The Structure of Sulfonium Ylides Stabilized by the Malonylide Moiety

J. Galloy and W. H. Watson*

Department of Chemistry, Texas Christian University,
Fort Worth, TX 76129

D. Craig, C. Guidry, Michael Morgan, Robert McKellar and A. L. Ternay, Jr.*

Department of Chemistry, University of Texas at Arlington,
Arlington, TX 76019

G. Martin

Department of Medicinal Chemistry, University of Houston,
Houston, TX 77004

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The crystal structures of four thioxanthenium bis(carbomethoxy)methylides and methylides of di-(*p*-nitrophenyl)sulfonium and dimethylsulfonium have been determined. The carbanion moiety in all cases is planar and the pi-system is rotated 90° with respect to the sulfur lone pair. All compounds exhibit a pseudoequatorial orientation of the carbanion system except for the 2,4-dimethylthioxanthenium ylide. The compounds are described in terms of the geometries around the sulfur atom, the interplanar angles and sulfur-oxygen and oxygen-oxygen interactions. Surprisingly, the sulfur atom is not symmetrically placed with respect to the two phenyl rings in the thioxanthenium compounds. The sulfur is coplanar with one phenyl ring but is significantly out of the plane of the other. The ^{13}C and ^{1}H spectra of the ylides are discussed along with the temperature dependence which indicates restricted rotation about the $^{+}S—C^{-}$ bond in several cases. The factors contributing to the stability of the ylides are analyzed.

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The chemistry of organosulfur compounds has been of interest for many years (1). In spite of this, there remains considerable controversy concerning the nature of sulfur bonding in hypervalent compounds (2,3,4). The value of ylides derived from organosulfur compounds has served to heighten this controversy (5,6,7). In most hypervalent compounds d-orbitals need not be invoked to rationalize molecular geometry and bonding; however, many theoretical calculations include some d-orbital participation in order to more accurately correlate specific physical properties.

If the sulfur atom possesses a formal positive charge, then the 3d-orbitals are contracted and provide for better overlap of the s and p orbitals of 2nd and 3rd row elments. Sulfonium ylides and oxysulfonium ylides may be considered as carbanions stabilized by an adjacent, positively-charged sulfur atom and, potentially, should be one of the better systems for observing d-orbital participation in bonding. Sulfonium ylides are stable if the anionic moiety is capable of electron delocalization. This stability has been rationalized in terms of "backbonding" from the carbon anion to sulfur 3d-orbitals or to σ^* orbitals associated with the other carbon-sulfur bonds (8,9). This view is supported by the C—S bond lengths of 1.709 (3) Å and 1.719(8) Å observed for 2-dimethylsulfuranylidene-1-indanedione (**1**) (10) and 2-dimethylsulfuranylidenemalononitrile (**2**) (11). A normal C=S bond is expected to be 1.65 Å in length (12,13) while a C—S single bond is greater than 1.8 Å. The C=S bonds in thiourea (14) and thioacetamide (15) are considered to be partial double bond in character and are reported to be 1.71 and 1.78 Å, respectively. Alternatively, the intermediate bond lengths in ylides have been rationalized in terms of electrostatic attraction between the positively-charged sulfur and the negatively-charged carbon which shortens the normal C—S bond.

Coupled with discussions of the structure and bonding in sulfur-containing ylides are analyses of the spectroscopic properties of these ylides (particularly ir and nmr). Superimposed upon this, in turn, is the issue of structural, stereochemical and spectroscopic parallels between such ylides and related sulfoxides, sulfinylimines and so forth. As part of a continuing study (16,17) of the structure, and the stereochemistry of such species we now present the single crystal X-ray analyses and relevant spectroscopic data for a series of ylides including: 2-chlorothioxanthenium bis(carbomethoxy)methylide (**3**), 2,4-dimethylthioxanthenium bis(carbomethoxy)methylide (**4**), thioxanthonium bis(carbomethoxy)methylide (**5**), 2-chlorothioxanthonium bis(carbomethoxy)methylide (**6**), di-(*p*-nitrophenyl)sulfonium bis(carbomethoxy)methylide (**7**) and dimethylsulfonium bis(carboethoxy)methylide (**8**). Compounds **3-6** represent conformationally-restricted diarylsulfonium species while **7** and **8** represent acyclic species.

Results and Discussion.

X-Ray Analyses.

The geometry around the sulfur atoms is intermediate between pyramidal (sp^3) and planar (sp^2). The phenyl rings in all compounds are planar with maximum deviations from planarity of the order of 0.01 Å. The pseudoequatorial compounds **3**, **5** and **6** exhibit interplanar angles of 177.3(6), 168.4(8) and 173.5(8)° while the pseudoaxial compound **4** has an interplanar angle of 155.3(6)°. Contrary to this trend the pseudoequatorial compound 9,9-dideuterio-

Table 1

Distances (Å) of Sulfur and Carbon C(9) from the Least-squares Planes of the Phenyl Rings

	9	3	4	5	6
S	0.18	0.11	0.22	0.17	0.13
	0.07	0.003	0.05	0.14	0.04
C(9)	0.02	0.001	0.03	0.06	0.03
	0.05	0.003	0.05	0.04	0.03

thioxanthenium bis(carboethoxy)methylide (**9**) (16) has an interplanar angle of 138.3(8)°. All phenyl groups were fitted to least-squares planes and the deviations of the sulfur and C(9) atoms from these planes were calculated, see Table 1. Of the compounds **3-6** and **9**, only **5** has the sulfur atom equidistant from the two phenyl planes. C(9) is equidistant from both planes and almost coplanar with the phenyl rings. It is difficult to believe the sulfur atom symmetry with respect to the phenyl planes will persist in solution, but it may represent a slight energy minimum which is frozen out in the solid state. Because of the wide range of values observed for the interplanar angle, the potential curve is probably broad which implies a relatively large bending vibration. In compounds such as **9** homoconjugative interactions should begin to be significant.

