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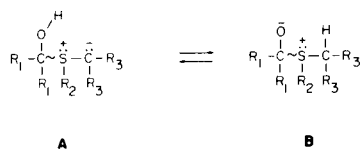
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The single-crystal X-ray structures of 9-hydroxy-1,4-dimethylthioxanthenium bis(carbomethoxy)methylide and 1,4-oxathianium bis(carbomethoxy)methylide are reported. The methylide carbon of the former is pseudo-axial while that of the latter is equatorial. The former exhibits a strong intramolecular hydrogen bond to a carbonyl oxygen atom.

J. Heterocyclic Chem., **19**, 1473 (1982).

Introduction.

Sulfonium ylides could, in principle, act as hydrogen bond acceptors at several sites, including (a) the sulfur atom, (b) the methylide carbon, and (c) functional groups bonded to the methylide carbon. In the case of bis-carboalkoxymethylides ($^+S^-(CO_2R)_2$) the oxygens of the carboalkoxy groups could serve as acceptors. While such hydrogen bonded species might be stable, they also could serve as precursors to zwitterions formed by proton transfer from an internal hydroxy group. A generalized example is shown below, the position of equilibrium being dictated by the substituents ($R_1 - R_3$) (1).



As part of a study of hydrogen bonding to stabilized carbanions we have prepared 9-hydroxy-1,4-dimethylthioxanthenium bis(carbomethoxy)methylide (**1**), and related thioxanthenium ylides. Compound **1** represents a model compound for transannular hydrogen bonding since the peri methyl groups constrain both the methylide carbon and the hydroxyl group to the pseudoaxial (a' , "flagpole") position.

Sulfonium ylides are unusually stable if groups capable of electron delocalization are attached to the carbanion. This stability has been rationalized in terms of $d\pi-p\pi$ backbonding interactions and the argument was supported by C-S bond lengths of 1.71 Å and 1.72 Å observed for 2-dimethylsulfuranylidene-1,3-indanedione (2) and 2-dimethylsulfuranylidene malonitrile (3). By comparison with several conjugated C=S bonds (4,5), an isolated C=S bond is expected to be about 1.61 Å while a single C-S bond is greater than 1.8 Å. The C=S bonds in thiourea (6) and thioacetamide (7) are considered to be partial double bond in character and are reported to be 1.71 Å.

Table 1

Atomic Positional Parameters ($\times 10^4$) for Compound 1

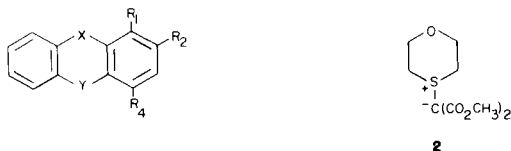
atom	x/a	y/b	z/c	Ueq (a)
C(1)	7229(3)	4711(4)	10080(2)	36
C(1')	8969(4)	6635(4)	10899(2)	46
C(2)	6228(4)	3112(4)	10197(2)	43
C(3)	4626(4)	1300(4)	9468(2)	42
C(4)	3964(3)	989(3)	8583(2)	35
C(4')	2220(4)	-1028(4)	7798(2)	45
C(5)	4405(4)	4601(4)	6738(2)	44
C(6)	5092(4)	6483(5)	6851(2)	52
C(7)	6505(4)	8281(4)	7708(2)	50
C(8)	7274(4)	8167(4)	8424(2)	45
C(9)	7658(3)	6280(3)	9106(2)	35
O(9)	9420(2)	6528(3)	8989(2)	45
S(10)	4048.2(6)	2056.9(8)	7293.1(4)	30
C(11)	6582(3)	4471(3)	9199(2)	31
C(12)	4989(3)	2590(3)	8459(2)	31
C(13)	5183(3)	4521(3)	7477(2)	32
C(14)	6644(3)	6286(3)	8324(2)	34
C(15)	4617(3)	429(3)	6415(2)	32
C(16)	2976(3)	-1380(3)	5588(2)	33
O(17)	1421(2)	-1616(3)	5486(1)	49
O(18)	3275(2)	-2827(3)	4939(1)	48
C(19)	1663(4)	-4679(4)	4121(2)	54
C(20)	6541(3)	1003(4)	6591(2)	33
O(21)	7814(2)	2638(3)	7318(1)	47
O(22)	6855(2)	-382(3)	5909(1)	47
C(23)	8768(4)	104(6)	6087(2)	59

(a) $U_{eq} = 1/3 \sum U_{ij} a_i^* a_j^* (a_i a_j)$.

