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Syntheses and Structure Studies of Stable Difluoro- and Dichlorosulfuranes. Apicophilicity Orders in Sulfuranes[1]

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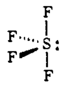
Contribution from the School of Chemical Sciences, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801. *Received October 16, 1978*

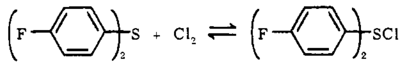
Abstract: Difluoroalkoxysulfurane **7** in solution is found to be in a conformation with an apical alkoxy ligand and an equatorial fluorine ligand. A similar conformation is postulated for dichloroalkoxysulfurane **8** in solution, but in the crystalline form **8** exists as a tetramer with bridging chlorine ligands and an octahedral arrangement of ligands around sulfur. Ring strain and electronegativity as factors affecting relative apicophilicities in sulfuranes and phosphoranes are discussed. Evidence that alkoxy groups may be more apicophilic than fluoro and chloro ligands in sulfuranes is also discussed.

Introduction

Tetracoordinate, tetravalent sulfur species, sulfuranes,[2] have been known for a long time. Sulfur tetrachloride was first reported in 1873[3] and sulfur tetrafluoride was reported in 1911.[4] Sulfur tetrachloride is unstable at temperatures above −20 °C; however, it has been employed in the synthesis of sulfur tetrafluoride.[5] Sulfur tetrafluoride is[6] a "trigonal bipyramid" (TBP) with the sulfur lone pair occupying an equatorial position. An approximate bonding scheme for this type of structure, the hypervalent bond model, has been described by Musher.[2]



Trichloro-[7] and dichlorosulfuranes,[8] like sulfur tetrachloride, are unstable with respect to the loss of chlorine at room temperature in solution, whereas trifluoro-[9] and difluorosulfuranes,[10] like sulfur tetrafluoride, do not show the analogous loss of fluorine. Wilson and Chang[8b] have reported the equilibrium constant for the formation of dichlorosulfurane **1** from the corresponding sulfide and chlorine to be 4.04 × 10^5 M^{-1} (eq 1). The first report, of which we are aware, of a dichlorosulfurane (**2**) was that by Price and Smiles;[11] however, controversy has surrounded this report.[12] Some workers[12a,b] have proposed that the true structure is **3** on the basis of products studies and IR data; however, others[12c,d] have supported the dichlorosulfurane structure on the basis of products and the IR spectrum of freshly made material. Livant and Martin[12d] have argued from the IR spectrum that the two compounds are in equilibrium. Some dichlorosulfuranes have been found to be useful synthetic intermediates[13] or reagents.[14]



(1)

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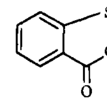

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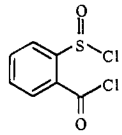

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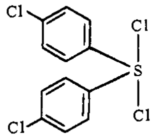
Dichlorosulfurane **4**[8a] was found to be a TBP, like sulfur tetrafluoride, with the chlorine ligands occupying the apical positions, as is expected from the relative apicophilicities of chlorine and carbon ligands that have been established[15] for phosphoranes. On the basis of ^{19}F NMR spectroscopic data, Denney et al.[10c] have determined that sulfurane **5**, like **4**, has its halogen ligands in the apical positions.



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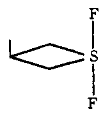

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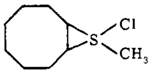
Monochloroalkoxysulfuranes have been implicated by spectroscopic methods as unisolated intermediates[16] or products[17] from the reaction of sulfides with alkyl hypochlorites. Chlorooxysulfuranes can be isolated when the oxygen ligand is incorporated into a ring connecting it to an equatorial ligand[12d,18a-c] or when the alkoxy is not susceptible to nucleophilic attack by chloride.[18d] The stabilizing effect of the ring system may be responsible for the stability of the unisolated intermediate postulated[19] to be chlorotrialkylsulfurane **6**.



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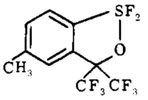

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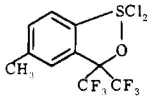

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Herein we report the syntheses and structures of the stable dihaloalkoxysulfuranes **7** and **8**. Factors affecting apicophilicities in sulfuranes are also discussed.

Experimental Section

Chemical shifts for ^{1}H and ^{13}C NMR are reported on the δ scale, parts per million downfield from internal Me_4Si, while ^{19}F NMR chemical shifts are reported on the ϕ scale, parts per million upfield from internal $CFCl_3$. Melting points were obtained using a sealed capillary tube and are uncorrected. Solvents were dried over P_2O_5, then distilled under N_2. Deuterated solvents were either distilled from P_2O_5 or filtered through a column of Woelm activity I basic alumina.

1,1-Difluoro-3,3-bis(trifluoromethyl)-5-methyl-[3*H*-2,1-benzoxathiole] (7). To a stirred slurry of 430 mg (2.9 mmol) of AgF_2 in 1 mL of 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) in a polyethylene container was added 202 mg (0.70 mmol) of sultene **9**[20] in 2 mL of Freon 113. The reaction mixture was stirred for 2 h. The stirring was stopped and the AgF and unreacted AgF_2 settled out. The colorless, supernatant liquid was transferred to a second polyethylene vial with a polyethylene pipet. The residue was washed twice with Freon 113 and the solutions were combined. The solvent was removed under vacuum to give 220 mg (0.68 mmol, 96%) of a white solid (mp 66–68 °C). The NMR spectra were obtained using a Teflon NMR tube insert to avoid reaction with glass. ^{1}H NMR (CD_2Cl_2): δ 2.60 (s, 3 H, CH_3), 7.64 (d, $J = 8$ Hz, H para to $C(CF_3)_2$, 7.67 (br s, H ortho to $C(CF_3)_2$, integral for last two peaks, 2 H), 8.30 (d, $J = 8$ Hz, 1 H, H ortho to S). ^{19}F NMR (CD_2Cl_2): ϕ −51.6 (d, $J = 31$ Hz, 1 F, axial S–F), 14.1 (br s, 1 F, equatorial S–F), 75.2 (q, $J = 10$ Hz, 3 F, CF_3), and 75.7 (q, $J = 10$ Hz, 3 F, CF_3). IR (CH_2Cl_2): 1603 (w), 1310 (m), 1230 (s), 1180 (s), 1066 (s), 980 (m), 823 cm^{-1} (m). Anal. ($C_{10}H_6F_8OS$) C, H, F, S.