In addition to the distances and angles reported in Tables 2 and 3, the geometry around the sulfur atom was further examined by calculating the distance of the sulfur atom

Table 2

Interatomic Distances (Å)

	9	3	4	5	6	7	8
C(1)—C(2)	1.392(11)	1.368(5)	1.371(4)	1.377(6)	1.373(6)	1.357(5)	—
C(1)—C(11)	1.393(14)	1.401(5)	1.389(4)	1.405(7)	1.394(6)	1.384(4)	—
C(2)—C(3)	1.391(13)	1.385(6)	1.379(4)	1.368(9)	1.379(5)	1.368(5)	—
C(3)—C(4)	1.387(14)	1.372(5)	1.396(4)	1.401(9)	1.372(7)	1.377(4)	—
C(4)—C(12)	1.385(9)	1.389(5)	1.400(3)	1.388(5)	1.369(5)	1.382(4)	—
C(12)—C(11)	1.386(11)	1.385(5)	1.393(3)	1.377(6)	1.409(5)	1.371(4)	—
S(10)–C(12)	1.789(9)	1.779(3)	1.781(2)	1.791(5)	1.773(4)	1.792(2)	1.785(3)
S(10)—C(13)	1.792(5)	1.779(4)	1.785(3)	1.771(3)	1.765(4)	1.790(3)	1.781(3)
S(10)—C(15)	1.706(8)	1.715(4)	1.722(2)	1.743(4)	1.711(4)	1.703(2)	1.731(2)
C(13)—C(14)	1.389(12)	1.373(6)	1.386(4)	1.381(6)	1.395(5)	1.380(3)	—
C(13)—C(5)	1.389(11)	1.404(6)	1.391(4)	1.393(7)	1.395(7)	1.389(3)	—
C(5)—C(6)	1.396(8)	1.367(8)	1.381(6)	1.381(6)	1.366(6)	1.376(4)	—
C(6)—C(7)	1.385(13)	1.375(10)	1.382(7)	1.389(9)	1.385(7)	1.369(4)	—
C(7)—C(8)	1.396(12)	1.368(7)	1.359(7)	1.373(9)	1.369(8)	1.378(3)	—
C(8)—C(14)	1.392(7)	1.398(6)	1.403(4)	1.394(6)	1.385(5)	1.382(4)	—
C(9)—C(14)	1.512(12)	1.493(5)	1.482(4)	1.503(8)	1.472(7)	—	—
C(9)—C(11)	1.509(10)	1.500(5)	1.504(4)	1.470(6)	1.463(5)	—	—
C(15)—C(16)	1.452(10)	1.445(5)	1.444(3)	1.436(6)	1.437(4)	1.444(4)	1.431(3)
C(15)—C(20)	1.439(8)	1.432(6)	1.439(3)	1.448(5)	1.432(4)	1.439(4)	1.431(3)
C(16)—O(17)	1.207(11)	1.201(4)	1.218(3)	1.199(6)	1.206(4)	1.207(3)	1.210(3)
C(16)—O(18)	1.367(8)	1.346(6)	1.336(3)	1.348(5)	1.347(4)	1.351(3)	1.361(3)
O(18)—C(19)	1.454(10)	1.436(7)	1.438(4)	1.449(5)	1.439(5)	1.441(5)	1.445(4)
C(20)—O(21)	1.220(10)	1.219(5)	1.208(3)	1.216(5)	1.211(4)	1.215(4)	1.214(3)
C(20)—O(22)	1.345(11)	1.349(4)	1.350(3)	1.348(5)	1.351(5)	1.349(3)	1.355(3)
O(22)–C(23)	1.459(7)	1.436(7)	1.422(3)	1.438(5)	1.437(5)	1.436(5)	1.446(4)
C(9)—O(9)	—	—	—	1.204(8)	1.229(6)	—	—
C(2)—X(2)	—	1.725(3)	1.500(4)	—	1.734(4)	—	—
C(4)—X(4)	—	—	1.490(4)	—	—	—	—
C(19)—C(24)	1.521(11)	—	—	—	—	—	1.466(6)
C(23)—C(25)	1.523(9)	—	—	—	—	—	1.457(6)
C(2)—N	—	—	—	—	—	1.494(4)	—
N—O(1)	—	—	—	—	—	1.214(6)	—
N—O(2)	—	—	—	—	—	1.192(6)	—
C(7)—N′	—	—	—	—	—	1.474(4)	—
N′—O(1′)	—	—	—	—	—	1.202(4)	—
N′—O(2′)	—	—	—	—	—	1.210(3)	—
S O(17,18)	2.730(6) (a)	2.738(4) (a)	2.857(2)	2.732(3) (a)	2.780(3)	2.749(2) (a)	2.709(2) (a)
S O(21)	2.935(5)	2.917(4)	2.947(2)	2.931(3)	2.931(3)	2.977(2)	2.972(2)
O(22) O(17,18)	2.748(6)	2.755(5)	2.608(3) (a)	2.757(4)	2.658(3) (a)	2.684(3)	2.711(3)

(a) Indicates ester oxygen O(18).