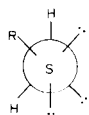
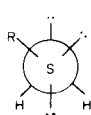
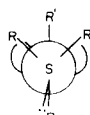
During the last decade the significance of backbonding involving second and third row elements has been brought into question. A study of the stability of carbanions adjacent to hetero atoms such as sulfur indicates the inclusion of d-orbitals lowers the energies of both the anion and the neutral parent compound (8,9); however, it was concluded that the stability of the anion relative to the neutral species could not be attributed to the $d\pi-p\pi$ backbonding. The authors suggested that the carbanion stability was related to polarization effects, stereoelectronic factors

(lone pair interactions) and, most importantly, interactions of the carbanion lone pair with a σ^* orbital involving the sulfur atom. For a series of compounds RSCH_2^- they demonstrated that conformation **C** was more stable than conformation **D** due to lone pair- σ^* (R-S) interaction. These interactions would decrease the S-C bond length and increase the R-S separation.

The above calculations were based upon a divalent sulfur species with a tetrahedral arrangement of bonds and lone pairs and a tetrahedral carbanion. The stable sulfonium ylides involve a positively-charged sulfur atom and an sp^2 -hybridized carbanion. The positive charge on the sulfur contracts the d-orbitals (10) and should provide the best opportunity for $d\pi$ - $p\pi$ backbonding if it is to occur. In order to provide additional insight into the sulfur-carbon bond in sulfonium ylides, we have determined the structures of **1** and 1,4-oxathienium bis(carbomethoxy)methylide, **2**. For comparison purposes the conformation about the C-S bond in these is shown in **E**.



	X	Y	R ₁	R ₂	R ₄
1	CHOH	*S-C(CO ₂ CH ₃) ₂	CH ₃	H	CH ₃
3	CHOH	*S-C(CO ₂ CH ₃) ₂	H	CH ₃	CH ₃
4	CHOH	S	CH ₃	H	CH ₃
5	CHOH	S	H	CH ₃	CH ₃
6	CHOH	S(O)	H	H	H
7	C=O	S	H	H	H
8	C=O	*S-C(CO ₂ CH ₃) ₂	CH ₃	H	CH ₃
9	C=O	*S-C(CO ₂ CH ₃) ₂	H	CH ₃	CH ₃

**C****D****E**

Results and Discussion.

X-Ray Analyses.

Figures 1 and 2 are ORTEP drawings (11) of compounds **1** and **2**, respectively. The two phenyl rings in compound **1** exhibit an interplanar angle of $158.7(2)^\circ$. The six-membered ring containing the sulfur atom is in a boat conformation with the C(9) and S(10) substituents occupying axial sites. The carbanion moiety is planar and the conformation about the S(10)-C(15) bond is determined primarily by electrostatic repulsion between the sulfur lone pair and the π -system of the carbanion. Normally,

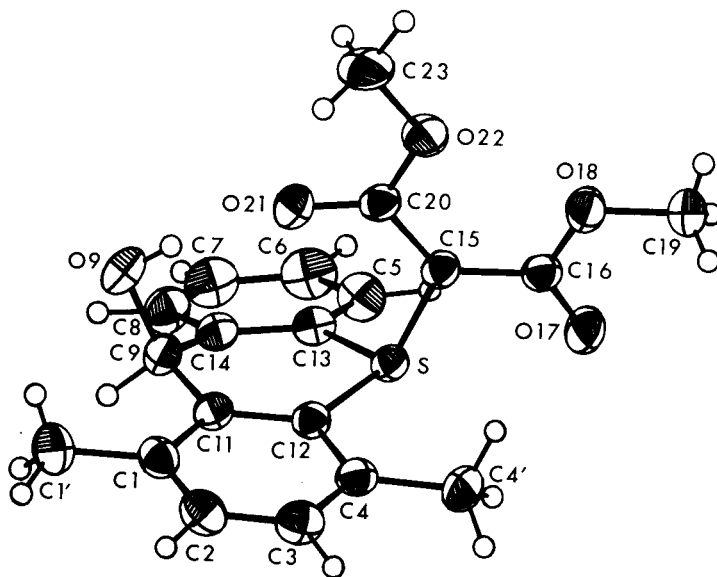


Figure 1. ORTEP drawing of 9-hydroxy-1,4-dimethylthioxanthenium bis(carbomethoxy)methylide (**1**). Thermal ellipsoids are drawn at the 35% probability level.

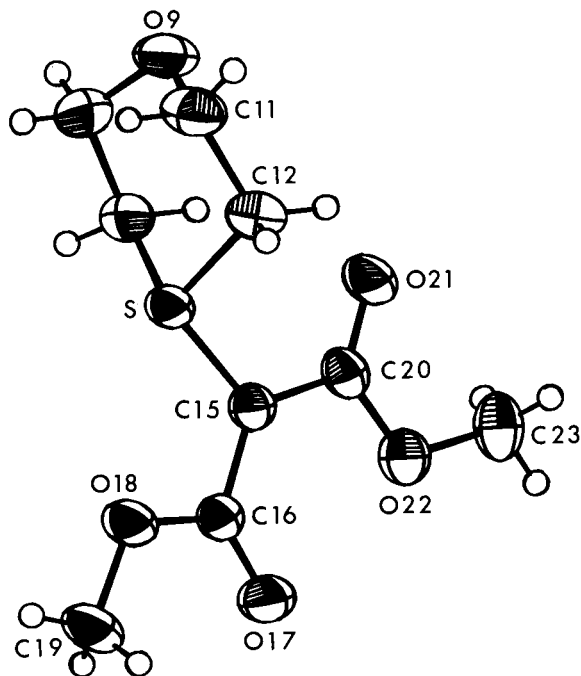


Figure 2. ORTEP drawing of 1,4-oxathianium bis(carbomethoxy)methylide (**2**). Thermal ellipsoids are drawn at the 35% probability level.