1,1-Dichloro-3,3-bis(trifluoromethyl)-5-methyl-[3H-2,1-benzoxathiole] (8). Through a solution of 34.1 g (0.117 mol) of mercaptan alcohol **10**[20] in 250 mL of CCl_4 was bubbled a mixture of Cl_2 and N_2 until no further precipitate was formed. The solution changed from faint yellow to bright yellow, then orange, then deep burgundy-red, followed by a cloudy orange and ending in a light yellow suspension of **8**. The solution was filtered, yielding 28.3 g (0.0788 mol, 67.4%) of **8** (mp 130–131 °C dec): ^{1}H NMR (CH_2Cl_2, 41 °C) δ 2.63 (br s, 3 H, CH_3), 7.69 (br s, H ortho to $C(CF_3)_2$), 7.76 (d, $J = 9$ Hz, H para to $C(CF_3)_2$) (integral for last two peaks, 2 H), and 9.27 (br d, $J = 8.5$ Hz, 1 H, H ortho to S); ^{1}H NMR (CH_2Cl_2, −85 °C) δ 2.72 (br s), 7.88 (br s), 7.97 (br d, $J =$ ca. 10 Hz), and 9.25 (d, $J = 9$ Hz); ^{19}F NMR (CH_2Cl_2, 41 °C) ϕ 74.08 (s, width at half height = 3 Hz); ^{19}F NMR (CH_2Cl_2, −85 °C) ϕ 71.77 (s, width at half height = 7 Hz); $^{13}C\{^{1}H\}$ (CD_2Cl_2) δ 150.6 (s), 137.48 (s), 135.8 (s), 134.7 (s) 133.0 (s), 127.1 (s), 121.5 (q, $^{1}J_{CF} = 290$ Hz, CF_3), 87.9 (heptet, $^{2}J_{CF} =$ 35 Hz, $C(CF_3)_2$), 22.1 (s, CH_3); IR (KBr) 3420 (s, br, H_2O), 1609 (m), 1485 (m), 1270 (s, br), 1250 (sh), 1185 (s), 1069 (s), 981 (s); IR (CH_2Cl_2) 1270 (sh), 1240 (s), 1228 (sh), 1178 (s), 1064 (s), 978 cm^{-1} (s). Anal. ($C_{10}H_6Cl_2F_6OS$) C, H, F, S.

Determination of the Molecular Weight of Dichlorosulfurane 8 in Solution. The solution molecular weight of **8** was determined using the isopiestic method. A sample of 4.96 mg of dichlorosulfurane **8** was placed in one side and 2.98 mg (0.0147 mmol) of diphenyl sulfoxide was placed in the second side of the isopiestic tube.[21] Dry $CFCl_3$ was bulb-to-bulb distilled into the apparatus, and the system was sealed under vacuum. The apparatus was placed in a freezer at −18 °C and the volumes were noted with time. After 2 weeks the volumes were completely equilibrated. The solutions of **8** and diphenyl sulfoxide were 1.26 and 1.30 mL, respectively, corresponding to a molecular weight of 347 (theoretical 359 for monomeric **8**) for **8** in solution.

X-ray Crystal Structure. Crystalline dichlorosulfurane **8** was recrystallized from dichloromethane utilizing a previously described[22] glass apparatus. A single crystal of approximate dimensions 0.5 × 0.5 × 0.8 mm was selected and wedged in a 0.5-mm thin-walled glass capillary which was sealed under a dry nitrogen atmosphere. This precaution was necessary to prevent loss of chlorine from the crystal and to protect it from moisture.

Crystal Data for 8: $C_{10}H_6Cl_2F_6OS$, mol wt 359.118, orthorhombic, $a = 25.766\,(15)$ Å, $b = 18.468\,(8)$ Å, $c = 11.159\,(3)$ Å, $V = 5310$ Å^3, $Z = 16$, $\rho_{calcd} = 1.80$ g cm^{-3}, $F(000) = 2848$, μ (Cu Kα) = 64.8 cm^{-1}, systematic absences for hkl when $h + k = 2n + 1$, for $0kl$ and for $h0l$ when $l = 2n + 1$, and for $hk0$ when $h = 2n + 1$ establish the space group as *Ccca*. The cell dimensions were obtained by a least-squares fit to the automatically centered settings for ten reflections on a Syntex P2$_1$ diffractometer equipped with a graphite monochromator, λ (Cu Kα_1) = 1.541 78 Å.

Solution and Refinement of the Structure of 8. Intensity data were collected on a computer-controlled four-angle Syntex P2$_1$ diffractometer using a 2θ scan mode with relatively fast variable scan speeds (5.0°/min to 15.0°/min) with the total background time/scan time set at 0.5. The fast 2θ scan mode was chosen to minimize data collection time in order to reduce crystal decomposition. Three standards from different parts of the reciprocal space were monitored every 50 reflections. By the end of the data collection the standards had deviated from initial values by ±5%. The crystal itself changed color from a pale straw yellow to a near black color indicating that some crystal decomposition had taken place. On another crystal decomposition was more severe with the standards falling to less than 50% of their original values before half of the data were collected. The hkl octant was collected out to $2\theta = 130°$ ($\sin\theta/\lambda = 0.588$). Out of the possible 2281 unique reflections collected, 1589 (69.7%) were observed using a 2σ criterion based on counting statistics. The data were corrected for Lorentz and polarization effects, but not for absorption.