Table 3

Valence Angles and Selected Angles Between Nonbonding Atoms

	9	3	4	5	6	7	8
C(1)C(2)C(3)	120.9(9)	122.0(3)	118.8(3)	120.6(6)	121.5(4)	123.2(2)	—
C(2)C(3)C(4)	119.3(7)	117.9(3)	122.1(3)	119.3(4)	119.2(4)	118.0(3)	—
C(3)C(4)C(12)	118.9(8)	120.7(4)	117.2(2)	119.5(4)	120.1(4)	119.6(3)	—
C(4)C(12)C(11)	123.0(8)	121.6(3)	121.9(2)	121.9(4)	121.6(4)	121.3(2)	—
C(12)C(11)C(1)	117.5(6)	117.1(3)	117.9(2)	117.2(3)	117.3(3)	118.9(3)	—
C(11)C(1)C(2)	120.4(8)	120.7(4)	122.1(3)	121.4(5)	120.2(3)	118.9(3)	—
C(5)C(6)C(7)	119.7(8)	119.1(5)	120.4(4)	119.0(6)	120.6(5)	118.7(2)	—
C(6)C(7)C(8)	120.7(6)	120.6(5)	120.3(4)	121.3(4)	119.4(4)	123.1(3)	—
C(7)C(8)C(14)	120.5(8)	122.0(5)	121.3(3)	120.2(5)	122.0(4)	118.3(2)	—
C(8)C(14)C(9)	121.3(7)	118.5(4)	119.5(3)	118.0(4)	118.7(4)	—	—
C(8)C(14)C(13)	117.8(7)	116.6(3)	117.4(3)	118.4(5)	117.7(4)	119.1(2)	—
C(14)C(13)C(5)	122.7(5)	121.7(4)	121.9(3)	121.5(3)	120.6(3)	121.7(2)	—
C(13)C(5)C(6)	118.6(8)	120.0(5)	118.6(3)	119.5(5)	119.7(4)	118.9(2)	—
C(9)C(11)C(1)	121.1(7)	118.0(3)	118.2(2)	118.3(4)	119.3(2)	—	—
C(9)C(11)C(12)	121.4(8)	124.8(3)	123.9(2)	124.4(4)	123.4(4)	—	—
C(11)C(12)S(10)	117.4(5)	123.8(2)	122.0(2)	122.5(3)	123.0(3)	113.9(2)	—
S(10)C(12)C(4)	119.6(6)	114.6(3)	115.9(2)	115.2(3)	115.2(3)	124.6(2)	—
C(12)S(10)C(13)	99.6(3)	103.1(2)	102.7(1)	102.6(2)	103.4(2)	103.9(1)	100.5(1)
S(10)C(13)C(14)	117.4(5)	124.4(3)	123.6(2)	122.8(3)	123.5(3)	119.4(2)	—
S(10)C(13)C(5)	119.7(6)	113.9(4)	114.5(2)	115.4(3)	115.7(3)	118.3(2)	—
C(13)C(14)C(9)	120.9(5)	124.9(3)	123.1(2)	123.6(3)	123.6(3)	—	—
C(14)C(9)C(11)	113.1(7)	118.9(4)	117.1(2)	119.8(4)	121.7(3)	—	—
C(12)S(10)C(15)	110.4(4)	108.0(2)	111.7(1)	105.2(2)	108.4(2)	111.5(1)	107.3(1)
C(13)S(10)C(15)	108.6(3)	106.4(2)	107.8(1)	107.3(2)	107.6(2)	107.8(1)	108.2(1)
S(10)C(15)C(16)	116.1(5)	116.3(3)	112.2(2)	116.4(3)	110.6(2)	116.4(2)	116.1(2)
S(10)C(15)C(20)	117.0(6)	116.4(3)	117.0(2)	116.0(3)	116.9(2)	118.2(2)	117.6(2)
C(15)C(16)O(17)	126.4(6)	126.5(4)	124.9(2)	126.1(4)	123.9(3)	125.7(2)	127.4(2)
C(15)C(16)O(18)	112.0(7)	112.1(3)	113.6(2)	111.8(3)	114.7(3)	112.5(2)	111.6(2)
O(17)C(16)O(18)	121.6(6)	121.5(4)	121.5(2)	122.2(3)	121.4(3)	121.8(2)	120.9(2)
C(16)O(18)C(19)	115.3(6)	116.9(3)	117.3(2)	116.8(4)	115.3(3)	115.2(2)	118.2(2)
C(15)C(20)O(21)	123.1(7)	123.7(3)	124.1(2)	123.3(4)	124.0(3)	124.6(2)	124.6(2)
C(15)C(20)O(22)	114.3(7)	114.8(3)	114.8(2)	114.3(3)	113.8(3)	113.5(2)	113.7(2)
O(21)C(20)O(22)	122.6(5)	121.5(4)	121.1(2)	122.3(3)	122.2(3)	121.8(2)	121.7(2)
C(20)O(22)C(23)	115.2(6)	115.2(3)	115.4(2)	114.8(4)	116.0(3)	114.8(2)	115.9(2)
C(16)C(15)C(20)	126.7(7)	127.1(3)	130.7(2)	127.6(4)	131.9(3)	125.2(2)	126.3(2)
O(18)C(19)C(24)	106.4(8)	—	—	—	—	—	111.3(3)
O(22)C(23)C(25)	111.2(6)	—	—	—	—	—	111.7(4)
C(11)C(9)O(9)	—	—	—	120.6(6)	119.2(4)	—	—
C(14)C(9)O(9)	—	—	—	119.4(5)	119.2(4)	—	—
C(1)C(2)X(2)	—	119.1(3)	119.6(3)	—	119.6(3)	—	—
C(3)C(2)X(2)	—	118.9(3)	121.6(3)	—	118.9(3)	—	—
C(3)C(4)X(4)	—	—	120.0(2)	—	—	—	—
C(12)C(4)X(4)	—	—	122.8(2)	—	—	—	—
C(1)C(2)N	—	—	—	—	—	119.5(3)	—
C(3)C(2)N	—	—	—	—	—	117.3(3)	—
C(2)NO(1)	—	—	—	—	—	115.6(4)	—
C(2)NO(2)	—	—	—	—	—	119.2(3)	—
O(1)NO(2)	—	—	—	—	—	125.3(4)	—
C(6)C(7)N′	—	—	—	—	—	118.7(2)	—
C(8)C(7)N′	—	—	—	—	—	118.1(2)	—
C(7)N′O(1′)	—	—	—	—	—	118.4(2)	—
C(7)N′O(2′)	—	—	—	—	—	118.0(3)	—
O(1′)N′O(2′)	—	—	—	—	—	123.6(3)	—
C(16)O(17,18)S	73.4*	73.6(2)*	67.0(1)	74.6(2)*	68.5(2)	72.7(1)*	74.5(1)*
C(20)O(21)S	66.2	66.6(2)	66.3(1)	67.5(2)	66.2(2)	65.0(1)	65.7(1)
O(17,18)SC(15)	—	57.3(2)	55.7(1)	57.0(1)*	56.8(1)	57.3(1)*	57.8(1)
O(21)SC(15)	—	53.3(2)	52.6(1)	53.2(1)	52.8(1)	52.1(1)	52.0(1)