the carbanion occupies a pseudo equatorial site in these sulfonium ylides (12,13); however, the methyl group at C(4) forces the carbanion into the sterically less-hindered axial conformation. A hydrogen bond involving the hydroxyl group at C(9) and the O(21) carbonyl oxygen atom further

Table 2

Interatomic Distances (Å) for Compound 1

C(1) - C(1')	1.501(3)	C(9) - C(14)	1.510(5)
C(1) - C(2)	1.387(5)	S(10) - C(12)	1.782(3)
C(1) - C(11)	1.400(4)	S(10) - C(13)	1.771(3)
C(2) - C(3)	1.380(3)	C(10) - C(15)	1.718(3)
C(3) - C(4)	1.379(4)	C(11) - C(12)	1.400(2)
C(4) - C(4')	1.510(3)	C(13) - C(14)	1.388(2)
C(4) - C(12)	1.399(4)	C(15) - C(16)	1.445(2)
C(5) - C(6)	1.380(6)	C(15) - C(20)	1.434(3)
C(5) - C(13)	1.396(5)	C(16) - O(17)	1.219(3)
C(6) - C(7)	1.389(3)	C(16) - O(18)	1.327(3)
C(7) - C(8)	1.379(6)	O(18) - C(19)	1.438(3)
C(8) - C(14)	1.394(5)	C(20) - O(21)	1.225(2)
C(9) - O(9)	1.433(3)	C(20) - O(22)	1.323(3)
C(9) - C(11)	1.520(4)	O(22) - C(23)	1.446(4)

Table 3

Valence Angles (°) for Compound 1

C(1')	- C(1)	- C(2)	119.0(2)
C(1')	- C(1)	- C(11)	122.3(2)
C(2)	- C(1)	- C(11)	118.8(2)
C(1)	- C(2)	- C(3)	121.6(2)
C(2)	- C(3)	- C(4)	121.3(3)
C(3)	- C(4)	- C(4')	119.7(3)
C(3)	- C(4)	- C(12)	117.1(2)
C(4')	- C(4)	- C(12)	123.2(3)
C(6)	- C(5)	- C(13)	119.4(2)
C(5)	- C(6)	- C(7)	119.9(4)
C(6)	- C(7)	- C(8)	119.8(4)
C(7)	- C(8)	- C(14)	121.7(2)
O(9)	- C(9)	- C(11)	111.3(3)
O(9)	- C(9)	- C(14)	109.5(2)
C(11)	- C(9)	- C(14)	116.7(2)
C(12)	- S(10)	- C(13)	103.7(1)
C(12)	- S(10)	- C(15)	108.9(1)
C(13)	- S(10)	- C(15)	111.0(1)
C(1)	- C(11)	- C(9)	117.7(2)
C(1)	- C(11)	- C(12)	118.4(3)
C(9)	- C(11)	- C(12)	123.9(2)
C(4)	- C(12)	- S(10)	114.2(1)
C(4)	- C(12)	- C(11)	122.8(2)
S(10)	- C(12)	- C(11)	123.0(2)
C(5)	- C(13)	- S(10)	114.9(1)
C(5)	- C(13)	- C(14)	121.7(3)
S(10)	- C(13)	- C(14)	123.2(2)
C(8)	- C(14)	- C(9)	118.2(2)
C(8)	- C(14)	- C(13)	117.4(3)
C(9)	- C(14)	- C(13)	124.3(3)
S(10)	- C(15)	- C(16)	111.2(2)
S(10)	- C(15)	- C(20)	118.5(1)
C(16)	- C(15)	- C(20)	130.2(2)
C(15)	- C(16)	- O(17)	124.0(2)
C(15)	- C(16)	- O(18)	114.5(2)
O(17)	- C(16)	- O(18)	121.4(2)
C(16)	- O(18)	- C(19)	116.2(2)
C(15)	- C(20)	- O(21)	123.3(2)
C(15)	- C(20)	- O(22)	115.0(1)
O(21)	- C(20)	- O(22)	121.7(2)
C(20)	- O(22)	- C(23)	116.4(2)