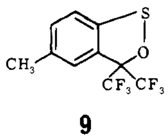
A version of the direct methods program MULTAN[23] was used to locate the sulfur atom and the two chlorine atoms. Two successive Fourier maps revealed the remainder of the nonhydrogen atoms. Initial refinement was carried out using the Gauss-Seidel blocked least-squares program supplied by Syntex[24] giving values for R and R_w of 0.139 and 0.171.[25] At this point evaluation of the data showed that six high-intensity reflections (200, 600, $20\bar{4}$, $40\bar{4}$, $11\bar{5}$, and $00\overline{10}$) were severely suffering from absorption or extinction ($|F_{obsd} - F_{calcd}|/\sigma(F_{obsd}) > 23$), and these were removed. Blocked least-squares refinement at this point gave values for R and R_w of 0.127 and 0.149. A difference map revealed the position of only one hydrogen atom (H10A) reliably. The rest of the hydrogen atoms were calculated at their theoretical positions. Full-matrix, least-squares refinement of the positional and anisotropic thermal parameters for the nonhydrogen atoms while holding the positional and thermal parameters for the hydrogen atoms constant gave final values for R and R_w of 0.126 and 0.147 for 1583 observed reflections. If the positional and thermal parameters for the hydrogen atoms were allowed to vary, the values shifted in a manner which could not be rationalized. The final value of $[\Sigma w(|F_{obsd}| - |F_{calcd}|)^2/(m - n)]^{1/2}$, where m is the number of observations and n is the number of parameters varied, was 4.04. A final difference map showed eight peaks roughly corresponding (90–130%) to the electron density observed for an average hydrogen atom. The largest of these (130% of an average hydrogen) is between S(1) and C(1). The next four (100–120% of an average hydrogen) were in the vicinity of S(1) and Cl(1). Two (95% of an average hydrogen) were in the vicinity of S(1) and Cl(2) while one (90% of an average hydrogen) was between S(1) and O(1). In addition four other peaks between 50 and 80% of an average hydrogen were located in the same areas mentioned above while the remainder of the peaks were less than 50% of an average hydrogen. The scattering curves were taken from the analytical expression used in the International Tables for X-ray Crystallography.[26] The final values of the atomic coordinates are given in Table IV in the microfilm edition. (See paragraph at end of paper regarding supplementary material.)

Results

Syntheses and Solution Dynamics of Dihalosulfuranes 7 and 8. Difluorosulfurane **7**, prepared by the reaction shown in eq 2, shows nonequivalent trifluoromethyl groups and S–F fluorines in its ^{19}F NMR spectrum.

Table I. Bond Lengths and Angles for Nonhydrogen Atoms in **8** with Estimated Standard Deviations in Parentheses

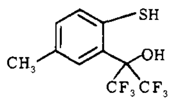
	Bond Lengths (Å)		
S(1)-Cl(1)	2.551 (5)	C(4)-C(10)	1.516 (17)
S(1)-Cl(2)	2.126 (5)	O(1)-C(7)	1.473 (14)
S(1)-O(1)	1.621 (8)	C(7)-C(8)	1.600 (23)
S(1)-C(1)	1.806 (11)	C(7)-C(9)	1.508 (21)
C(1)-C(2)	1.380 (16)	C(8)-F(1)	1.317 (16)
C(2)-C(3)	1.402 (17)	C(8)-F(2)	1.268 (19)
C(3)-C(4)	1.371 (18)	C(8)-F(3)	1.292 (17)
C(4)-C(5)	1.418 (17)	C(9)-F(4)	1.284 (16)
C(5)-C(6)	1.402 (16)	C(9)-F(5)	1.267 (19)
C(1)-C(6)	1.349 (15)	C(9)-F(6)	1.314 (18)
C(6)-(7)	1.513 (16)		
	Bond Angles (deg)		
O(1)-S(1)-C(1)	92.1 (5)	C(3)-C(4)-C(10)	122.0 (11)
Cl(1)-S(1)-Cl(2)	167.6 (2)	C(5)-C(4)-C(10)	117.5 (11)
Cl(1)-S(1)-O(1)	94.0 (3)	C(6)-C(7)-C(8)	110.8 (11)
Cl(1)-S(1)-C(1)	88.3 (4)	O(1)-C(7)-C(8)	105.1 (10)
Cl(2)-S(1)-O(1)	97.3 (3)	C(6)-C(7)-C(9)	114.0 (11)
Cl(2)-S(1)-C(1)	96.2 (4)	O(1)-C(7)-C(9)	108.9 (10)
S(1)-O(1)-C(7)	117.6 (7)	C(8)-C(7)-C(9)	113.0 (11)
S(1)-C(1)-C(6)	110.1 (8)	C(7)-C(8)-F(1)	109.7 (12)
S(1)-C(1)-C(2)	125.1 (9)	C(7)-C(8)-F(2)	113.1 (13)
O(1)-C(7)-C(6)	104.2 (9)	C(7)-C(8)-F(3)	111.1 (13)
C(7)-C(6)-C(1)	115.7 (10)	F(1)-C(8)-F(2)	106.8 (13)
C(6)-C(1)-S(1)	110.1 (8)	F(1)-C(8)-F(3)	104.3 (13)
C(6)-C(1)-C(2)	124.7 (11)	F(2)-C(8)-F(3)	111.4 (14)
C(1)-C(2)-C(3)	115.5 (11)	C(7)-C(9)-F(4)	112.5 (12)
C(2)-C(3)-C(4)	122.1 (11)	C(7)-C(9)-F(5)	110.2 (13)
C(3)-C(4)-C(5)	120.5 (11)	C(7)-C(9)-F(6)	111.9 (13)
C(4)-C(5)-C(6)	117.3 (11)	F(4)-C(9)-F(5)	106.1 (13)
C(5)-C(6)-C(1)	119.9 (11)	F(4)-C(9)-F(6)	108.8 (13)
C(5)-C(6)-C(7)	124.4 (11)	F(5)-C(9)-F(6)	107.1 (13)



$+\ 2\ \mathrm{AgF_2}$ (excess) $\longrightarrow$ **7** $+\ 2\ \mathrm{AgF}$ (2)

9

Dichlorosulfurane **8** is easily prepared from mercaptan alcohol **10** in carbon tetrachloride by bubbling chlorine into the solution until no further precipitation of **8** occurs (eq 3). The progress of the reaction is easily followed by the color changes that occur at different stages of the reaction. The color progresses from that of the almost colorless **10** to the bright yellow of sultene **9**, then through shades of orange until a deep burgundy-red solution is obtained. It then proceeds through a cloudy orange and ends as a light yellow suspension of the sparingly soluble dichlorosulfurane **8**. Dichlorosulfurane **8** is very stable and can be stored as the solid for several months before any appreciable decomposition (the loss of chlorine to yield sultene **9**) is observed.



