Crystal Structure and Nuclear Magnetic Resonance and Infrared Spectra of 9,9-Dideuteriothioxanthenium Bis(carboethoxy)methylide, Dimethyl 9-(1,4-Dimethylthioxanthenyl)malonate, Thioxanthonium Bis(carbomethoxy)methylide, and Related Compounds

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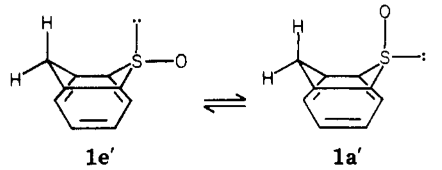
The single-crystal X-ray structures of the sulfonium ylides 9,9-dideuteriothioxanthenium bis(carboethoxy)methylide and thioxanthonium bis(carbomethoxy)methylide reveal that both molecules are folded about an imaginary line connecting C(9) and S (138° and 169°, respectively). Like the corresponding sulfoxides, the methylide carbon is pseudoequatorial (e′) in both ylides. The malonylide fragment resides in the plane which bisects the "angle of the fold" of the heterocycle. The oxygen of one carbonyl group ("endo") is arrayed essentially trans to the nonbonding electron pair on sulfur. Dimethyl 9-(1,4-dimethylthioxanthenyl)malonate exists with the malonyl fragment in the pseudoaxial (a′) position. ^{13}C resonances of a′ methylide carbons in these thioxanthenium ylides occur downfield of corresponding e′ methylide carbons (67 vs. 54 ppm). The methylide carbons of related thioxanthonium ylides resonate near 60 ppm, reflecting their intermediate geometry. Both ^1H and ^{13}C NMR spectra indicate a relatively high rotational barrier about the $S^+–C^-$ bond in bis(carbomethoxy)methylides derived from thioxanthone, 2-chlorothioxanthone, and 2,4-dimethylthioxanthone. Infrared spectra can be used to distinguish isomeric ylides and thioxanthenes.

Sulfonium ylides, like sulfonium salts and sulfoxides, are pyramidally stable and, in appropriate ring systems, give rise to conformational and configurational isomers. The consequences of such isomerism in a series of thioxanthene sulfoxides have been explored by us.[1] Among the conclusions reached in these studies, one was that the preferred conformation of the sulfinyl oxygen in simple thioxanthene sulfoxides, including thioxanthene sulfoxide (1)



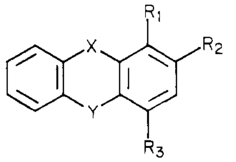
1e′ **1a′**

itself, generally was pseudoequatorial (e′) rather than pseudoaxial (a′). It also was shown that the conformation of such e′ sulfoxides could be biased toward the a′ position by incorporating a substituent at C(4) (i.e., peri to the sulfinyl group).[2,3]

Thioxanthone sulfoxide (**2**, Chart I) also exists in the e′ conformation.[5] However, this system is much less folded than are similar thioxanthene sulfoxides.

As part of our continuing study of the stereochemistry of heterocycles, particularly those of biomedical significance, we have begun to investigate the structure of ylides of neuroleptic agents. In this report we present the structures of an e′ thioxanthenium methylide [9,9-dideuteriothioxanthenium bis(carboethoxy)methylide (**3**)], a related thioxanthene [dimethyl 9-(1,4-dimethylthioxanthenyl)malonate (**4**)], and an e′ thioxanthonium meth-

Chart I



	X	Y	R_1	R_2	R_3
1	CH_2	S(O)	H	H	H
2	C=O	S(O)	H	H	H
3	CD_2	$S^+–C^-(CO_2C_2H_5)_2$	H	H	H
4	$CHCH(CO_2CH_3)_2$	S	CH_3	H	CH_3
5	C=O	$S^+–C^-(CO_2CH_3)_2$	H	H	H
6	C=O	S	H	H	H
7	C=O	S	H	Cl	H
8	C=O	S	H	CH_3	CH_3
9	C=O	S	CH_3	H	CH_3
10	O	S	H	H	H
11	S(O)	S(O)	H	H	H
12	$CHCH_3$	S(O)	H	CH_3	CH_3
13	CH_2	S(O)	CH_3	H	CH_3
14	O	S(O)	H	H	H
15	$CHCH_3$	S(O)	H	H	H
16	CD_2	$S^+–C^-(CO_2C_2H_5)_2$	CH_3	H	CH_3
17	CH_2	$S^+–C^-(CO_2CH_3)_2$	CH_3	H	CH_3
18	CH_2	$S^+–C^-(CO_2CH_3)_2$	H	Cl	H
19	CH_2	$S^+–C^-(CO_2CH_3)_2$	H	H	H
20	CH_2	S	CH_3	H	CH_3
21	C=O	$S^+–C^-(CO_2CH_3)_2$	H	Cl	H
22	C=O	$S^+–C^-(CO_2CH_3)_2$	H	CH_3	CH_3
23	C=O	$S^+–C^-(CO_2CH_3)_2$	CH_3	H	CH_3

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[1] For the most recent publication see A. L. Ternay, Jr., J. Herrmann, B. R. Hayes, and P. Joseph-Nathan, *J. Org. Chem.*, **45**, 189 (1980).

[2] A. L. Ternay, Jr., L. Ens, J. Herrmann, and S. Evans, *J. Org. Chem.*, **34**, 940 (1969).

[3] The conformation may be altered (e′ → a′) by complexing with halogens[4] and by hydrogen bond formation.[1]

[4] A. L. Ternay, Jr., J. Herrmann, M. Harris, and B. R. Hayes, *J. Org. Chem.*, **42**, 2010 (1977).

[5] S. S. C. Chu, *Acta Crystallogr., Sect. B*, **B32**, 1583 (1976).

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Table I. Interatomic Distances (Å) for Dimethyl 9-(1,4-Dimethylthioxanthenyl)malonate (4)

S(10)-C(12)	1.770 (3)	C(9)-C(11)	1.513 (4)
S(10)-C(13)	1.755 (3)	C(9)-C(14)	1.510 (5)
C(1)-C(2)	1.401 (4)	C(9)-C(17)	1.556 (4)
C(1)-C(11)	1.410 (3)	C(11)-C(12)	1.403 (3)
C(1)-C(15)	1.496 (4)	C(13)-C(14)	1.385 (3)
C(2)-C(3)	1.366 (4)	C(17)-C(18)	1.513 (5)
C(3)-C(4)	1.384 (4)	C(18)-O(19)	1.201 (3)
C(4)-C(12)	1.393 (4)	C(18)-O(20)	1.327 (4)
C(4)-C(16)	1.497 (4)	O(20)-C(21)	1.436 (6)
C(5)-C(13)	1.402 (5)	C(17)-C(22)	1.518 (4)
C(5)-C(6)	1.368 (5)	C(22)-O(23)	1.194 (4)
C(6)-C(7)	1.373 (4)	C(22)-O(24)	1.322 (3)
C(7)-C(8)	1.388 (6)	O(24)-C(25)	1.440 (5)
C(8)-C(14)	1.388 (15)		

ylide [thioxanthonium bis(carbomethoxy)methylide (**5**)].