Table 4

Torsion Angles (°) for Compound 1

C(9) - C(11) - C(12) - S(10)	1.5(4)
C(11) - C(12) - S(10) - C(13)	- 14.1(3)
C(12) - S(10) - C(13) - C(14)	8.2(3)
S(10) - C(13) - C(14) - C(9)	10.8(4)
C(13) - C(14) - C(9) - C(11)	- 25.6(4)
C(14) - C(9) - C(11) - C(12)	18.9(4)
C(11) - C(12) - S(10) - C(15)	104.2(2)
C(14) - C(13) - S(10) - C(15)	- 108.6(2)
C(12) - S(10) - C(15) - C(16)	126.8(2)
C(13) - S(10) - C(15) - C(16)	- 119.6(2)
C(12) - S(10) - C(15) - C(20)	- 52.8(3)
C(13) - S(10) - C(15) - C(20)	60.7(3)
S(10) - C(15) - C(16) - O(17)	6.7(4)
S(10) - C(15) - C(16) - O(18)	- 172.1(2)
C(15) - C(16) - O(18) - C(19)	178.2(3)
O(17) - C(16) - O(18) - C(19)	- 6(5)
S(10) - C(15) - C(20) - O(21)	- 3.1(5)
S(10) - C(15) - C(20) - O(22)	176.4(2)
C(15) - C(20) - O(22) - C(23)	- 177.1(3)
O(21) - C(20) - O(22) - C(23)	2.3(5)
O(17) - C(16) - C(15) - C(20)	- 173.8(3)
O(18) - C(16) - C(15) - C(20)	7.5(5)
C(16) - C(15) - C(20) - O(21)	177.4(3)
C(16) - C(15) - C(20) - O(22)	- 3.2(5)
O(9) - C(9) - C(11) - C(12)	- 107.9(3)
O(9) - C(9) - C(14) - C(13)	102.1(3)
O(9) - C(9) - C(11) - C(1)	72.2(3)
O(9) - C(9) - C(14) - C(8)	- 74.2(3)
C(9) - C(11) - C(1) - C(1')	- 2.7(4)
C(9) - C(11) - C(1) - C(2)	177.5(3)
C(9) - C(11) - C(12) - C(4)	- 176.4(3)
C(9) - C(14) - C(8) - C(7)	175.5(3)
C(9) - C(14) - C(13) - C(5)	- 174.4(3)
C(11) - C(1) - C(2) - C(3)	.3(5)
C(1) - C(2) - C(3) - C(4)	.9(5)
C(1) - C(11) - C(9) - C(14)	- 161.0(2)
C(11) - C(9) - C(14) - C(8)	158.2(2)
C(1) - C(11) - C(12) - S(10)	- 178.6(2)
C(2) - C(3) - C(4) - C(4')	179.2(3)
C(2) - C(3) - C(4) - C(12)	.1(4)
C(3) - C(4) - C(12) - C(11)	- 2.3(4)
C(3) - C(4) - C(12) - S(10)	179.6(2)
C(1') - C(1) - C(2) - C(3)	- 179.5(3)
C(1') - C(1) - C(11) - C(12)	177.4(3)
C(4') - C(4) - C(12) - C(11)	178.6(3)
C(4') - C(4) - C(12) - S(10)	.5(4)
C(4) - C(12) - C(11) - C(1)	3.5(4)
C(4) - C(12) - S(10) - C(15)	- 77.7(2)
C(5) - C(13) - S(10) - C(15)	76.2(2)
C(4) - C(12) - S(10) - C(13)	164.0(2)
C(12) - S(10) - C(13) - C(5)	- 167.0(2)
S(10) - C(13) - C(5) - C(6)	174.8(3)
S(10) - C(13) - C(14) - C(8)	- 172.9(2)
C(13) - C(5) - C(6) - C(7)	- 2.0(5)
C(5) - C(6) - C(7) - C(8)	2.9(5)
C(6) - C(7) - C(8) - C(14)	- 1.3(5)
C(7) - C(8) - C(14) - C(13)	- 1.0(4)
C(8) - C(14) - C(13) - C(5)	1.9(4)
C(8) - C(14) - C(13) - S(10)	- 172.9(2)
C(14) - C(13) - C(5) - C(6)	- 4(5)

stabilizes the conformation, $O(9)..O(21) = 2.725(2) \text{ \AA}$, $O(9)..H(9) = 0.82(3) \text{ \AA}$, $H(9)..O(21) = 1.92(3) \text{ \AA}$, and $O(9)H(9)O(21) = 169(4)^\circ$. Short intramolecular contacts exist between the carbonyl oxygen atoms and S(1) with $S(10)..O(17) = 2.816(2) \text{ \AA}$ and $S(10)..O(21) = 2.969(2) \text{ \AA}$. Whether this represents an attractive interaction or occurs as a result of repulsion between O(18) and O(22), $O(18)..O(22) = 2.612(2) \text{ \AA}$, cannot be ascertained; however, a small twist away from coplanarity would reduce the interaction without any significant decrease in delocalization energy. The C(4') methyl to C(15) distance is $3.428(4) \text{ \AA}$. The methyl group remains coplanar with the phenyl ring, but is slightly bent away from C(15); $C(3)C(4)C(4') = 119.7(3)^\circ$, $C(12)C(4)C(4') = 123.2(3)^\circ$, $C(4')..C(3) = 2.499(3) \text{ \AA}$ and $C(4')..C(12) = 2.560(3) \text{ \AA}$. The S(10)-C(13) distance of $1.771(3) \text{ \AA}$ is slightly shorter than the S(10)-C(12) distance of $1.782(3) \text{ \AA}$. This may be related to the steric interactions involving the C(4) methyl group.

