrystallization from petroleum ether afforded 6.7 g (83%) of **56** as colorless prisms: mp 68–69 °C; ^1H NMR ($CDCl_3$) δ 2.10 (dt, J = 7.6 and 6.0 Hz, CH_2CH_2Cl), 3.31 (t, J = 6 Hz, CH_2CH_2Cl), 4.32 (t, J = 7.6 Hz, H_9), 6.98–7.45 (m, ArH). Anal. Calcd for $C_{15}H_{13}ClS$: C, 69.09; H, 5.02. Found: C, 69.30; H, 4.99.

9-(2-Iodoethyl)thioxanthene (57). A mixture of **56** (2 g), sodium iodide (1.7 g), and acetone (40 mL) was refluxed for 36 h. The solvent was evaporated to dryness and the residue was extracted with ether. The extract was concentrated to give an oil which soon solidified. Recrystallization from hexane gave 2.4 g (89%) of **57** as colorless needles: mp 102–104 °C; ^1H NMR ($CDCl_3$) δ 2.15 (dt, J = 7.1 and 6.3 Hz, CH_2CH_2I), 4.19 (t, J = 7.1 Hz, H_9), 6.98–7.51 (m, ArH), 2.96 (t, J = 6.3 Hz, CH_2CH_2I). Anal. Calcd for $C_{15}H_{13}IS$: C, 51.15; H, 3.72. Found: C, 51.33; H, 3.74.

Diethyl (9-Phenylthioxanthen-9-yl)malonate (63). To a solution of diethyl malonate (5.7 g) in THF (60 mL) were added NaH (1.1 g, 50% dispersion in oil) and then **60** (8 g) in limited amounts with stirring. After the mixture was stirred for 1 h at room temperature, the reaction mixture was poured into cold water and extracted with ether. The extract was washed with water and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave an oil which was crystallized by adding petroleum ether. Recrystallization from CH_2Cl_2–hexane afforded 8.1 g (87%) of **63** as colorless prisms: mp 104–106 °C (lit.[8] 105 °C).

(9-Phenylthioxanthen-9-yl)acetic Acid (64). A mixture of **63** (3.25 g), NaOH (4 g), and methyl cellosolve (40 mL) was refluxed for 5 h. The reaction mixture was poured into cold water, acidified with concentrated HCl, and extracted with CH_2Cl_2. The extract was washed with water and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the residue recrystallized from acetone–hexane gave 2 g (80%) of **64** as colorless leaflets: mp 199–201 °C; IR (KBr) 3310–2700 (CO_2H), 1720 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ 3.40 (s, 9-CH_2), 6.68 (br, CO_2H), 6.83–7.60 (m, ArH). Anal. Calcd for $C_{21}H_{16}O_2S$: C, 75.88, H, 4.85. Found: C, 76.04; H, 4.79.

Ethyl (9-Phenylthioxanthen-9-yl)acetate (65). A mixture of **64** (2 g), sulfuric acid (3 drops), and EtOH (30 mL) was refluxed for 10 h. After cooling, the reaction mixture was poured into cold water and extracted with CH_2Cl_2. The extract was washed with a Na_2CO_3 solution and then water and dried over $MgSO_4$. Removal of the solvent gave an oil which soon solidified, was recrystallized from CH_2Cl_2–EtOH, and afforded 1.99 g (92%) of **65** as colorless prisms: mp 136–138 °C; IR (KBr) 1732 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ 0.99 (t, J = 7 Hz, CH_2CH_3), 3.36 (s, 9-CH_2), 3.85 (q, J = 7 Hz, CH_2CH_3), 6.83–7.43 (m, ArH). Anal. Calcd for $C_{23}H_{20}O_2S$: C, 76.64; H, 5.59. Found: C, 76.64; H, 5.46.

2-(9-Phenylthioxanthen-9-yl)ethanol (66). To a solution of **65** (1 g) in ether (15 mL) was added $LiAlH_4$ (300 mg) in limited amounts with stirring and the mixture was refluxed for 3 h. The reaction mixture was treated with an NH_4Cl solution and the organic layer was separated and dried over anhydrous $MgSO_4$. Removal of the solvent gave an oil which was distilled to afford 810 mg (92%) of **66** as a colorless oil: bp 190 °C (0.1 mmHg);

(12) (a) Cappozzi, G.; Melloni, G.; Modena, G. *J. Chem. Soc., Perkin Trans 1* **1973**, 2250. (b) Price, C. C.; Hori, M.; Parasaran, T.; Polk, M. *J. Am. Chem. Soc.* **1963**, *85*, 2278. (c) Schönberg, A.; Asker, W. *J. Chem. Soc.* **1942**, 274.