Recently,[6] we prepared thioxanthenium methylides which, because of peri substitution at C(4),[2] *must* exist with the methylide carbon in the a′ position. Using these as model compounds, and not making any other assumptions, it was possible to demonstrate that simple ylides of thioxanthene (i.e., those lacking substituents at C(4)/C(5) and C(9)) exist in the e′ conformation. Our ^1H NMR data also established that a′ or e′ S^+–C^- $(CO_2R)_2$ moieties influenced the chemical shifts of protons at C(9) in a manner similar to what we had already observed for the corresponding sulfoxides. For example, in an a′ ylide the C(9) $H_{a'}$ was significantly deshielded, as in the corresponding sulfoxide.[7]

Results thus far[1] have indicated that sulfoxides of thioxanthene generally have the same conformation in solution as is found in the solid state. Such studies have drawn heavily upon ^1H NMR spectroscopy. While ^1H NMR has been of value in the study of simple thioxanthenium ylides, it is not as valuable for conformational analysis when (a) there are no protons at C(9) (e.g., C=O), (b) C(9) has been replaced by a heteroatom (e.g., S), or (c) there are two magnetically similar groups on S (e.g., O^- and $^-CR_2$). In order to surmount such limitations, we have begun to probe the conformation of the methylide fragment directly, with the aid of ^{13}C NMR. In this manuscript we describe the solution conformational analysis (a′ vs. e′) of sulfonium ylides derived from thioxanthenes and thioxanthones based upon ^{13}C NMR spectra. A rationale for the observed rotomeric distribution found about the S^+–C^- bonds in such ylides, based upon repulsions between nonbonding electron pairs, also is presented.

Results and Discussion.

Syntheses. The compounds used in this study have been prepared by the elegant procedure employed extensively by Ando,[9] i.e., the reaction of a sulfide with a dialkyl diazomalonate in the presence of anhydrous copper(II) sulfate. It was observed that yields could be improved to approximately 80% through the use of a "solvent" (e.g., toluene). To date, we have failed to identify epoxide formation during the reaction of thioxanthone (**6**), 2-chlorothioxanthone (**7**), 2,4-dimethylthioxanthone (**8**), or

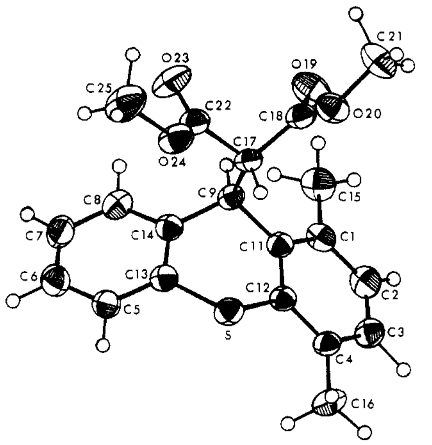

Figure 1. ORTEP drawing of dimethyl 9-(1,4-dimethylthioxanthenyl)malonate.

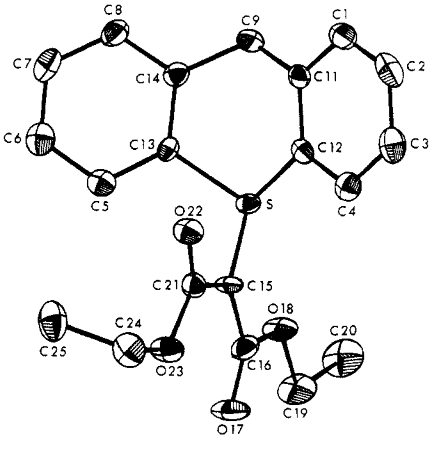

Figure 2. ORTEP drawing of 9,9-dideuteriothioxanthenium bis(carboethoxy)methylide.

1,4-dimethylthioxanthone (**9**) with dialkyl diazomalonates in the presence of copper(II).[10] However, we have observed that 1,4-dimethylthioxanthene can react with diethyl diazomalonate to form **4**.[11]

X-ray Analyses. Dimethyl 9-(1,4-Dimethylthioxanthenyl)malonate (4). Tables I and II list the interatomic distances and valence angles for **4**. Figure 1 is an ORTEP[12] drawing of the molecule and indicates the numbering scheme used in these tables. The final atomic positional coordinates are presented in Table I of the supplementary material. (See the paragraph at the end of the paper about supplementary material.)

In the malonylide unit all chemically equivalent bonds are statistically identical. The C(9)–C(11) and C(9)–C(14) distances of 1.513 (4) and 1.510 (5) Å are statistically equivalent; however, the S–C(12) and S–C(13) distances of 1.770 (3) and 1.755 (3) Å differ significantly. The dihedral angle between the planes of the two phenyl rings is 134.9°. C(15) and C(16) lie slightly more than 0.1 Å out of the phenyl plane.

The two halves of the malonate ester are planar as indicated by torsion angles C(17)–C(18)–O(20)–C(21) = −175.1°, O(19)–C(18)–O(20)–C(21) = 4.3°, C(17)–C(22)–

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[6] A. L. Ternay, Jr., D. Craig, and H. R. O'Neal, *J. Org. Chem.*, 45, 1529 (1980). The current work was presented at the 9th International Symposium on Organic Sulphur Chemistry, Riga, Latvia, June 1980.

[7] Recently Tamura and co-workers[8] concluded that simple thioxanthenium methylides exist in the e′ conformation. Their conclusions were based upon ". . . NMR spectral comparison. . .with the corresponding sulfoxide and *N*-(*p*-toluenesulfonyl)sulfilimine" and were made without employment of an isomeric a′ ylide.

[8] Y. Tamura, C. Mukai, and M. Ikeda, *Heterocycles*, 12, 1179 (1979).

[9] W. Ando, T. Yagihara, S. Tozume, I. Imai, J. Suzuki, T. Toyama, S. Nakaido, and T. Migita, *J. Org. Chem.*, 37, 172 (1972).

[10] By way of contrast, thioxanthenethione reacts to produce an episulfide (unpublished results with P. Staudt).