*Indicates O(18).

from the plane composed of the three attached carbon atoms. The distances for compounds **3-6** and **9** are 0.68, 0.64, 0.70, 0.67 and 0.67 Å, respectively, while compounds **7** and **8** which are not constrained by ring fusion exhibit distances of 0.63 and 0.70 Å. There is no obvious trend in these data.

In all of the compounds examined, the malonylide fragment is planar and oriented with its π-system perpendicular to the lone pair of the sulfur atom. This orientation brings two oxygen atoms of the anion in close proximity to the positively-charged sulfur atom. A carbonyl oxygen atom of one ester group approaches the sulfur from below the basal plane of the pyramid to an average distance of 2.932(9) Å in compounds **2-6** and **9** and an average of 2.914(3) Å in compounds **7** and **8**. An oxygen from the second ester group approximately bisects the angle between the sulfur lone pair and the S—C(15) bond. In structures **4** and **6** the carbonyl oxygen occupies the bisecting site at distances of 2.857(2) and 2.780(3) Å while the ester oxygen is found at an average distance of 2.73(1) Å in the remaining structures. The planar array of the anion moiety leads to the backside interaction between oxygen atoms which averages 2.63(2) Å for the ester-oxygen:ester-oxygen interactions and 2.753(4) and 2.70(2) Å for ester-oxygen:carbonyl-oxygen interactions in **3, 5, 9** and **7** and **8**, respectively. The distances within the malonylide moiety are surprisingly constant throughout the series with average values C(15)—C(16) = 1.441(6), C(15)—C(20) = 1.437(6), C(16)—O(17) = 1.207(6), C(20)—O(21) = 1.215(4), C(16)—O(18) = 1.35(1) and C(20)—O(22) = 1.350(3) Å.

The orientation of the anion moiety with respect to the sulfur atom is determined by the sulfur lone-pair:carbon π-electron repulsion. The oxygen atoms are forced into close proximity of the sulfur atom by the planarity of the anion, the orientation effects of the lone-pair:π-electron repulsion and the backside oxygen-oxygen repulsion. The malonylide anion is isoconjugate with the pentadienyl anion, and PMO theory predicts the charge density in the pentadienyl system to be evenly distributed on atoms 1, 3 and 5. Replacement of atoms 1 and 3 by more electronegative oxygen atoms results in a greater charge density being associated with the carbonyl oxygen atoms. Some charge is returned to position 3 by σ-bond formation to the positively charged sulfur atom. One might expect additional stabilization of the ylide structure by an electrostatic interaction between the carbonyl oxygen atoms and the positively charged sulfur atom. Of the seven compounds investigated only two have both carbonyl groups oriented toward the positively charged sulfur atom. The bisecting carbonyl-sulfur interaction may provide less stabilization due to the proximity of the sulfur lone pair.

The $^{+}$S—C^{-} bond distances range from 1.703(2) Å to 1.743(4) Å with an average value of 1.72(1) Å. It is difficult to attribute either stability or bond length reduction to an electrostatic interaction between the positively charged sulfur atom and the negatively charged ylide carbon since the most stable structures are those in which the negative charge is delocalized. Any significant variations in bond lengths in the current series may be attributable to changes in geometry around the sulfur atom or to the effects of the other sulfur substituents.

The shortening of the $^{+}$S—C^{-} bond also has been attributed to backdonation to the σ^{*}-orbitals of the other sulfur-carbon bonds. Overlap with these orbitals is not favored by pyramidal geometry around the sulfur atom. Sulfur 3d-orbitals have the proper orientation to participate in backbonding with the carbanion π-system and the nonbonding electrons of the carbonyl groups. While d-orbital participation cannot be demonstrated in the current series, it is an obvious rationalization that cannot be eliminated by structural considerations.