In compound **2** a crystallographic mirror plane bisects the 1,4-oxathiane ring while the carbanion moiety lies entirely within the plane. The six-membered ring exhibits a chair conformation with the carbanion occupying an equatorial site. The conformation about the S(10)-C(15) bond is again determined by electrostatic repulsion between the sulfur lone pair and the pi-system of the carbanion. The S(10)-C(12) distance of $1.804(2) \text{ \AA}$ is longer than that observed in compound **1** due to changes in hybridization of C(12). The S(10)-C(15) distance of $1.723(2) \text{ \AA}$ is statistically equivalent to the $1.718(3) \text{ \AA}$ distance in **1**. The carbanion moiety conformation in **2** has one carbonyl oxygen atom O(18) and one ester oxygen atom O(21) oriented toward the sulfur atom with short intramolecular contacts of $S(10)..O(18) = 2.716(2) \text{ \AA}$, $S(10)..O(21) = 2.988(2) \text{ \AA}$ and $O(17)..O(22) = 2.700(3) \text{ \AA}$.

Four conformations differing only in the orientation of the carbonyl and ester oxygen atoms are possible. For structures where the carbanion group occupies a pseudo axial site only the conformation with both carbonyls oriented toward the sulfur atom have been observed in the solid state. For structures with the carbanion group occupying a pseudo equatorial site all four conformations have been observed; however, the conformer with one carbonyl oriented toward the sulfur lone pair and the other away from the sulfur atom appears to be less common (14,15). In structure **1** the carbanion bond *trans*, antiperiplanar, to the sulfur lone pair, $C(15)-C(20) = 1.434(3) \text{ \AA}$, is shorter than the bond *syn* to the lone pair, $C(15)-C(16) = 1.445(2) \text{ \AA}$; however, the bond length variation is reversed in **2** with the *syn* bond being $1.434(4) \text{ \AA}$ and the *trans* bond $1.446(4) \text{ \AA}$. If a sulfur lone-pair σ^* interaction is present, the *trans* C-C bond would be lengthened as observed in **2**. However, in the case of **1** if the sulfur lone pair is con-

Table 5

Atomic Positional Parameters ($\times 10^4$) for Compound **2**

atom	x/a	y/b	z/c	Ueq (a)
O(9)	4830(1)	2500	6344(3)	56
S(10)	3249.8(3)	2500	5733.9(6)	39
C(11)	4446(1)	4195(4)	6698(3)	54
C(12)	3850(1)	4485(3)	5550(3)	47
C(15)	2720(1)	2500	4089(3)	37
C(16)	1990(1)	2500	4405(3)	35
O(17)	1529(1)	2500	3426(2)	50
O(18)	1847(1)	2500	5969(2)	49
C(19)	1135(2)	2500	6399(5)	55
C(20)	3041(1)	2500	2539(3)	39
O(21)	3659(1)	2500	2312(2)	50
O(22)	2587(1)	2500	1330(2)	50
C(23)	2886(2)	2500	-242(4)	53

(a) $U_{eq} = 1/3 \sum U_{i,j,k} \lambda_i \lambda_j \lambda_k$.

Table 6

Interatomic Bond Distances and Angles for Compound **2**

O(9) - C(11)	1.420(3)	C(16) - O(17)	1.214(3)
S(10) - C(12)	1.804(2)	C(16) - O(18)	1.346(3)
S(10) - C(15)	1.723(2)	O(18) - C(19)	1.423(4)
C(11) - C(12)	1.516(3)	C(20) - O(21)	1.208(3)
C(15) - C(16)	1.434(4)	C(20) - O(22)	1.344(3)
C(15) - C(20)	1.446(4)	O(22) - C(23)	1.444(4)
C(11) - O(9) - C(11)			111.3(2)
C(12) - S(10) - C(12)			99.14(9)
C(12) - S(10) - C(15)			108.24(9)
O(9) - C(11) - C(12)			111.9(2)
S(10) - C(12) - C(11)			109.4(2)
S(10) - C(15) - C(16)			115.8(2)
S(10) - C(15) - C(20)			118.1(2)
C(16) - C(15) - C(20)			126.1(2)
C(15) - C(16) - O(17)			126.5(2)
C(15) - C(16) - O(18)			112.5(2)
O(17) - C(16) - O(18)			121.0(2)
C(16) - O(18) - C(19)			116.5(2)
C(15) - C(20) - O(21)			124.6(2)
C(15) - C(20) - O(22)			113.8(2)
O(21) - C(20) - O(22)			121.7(2)
C(20) - O(22) - C(23)			115.6(2)

sidered to be a fixed spatial entity, then a significant stereoelectronic interaction should occur between the lone pair on sulfur and the *syn* keto function. The resonance form with the negative charge residing on the carbonyl oxygen adjacent to the sulfur lone pair would be a minor contributor compared to the resonance form with the negative charge on the other carbonyl. In addition, any delocalization or redistribution of the sulfur lone pair should be energetically beneficial.