[11] Unlike the base-induced reactions noted by Tamura,[8] this reaction produces a 9-substituted thioxanthene without use of a strong base. Thus far we have not determined if an ylide is an intermediate but presume so.

[12] C. K. Johnson, Report ORNL 3711, Oak Ridge National Laboratory, Oak Ridge, TN.

Table II. Valence Angles (Degrees) for Dimethyl 9-(1,4-Dimethylthioxanthenyl)malonate (4)

C(12)-S(10)-C(13)	100.0 (1)	S(10)-C(12)-C(11)	120.1 (2)	C(5)-C(6)-C(7)	120.9 (3)	C(18)-C(17)-C(22)	105.9 (2)
C(2)-C(1)-C(11)	117.7 (2)	C(4)-C(12)-C(11)	122.6 (2)	C(6)-C(7)-C(8)	119.7 (4)	C(17)-C(18)-O(19)	125.8 (3)
C(2)-C(1)-C(15)	118.8 (2)	S(10)-C(13)-C(5)	118.4 (2)	C(7)-C(8)-C(14)	120.9 (2)	C(17)-C(18)-O(20)	110.5 (2)
C(11)-C(1)-C(15)	123.5 (2)	S(10)-C(13)-C(14)	120.6 (3)	C(11)-C(9)-C(14)	110.9 (2)	O(19)-C(18)-O(20)	123.6 (3)
C(1)-C(2)-C(3)	122.2 (2)	C(5)-C(13)-C(14)	121.0 (3)	C(11)-C(9)-C(17)	110.3 (3)	C(18)-O(20)-C(21)	116.2 (2)
C(2)-C(3)-C(4)	121.3 (3)	C(8)-C(14)-C(9)	122.1 (2)	C(14)-C(9)-C(17)	110.0 (2)	C(17)-C(22)-O(23)	124.3 (2)
C(3)-C(4)-C(12)	117.4 (2)	C(8)-C(14)-C(13)	118.2 (3)	C(1)-C(11)-C(9)	122.1 (2)	C(17)-C(22)-O(24)	111.6 (2)
C(3)-C(4)-C(16)	120.1 (2)	C(9)-C(14)-C(13)	119.7 (3)	C(1)-C(11)-C(12)	118.6 (2)	O(23)-C(22)-O(24)	124.0 (3)
C(12)-C(4)-C(16)	122.5 (2)	C(9)-C(17)-C(18)	113.0 (2)	C(9)-C(11)-C(12)	119.2 (2)	O(22)-O(24)-C(25)	116.4 (3)
C(6)-C(5)-C(13)	119.2 (2)	C(9)-C(17)-C(22)	110.5 (3)	S(10)-C(12)-C(4)	117.3 (2)		

Table III. Interatomic Distances and Intermolecular Contacts (Å) for 9,9-Dideuteriothioxanthenium Bis(carboethoxy)methylide (3)

Interatomic Distances			
S-C(12)	1.789 (3)	C(9)-C(11)	1.509 (10)
S-C(13)	1.792 (5)	C(9)-C(14)	1.512 (12)
S-C(15)	1.706 (8)	C(11)-C(12)	1.386 (11)
C(1)-C(2)	1.392 (11)	C(13)-C(14)	1.389 (12)
C(1)-C(11)	1.393 (14)	C(15)-C(16)	1.452 (10)
C(2)-C(3)	1.397 (13)	C(16)-O(17)	1.207 (11)
C(3)-C(4)	1.387 (14)	C(16)-O(18)	1.367 (8)
C(4)-C(12)	1.385 (3)	O(18)-C(19)	1.454 (10)
C(5)-C(6)	1.396 (8)	C(19)-C(20)	1.521 (11)
C(5)-C(13)	1.389 (11)	C(15)-C(21)	1.439 (8)
C(6)-C(7)	1.385 (13)	C(21)-O(22)	1.220 (10)
C(7)-C(8)	1.396 (12)	C(21)-O(23)	1.345 (11)
C(8)-C(14)	1.392 (7)	O(23)-C(24)	1.459 (7)
		C(24)-C(25)	1.523 (9)
Intramolecular Contacts			
S···O(18)	2.730 (6)	S···O(22)	2.935 (5)

O(24)–C(25) = 178.9°, and O(23)–C(22)–O(24)–C(25) = 1.4°; however, the halves are not coplanar, O(19)–C(18)–C(17)–C(22) = -88.8°, O(20)–C(18)–C(17)–C(22) = 88.5°, O(23)–C(22)–C(17)–C(18) = 60.1°, and O(24)–C(22)–C(17)–C(18) = -120.0°.

The two methine hydrogens exist anti to one another with H(9)–C(9)–C(17)–H(17) = -173.1°.

9,9-Dideuteriothioxanthenium Bis(carboethoxy)methylide (3). Tables III and IV list the interatomic distances and valence angles for 3. Figure 2 is an ORTEP[12] drawing of the molecule and indicates the numbering scheme used in these tables. The final positional coordinates are presented in Table II of the supplementary material.

All chemically equivalent bonds in the thioxanthene system are also of statistically equivalent length. The two phenyl rings are planar; however, the sulfur atom and C(9) are considerably out of the plane of the rings. A least-squares plane fitted to C(1)–C(2)–C(3)–C(4)–C(11)–C(12) shows a maximum deviation of 0.008 Å while S and C(9) are 0.066 and 0.046 Å out of the plane. A least-squares plane fitted to C(5)–C(6)–C(7)–C(8)–C(13)–C(14) shows a maximum deviation of 0.010 Å, with S and C(9) out of the plane by 0.193 and 0.020 Å, respectively. The dihedral angle between the two planes is 138.3°. This value is similar to the angle in phenoxathiin (10; 138°)[13] and *trans*-thianthrene disulfoxide (11; 133°)[14] but smaller than what has been found for *cis*-2,4,9-trimethylthioxanthene sulfoxide (12; 147°),[15] 1,4-dimethylthioxanthene sulfoxide (13; 144°),[16] and phenoxathiin sulfoxide (14; 153°).[17] This angle is similar to that in *cis*-9-methylthioxanthene sulfoxide (15).[18]

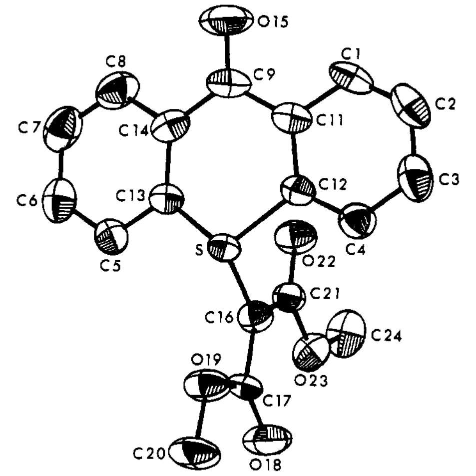

Figure 3. ORTEP drawing of thioxanthonium bis(carbomethoxy)methylide.