(13) Ohno, S.; Shimizu, H.; Kataoka, T.; Hori, M. *Chem. Pharm. Bull.*, in press.

(14) Maryanoff, B. E.; Stackhouse, J.; Senkler, G. H., Jr.; Mislow, K. *J. Am. Chem. Soc.* **1975**, *97*, 2718.

IR (neat) 3325 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 1.47 (br, OH), 2.58 (t, J = 6.9 Hz, 9-CH_2), 3.49 (t, J = 6.9 Hz, CH_2OH), 6.64-7.36 (m, ArH).

9-(2-Chloroethyl)-9-phenylthioxanthene (58). To a solution of **66** (700 mg) in benzene (10 mL) was added dropwise thionyl chloride (2 mL) and the mixture was refluxed for 1 h. Evaporation of the solvent gave an oil which soon solidified, was recrystallized from CH_2Cl_2-MeOH, and afforded 697 mg (94%) of **58** as colorless needles: mp 126-128 °C; ^1H NMR ($CDCl_3$) δ 2.60-2.99 (m, 9-CH_2), 3.10-3.47 (m, CH_2Cl), 6.58-7.38 (m, ArH). Anal. Calcd for $C_{21}H_{17}ClS$: C, 74.87; H, 5.09. Found: C, 74.84; H, 5.00.

9-Phenyl-9-(3-(phenylthio)propyl)thioxanthene (67). To a solution of (3-(phenylthio)propyl)magnesium bromide prepared from 3-(phenylthio)propyl bromide[10] (6.2 g), Mg (650 mg), ether (50 mL), and catalytic amounts of I_2 was added **60** (4 g) in limited amounts with stirring. After refluxing for 30 min, the reaction mixture was treated with an NH_4Cl solution. The organic layer was separated, dried over anhydrous $MgSO_4$, and evaporated to dryness to give an oil which was purified by column chromatography on silica gel using CH_2Cl_2-petroleum ether (1:4). Recrystallization of the resulting solids from hexane gave 3 g (66%) of **67** as colorless needles: mp 95-97 °C; ^1H NMR ($CDCl_3$) δ 1.19-1.75 (m, 9-CH_2CH_2), 2.29-2.68 (m, 9-CH_2), 2.75 (t, J = 6.5 Hz, CH_2S), 6.55-7.35 (m, ArH). Anal. Calcd for $C_{28}H_{24}S_2$: C, 79.20; H, 5.70. Found: C, 79.27; H, 5.69.

9-(3-Iodopropyl)-9-phenylthioxanthene (59). A mixture of **67** (1.4 g), sodium iodide (1.5 g), methyl iodide (5 mL), and DMF (10 mL) was refluxed for 24 h. The reaction mixture was poured into cold water and extracted with ether. The extract was washed with water, dried over anhydrous $MgSO_4$, and evaporated in vacuo. The residue was recrystallized from hexane to afford 1.27 g (87%) of **59** as colorless prisms: mp 111-113 °C; ^1H NMR ($CDCl_3$) δ 1.35-1.88 (m, 9-CH_2CH_2), 2.22-2.60 (m, 9-CH_2), 2.98 (t, J = 6.4 Hz, CH_2I), 6.50-7.37 (m, ArH). Anal. Calcd for $C_{22}H_{19}IS$: C, 59.73; H, 4.33. Found: C, 59.89; H, 4.32.

X-ray Analysis of 1'. Crystal data: $C_{20}H_{17}BF_4S$, FW = 376.22, orthorhombic, $P2_12_12_1$, a = 9.976 (7) Å, b = 12.099 (5) Å, c = 14.700 (8) Å, U = 1774.2 Å^3, Z = 4, D_x = 1.41 g/cm^3, μ(Mo Kα) = 2.3 cm^{-1}. The cell dimensions and intensities were measured on a Syntex R3 four-circle diffractometer with graphite-monochromated Mo Kα radiation with ω-scan mode within 2θ less than 50°. A total of 1805 independent reflections were collected, among which 1130 reflections ($I > 1.96\sigma(I)$) were stored as observed. The structure was solved by the direct method using MULTAN in Syntex XTL program.[15] A block-diagonal least-squares method was applied to the refinement with anisotropic temperature factors for all the non-hydrogen atoms. The R value was 0.08. Atomic co-ordinates and thermal parameters, bond distances and angles, and the deviations of atoms from the least-squares planes are listed in Tables III, IV, and V (see the paragraph at the end of the paper about supplementary material concerning X-ray data tables for the compound 1'). The structure factor table (33 pages) is available from the author.