We have suggested that the most important factor determining the stability of ylides may be the change in geometry associated with the sp^2 hybridization and not the delocalization. In addition to reducing the covalent radius of the carbanion carbon, the rehybridization permits the minimization of lone pair:π-electron repulsion and a possible π-σ^{*} interaction involving the two C—S bonds and the carbanion system (17).

NMR Spectra.

All of the nmr spectra of these ylides share general common characteristics. Thus, all exhibit the OCH_3 resonance near 50 ppm, the —C(O)—O— resonance near 166 ppm and the methylide carbon in the region near 50-70 ppm. We have already demonstrated that the range of the latter is, at least in part, a conformational dependence. Thus, in the thioxanthenium methylide series e′ methylide carbons resonate near 50 ppm while the a′ analogs absorb near 70 ppm (16). The thioxanthonium methylides, with an intermediate geometry, resonate near 60 ppm. The acyclic analog diphenylsulfonium bis(carbomethoxy)methylide (**10**) exhibits a methylide resonance at 59.6 ppm well within the range of these heterocyclic analogs. That electronic effects can perturb the methylide resonance is seen by the methylide carbon resonances of **7** (58.2 ppm).

While there are the similarities described above, there is one spectral feature present in the thioxanthonium methylides but absent in the other compounds. Both the proton and the carbon resonances indicate a comparatively high rotational barrier about the $^{+}$S—C^{-} bond in **5** and **6**. This is most obvious in their extremely broad —OCH_3 resonances at +34° (60 MHz). At 200 MHz, at this temperature, the methoxy signals appear as overlapping, broadened singlets. Increasing the temperature leads to coalescence of these signals. A complete lineshape analysis of **6**, in benzene-d_6, indicates a $\Delta H^{\ddagger}$ = 12.1 kcal/mole,

$\Delta S^{\ddagger} = -7.1$ eu and $\Delta G^{\ddagger}_{298} = 14.3$ kcal/mole.

At lower temperatures (approximately $-30°$ at 200 MHz) the upfield ^1H methoxy resonance of **6** (and related thioxanthonium methylides) begins to broaden relative to the downfield methoxy resonance. Near $-90°$ it sharpens again. In addition, the chemical shift of the upfield signal is quite temperature sensitive. For example, at $-35°$ (200 MHz, deuteriochloroform) the downfield methoxy signal of **5** occurs at 775 Hz while the upfield occurs at 676 Hz. (The relative widths at half-height are 1:2.2). At $-65°$ the downfield signal has shifted to 772 Hz while the upfield has shifted to 703 Hz. (Relative widths are approximately 1.2:1). This second rotational barrier is related to rotation around the C⁻—C(O) bond in the endo carbomethoxy group. Such slowed rotation is consistent with attraction between the positively-charged sulfur and the endo carbonyl oxygen.

Both of these rotational barriers are sensitive to the substituent at the C(2) position and this dependence will be discussed, in detail, in a subsequent manuscript. However, it is clear that the C(2) substituent influences interactions between sulfur and the moiety to which it is bonded. In this instance these may be viewed as Lewis acid-base complexes between a sulfide and a carbene. This is, we believe, quite significant since C(2)-substituted systems of this and related types (*e.g.*, phenothiazines) often show substantial pharmacological activity. Moreover, this activity depends, in part, upon the nature of the C(2) substituent.

EXPERIMENTAL

X-Ray Structure Determination and Refinement.

All data were collected on a Syntex $P2_1$ diffractometer system by the $\theta:2\theta$ scanning technique using a variable scan speed and graphite monochromatized CuKα radiation (λ = 1.54178 Å). Room-temperature lattice parameters were refined by a least-squares procedure using 15 reflections whose angles were measured by a centering routine associated with the diffractometer. Space groups were determined by systematic absences and statistics. Periodically monitored reference reflections showed no significant changes in intensity. Lorentz and polarization corrections were applied, but no absorption corrections were made.

The direct-methods program MULTAN (19) was used to calculate phases for the larger |E| values. The phase set with the largest combined figure of merit revealed the molecular framework for all compounds except (**5**). Difference Fourier calculations yielded the coordinates of all hydrogen atoms after anisotropic refinement of the heavy atoms. Full-matrix least-squares refinements were terminated when the R value became stationary. R is defined as $\Sigma||F_o|-|F_c||/\Sigma|F_o|$. The function minimized in the refinement was $\Sigma\omega(|F_o|-|F_c|)^2$ where $\omega = 1/\sigma^2(F_o)$ was determined by counting statistics. H atom thermal parameters were not refined.

Final difference maps were checked for residual electron density and the shift/error for all parameters was examined. Atomic scattering factors were calculated by the XRAY76 program (20). Bond distances, valence angles and selected intramolecular distances and angles are presented in Tables 2 and 3. Lists of atomic positional parameters and anisotropic thermal parameters may be obtained from the author (WHW).

2-Chlorothioxanthenium Bis(carbomethoxy)methylide (**3**).

The following data are reported: $C_{18}H_{15}ClO_4S$: MW = 362.83; crystal dimensions 0.30 × 0.33 × 0.09 mm; space group $P2_1/c$; a = 8.155(2), b = 17.778(4), c = 13.226(2) Å, β = 121.02(1)°; V = 1643.2(5) Å^3; Z = 4; dc = 1.47 gcm^{-3}; μ = 33.75 cm^{-1}. Of the 2667 independent reflections measured 2079 had intensities greater than 3σ(I). A twenty atom fragment was found in the E map with the highest CFOM. A final R of 0.060 was achieved with a mean shift/error in the final cycle of refinement of 0.03. The largest peak in the final difference Fourier map was 0.3 eÅ^{-3}. An ORTEP drawing (21) of compound **3** is presented in Figure 1.