The C_{aryl}–S distances (1.792 (5) and 1.789 (3) Å) are comparable to those in the three-coordinate thioxanthene sulfoxides, which exhibit a mean value of 1.781 Å. The C_{aryl}–S–C_{aryl} angle of 99.6 (3)° is larger than the corresponding angle in thioxanthene sulfoxides[19] and in phenoxathiin sulfoxide.[17] The most notable feature of the structure is the intramolecular interactions between one carbonyl oxygen and sulfur, S–O(22) = 2.935.5 Å, and one ester oxygen and sulfur, S–O(18) = 2.730 (6) Å. The general plane of the malonylide unit is essentially perpendicular to the plane of the thioxanthene system, reducing any possible sulfur–carbon double bond character: S–C(15) = 1.706 (8) Å. Although the standard deviations were large, the sulfur–oxygen interactions are reflected in the bond distances in the pseudo-five- and -six-membered rings. The C=O distance in the interacting carbonyl is 1.220 Å compared with 1.207 Å for the other. The C-O bond for the ester oxygen is 1.367 Å for the one involved in the sulfur interaction as compared to 1.345 Å for the other. The two C–C bonds involving the ylide carbon are 1.439 and 1.452 Å, consistent with greater double bond character in the former.

Thioxanthonium Bis(carbomethoxy)methylide (5). Tables V and VI list the interatomic distances and valence angles for 5. Figure 3 is an ORTEP[12] drawing of the molecule and indicates the numbering scheme used in the tables.

The X-ray analysis reveals that the malonylide fragment is essentially planar. One ester group ("endo") presents its carbonyl oxygen to the sulfur atom in a geometry anti to the nonbonding electron pair on sulfur. The separation,

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(13) S. Hosoya, *Acta Crystallogr.*, **20**, 429 (1966).

(14) H. L. Ammon, P. H. Watts, and J. M. Steward, *Acta Crystallogr., Sect. B*, **B26**, 451 (1970).

(15) S. S. C. Chu, R. D. Rosenstein, and A. L. Ternay, Jr., *Acta Crystallogr., Sect. B*, **B35**, 2430 (1979).

(16) S. S. C. Chu and B. Chung, *Acta Crystallogr., Sect. B*, **B30**, 235 (1974).

(17) J. S. Chen, W. H. Watson, D. Austin, and A. L. Ternay, Jr., *J. Org. Chem.*, **44**, 1989 (1980).

(18) J. Jackobs and M. Sundaralingam, *Acta Crystallogr., Sect. B*, **B25**, 2487 (1969).

(19) S. S. C. Chu, *Acta Crystallogr., Sect. B*, **B31**, 1082 (1975).

Table IV. Valence Angles (Degrees) for 9,9-Dideuteriothioxanthenium Bis(carboethoxy)methylide (3)

C(12)-S-C(13)	99.6 (3)	S-C(13)-C(5)	119.7 (6)	C(6)-C(7)-C(8)	120.7 (6)	C(15)-C(16)-O(17)	126.4 (6)
C(12)-S-C(15)	110.4 (4)	S-C(13)-C(14)	117.4 (5)	C(7)-C(8)-C(14)	120.5 (8)	C(15)-C(16)-O(18)	112.0 (7)
C(13)-S-C(15)	108.6 (3)	C(5)-C(13)-C(14)	122.7 (5)	C(11)-C(9)-C(14)	113.1 (7)	O(17)-C(16)-O(18)	121.6 (6)
C(2)-C(1)-C(11)	120.4 (8)	C(8)-C(14)-C(9)	121.3 (7)	C(1)-C(11)-C(9)	121.1 (7)	C(16)-O(18)-C(19)	115.3 (6)
C(1)-C(2)-C(3)	120.9 (9)	C(8)-C(14)-C(13)	117.8 (7)	C(1)-C(11)-C(12)	117.5 (6)	O(18)-C(19)-C(20)	106.4 (8)
C(2)-C(3)-C(4)	119.3 (7)	C(9)-C(14)-C(13)	120.9 (5)	C(9)-C(11)-C(12)	121.4 (8)	C(15)-C(21)-O(22)	123.1 (7)
C(3)-C(4)-C(12)	118.9 (8)	S-C(15)-C(16)	116.1 (5)	S-C(12)-C(4)	119.6 (6)	C(15)-C(21)-O(23)	114.3 (7)
C(6)-C(5)-C(13)	118.6 (8)	S-C(15)-C(21)	117.0 (6)	S-C(12)-C(11)	117.4 (5)	O(22)-C(21)-O(23)	122.6 (5)
C(5)-C(6)-C(7)	119.7 (8)	C(16)-C(15)-C(21)	126.7 (7)	C(4)-C(12)-C(11)	123.0 (8)	C(21)-O(23)-C(24)	115.2 (6)
						O(23)-C(24)-C(25)	111.2 (6)

Table V. Interatomic Distances and Intermolecular Contacts (Å) for Thioxanthonium Bis(carbomethoxy)methylide (5)

Interatomic Distances

S-C(12)	1.736 (6)	C(9)-C(11)	1.455 (7)
S-C(13)	1.761 (4)	C(9)-C(14)	1.490 (10)
S-C(16)	1.747 (5)	C(9)-O(15)	1.206 (9)
C(1)-C(2)	1.345 (8)	C(11)-C(12)	1.393 (7)
C(1)-C(11)	1.409 (9)	C(13)-C(14)	1.382 (8)
C(2)-C(3)	1.373 (11)	C(16)-C(17)	1.435 (6)
C(3)-C(4)	1.401 (11)	C(17)-O(18)	1.130 (7)
C(4)-C(12)	1.377 (6)	C(17)-O(19)	1.352 (6)
C(5)-C(6)	1.405 (7)	O(19)-C(20)	1.452 (6)
C(5)-C(13)	1.392 (9)	C(16)-C(21)	1.440 (6)
C(6)-C(7)	1.357 (11)	C(21)-O(22)	1.219 (6)
C(7)-C(8)	1.387 (11)	C(21)-O(23)	1.345 (7)
C(8)-C(14)	1.393 (7)	O(23)-C(24)	1.428 (7)

Intramolecular Contacts

S···O(13)	2.733 (4)	S···O(22)	2.932 (4)

2.932 Å, corresponds closely to that found in 9,9-dideuteriothioxanthenium bis(carboethoxy)methylide (**3**; 2.935 Å). The etherlike oxygen of the "exo" ester fragment of **5** shows a significant intramolecular contact with the sulfur (2.733 Å). Again, this distance is similar to the corresponding distance in **3** (2.771 Å). The general arrangement of atoms in the malonylide fragments of **5** and **3** is, in fact, quite similar. The plane of the malonylide fragment is essentially perpendicular to the idealized plane of the thioxanthone system, reducing any possible sulfur–carbon double bond character: S–C(16) = 1.747 (5) Å.