$+\ 2\ \mathrm{Cl_2}$ (excess) $\longrightarrow$ **8** $+\ 2\ \mathrm{HCl}$ (3)

10

The molecular weight of dichlorosulfurane **8** in solution (0.011 M) was found to be 347 g/mol (theoretical 359 g/mol for monomeric **8**) by the isopiestic method.[21]

X-ray Crystal Structure of Dichlorosulfurane 8. Table I lists selected bond lengths for the structure determined in the analysis and Figure 1 is a stereoscopic view of a single molecule showing two close S(1)···Cl(1) intermolecular[27] contacts with molecules at $-x, y, 0.5-z$ and $x, 1.5-y, 0.5-z$ from the reference molecule at $0.5-x, 1-y, z$. Table II lists the bond angles and bond lengths around sulfur involving the interactions of the two molecules previously listed with the reference molecule. Figure 2 shows a stereoscopic view of a simplified molecular packing diagram illustrating S···Cl interactions and the tetrameric nature of **8** in the crystal. Figure 3 gives an enlarged stereoscopic view of the sulfur atoms and attached atoms in a single tetramer unit in the crystal. A stereoscopic view of the complete molecular packing diagram (Figure 4) is in the microfilm edition (see paragraph at end of paper regarding supplementary material).

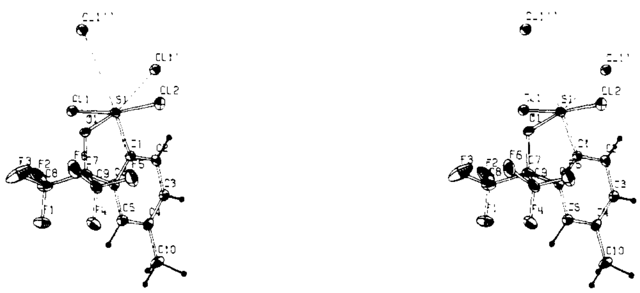


Figure 1. Stereoview indicating the octahedral nature of the sulfur of sulfurane **8**.

Table II. Intermolecular[a] Interactions of the Sulfur and Chlorine Atoms in **8** with Estimated Standard Deviations in Parentheses

	Intermolecular Contact Distance (Å)		
S(1)···Cl(1)′[b]	2.879 (4)	Cl(1)···Cl(2)′	3.505 (4)
S(1)···Cl(1)″	3.338 (4)	Cl(1)···Cl(1)″	4.250 (5)
S(1)···S(1)′	4.145 (4)	Cl(1)···Cl(2)″	3.784 (5)
S(1)···S(1)″	4.069 (5)	Cl(1)···Cl(1)‴	4.222 (5)
S(1)···S(1)‴	4.587 (4)	Cl(2)···Cl(2)‴	4.172 (4)
Cl(1)···Cl(1)′	3.516 (4)		

Selected Intermolecular Bond Angles (deg)	
O(1)-S(1)···Cl(1)′	169.5 (3)
C(1)-S(1)···Cl(1)″	178.0 (4)
Cl(1)′···S(1)···Cl(1)″	85.2 (1)
Cl(1)-S(1)···Cl(1)′	80.5 (1)
Cl(1)-S(1)···Cl(1)″	91.4 (1)
C(1)-S(1)···Cl(1)′	96.7 (4)
O(1)-S(1)···Cl(1)″	86.0 (3)
Cl(2)-S(1)···Cl(1)′	87.5 (2)
Cl(2)-S(1)···Cl(1)″	86.6 (1)
S(1)-Cl(1)···Cl(1)′	53.9 (1)
S(1)-Cl(1)···Cl(2)′	136.1 (1)

[a] See ref 27. [b] The primed atoms are at the position $-x, y, 0.5-z$ from the reference molecule at $0.5-x, 1-y, z$. The doubly primed atoms are at the position $x, 1.5-y, 0.5-z$ from the reference molecule, and the triply primed atoms are at the position $-x, 1.5-y, z$ from the reference molecule.

As can be seen from Figures 1 and 3 as well as from the bond angles, the configuration about the sulfur atom in dichlorosulfurane **8** is approximately octahedral. Of the angles around the "octahedral" sulfur atom of **8**, the 12 angles approximating right angles range from 80.5 to 97.3° while the angles approximating linearity range from 167.6–178° (Tables II and III).

The six carbon atoms making up the phenyl ring together with the carbon atom of the methyl group (C(10)) are coplanar within the accuracy of the analysis. The atoms of the five-membered ring [S(1), O(1), C(7), C(6), and C(1)] form an approximate plane from which C(7) deviates by 0.05 Å above the plane and C(1) and O(1) deviate by 0.03 Å below the plane. The plane defined by Cl(1), S(1), and Cl(2) makes a dihedral angle of 86.9° with the plane defined by O(1), S(1), and C(1).

Discussion

Structure of Difluorosulfurane 7. There are two covalent

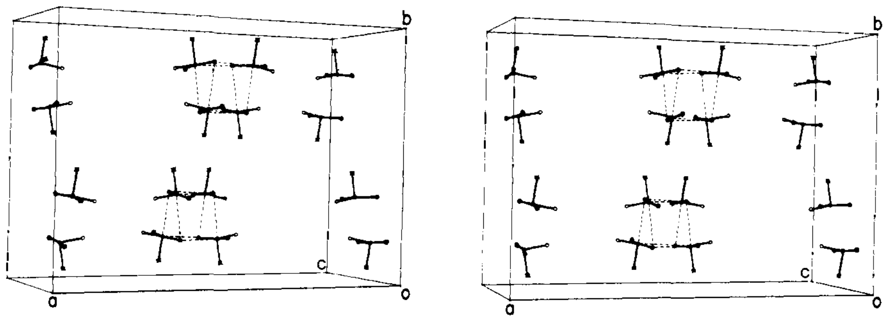


Figure 2. A simplified stereoview of the unit cell for sulfurane **8** showing only the sulfur atom and the atoms bonded to it.