The question concerning the nature of the sulfur-carbon bond and the reasons for the unusual stability of the sulfonium ylides when the carbanion is attached to groups capable of electron delocalization must be addressed. Un-

Table 7

Torsion Angles (°) for Compound **2**

O(9) - C(11) - C(12) - S(10)	63.0(2)
C(11) - C(12) - S(10) - C(15)	-163.7(1)
C(11) - C(12) - S(10) - C(12')	-51.0(2)
C(12) - S(10) - C(12') - C(11')	51.0(2)
C(11) - O(9) - C(11') - C(12')	70.5(3)
C(12) - C(11) - O(9) - C(11')	-70.5(3)
C(12) - S(10) - C(15) - C(16)	-126.7(1)
C(12) - S(10) - C(15) - C(20)	53.3(1)
S(10) - C(15) - C(16) - O(17)	180.0
S(10) - C(15) - C(16) - O(18)	0.0
C(15) - C(16) - O(18) - C(19)	180.0
O(17) - C(16) - O(18) - C(19)	0.0
S(10) - C(15) - C(20) - O(21)	0.0
S(10) - C(15) - C(20) - O(22)	180.0
C(15) - C(20) - O(22) - C(23)	180.0
O(21) - C(20) - O(22) - C(23)	0.0
O(17) - C(16) - C(15) - C(20)	0.0
O(18) - C(16) - C(15) - C(20)	180.0
C(16) - C(15) - C(20) - O(21)	180.0
C(16) - C(15) - C(20) - O(22)	0.0

doubtedly, there is some benefit derived from the higher polarizability of the sulfur atom and the delocalized carbanion moiety; however, we suggest the most important factor may be the rehybridization of the carbanion carbon. The major increase in stability in going from a tetrahedral carbanion to a delocalized sp^2 -hybridized carbanion may be related primarily to the symmetry of the carbanion carbon and not 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 π - σ^* interaction involving the two C-S bonds and the carbanion system may exist. The first interaction determines primarily the conformation about the $^*S-C^-$ bond while the second leads to a shortening of the $^*S-C^-$ bond, partial neutralization of the charges and a lengthening of the S-C(12) and S-C(13) bonds. Except for the lengthening of the two adjacent S-C bonds, the latter interaction is indistinguishable from a $d\pi$ - $\pi\pi$ contribution.

NMR Spectra.

It has previously been shown that in the thioxanthenium bis(carbomethoxy)methylides, and related systems, an a' methylide carbon resonates downfield of the corresponding e' methylide carbon (approximately 65 *vs.* 55 ppm). The carbon-13 nmr spectrum of **1** exhibits the corresponding resonance at 64 ppm, supporting the maintenance in solution of the conformation observed in the solid state.

The hydrogen bond demonstrated in the solid state also is observed in solution. Thus, in deuteriochloroform, at 25°, both C9-H and OH appear as doublets ($J = 11.6$ Hz). The magnitude of the coupling constant is consistent with

an anti conformation for the H-C-O-H fragment (16). The identity of these signals was established by the addition of deuterium oxide to the sample. Although the doublet centered at 6.40 ppm *ultimately* disappeared (and the doublet centered at 5.73 ppm collapsed to a singlet), even after twenty minutes contact with deuterium oxide the exchange was only 50% complete. This implies a strong hydrogen bond in this system.

The methoxy resonance appears at 3.68 ppm as a broadened singlet. The aryl methyl groups appear at 2.53 and 2.64 ppm. These values are consistent with previous results. The resonance at 2.53 ppm is assigned to C4- CH_3 , while C1- CH_3 occurs at 2.64 ppm.

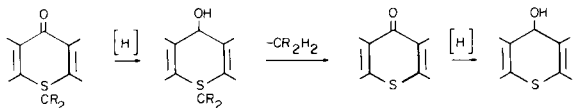
9-Hydroxy-2,4-dimethylthioxanthenium bis(carbomethoxy)methylide (**3**) was prepared by the borohydride reduction of the corresponding ketone. While two isomers are, in principle, possible, this method produced only one pure isomer. While the C4 methyl group assured an a' methylide carbon, the hydroxyl group could have been an a' or e' . The proton nmr spectrum of **3** exhibited two doublets for the H-C-O-H fragment ($J = 11.4$ Hz). The lower-field doublet (6.51 ppm) is ascribed to the hydroxyl group, the upfield doublet (5.74 ppm) to C9-H. The values of δ and J , when compared to those of **1** and considered along with the observed coupling in deuteriochloroform, indicate a strong hydrogen bond in **3** and a *cis*, di- a' geometry.