The bond distance of the "endo" carbonyl group is 1.213 (6) Å while that of the "exo" carbonyl group is 1.130 (7) Å. The greater distance (hence single bond character) of the endo carbonyl group is parallel to what was found in **3**.

The heterocyclic ring is essentially planar, the "angle of fold" being 168.6°. This is much greater than that found in **3** and is significantly larger than what has been found for **2** (155.7°).[20] The C$_{\mathrm{aryl}}$–S distances (1.796 (6) and 1.761 (4) Å) are comparable to those found in **3** and **2**.

NMR Studies. Thioxanthenium Ylides. The data in Table VII indicate that the chemical shift of the methylide carbon in thioxanthenium methylides is conformation dependent. Thus, 9,9-dideuterio-1,4-dimethylthioxanthenium bis(carboethoxy)methylide (**16**) and 1,4-dimethylthioxanthenium bis(carbomethoxy)methylide (**17**), both of which possess an a′ methylide carbon, exhibit their resonance near 67 ppm. In 9,9-dideuteriothioxanthenium bis(carboethoxy)methylide (**3**), 2-chlorothioxanthenium bis(carbomethoxy)methylide (**18**), and thioxanthenium bis(carbomethoxy)methylide (**19**) the corresponding resonance occurs at 54 ppm.[21] Whether these chemical shift differences reflect a differing amount of electron density at the a′ and e′ methylide carbon and/or a different position relative to anisotropic groups within the molecule remains to be clarified. However, a $\Delta\delta$ of approximately 15 ppm is large enough to permit unambiguous stereochemical assignment (a′ vs. e′). This resonance is, of itself, *also sufficient to distinguish between an ylide and a 9-substituted thioxanthene.*

While the chemical shift of the methylide carbon is sensitive to conformation, it appears that in these types of ylides the carbonyl carbons are not. Thus, the carbonyl carbons of dimethyl malonate and of the thioxanthenium ylides examined in this study absorb at 166 ppm. These values differ from those observed for the diasterotopic carbonyl carbons of **4** (167.9 and 168.2 ppm).

The carbons of the aryl methyl groups are anisochronous in 1,4-dimethylthioxanthene (**20**; 19.8 and 20.2 ppm) and in **4** (19.6 and 20.8 ppm). However, this difference disappears in the ylides **16** and **17** (Table VII).

Proton NMR studies cannot *readily* provide conformational information beyond assigning a′ or e′ geometries to the ylide fragment. However, in compounds such as **4** the magnitude of J_{AB} can indicate the rotational distribution about the bond connecting C(9) to its substituent. The large (12 Hz) coupling strongly suggests a rotomeric distribution in which both methine hydrogens are anti to one another, a geometry similar to what we have observed in the solid state.

Thioxanthonium Ylides. The ^{1}H NMR spectra of thioxanthonium bis(carbomethoxy)methylide (**5**), 2-chlorothioxanthonium bis(carbomethoxy)methylide (**21**), 2,4-dimethylthioxanthonium bis(carbomethoxy)methylide (**22**), and 1,4-dimethylthioxanthonium bis(carbomethoxy)methylide (**23**) exhibit resonances consistent with the assigned structures (Table VIII).

The most striking characteristic of these ^{1}H NMR spectra is the appearance of the methoxy signal. In **5**, **21**, and **22** the methoxy resonance is quite broad, suggesting that rotation about the S^+–C^- bond is hindered in these systems. Since **5** and **21** possess protons at C(4) while **22** possesses a methyl group at C(4), yet all three exhibit broadened signals, one concludes that a methyl group at C(4) is, of itself, insufficient to substantially alter the ease of rotation in these systems. These results also suggest that a methyl group at C(4), by itself, is incapable of *drastically* altering the geometry of the system.

While both **22** and **23** possess methyl groups peri to sulfur, the sharp methoxy resonance in **23** indicates a lower rotational barrier in **23** than in **22**. Since a methyl group at C(1) should not directly alter electron distribution at *the ylide fragment, the effect of the C(1) methyl group* is presumed to be steric. (Of course, changes in geometry will, in turn, lead to changes in electron density.) Repulsion between the C(9) carbonyl oxygen and the C(1)

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(20) The angle of fold is also substituent dependent. Thus, 2-chlorothioxanthonium bis(carbomethoxy)methylide possess an even more planar ring (unpublished results).

(21) These resonances are absent in the quaternary-carbon supressed spectra of these compounds and in the spectrum of 4.

Table VI. Valence Angles (Degrees) for Thioxanthonium Bis(carbomethoxy)methylide (5)

C(12)-S-C(13)	102.7 (2)	S-C(12)-C(11)	121.2 (3)	C(6)-C(7)-C(8)	122.3 (5)	S-C(16)-C(21)	116.0 (3)
C(12)-S-C(16)	104.4 (2)	C(4)-C(12)-C(11)	122.9 (5)	C(7)-C(8)-C(14)	119.2 (6)	C(17)-C(16)-C(21)	127.4 (4)
C(13)-S-C(16)	107.5 (2)	S-C(13)-C(5)	114.6 (4)	C(11)-C(9)-C(14)	120.2 (5)	C(16)-C(17)-O(18)	126.1 (4)
C(2)-C(1)-C(11)	123.0 (6)	S-C(13)-C(14)	123.1 (4)	C(11)-C(9)-O(15)	119.9 (7)	C(16)-C(17)-O(19)	111.7 (4)
C(1)-C(2)-C(3)	120.8 (7)	C(5)-C(13)-C(14)	122.0 (4)	C(14)-C(9)-O(15)	119.6 (6)	O(18)-C(17)-O(19)	122.2 (4)
C(2)-C(3)-C(4)	119.0 (5)	C(8)-C(14)-C(9)	118.0 (6)	C(1)-C(11)-C(9)	120.0 (5)	C(17)-O(19)-C(20)	116.7 (5)
C(3)-C(4)-C(12)	119.1 (6)	C(8)-C(14)-C(13)	118.7 (6)	C(1)-C(11)-C(12)	115.2 (4)	C(16)-C(21)-O(22)	123.5 (5)
C(6)-C(5)-C(13)	118.4 (6)	C(9)-C(14)-C(13)	123.3 (4)	C(9)-C(11)-C(12)	124.8 (5)	C(16)-C(21)-O(23)	114.5 (4)
C(5)-C(6)-C(7)	119.4 (7)	S-C(16)-C(17)	116.5 (3)	S-C(12)-C(4)	115.4 (4)	O(22)-C(21)-O(23)	121.9 (4)
						C(21)-O(23)-C(24)	115.4 (5)