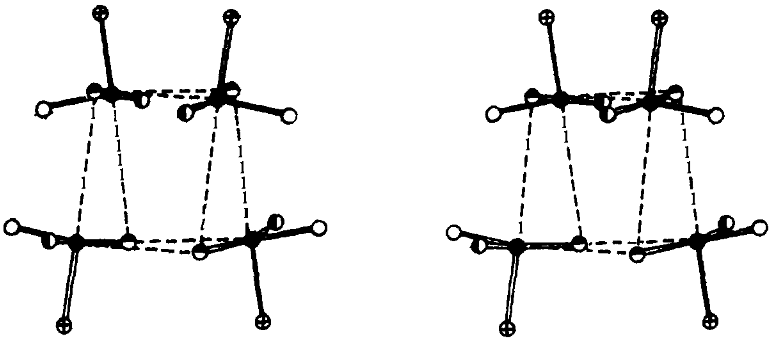
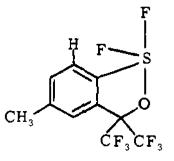


Figure 3. Enlarged view of a single tetrameric unit in unit cell for sulfurane **8**: ●, sulfur atom; ⊕, carbon atom; ○, oxygen atom; ⊖, chlorine atom involved in "intermolecular" S-Cl bonding; ◑, chlorine atom not involved in "intermolecular" S-Cl bonding.

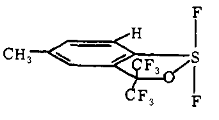
Table III. Apical and Equatorial Bond Lengths (Å) and Angles (deg) for Some Selected Sulfuranes

	bond lengths				bond angles	
sulfurane	S-O$_{(a)}$	S-O$_{(e)}$	S-C	S-Cl	e-S-e[a]	a-S-a[b]
17[c]	1.916 (4)		1.803 (6)		104.4 (3)	175.1 (2)
	1.889 (4)		1.810 (7)			
18[d]	1.832 (5)		1.787 (8)		108.1 (4)	177.1 (2)
	1.819 (5)		1.803 (8)		107.6 (3)[e]	178.2 (2)[e]
	1.831 (5)[e]		1.803 (7)[e]			
	1.816 (5)[e]		1.798 (8)[e]			
12[f]	1.840 (10)	1.630 (9)	1.777 (14)		95.0 (6)	172.0 (4)
	1.829 (10)					
15[g]	1.754 (3)	1.630 (4)			104.6 (2)	171.5 (2)
	1.756 (3)	1.633 (3)				
4[h]			1.767 (7)	2.259 (3)	108.6 (4)	185.5 (11)
			1.797 (9)	2.323 (3)		
8		1.621 (8)[i]	1.806 (11)	2.126 (5)	92.1 (5)[i]	167.6 (2)[i]
				2.551 (5)		
				2.879 (4)		
				3.338 (4)		

[a] Angle between equatorial bonds. [b] Angle between apical bonds is measured from the side of the equatorial ligands. [c] References 22 and 34. [d] Reference 35. [e] Sulfurane **18** has two unique molecules in the solid; this number is for molecule two. [f] Reference 1. [g] Reference 31. [h] Reference 8a. [i] The method used for the assignment of equatorial and apical ligands is discussed in the text.



7a



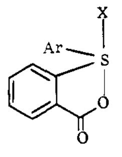
7b

conformers for difluorosulfurane **7** (**7a** and **7b**) that honor both the stricture against diapical linkage of five-membered rings and the poor apicophilicity of carbon. The ^{19}F NMR spectrum of difluorosulfurane **7** shows nonequivalent trifluoromethyl groups and nonequivalent fluorines bonded to sulfur; structure **7a** is the only one that satisfies the ^{19}F NMR data. Difluorosulfurane **7** shows a downfield chemical shift for the proton ortho to sulfur to δ 8.30. While the magnitude of this shift is not as great as it is for chlorosulfuranes,[20b] it is similar to the shift observed when an alkoxy ligand occupies the apical position with the S-O bond coplanar with the C-H bond ortho to sulfur.[20b] This lends further support to structure **7a** since the apical-equatorial (a-e) five-membered ring holds the ortho proton coplanar with the apical S-F bond.

A referee has noted that **7a** may be in equilibrium with the permutational isomer which has an apical aryl group and an equatorial alkoxy ligand. Such a species could be reached by a single pseudorotation step of the type usually called Berry pseudorotation (BPR).[28] Compound **7** might indeed have a geometry intermediate between these two idealized TBP geometries, an approximate rectangular pyramidal geometry. Rapid interconversions of such species would not interconvert the nonequivalent CF_3 groups or fluoro ligands on sulfur. The problems associated with considering such processes have been discussed[18b] in connection with studies of the racemization of a chiral sulfurane, a process entirely analogous to that which interconverts CF_3 groups of **7a**. An unsymmetrically substituted molecule such as **7** is expected to have an equilibrium geometry considerably distorted from any of these idealized geometries.

Crystal and Solution Structures of Dichlorosulfurane 8. Crystalline dichlorosulfurane **8** is a tetramer (Figures 2 and 3) with bridging chlorine atoms. The geometry around the sulfur atoms in the tetramer is essentially octahedral (Figure 1) with one chlorine atom from each of two neighboring sulfurane molecules of the tetramer occupying the other two sites in the hexacoordinate structure. The S-Cl bond lengths vary from 2.126 to 3.338 Å (Tables I and II). Other sulfuranes,[28] including dichlorosulfurane **4**,[8a] have simple monomeric "TBP" geometries.

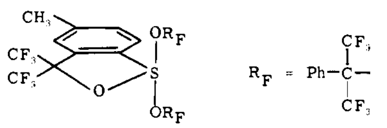
The shortest S-Cl bond is that to Cl(2) (2.126 Å), an atom not involved in any intermolecular S—Cl interactions. The other S-Cl bonds to Cl(1) (2.551 Å), Cl(1)′ (2.879 Å), and Cl(1)″ (3.338 Å) involve chlorine atoms that are intermolecularly coordinated, the bridging atoms of the tetramer. Note (Figure 1) that Cl(1) is trans to Cl(2), Cl(1)′ is trans to O(1), and Cl(1)″ is trans to C(1). The order of S-Cl bond lengths Cl(1)″ > Cl(1)′ > Cl(1) is therefore that expected from a consideration of the ability of the trans ligand to withdraw electrons toward itself in the three-center bond. It has been shown[12d] from carbonyl stretch frequencies in sulfuranes with the general structure **11** that chlorine ligands are more effective than alkoxy ligands in withdrawing electron density from the carboxy ligand.