Registry No. 1, 73083-61-1; 1', 91127-92-3; 2, 73083-59-7; 2', 53996-55-7; 3, 91127-40-1; 4, 91127-41-2; 5, 91199-12-1; 6, 54053-51-9; 7, 91127-43-4; 8, 91156-92-2; 9, 73083-67-7; 10, 73083-65-5; 11, 73083-71-3; 12, 73083-69-9; 13, 91127-45-6; 14, 91127-47-8; 15, 91127-49-0; 16, 91127-51-4; 17, 91127-53-6; 18, 91127-55-8; 19, 91127-57-0; 20, 73083-87-1; 21, 73083-85-9; 22, 91127-59-2; 23, 91127-61-6; 24, 90133-33-8; 25, 90133-62-3; 26, 90133-64-5; 27, 73083-79-1; 28, 73083-77-9; 29, 91127-63-8; 30, 66571-82-2; 31, 66571-84-4; 32, 66571-86-6; 33, 91127-65-0; 34, 91127-67-2; 35, 91127-69-4; 36, 90133-42-9; 37, 91127-71-8; 38, 91127-72-9; 39, 73083-90-6; 40, 91127-74-1; 41, 35500-04-0; 42, 71031-54-4; 43, 41959-21-1; 44, 91127-75-2; 45, 91127-76-3; 46, 91127-77-4; 47, 91127-78-5; 48, 59181-69-0; 49, 91127-79-6; 50, 53512-25-7; 51, 90133-34-9; 52, 66572-01-8; 53, 91127-80-9; 54, 91127-81-0; 55, 90133-60-1; 56, 91127-82-1; 57, 91127-83-2; 58, 91127-84-3; 59, 91127-85-4; 60, 42528-40-5; 61, 91127-87-6; 62, 40020-62-0; 63, 42528-50-7; 64, 91127-88-7; 65, 91127-89-8; 66, 91127-90-1; 67, 91127-91-2; methyl iodide, 74-88-4; propyl bromide, 106-94-5; duryl bromide, 1646-53-3; diethyl malonate, 105-53-3; 3-(phenylthio)propyl bromide, 3238-98-0.

Supplementary Material Available: ^1H NMR spectra of 1 and 7 (Figure 2) and 9 and 10 (Figure 3), X-ray data tables for the compound 1', atomic co-ordinates (x10^4) and thermal parameters for non-hydrogen atoms with their estimated standard deviations (Table III), bond distances (Å) and angles (deg) involving non-hydrogen atoms with their estimated standard deviations (Table IV), the deviations of atoms from the least-squares planes (Å) with their estimated standard deviations (Table V) (5 pages). Ordering information is given on any current masthead page.

(15) Mermain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A.* **1971**, *27*, 368.

3,8-Bis(trimethylsiloxy)-6-bromo-6,7-dihydro-1-phenyl-1*H*-phosphonin 1-Oxide and Its Conversion to a Phosphonin Oxide and a Cyclopenta-λ^5-phosphorin[1]

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Quantitative silylation of 5,6-dibromo-1-phenyl-3,8-phosphonanedione 1-oxide occurs with bis(trimethylsilyl)trifluoroacetamide, providing the 3,8-bis(trimethylsiloxy) derivative. Reaction of this water-sensitive compound with 1 equiv of triethylamine accomplishes elimination of HBr to give the title dihydrophosphonin derivative. Heating this compound in an inert solvent at 80 °C effects intramolecular ring closure with an accompanying silyl migration from C-O to P-O, providing the novel 1,3-bis(trimethylsiloxy)-1-phenylcyclopenta[*b*]-λ^5-phosphorin-7-one. Hydrolysis of this compound gave a crystalline diketo phosphoryl derivative of the bicyclic system. When the monobromo compound was reacted further with triethylamine, 3,8-bis(trimethylsiloxy)-1-phenyl-1*H*-phosphonin 1-oxide was formed along with the bicyclic product.

The bis(trimethylsilyl) ethers (1) of the bis(enolic) form of 3,8-phosphonane oxides[2] can be viewed as tetrahydrophosphonin derivatives, and are therefore of interest in synthetic work designed to achieve the fully unsaturated phosphonin system.[3] Such a synthesis would be facilitated by using 3,8-phosphonanediones that possess additional substituents on the ring in proper locations for elimination reactions. The 5,6-epoxy (2) and 5,6-dibromo (3) deriva-

(1) Taken from the doctoral dissertation of Rao, N. S., 1983. Supported by National Science Foundation Grant CHE-7717876.

(2) Quin, L. D.; Middlemas, E. D.; Rao, N. S. *J. Org. Chem.* **1982**, *47*, 905.

(3) Quin, L. D.; Rao, N. S. *J. Am. Chem. Soc.* **1983**, *105*, 5960.

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