Sulfuranes with Oximate Axial Ligands

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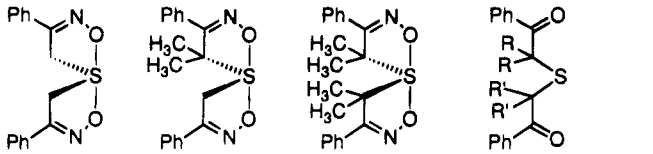
New sulfuranes having one or two axial oximate (R_2C=NO) ligands were synthesized. An improved sulfurane-forming step, involving a rapidly stirred suspension of $NaHCO_3$, is described. The failure of sulfide oximes in which sulfur bears one or two tertiary carbons to form sulfuranes is explained by a C–S bond cleavage leading to tertiary carbocations. This represents a hitherto unanticipated limitation to the standard method of sulfurane synthesis. The X-ray crystal structure of one of the new sulfuranes, namely 2,2′-spirobi(4-phenyl-3*H*-1,2,5-oxathiazoline), is reported (R = 0.0368). An unusual feature was the quite compressed equatorial (C–S–C) angle, 102.6(1)°. The S–O bond length, 1.846(2) Å, was similar to S–O bond lengths of sulfuranes having two axial carboxylate ligands. Since the oximate ligand has not been used previously in a 10-S-4 species, an assessment of its apicophilicity relative to other more common axial ligands was made by considering X-ray structural data, IR data, and *ab initio* calculations. These suggest that the R_2C=NO ligand is as apicophilic as the hexafluorocumyloxy ($ArC(CF_3)_2O$) ligand.

Most sulfuranes containing a five-membered ring reported to date are of the "Martin type" (Figure 1), with benzoannulation at the 4-5 positions of the sulfur-containing five-membered ring.[1] Benzoannulation is salutary in some respects—ease of synthesis, proper placement of a π-acceptor to delocalize the sulfur lone pair[1]—but it is not a *sine qua non* for sulfurane design.



1 **2** **3**

4a R = R′ = H
b R = H, R′ = CH_3
c R = R′ = CH_3

How radically can the Martin five-membered ring layout be altered? Earlier work had shown that even small modifications could cause major changes in reactivity.[2]

This question was of interest to us in another context. Extended Hückel calculations had linked the expansion of the equatorial angle, α, with a decrease in the distances S–Ax and an increase in the stability of the sulfurane.[3] *Ab initio* calculations (4-31G(*) basis) on the contrary had found little correlation between equatorial angle and apical bond length in SH_2F_2.[4] Therefore, it was of interest to shed light on the issue experimentally, *viz.* to prepare a series of similar sulfuranes in which the equatorial angle is progressively increased and to characterize the members of the series with regard to axial bond length and, as a measure of relative kinetic stability at least, with regard to rate of a standard reaction like hydrolysis.

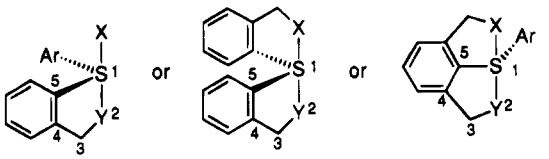
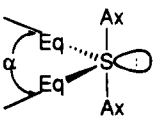


Figure 1. Sulfuranes with "Martin-type" five-membered rings.

In designing such a series of sulfuranes, we made an effort to avoid rare or exotic reagents. This resulted in sulfurane targets **1**–**3**, which, we hoped, could be easily made from the oximes of the venerable and readily prepared phenacyl sulfides **4**. Synthesis of any one of the target molecules would be interesting since 10-S-4[5] species having oximate ligands were unknown prior to our undertaking this work. Note that, contrary to the Martin layout of the five-membered ring in which sp^2 carbons occupy positions 4 and 5, **1**–**3** have an sp^3 carbon in the equatorial position (position 5) and sp^2 atoms in positions 3 and 4. Thus, while **1**–**3** have two sp^2 atoms,



two sp^3 atoms, and sulfur in their five-membered rings, as do sulfuranes with the Martin five-membered ring layout, these atoms are in the ring at novel positions. There is no π-acceptor (or π-donor, for that matter) at the equatorial position.

The equatorial angle would be expected to increase in the order **1** < **2** < **3** (*cf.* the C–S–C angles of di-*tert*-butyl sulfide, 113.2(12)°,[6] and methyl sulfide, 98.87(17)°,[7] or 99.05(4)°[8]) and thus provide a series to assess the effect of increasing equatorial angle on axial bond length and on stability.

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1995.