The methoxy resonance of **3** occurs as a broadened singlet at 3.69 ppm while the aryl methyl groups resonate at 2.42 ppm (C1) and 2.54 (C4).

Stability.

Compounds **1** and **3** were prepared by reducing the corresponding ketone with sodium borohydride. If the reduction was performed in the presence of excess reductant and at elevated temperatures or in alkaline solution (sodium hydroxide) then the major heterocyclic species was the "alcohol-sulfide". Thus attempts to prepare **1** yielded 1,4-dimethylthioxanthen-9-ol (**4**) while those designed to prepare **3** yielded 2,4-dimethylthioxanthen-9-ol (**5**). (Other reductions conducted in alkaline solution or acid solution also resulted in the cleavage of the $^*S-C^-$ bond.)

This behavior parallels our earlier observation (17) that thioxanthen-9-ol 10-oxide (**6**) is unstable in acidic or basic solution, or upon heating, and undergoes an internal redox reaction to form thioxanthone (**7**). The production of "alcohol-sulfides" from ylides **1** and **3** is presumed to involve initial reduction of the "ketone-ylide" to the "alcohol-ylide" which, in turn, decomposed to the "ketone-sulfide". Excess reductant converted this, in the end, to the alcohol.



Heating these alcohol-ylides in a sealed tube ($\sim 200^\circ$; 10 minutes) produced a mixture which included the corresponding ketone-sulfide.

EXPERIMENTAL

Structure Determination and Refinement.

All X-ray data were collected on a Syntex P2, diffractometer system by the $\theta:2\theta$ scanning technique using a variable scan speed, $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) and a graphite monochromator. Room-temperature lattice parameters were refined by a least-squares procedure utilizing 15 reflections whose angles were measured by a centering routine associated with the diffractometer. Periodically monitored reflections showed no significant changes in intensities. The data were corrected for Lorentz and polarization factors but no absorption corrections were made. The direct methods program MULTAN78 (18) was used to calculate phases for the larger $|E|$ values. The phase set with the largest combined figure of merit was selected, and the E map calculated with these phases revealed the positions of all nonhydrogen atoms. After several cycles of anisotropic least-squares refinement, a difference Fourier map revealed the positions of the hydrogen atoms. Full-matrix least-squares refinement was terminated when the shift/error was of the order of 0.1. The heavy atoms were refined anisotropically while the hydrogen atoms were refined isotropically. The R factor 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 $\omega = 1/\sigma^2(F_o)$. Atomic scattering factors were calculated by the XRAY76 program (19).

Compound 1.

A crystal of dimensions $0.33 \times 0.25 \times 0.25 \text{ mm}$ was used to collect all intensity data. The unit cell is triclinic and intensity statistics are consistent with space group P1.

Crystal Data.

The following data are reported: $\text{C}_{20}\text{H}_{20}\text{O}_5\text{S}$, $M = 372.44$, $a = 8.384(1)$, $b = 8.653(1)$, $c = 16.378(2) \text{ \AA}$, $\alpha = 119.10(1)$, $\beta = 92.53(1)$, $\gamma = 115.64(1)^\circ$, $V = 885.7(2) \text{ \AA}^3$, $Z = 2$, $d_c = 1.40 \text{ MgM}^{-3}$, $\mu(\text{CuK}\alpha) = 18.33 \text{ cm}^{-1}$.

The structure was refined to an R factor of 0.036 and the largest peak in the final difference electron density map was $0.3 \text{ e}\text{\AA}^{-3}$. Table 1 contains the atomic positional parameters and U_{eq} values while Tables 2, 3, and 4 list the interatomic distances, valence angles and torsion angles.

Compound 2.

A crystal of dimensions $0.38 \times 0.33 \times 0.33 \text{ mm}$ was used to collect all intensity data. The unit cell is orthorhombic and systematic extinctions are consistent with space group Pnma.

Crystal Data.

The following crystal data are reported: $\text{C}_8\text{H}_{14}\text{O}_5\text{S}$, $M = 234.27$, $a = 19.312(4)$, $b = 6.917(1)$, $c = 8.421(1) \text{ \AA}$, $V = 1125.0(3) \text{ \AA}^3$, $Z = 4$, $d_c = 1.38 \text{ MgM}^{-3}$, $\mu(\text{CuK}\alpha) = 25.3 \text{ cm}^{-1}$.

The structure was refined to an R factor of 0.044 and the largest peak in the final difference electron density map was $0.25 \text{ e}\text{\AA}^{-3}$. During the final cycles of least-squares refinement the data were corrected for extinction through use of the equation $F_o^* = k|F_c| \{1 + 2r^*|F_c|^2\delta\}^{-1/4}$ where δ is a dimensionless constant for each reflection and r^* was refined to a value of $11(1) \times 10^{-3} \text{ e}^{-2}$ (20). Table 5 presents the atomic positional parameters and U_{eq} values while Tables 6 and 7 list the interatomic distances, valence angles and torsion angles (21).