Table VII. ^{13}C NMR Spectra[a]

	chemical shift, δ					
compd	C(1)/C(4)[b]	CH_2	C=O	$C(CO_2R)_2$	OR[c]	C_{aryl}[d]
3			165.76	53.76	59.04, 13.97	132.38, 129.24, 129.94, 128.58, 127.35, 124.54
4	20.08, 19.66	49.74, 44.00[e]	168.18, 167.89		52.15, 52.01[f]	135.19, 134.21, 133.49, 133.00, 132.07, 129.79, 128.44, 127.85, 127.18, 126.94, 126.31
16	19.89		166.19	66.92	59.07, 14.48	138.10, 137.52, 136.50, 133.98, 125.68, 122.80, 132.30, 130.56, 129.34, 129.05, 127.70
17	19.60	31.44	166.28	66.91	50.54	138.14, 137.60, 136.24, 133.87, 124.94, 122.12, 132.21, 130.51, 129.10, 128.90, 127.51
18		35.17	165.88	53.75	50.75	136.34, 134.63, 132.16, 127.94, 126.87, 130.22, 128.76, 127.65, 125.91, 124.09[g]
19		35.56	166.15	53.77	50.71	132.81, 128.34, 130.09, 128.74, 127.47, 124.47
20	20.23, 19.83	35.21				136.83, 134.20, 134.06, 133.44, 132.69, 132.40, 127.81, 127.64, 126.98, 126.72, 126.38, 126.30
dimethyl malonate		40.51	166.42		51.86	

[a] $CDCl_3$; probe temperature 33 °C. [b] Unassigned. [c] When R = CH_3, a single value is given. When R = C_2H_5, the methylene resonance is given first. [d] No attempt has been made to assign these; however, values for quaternary carbons are given first. [e] Methine. [f] Diastereotopic. [g] Absorption at δ 128.76 and 127.65 each appears to represent two carbons.

Table VIII. ^1H NMR Spectra of Thioxanthonium Bis(carbomethoxy)methylides[a]

compd	Ar CH_3	OCH_3	Ar H
5		3.59[b]	7.2-8.5
21		3.60[b]	7.2-8.5
22	2.42, 2.57	3.56[b,c]	7.2-8.4
23	2.63, 2.73	3.57	7.5-8.4

[a] Spectra recorded in $CDCl_3$ at 33 °C with chemical shifts in parts per million downfield from Me_4Si. Integrations are consistent with the assigned structure. All signals are singlets except for the aryl protons. [b] Broad. [c] At 24 °C (250 MHz, $CDCl_3$) these appear as two broad signals at 3.84 and 3.37 ppm.

methyl group should lead to a decrease in the dihedral angle formed by the planes containing the aryl rings, and it has been shown that thioxanthenium methylides of this type, which do have smaller dihedral angles (approximately 140°), have a lower rotational barrier (i.e., a sharp methoxy resonance).

The ^{13}C NMR spectra (Table IX) of these compounds are consistent with the proposed ylide structures. The methylide carbon in these compounds resonates at 61–63 ppm, between the values observed for thioxanthenium bis(carboalkoxy)methylides. This suggests that these thioxanthonium methylides should have a relatively planar central ring in solution since a planar structure, rather than having a′ and e′ positions, will have two equivalent positions of intermediate geometry.

At 33 °C (25 MHz) the ^{13}C NMR spectra of **5** and **21–23** contain a sharp resonance for the C(9) carbonyl group near 180 ppm. (Its presence, of course, confirms that these compounds are not epoxides.) By way of contrast, the ester carbonyl resonances are broad for **5**, **21**, and **22** at 33 °C (25 MHz, $CDCl_3$) and could be detected only with difficulty under conditions which led to the facile detection of all other resonances. This stems from the proximity of these conditions to those of coalescence.[22]

Conformational Analysis of Thioxanthenium Ylides. Thioxanthenium methylides of the type under discussion (i.e., those lacking substituents at C(4) and with a methylide carbon stabilized by an alkoxycarbonyl group) exist, preferentially, in the pseudoequatorial conformation. This preference for the e′ conformation, and for that rotomer which places the plane of the malonylide fragment

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[22] At 200 MHz, the ^1H methoxy resonances of **21** coalesce near 40 °C. At 250 MHz, those of **22** coalesce near 50 °C. The related coalescence appears in ^{13}C spectra, as well as being reflected in the appearance of distinct OCH_3 and C(O)O resonances. At still lower temperatures (approximately −20 °C) the upfield OCH_3 signal begins to broaden relative to the downfield signal. This is taken to indicate a rotational barrier between the methylide carbon and the *endo*-carbonyl carbon, consistent with attraction between the *endo*-carbonyl oxygen and the positively charged sulfur.

Table IX. ^{13}C NMR Spectra of Thioxanthonium Bis(carbomethoxy)methylides[a]

compd	Ar CH_3	OCH_3	C^-	C(O)O	C(9)=O	aryl[b]
5		51.14	61.14	164[c]	177.78	133.77, 131.45, 134.05, 131.11, 129.79, 126.69
21		51.19	61.00	164[c]	176.76	138.05, 133.57, 132.57, 131.84, 131.10, 134.31, 134.07, 131.26, 129.85, 129.50, 128.25, 126.74
22	21.11, 19.42	50.80	63.08	165.75[d]	179.62	138.81, 134.36, 133.34, 132.28, 125.58, 141.93, 136.84, 133.72, 131.40, 128.87, 128.63, 127.81
23	22.85, 19.68	50.83	62.91	165.79	182.57	140.35, 137.31, 136.53, 135.51, 134.74, 133.04, 131.58, 130.22, 128.60, 129.58, 128.34[e]

[a] Spectra obtained at 33 °C at 25 MHz in $CDCl_3$. All signals are sharp unless otherwise noted. [b] Quaternary carbons presented first. [c] Approximate center of *very* broad signal. [d] Broad. [e] Because of overlap, assignments are unclear.