11

In the following discussion of dichlorosulfurane **8** as a highly distorted TBP we are arbitrarily defining the two chlorine ligands of the "basic" sulfurane in the tetramer as the two nearest to sulfur (Cl(1) and Cl(2)). This assignment of the "basic" sulfurane structure places the five-membered ring in a diequatorial (e-e) disposition relative to sulfur. (The choice of Cl(1)′ and Cl(2) would make the ring apical-equatorial, a-e.)

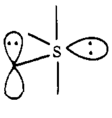
Sulfurane **12** has been determined[1] to have an e-e five-



12

membered ring in the solid state and probably also in solution.[20] Chen and Hoffman[29] have suggested, on the basis of extended Hückel calculations, that an equatorial π donor should prefer the geometry depicted in generalized structure **13**, which is the orientation observed for sulfuranes **12** and **8**, over that shown in structure **14**.

Sulfuranes **15**[30] and **16**,[31] on the other hand, have been reported to have geometries of the type of **14**, similar to the geometries observed[32] and calculated[33] to be favored for π-donor equatorial ligands in phosphoranes. Both orientations of π-donor ligands are therefore seen in sulfuranes and it appears that any conformational preference is small, too small



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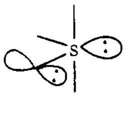

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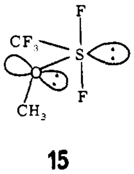

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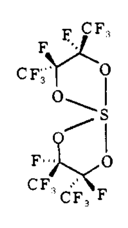
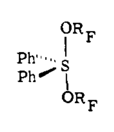


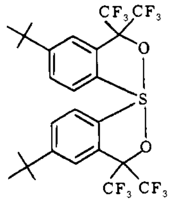
16

to be reflected in equatorial S-O bond lengths (see **8**, **12**, and **16** in Table III). Apical S-O bond lengths (Table III) do decrease, as expected,[36] with increasing numbers of electronegative substituents to sulfur, while bonds to equatorial ligands (S-O bonds of **8**, **12**, and **15** and S-C bonds of **4**, **8**, **12**, **17**, and **18**) are much less sensitive to such changes.



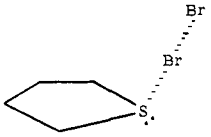
$R_F = PhC(CF_3)_2$

17



18

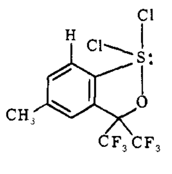
The intermolecular Cl—Cl interactions in **8** (as reflected in long contact distances, Table II) are relatively insignificant in comparison with the intermolecular S—Cl interactions responsible for its tetramerization. This is to be contrasted to the importance of such X—X interactions reported[8a] in other adducts of halogens to organic chalcogenides. Indeed, many such adducts, especially those[37] such as **19**,[38] which has an



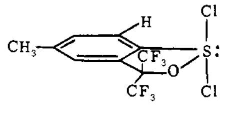
19

S-Br-Br angle of ca. 178°, are best described as charge-transfer complexes of X_2 with the chalcogenide.

An isopiestic molecular weight determination indicates that **8** is monomeric in solution and, in accord with this, the solid and solution infrared spectra of **8** are different. We need consider only two TBP structures for **8** in solution, **8a** and **8b**.



8a



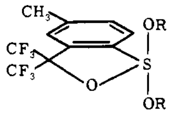
8b

Structure **8b** is closer to the basic sulfurane of the tetramer observed in the crystalline state than is **8a**. The ^{19}F NMR spectrum of **8** exhibits a singlet for its CF_3 groups as expected for structure **8b**. Cooling a sample to −85 °C results in only slight broadening and a downfield shift. However, a very rapid exchange between dichlorosulfurane **8** and sultene **9**, evidenced[39] by coalescence of ^{19}F peaks for solutions containing both compounds, suggests that the equilibrium shown in eq 4, or another process which might interconvert the enantiomers of **8a**, may be responsible for the observed equivalence of the trifluoromethyl groups of **8**. Structure **8a** is therefore also consistent with the ^{19}F NMR spectrum.

$$8 \rightleftharpoons 9 + Cl_2 \qquad (4)$$

The ^{1}H NMR spectrum of **8** exhibits a large downfield shift for the proton ortho to sulfur (δ 9.27). Such shifts have been observed[20b] only for systems in which the ortho proton is in a geometry with the ortho C–H bond held essentially coplanar with an apical S–Cl bond, as in structure **8a**. Dichlorosulfurane **4**, which does not have the ortho proton held in such a configuration, shows no absorption at fields lower than δ 7.6.[40] The ^{1}H NMR spectrum of **8** therefore lends strong support to the postulate that conformer **8a** is at least one of the conformers present in solutions of **8**. Since the more stable conformer of difluorosulfurane **7** has an a–e five-membered ring, one might expect dichlorosulfurane **8** also to have an a–e ring. (Chlorine is generally considered to be less apicophilic than fluorine.)[15]

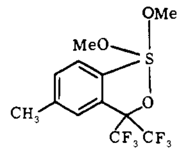
Apicophilicites in Sulfuranes. The structures of difluorosulfurane **7** and dichlorosulfurane **8** raise intriguing questions concerning the factors determining apicophilicities in sulfuranes. One might ask, for example, why sulfuranes **7**, **8**, and **21**[20b] have a–e five-membered rings, while sulfuranes **12**, **20a**, and **20b** have e–e five-membered rings. In the case of trialkoxysulfurane **21** the a–e ring geometry is easily explained on the basis of apicophilicities since one would expect the more electronegative fluoroalkoxy ligand to be more apicophilic than the methoxy ligands. The geometries of dihalosulfuranes **7** and **8** cannot, however, be rationalized so easily. In phosphoranes,[15] fluorine and chlorine ligands are more apicophilic than alkoxy ligands.