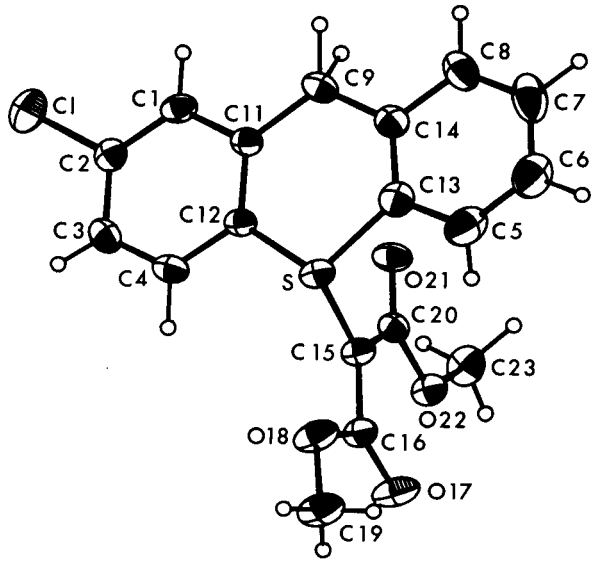

Figure 1. ORTEP drawing of 2-Chlorothioxanthenium bis(carbomethoxy)methylide **3**.

2,4-Dimethylthioxanthenium Bis(carbomethoxy)methylide (**4**).

The following data are reported: $C_{20}H_{20}O_4S$: MW = 356.44; crystal dimensions 0.33 × 0.25 × 0.20 mm; space group $P2_1/c$; a = 11.005(2), b = 10.161(2), c = 15.687(2) Å, β = 93.53(1)°; V = 1750.8(4) Å^{-3}; Z = 4; dc = 1.35 gcm^{-3}; μ = 17.85 cm^{-1}. Of the 2919 independent reflections measured 2278 had intensities greater than 3σ(I). All nonhydrogen atoms were located in the E map with the highest CFOM. A final R of 0.048 was achieved with a largest shift/error of 0.05 in the final cycle of refinement. The largest peak in the final difference Fourier map was 0.03 eÅ^{-3}. An ORTEP drawing of compound **4** is presented in Figure 2.

Thioxanthonium Bis(carbomethoxy)methylide (**5**).

The following data are reported: $C_{18}H_{14}O_5S$: MW = 342.37; crystal dimensions 0.40 × 0.33 × .18 mm; space group $P2_1$; a = 11.728(3), b = 9.425(2), c = 8.197(2) Å, β = 119.45(2)°; V = 789.0(3) Å^3; Z = 2; dc = 1.44 gcm^{-3}; μ = 20.10 cm^{-1}. Of the 1370 independent reflections measured 1326 had intensities greater than 3σ(I). The structure was solved by use of Harker planes and subsequent Fourier syntheses. A final R of 0.063 was achieved with a largest shift/error of 0.06 during the final cycle of refinement. Four reflections were omitted because of secondary extinction. A final difference Fourier map contained a maximum electron density of 0.04 eÅ^{-3}. An ORTEP drawing of compound **5** is presented in Figure 3.

2-Chlorothioxanthonium Bis(carbomethoxy)methylide (**6**).

The following data are reported: $C_{18}H_{13}ClO_5S$: MW = 376.82; crystal dimensions 0.38 × 0.16 × 0.07 mm; space group $P\bar{1}$; a = 5.553(2), b = 12.167(4), c = 12.992(5) Å, α = 93.91(3), β = 105.03(3), γ = 101.62(2)°; V = 823.7(5) Å^3; Z = 2; dc = 1.52 gcm^{-3}; μ = 34.41 cm^{-1}. Of the 2394

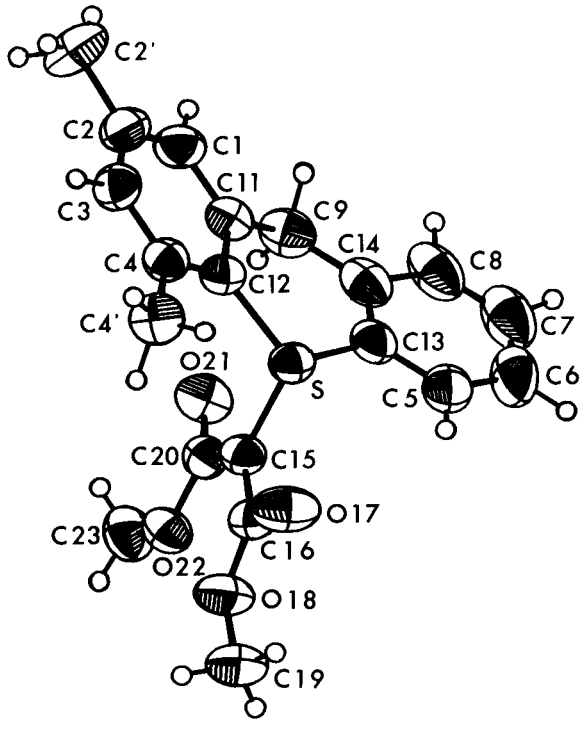

Figure 2. ORTEP drawing of 2,4-Dimethylthioxanthenium bis(carbomethoxy)methylide **4**.