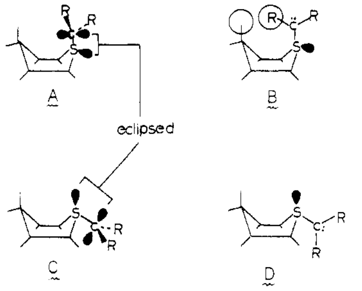

Figure 4. Conformational analysis of simple thioxanthenium methylides and related, conformationally restricted diarylsulfonium ylides.

within the plane which bisects the dihedral angle of the heterocycle, can be understood with the aid of the four structures shown in Figure 4.

In Figure 4, structures A and B represent a′ conformations while C and D are e′ conformations. The energy of A is raised by the eclipsing of the nonbonding electron pair on sulfur and the p orbital of the sp^2-hybridized methylide carbon. Rotation about the ylide bond has made these electron pairs orthogonal in structure B; however, B exhibits a repulsive interaction between one ester moiety and the other meso position (C(9)). Structure C possesses an e′ methylide carbon and contains two unfavorable interactions: (a) repulsions between ester groups and their respective peri positions and (b) eclipsing between nonbonding electron pairs. Structure D, on the other hand, is devoid of both of these. Thus, on consideration of A–D, D appears to be the most reasonable conformer.[23,24]

Conformer D, in addition to aligning adjacent nonbonding electron pairs orthogonally, also offers the opportunity for the "endo" R group to directly stabilize the charge on sulfur. In the structures under discussion the endo alkoxycarbonyl group is oriented so as to align the carbonyl oxygen trans to the nonbonding electron pair on sulfur. This stabilizing interaction is used to explain the rotomeric distribution about the bond between the methylide carbon and the *endo*-alkoxycarbonyl group.[25]

Table X. Infrared Spectra[a]

compd	conformation	absorptions,[b] cm^{-1}
3	e′	1684 (s), 1648 (s)
4	a′	1748 (sh), 1738 (s), 1717 (mw)
17	a′	1625 (s)[c]
18	e′	1677 (s), 1641 (s)
29	e′	1697 (s), 1656 (s)

[a] Nujol mulls. [b] Only absorptions between 1800 and 1600 cm^{-1} are included. Frequencies were calibrated by using a polystyrene film. [c] Broad.

Infrared Spectra of Thioxanthenium Ylides. The carbonyl groups of 4 absorb above 1700 cm^{-1} (Table X). However, the ylides prepared in this study, regardless of their conformation, absorb below 1700 cm^{-1} (solid state). Thus, IR spectroscopy can serve to distinguish between thioxanthenes such as 4 and ylides such as 17 or 18.

Furthermore, it appears that IR spectroscopy can distinguish between some e′ and a′ ylides in this series. For example, thioxanthenium bis(carbomethoxy)methylide (19), an e′ ylide, absorbs at 1697 and 1656 cm^{-1}.[26] This can be compared to the spectrum of 17 which possesses an a′ ylide fragment and exhibits a single, broad absorption at 1625 cm^{-1}. The presence of two carbonyl absorptions for the e′ ylides is consistent with the X-ray structure for 3 which shows that the endo carbonyl group is longer (1.220 Å) than the exo (1.207 Å). It seems, therefore, that the 1697-cm^{-1} absorption in 19 is due to the exo moiety while the lower frequency is due to the endo moiety.

Experimental Section

^1H NMR spectra were obtained on Varian Models HA-100 and T-60 spectrometers. ^{13}C NMR spectra were obtained on a Varian Model XL-100-15 spectrometer operating at 25.158 MHz in the Fourier transform mode. The spectrometer was equipped with a Nicolet Technology Model TT-100 data system, a Model NT-440 frequency synthesizer, and a TT-760 decoupler operating at a power level such that $\gamma_{H_2}/2\pi$ = 2.9 kHz. Sufficient acquisitions were acquired in each case to provide adequate signal to noise ratios such that discrimination of the quaternary carbon signals was completely unambiguous. Infrared spectra were recorded, as Nujol mulls, on a Perkin-Elmer Model 621 infrared spectrophotometer.

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(23) This analysis suggests that, in the absence of *severe* repulsions between an a′ substituent on C(9) and the proximal R group bonded to the methylide carbon, conformer B would be preferred over A in those structures where the methylide carbon is forced to be a′. Conformer B renders orthogonal those nonbinding electron pairs which are adjacent. This is supported by our study of the structure of 17 (unpublished results).

(24) We have observed that thianthrenium bis(carboethoxy)methylide exists in the e′ conformation and possesses the same general features observed for thioxanthenium ylides. The corresponding cis diylide is di-e′ (unpublished results with J. Baack).

(25) A similar ylide derived from *N*-methylphenothiazine exists in the a′ array. We must conclude, therefore, that while attractive interactions may influence the orientation of the *endo*-alkoxycarbonyl moiety within a given e′ isomer, they may not be the major factor in controlling the a′ vs. e′ distribution in structures possessing certain heteroatoms in place of C9 (unpublished results with J. Baack).

(26) Tamura[8] has reported values of 1710 and 1650 cm^{-1} ($CHCl_3$) for 19.

X-ray data were collected on a Syntex $P2_1$ diffractometer system. Room-temperature unit-cell dimensions were determined by a least-squares procedure utilizing 15 reflexions whose angles were measured by a centering routine associated with the Syntex diffractometer. Intensity data were collected by the 0.20 scanning technique with a variable scan speed, a graphite monochromator, and Cu Kα radiation ($\lambda = 1.541\,78$). A reference reflexion was monitored periodically to check for variations in intensity. Lorentz and polarization corrections were applied, but no absorption corrections were made. Structures were solved by application of the direct-methods program MULTAN.[27] Least-squares refinements and difference Fourier calculations were used to locate all atoms not found in the original E map. The R factor is defined as $R = \sum||F_o| - |F_c||\sum|F_o|$. The function minimized in the refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma(I)$ was determined from counting statistics. H atom thermal parameters were refined isotropically. A final difference Fourier map was checked for any unaccounted for electron density.

Compound **3** was recrystallized from benzene-ethyl acetate (1:1 v/v), and a crystal of dimensions 0.75 × 0.6 × 0.5 mm was selected for all X-ray measurements. The unit cell was found to be triclinic and space group $\bar{P}\bar{1}$ was consistent with statistics. Crystal data: $C_{20}H_{18}D_2O_4S$, $M_r = 358.43$, $a = 8.082$ (1) Å, $b = 10.365$ (1) Å, $c = 13.355$ (2) Å, $\alpha = 122.32$ (1), $\beta = 98.85$ (1), $\gamma = 103.96$ (1)°, $V = 861.1$ (2) Å^3, $Z = 2$, $d_{\text{calcd}} = 1.38$ g cm^{-3}, $\mu = 18.2$ cm^{-1}.