a, R = C(CF$_3$)$_2$C$_6$H$_4$-*p*-*t*-Bu
b, R = C(CF$_3$)$_3$

20

The a–e ring disposition in dihalosulfuranes **7** and **8** might be the result of a greater ring strain in an e–e ring than in an a–e ring. In phosphorane **22**[41] this ring strain factor is enough to force an oxygen ligand into an apical position, pushing a more electronegative fluorine ligand into an equatorial position. The ring strain effect in sulfuranes is clearly much less important,[28] because of the smaller angle between the two bonds to equatorial ligands in sulfuranes compared with the approximately 120° angle between the equatorial bonds of phosphoranes. Sulfurane **5**[10c] has an e–e four-membered ring, whereas the closely analogous phosphorane **23**[42] has appreciable amounts of both conformers, **23a** (a–e ring) and **23b** (e–e ring), with the conformer (**23a**) with apical carbon and equatorial fluorine being the major component. The finding of an e–e ring in trialkoxysulfuranes **12**, **20a**, and **20b** rules out the argument that the ring strain effect is the only factor involved in forcing the five-membered ring of dihalosulfuranes **7** and **8** into a–e orientations. While it is not clear whether ring strain considerations favor a–e or e–e conformations of sulfuranes, the present data are consistent with a small conformational preference for a–e five-membered rings.



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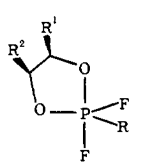

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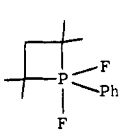
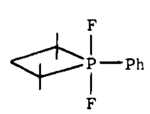
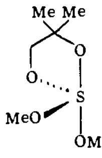


23a



23b

Trialkoxysulfuranes **12** and **20a** have alkoxy ligands of similar electronegativities. The electronegativity difference factor which forces the e–e ring in difluorosulfurane **5** is therefore not operative in **12** and **20a**. Tetraalkoxysulfurane **24**,[43] which has four alkoxy ligands of approximately equal electronegativity, has an a–e five-membered ring. If ring strain is responsible for sulfuranes **7**, **8**, and **24** having a–e rings, then some factor other than electronegativity differences must be responsible for forcing the e–e rings in sulfuranes **12**, **20a**, and **20b**.

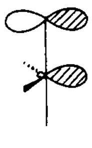


24

We suggest that the additional factor may be steric bulk. The apical alkoxy ligands in sulfuranes containing an e–e ring (**12**, **20a**, and **20b**) are relatively bulky tertiary alcohols. While it is generally accepted[15b] that bulky ligands in TBP phosphoranes prefer equatorial positions (since there are only two nearest neighbors at approximately 90° angles), the situation is different for sulfuranes. Both apical and equatorial ligands have only two nearest neighbors at 90° angles, while the equatorial ligand has an additional neighbor at an angle of less than 110°.[1,6,22,34,35,44] It is therefore possible that bulky ligands in sulfuranes prefer the apical positions of the TBP. This explains the e–e ring preference in trialkoxysulfuranes **12**, **20a**, and **20b**. In tetraalkoxysulfurane **24** the methoxy ligands are not bulky enough to overcome the ring strain effect. In dihalosulfuranes **7** and **8** the greater electronegativity of chlorine or fluorine ligands, when coupled with the small size of these groups, is not enough to overcome the ring strain effect; therefore, dihalosulfuranes **7** and **8** have a–e rings dictated primarily by ring strain effects.

The ^{19}F NMR spectra of $X_2P[OCH(CF_3)_2]_3$, with X = F or Cl, show no evidence for nonequivalent fluoroalkoxy ligands at very low temperatures.[46] An explanation of this based on a conformational preference for structures with two apical halogens leads to the conclusion that both Cl and F have greater apicophilicities than the fluoroalkoxy group. The fluoroalkoxy groups of sulfurane **12**, in contrast, are by definition *more* apicophilic than the F ligands of **7a** or the Cl ligands of **8a**. This difference in order of apicophilicities for phosphoranes and for sulfuranes is explicable in part by reference to the steric argument outlined above.

In addition, one can invoke electronic effects which favor an apical alkoxy ligand (relative to an equatorial alkoxy ligand) more than an apical fluorine is favored (relative to an equatorial fluorine) in sulfuranes. Let us consider π-donor interactions with the framework σ and σ^* orbitals and the sulfur 3d orbitals. Hoffman et al.,[33] using extended Hückel calculations, determined that in phosphoranes the π-donor interaction with framework σ orbitals (destabilizing) is more important than the π-donor interaction with σ^* orbitals or phosphorus 3d orbitals (stabilizing). Apical π donors in phosphoranes have little orientational preference due to the threefold axis of the equatorial plane. In sulfuranes this is not the case since sulfuranes have a sulfur lone pair occupying an equatorial position. According to Chen and Hoffman[29] interactions with the sulfur lone pair (**25**) are more destabilizing than interactions with the framework σ orbitals. Any stabilization from interaction with the framework σ^* orbitals can come only with the π donor's p orbital in the orientation shown in **26** (or **27**). The same orientation (**27**) minimizes the destabilizing interaction between the sulfur lone pair and the oxygen lone pairs (**25**) and maximizes the stabilizing interaction between the sulfur lone pair and the σ^* O–C orbital of the apical alkoxy group. While ligands such as chlorine and fluorine with two p-orbital lone pairs cannot avoid the destabilizing interaction depicted in **25**, oxygen ligands, with only one p orbital lone pair, can orient themselves in such a way as to minimize the interaction shown in **25** and maximize the interaction shown in **26** and **27**. The destabilizing lone pair-lone pair interaction forced upon fluorine and chlorine but not alkoxy ligands in sulfuranes may be enough to change the relative apicophilicities of these ligands.



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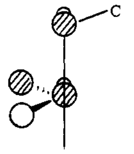

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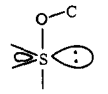
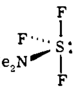


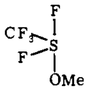
27

It is apparent that electronegativity differences, if large enough, may still be the predominating factor in determining sulfurane apicophilicities. For example, compound **28** gives[45] an ^{19}F NMR spectrum consistent with the structure with apical fluorines and an equatorial dimethylamino ligand.