9-Hydroxy-1,4-dimethylthioxanthenium Bis(carbomethoxy)methylide (1).

1,4-Dimethylthioxanthenium bis(carbomethoxy)methylide (12b) (3.7 g, 0.10 mole) was suspended in 100 ml 95% ethanol. To this was added sodium borohydride (1.12 g, 0.04 mole) and the reaction mixture stirred, overnight, at 20° . The reaction mixture was treated with 200 ml of water and extracted with chloroform ($4 \times 75 \text{ ml}$). The chloroform extracts were combined and dried (magnesium sulfate) and the volatiles removed under reduced pressure (0.5 torr). The residue was recrystallized several times from methanol to afford **1** (1.5 g, 0.0041 mole, 41%), mp 206-207. This material was homogeneous on tlc (22) and had ^1H and ^{13}C nmr spectra consistent with the structure (23).

Anal. Calcd. for $\text{C}_{20}\text{H}_{20}\text{O}_5\text{S}$: C, 64.50; H, 5.41. Found: C, 64.30; H, 5.17.

9-Hydroxy-2,4-dimethylthioxanthenium Bis(carbomethoxy)methylide (3).

2,4-Dimethylthioxanthenium bis(carbomethoxy)methylide (9) was reduced in a manner similar to that described above. The product, **3**, was isolated in 34% yield with a mp 201-202°. This material was homogeneous on tlc (22) and had ^1H and ^{13}C nmr spectra consistent with the structure (23,24).

Anal. Calcd. for $\text{C}_{20}\text{H}_{20}\text{O}_5\text{S}$: C, 64.50; H, 5.41. Found: C, 64.72; H, 5.23.

1,4-Oxathianium Bis(carbomethoxy)methylide (2).

1,4-Oxathiane (5.2 g, 0.05 mole) was added to a mixture of 10 ml of toluene, 150 mg of anhydrous copper(II) sulfate and 16 g (0.10 mole) of dimethyl diazomalonnate and the reaction mixture heated, under nitrogen, for 4 hours at 100° (25). After cooling to room temperature chloroform (25 ml) was added and the insoluble material removed by filtration. The filtrate was concentrated under reduced pressure (0.2 torr) and the residue recrystallized (twice) from ethanol to afford **2** (6.1 g, 0.27 mole, 52%), mp 163-164.5°. The mass spectrum of **2** exhibited a molecular ion at 234 amu and intense peaks at 59, 103 and 191 amu. The carbon-13 spectrum included the following resonances $\text{C}=\text{O}$: 166.6 ppm; $\text{C}-\text{O}$: 66.2 ppm; C^- : 57.7 ppm; OCH_3 : 50.7 ppm. The ring carbons appeared at 66.2 and 37.0 ppm.

Anal. Calcd. for $\text{C}_8\text{H}_{14}\text{O}_5\text{S}$: C, 46.14; H, 6.02. Found: C, 46.23; H, 5.68.

Reduction Under Alkaline Conditions.

Reduction of 1,4-dimethylthioxanthenium bis(carbomethoxy)methylide was carried out as described above except that 2 g of sodium hydroxide pellets were added to the reaction mixture. After stirring overnight, 1,4-dimethylthioxanthen-9-ol was isolated in 40% yield. The nmr analysis indicated that the reaction product contained small quantities (approximately 10%) of the desired product.

If reduction was conducted using the same quantities of reagents, but with the reaction mixture refluxed for 4 hours, essentially all of the starting material was converted to 1,4-dimethylthioxanthen-9-ol.

An attempted reduction using sodium dithionite in the presence of sodium carbonate produced significant (approximately 25%) amounts of 1,4-dimethylthioxanthen-9-ol (26).

Thermal Stability.

cis-9-Hydroxy-1,4-dimethylthioxanthenium bis(carbomethoxy)methylide (200 mg) was heated in a sealed micro Carius tube (nitrogen atmosphere) for 2 minutes at 250° and the product analyzed by ^1H and ^{13}C nmr as well as by tlc (22). While the tlc showed the presence of six compounds, one of these was shown (rf value using authentic 1,4-dimethylthioxanthenone and characteristic fluorescence under uv) to be 1,4-dimethylthioxanthenone (27).

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- (22) Silica gel substrate, chloroform and benzene eluents.
- (23) The nmr spectra were recorded on Varian T-60 and Varian NT-200 spectrometers. Probe temperature maintained at 20° in the NT-200 and 36° in the T-60. All spectra were recorded in deuteriochloroform which had *not* been treated to remove stabilizing agents, and so forth. Mass spectra were obtained at the gc/ms lab of The University of Texas at Arlington using the direct inlet system of a DuPont 321 mass spectrometer equipped with a Ribermag GG/MS Data System.
- (24) While two stereoisomers are, in principal, possible, only one was isolated from the reaction mixture.
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- (26) Essentially the same results were observed when the starting material was 2,4-dimethylthioxanthonium bis(carbomethoxy)methylide.
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