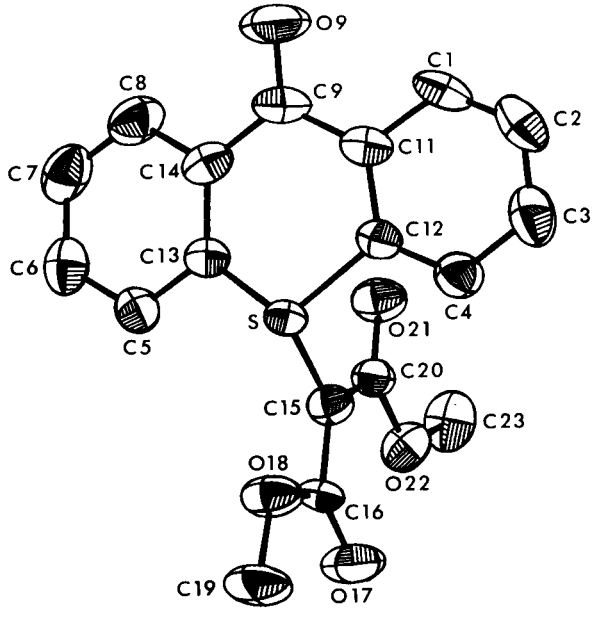

Figure 3. ORTEP drawing of Thioxanthonium bis(carbomethoxy)methylide **5**.

independent reflections measured 1816 had intensities greater than $3\sigma(I)$. All nonhydrogen atoms were located in the E map with the highest CFOM. A final R of 0.053 was achieved with a largest shift/error of 0.07 in the final cycle of refinement. The largest peak in the final difference Fourier map was 0.04 e Å^{-3}. An ORTEP drawing of compound **6** is presented in Figure 4.

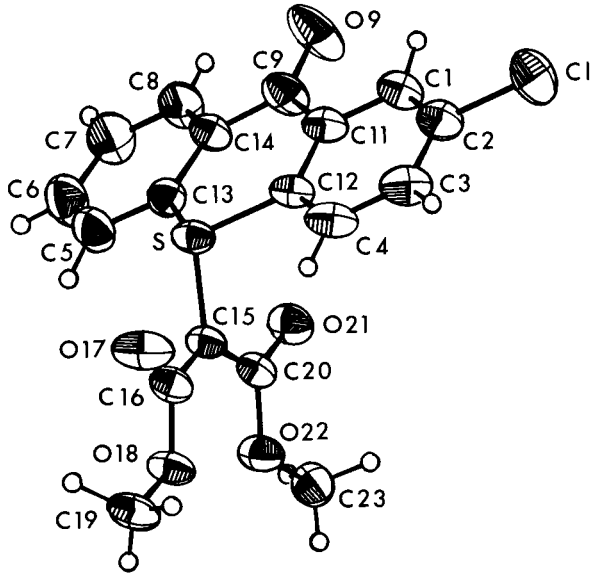

Figure 4. ORTEP drawing of 2-Chlorothioxanthonium bis(carbomethoxy)methylide **6**.

Di(*p*-nitrophenyl)sulfonium Bis(carbomethoxy)methylide (**7**).

The following data are reported: $C_{17}H_{14}N_2O_8S$: MW = 406.37; crystal dimensions 0.45 × 0.35 × 0.22 mm; space group $P2_1/c$; a = 17.491(5); b = 8.435(2), c = 13.347(3) Å; β = 113.30(2)°; V = 1808.6(7) Å^3; Z = 4; dc = 1.49 gcm^{-3}; μ = 20.14 cm^{-1}. Of the 3018 independent reflections measured 2598 had intensities greater than $3\sigma(I)$. All nonhydrogen atoms were located in the E map with the highest CFOM. A final R of 0.055 was achieved with an average shift/error of 0.1 in the final cycle of refinement. The largest peak in the final difference Fourier map was 0.3 e Å^{-3}. An ORTEP drawing of compound **7** is shown in Figure 5.

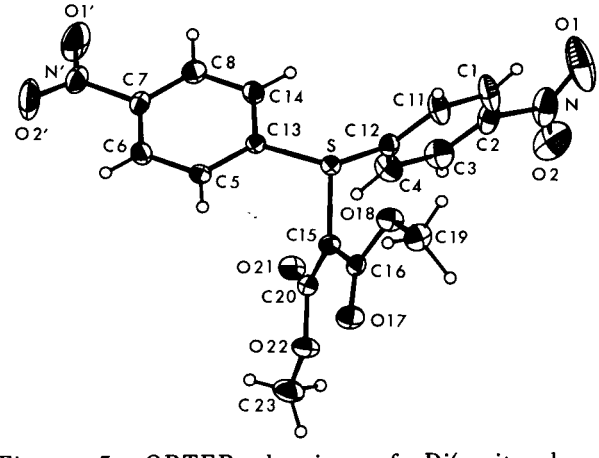

Figure 5. ORTEP drawing of Di(*p*-nitrophenyl)-sulfonium bis(carbomethoxy)methylide **7**.

Dimethylsulfonium Bis(carbomethoxy)methylide (**8**).