28

If in fact electronic factors favor apical alkoxy ligands over apical fluorine ligands in sulfuranes, then an alternative explanation exists for the observed nonequivalence of fluorine ligands in the compound that Sprenger and Cowley[30] described as structure **15**, which they attributed to restricted rotation around the equatorial S–O bond. Since our data are consistent with there being little orientational preference for equatorial π donors in sulfuranes, structure **29** may provide a better explanation of the observed nonequivalence of the fluorine ligands.



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From the above discussion of possible differences in the apicophilicity scales for sulfuranes and phosphoranes it is obvious that the differences arise as a result of the substitution of an equatorial lone pair in sulfuranes for one of the equatorial substituents in phosphoranes. Sulfurane oxides and imines, being pentacoordinate, would therefore be expected to have an apicophilicity scale very similar to that for phosphoranes. A recent report[47] of two sulfurane imines postulates structures that are not consistent with the apicophilicities found for phosphoranes; however, alternative structures that are consistent with the relative apicophilicities in phosphoranes appear more consistent with the reported[47] NMR spectra and spectroscopic trends observed[48] for sulfuranes and phosphoranes.

It is evident, from the above discussion of relative apicophilicities in sulfuranes and phosphoranes, that the apicophilicity scale for phosphoranes[15] should be viewed as only a tentative guideline for sulfuranes and, by extension, for derivatives of other hypervalent elements as well.

Acknowledgment. We thank Drs. Iain C. Paul and Eileen N. Duesler for helpful discussions relating to the crystallographic portions of this problem. This work was supported in part by a grant to J.C.M. from the National Cancer Institute (CA 13963) and by fellowships to L.D.M. from Standard Oil of California (1973 and 1975–1976) and Exxon (1974–1975). The X-ray work was carried out using equipment purchased under the terms of an NSF Major Equipment Chemistry Department Grant (MPS 75-05911).

Supplementary Material Available: A listing of the final atomic coordinates (Table IV), final values of the thermal parameters (Table V), observed and calculated structure factors (Table VI), and a stereoscopic view of a complete unit cell (Figure 4) (12 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Part 39 in a series on sulfuranes. For part 38 see E. F. Perozzi and J. C. Martin, *J. Am. Chem. Soc.*, **101**, 1591 (1979). Abstracted in part from the Ph.D. Thesis of L.D.M., University of Illinois at Urbana-Champaign, 1979.
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Synthesis of Alkenes by Reductive Elimination of β-Hydroxysulfoximines

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Abstract: β-Hydroxysulfoximines, obtained in high yield by the addition of α-lithio derivatives of *S*-alkyl-*N*-methyl-*S*-phenylsulfoximines to aldehydes and ketones, undergo reductive elimination to yield alkenes upon treatment with aluminum amalgam in a mixture of tetrahydrofuran, water, and acetic acid. Dienes and trienes were obtained from enones and dienones, respectively. Diastereomers of 5-(*N*-methylphenylsulfonimidoyl)-4-octanol were prepared in stereochemically pure forms; reductive elimination of each diastereomer gave rise to a mixture of *cis*- and *trans*-4-octene (60–84% trans). β-Hydroxy sulfides, sulfoxides, and sulfones do not eliminate under comparable conditions. A 1,3 elimination did not occur when 3-(*N*-methylphenylsulfonimidoyl)-1-phenyl-1-propanol was treated with aluminum amalgam; the reaction gave 1-phenyl-1-propanol.

The transformation of a carbonyl group to a carbon–carbon double bond, a reaction of broad significance, has received considerable attention in the chemical literature. Foremost among the methods available for effecting this transformation is the reaction of an aldehyde or ketone with a phosphorus ylide. Known as the Wittig reaction, this procedure is uncommonly versatile and has been extensively employed in synthetic chemistry.[1] Nevertheless, it has its limitations and alternative methods have been and will continue to be developed.

The use of sulfur-derived reagents to effect the methylenation of carbonyl compounds is a relatively recent innovation and in most instances has not proven to be as general or as simple as the Wittig reaction. (Sulfur ylides that are analogous to the Wittig reagent react with carbonyl compounds to give oxiranes, not alkenes.)[2] Corey has introduced a method of carbonyl methylenation involving β-hydroxysulfinamides which thermally decompose to yield alkenes.[3] The β-hydroxysulfinamides in turn are derived from the reaction of *N*-*p*-tolylmethanesulfinamide dianion with an aldehyde or ketone. Durst has developed an interesting and general procedure for carbonyl methylenation that is based upon β-hydroxy sulfoxides.[4] It was found that the β-hydroxy sulfoxides derived from a carbonyl compound and the anion of a *tert*-butyl alkyl sulfoxide undergo reaction with positive halogen to yield alkenes. Overall yields for this procedure are high; the reaction appears to be quite general. The use of positive halogenating agents precludes the presence of sensitive functionality in the molecule.

Reductive elimination of sulfur-containing molecules is a recent innovation in this field. Coates has shown that the *O*-acetates or benzoates of β-hydrosulfides undergo reductive elimination in the presence of dissolving alkali metals to yield alkenes.[5] β-Hydroxy sulfides also yield alkenes by electroreduction.[6] A similar procedure has recently appeared that involves the use of 2-methylthiopyridine, which is reacted as its anion with a carbonyl compound to yield a β-hydroxy sulfide.[7] This, on successive treatment with titanium tetrachloride, ammonia, and zinc, undergoes reductive elimination to yield an alkene. A methylenation procedure based on the reductive elimination of β-hydroxy sulfones has been described by Julia.[8] The β-hydroxy sulfones (derived from the reaction of anions of alkyl phenyl sulfones with carbonyl compounds), upon reduction with sodium amalgam in ethanol, give rise to alkenes. Where geometric isomers are possible, the reaction produces equal amounts of cis and trans alkenes.[9]

Several intriguing procedures based on 1,2 eliminations initiated by treatment of sulfur-containing substrates with tin hydrides have been described recently;[10,11] these eliminations apparently proceed by a radical mechanism. In the present paper we present a procedure for the reductive elimination of β-hydroxysulfoximines which we believe offers experimentalists a useful method for achieving methylenation of carbonyl compounds. The method is based on the readily available *S*-alkyl-*N*-methyl-*S*-phenylsulfoximines.[12]

Results and Discussion

(*N*-Methylphenylsulfonimidoyl)methyllithium (**2**), gen-

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