Of the 2249 independent reflexions, 2220 had intensities greater than $3\sigma(I)$. Full-matrix, least-squares refinement with anisotropic thermal parameters led to a final R of 0.076.

Compound **4** was recrystallized from benzene and a crystal of dimensions 0.66 × 0.41 × 0.20 mm was selected for all X-ray measurements. The unit cell was found to be monoclinic, and systematic extinctions were consistent with space group $P2_1/c$. Crystal data: $C_{20}H_{20}O_4S$, $M_r = 356.44$, $a = 9.553$ (2) Å, $b = 27.65$ (1) Å, $c = 7.778$ (a) Å, $\beta = 122.05$ (1)°, $V = 1742$ (1) Å^3, $Z = 4$, $d_{\text{calcd}} = 1.36$ g cm^{-3}, $\mu = 17.95$ cm^{-1}.

Of the 2872 independent reflexions ($2\theta < 130°$), 2394 had intensities greater than $3\sigma(I)$. Full-matrix, least-squares refinement with anisotropic thermal parameters led to a final R of 0.064.

Compound **5** was recrystallized from ethanol, and a crystal of dimensions 0.40 × 0.33 × 0.18 mm was used to collect all X-ray data. The unit cell was found to be monoclinic, and room-temperature cell dimensions were obtained by a least-squares fit to 15 medium angle reflexions. Systematic absences were consistent with space group $P2_1$. Crystal data: $C_{18}H_{14}O_5S$, $M_r = 342.37$, $a = 11.728$ (3) Å, $b = 9.425$ (2) Å, $c = 8.197$ (2) Å, $\beta = 119.45$ (2)°, $V = 789.0$ (3) Å^3, $Z = 2$, $d_{\text{calcd}} = 1.44$ g cm^{-3}, $\mu = 20.10$ cm^{-1}.

Of the 1370 independent reflexions measured, 1326 had intensities greater than $3\sigma(I)$, where $\sigma(I)$ was estimated from counting statistics. Lorentz and polarization corrections were applied, but no absorption corrections were made.

The structure was solved by utilizing the u, 1/2, w Harker plane to find the x and z coordinates of the sulfur atom. The remainder of the carbon and oxygen atoms were found by alternate Fourier and least-squares calculations. Full-matrix, least-squares refinement with isotropic thermal parameters yielded an R value of 0.106 while anisotropic refinement lowered the R to 0.065, where $R = \sum\Delta F_{\text{meas}}/\sum|F_{\text{meas}}|$. Eleven hydrogen atoms were located in a difference Fourier map, but three methyl hydrogen atoms could not be found. Anisotropic least-squares refinement with fixed H atom positions led to a final R of 0.063. Four strong reflexions were dropped from the refinement because of possible secondary extinction. The scattering factors of all atoms were calculated by the X-ray program, and the sulfur atom was corrected for anomalous dispersion.

2-Chlorothioxanthenium Bis(carbomethoxy)methylide (18). A mixture of 2-chlorothioxanthene (2.0 g, 8.6 mmol), dimethyl diazomalonate (2.72 g, 17.2 mmol), toluene (10 mL), and anhydrous copper sulfate was heated for 3 h at 100 °C under a nitrogen atmosphere. After cooling, the mixture was suspended in chloroform and filtered. The filtrate was concentrated to a brown oil and then triturated with hexane (10 × 2 mL) and with chloroform (2 × 1 mL) to afford 1.9 g (48%) of **18**, mp 186–188 °C.

This material has mass, NMR (^{1}H and ^{13}C), and IR (Nujol) spectra and an elemental analysis (C, H) consistent with the assigned structure.

2-Chlorothioxanthonium Bis(carbomethoxy)methylide (21). 2-Chlorothioxanthone (2.46 g, 9.97 mmol), dimethyl diazomalonate (3.16 g, 20 mmol), anhydrous copper(II) sulfate (0.45 g, 0.27 mmol), and toluene (12 mL) were mixed together, and the reaction mixture was heated for 5 h at 95–100 °C. After cooling, the reaction mixture was diluted with chloroform (25 mL) and the insoluble residue removed by filtration. The filtrate was concentrated to dryness (N_2 steam) and the resulting solid recrystallized from ethanol to afford 2.89 g (77%) of **21** (mp 182–184 °C) as shining yellow crystals.

Thioxanthonium Bis(carbomethoxy)methylide (5). A mixture of thioxanthone (0.530 g, 2.50 mmol), dimethyl diazomalonate (0.800 g, 5.06 mmol), anhydrous copper(II) sulfate (0.02 g), and toluene (8 mL) was reacted and worked up as described above. Recrystallization of the crude product from benzene–ethyl acetate (2:1 v/v) afforded **5** in 70% yield; mp 203–204 °C.

2,4-Dimethylthioxanthonium Bis(carbomethoxy)methylide (22). A mixture of 2,4-dimethylthioxanthone (0.542 g, 2.25 mmol), dimethyl diazomalonate (0.747 g, 4.72 mmol), anhydrous copper(II) sulfate (0.02 g), and toluene (10 mL) was reacted and worked up as described above. The final product was obtained in 70% yield; mp 201–203 °C [after recrystallization from benzene–ethanol (2:1 v/v)].

1,4-Dimethylthioxanthonium Bis(carbomethoxy)methylide (23). A mixture of **8** (0.970 g, 4.04 mmol), dimethyl diazomalonate (1.29 g, 8.13 mmol), anhydrous copper(II) sulfate (0.03 g), and toluene was reacted and worked up as described above. Recrystallization from benzene–ethanol (1:2 v/v) afforded the final product in 72% yield; mp 206–208 °C.

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Registry No. **1**, 10133-81-0; **2**, 7605-15-4; **3**, 76529-32-3; **4**, 76550-01-1; **5**, 76293-14-6; **6**, 492-22-8; **7**, 86-39-5; **8**, 76293-13-5; **9**, 25942-61-4; **10**, 262-20-4; **11**, 2748-50-7; **12**, 71901-19-4; **13**, 51517-43-2; **14**, 948-44-7; **15**, 19018-80-5; **16**, 72844-62-3; **17**, 72844-61-2; **18**, 76529-33-4; **19**, 72447-77-9; **20**, 17394-13-7; **21**, 76293-15-7; **22**, 76307-78-3; **23**, 76529-34-5; 2-chlorothioxanthene, 92-38-6; dimethyl diazomalonate, 6773-29-1; thioxanthone, 492-22-8; 2,4-dimethylthioxanthone, 76529-35-6.

Supplementary Material Available: Atomic coordinates for **3–5** (5 pages). Ordering information is given on any current masthead page.

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