The following data are reported: $C_9H_{16}O_4S$: MW = 220.29; crystal dimensions 0.25 × 0.25 × 0.25 mm; space group $P2_1/c$; a = 7.273(2), b = 16.262(3), c = 9.828(2) Å, β = 95.22(2)°; V = 1157.6(4) Å^3; Z = 4; dc = 1.26 gcm^{-3}; μ = 23.50 cm^{-1}. Of the 1940 reflections measured 1651 had intensities greater than $3\sigma(I)$. All nonhydrogen atoms were found in the E map with the highest CFOM. A final R of 0.050 was achieved with a mean shift/error of 0.02 in the final cycle of refinement. The largest peak in the final difference Fourier map was 0.25 e Å^{-3}.

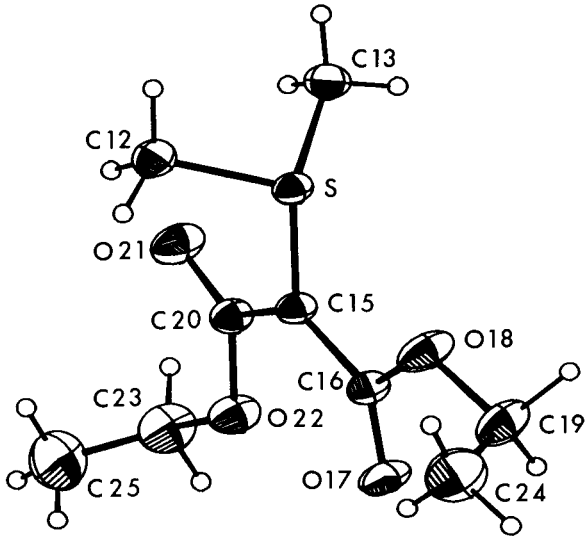

Figure 6. ORTEP drawing of Dimethylsulfonium bis(carboethoxy)methylide **8**.

Synthesis.

Diphenylsulfonium Bis(carbomethoxy)methylide (**10**).

A mixture of diphenyl sulfide (2.79 g, 0.015 mole), dimethyl diazomalonate (4.74 g, 0.0300 mole), toluene (9 ml) and anhydrous copper(II) sulfate (100 mg) (21) were heated in a nitrogen atmosphere for 5 hours at 103-107°. After cooling to room temperature, the mixture was triturated with chloroform (50 ml) and the insoluble material removed by filtration. The volatiles were removed *in vacuo*, to afford the crude reaction product. Two recrystallizations from ethanol yielded 1.23 g (0.00393 mole, 26%) of diphenylsulfonium bis(carbomethoxy)methylide, mp 121-122°; ^{13}C nmr (25 MHz, deuteriochloroform, 30°): C=O, 166.23; aryl-C, 131.00, 130.13 (quat), 129.14, 128.97; $^{+}S—C^{-}$, 59.58; CH_3, 150.66; ^{1}H nmr (250 MHz deuteriochloroform, 24°): Ar-4, δ 7.4-8.2 (8H, multiplet); OCH_3, δ 3.8 (6H, band-width at half-height 0.37 Hz).

Anal. Calcd. for $C_{17}H_{16}O_4S$: C, 64.54; H, 5.10. Found: C, 64.21; H, 5.01.

Di(4-nitrophenyl)sulfonium Bis(carbomethoxymethylide) (**7**).

A mixture of di(4-nitrophenyl)sulfide (2.76 g, 0.0100 mole), dimethyl diazomalonate (3.16 g, 0.0200 mole) and anhydrous copper(II) sulfate (100 mg) was heated for 4 hours at 100-110° in a nitrogen atmosphere. After cooling to room temperature, the reaction mixture was triturated with chloroform (50 ml) and the insoluble material removed by filtration. The volatiles were removed, *in vacuo*, to afford the crude product. Two recrystallizations from ethanol followed by one from ethyl acetate afforded 2.29 g (0.00564 mole, 56%) of di(4-nitrophenyl)sulfonium bis(carbomethoxy)methylide, mp 184-186°; ^{13}C nmr (25 MHz, deuteriochloroform, 30°): C=O, 165.82; aryl—C—NO, 149.57; aryl-C, 136.28 (quat), 130.35, 124.60; $^{+}S—C^{-}$, 58.15; CH, 51.47.

Anal. Calcd. for $C_{17}H_{14}N_2O_8S$: C, 50.25; H, 3.47. Found: C, 50.31; H, 3.69.

Dimethylsulfonium Bis(carboethoxy)methylide (**8**).

A mixture of dimethyl sulfide (0.62 g, 0.010 mole), diethyl diazomalonate (3.72 g, 0.020 mole) and anhydrous copper(II) sulfate (0.010 g) were heated for 4 hours at 100-110° in a nitrogen atmosphere. After cooling to room temperature chloroform (50 ml) was added to the reaction mixture and the insoluble material removed by filtration. The volatiles were removed, *in vacuo*, and the resulting crude reaction product recrystallized from ethanol to form dimethylsulfonium bis(carboethoxy)methylide (0.34 g, 0.00158 mole, 16%), mp 133-135°.

Anal. Calcd. for $C_9H_{14}O_4S$: C, 49.07; H, 7.32. Found: C, 49.12; H, 7.01.

2-Chlorothioxanthenium Bis(carbomethoxy)methylide (**3**), 2,4-Dimethylthioxanthenium Bis(carbomethoxy)methylide (**4**), Thioxanthonium Bis(carbomethoxy)methylide (**5**), 2-Chlorothioxanthonium Bis(carbomethoxy)methylide (**6**), and Thioxanthenium Bis(carboethoxy)methylide (**9**).

These compounds were prepared as described in the literature (16).

Acknowledgement.

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