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We report herein our efforts at preparing targets **1**–**3**, which were not completely successful. Thus, although our goal of studying a series of sulfuranes with rationally varied equatorial angles has not been met at present, we describe here the synthesis and structure of the novel sulfurane **1** as well as some related oximate sulfuranes and a thorough evaluation of the oximate functionality as an apical ligand in sulfuranes. Further, the causes for our failure to prepare **2** and **3** have been investigated. These investigations point to a significant, but hitherto unanticipated, limitation of standard methods of sulfurane construction.

Experimental Section

General. Diethyl ether was dried by distillation under nitrogen from $LiAlH_4$. Chloroform and methylene chloride were distilled under nitrogen from P_2O_5 onto type 4A molecular sieves. All other solvents were dried by storage over type 4A molecular sieves. Melting points were determined using a Mel-Temp apparatus and are uncorrected. CI mass spectra were recorded on a VG7070-EHF mass spectrometer using NH_3 as the reactant gas. EI mass spectra were obtained on a Finnigan 3300 GC/MS. IR spectra were obtained using a Perkin-Elmer Model 983 IR spectrophotometer. NMR spectra were obtained on either a Varian EM-390 (90 MHz ^{1}H) or Bruker AM-400 (400.142 MHz ^{1}H, 100.620 MHz ^{13}C) NMR spectrometer. Chemical shifts are reported on the δ scale, ppm downfield from internal TMS. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, or Atlantic Microlab, Inc., Norcross, GA. Commercial chemicals used in this work were checked for purity and, if necessary, purified by distillation or recrystallization, as appropriate, prior to use.

2,2′-Thiobis(acetophenone), 4a.[9] To a stirred suspension of 0.154 g (3.35 mmol) of anhydrous Li_2S in 10 mL dry DMF was added a solution of 0.945 g (4.75 mmol) of 2-bromoacetophenone in 20 mL of dry DMF. After a few minutes the reaction mixture became warm and turned orange-brown. Stirring was continued for 2 h at room temperature. The reaction mixture was poured into 200 mL of water; the precipitated product was collected and recrystallized from methanol, to give 0.300 g (46.7% yield) of colorless needles, mp 78–80 °C (lit.[10] 77 °C). ^{1}H-NMR ($CDCl_3$): 7.3–8.2 (m, 10H, arom), 3.99 (s, 4H, CH_2). ^{13}C-NMR ($CDCl_3$): 37.36 (CH_2), 128.26, 128.36, 133.17, 135.04, 193.80 (C=O). EI-MS (*m/e*, (rel abund)): 270 (M, 1.62), 165 (M − PhCO, 17.84), 105 (PhCO, 100.00), 77 (43.47), 57 (31.20). IR (KBr; cm^{-1}): 1674(s), 1598(m), 1580(m), 1477(s), 1315(m), 1276(s), 1197(s), 1180(m), 1015(m), 1000(m), 988(m), 685(s).

2,2′-Thiobis(acetophenone) Bis-oxime, 5. A mixture of 0.351 g (7.36 mmol) of 85% KOH, 0.511 g (7.36 mmol) of NH_2-OH·HCl, 25 mL of H_2O, and 25 mL of abs EtOH was treated with 0.497 g (1.84 mmol) of **4a**, refluxed 1 h, and poured into 500 mL of cold water. The product which precipitated was collected, dried, and recrystallized from EtOH/H_2O to give 0.413 g (74.8%) of colorless needles, mp 150–152 (lit.[10] 151 °C). Anal. Calcd for $C_{16}H_{16}N_2O_2S$: C 63.98%, H 5.37%, N 9.33%, S 10.67%. Found: C 64.06%, H 5.41%, N 9.22%, S 10.50%. ^{13}C-NMR (DMSO-d_6): 24.63 (CH_2), 125.76, 128.16, 128.66, 134.77, 152.78 (C=N). EI-MS (*m/e* (rel abund)): 300 (M, 0.77), 237 (37.90), 135 (41.91), 134 (37.17), 117 (31.45), 104 (68.85), 103 (100.00), 91 (38.10), 77 (68.58). IR (KBr; cm^{-1}) 1629(w), 1579(w), 1498(m), 1462(m), 1440(m), 1421(m), 1317(m), 1302(m), 1238(m), 1190(w), 1057(s), 1029(w), 999(m), 950(s), 921(m), 918(m), 890(w), 842(w), 801(w), 778(m), 768(m), 748(s), 689(s), 653(m), 578(w), 490(w), 434(w).

2,2′-Spirobi(4-phenyl-3*H*-1,2,5-oxathiazoline), 1. Glassware, filter paper, and $NaHCO_3$ were oven-dried overnight at 100 °C. A vigorously stirred suspension of 0.045 g (0.13 mmol) of **5** (84% *ZZ* form, see text) and 1.00 g (11.9 mmol) of dry $NaHCO_3$ in 40 mL dry CH_2Cl_2 was treated dropwise with 17 μL (0.15 mmol) of *tert*-butyl hypochlorite.[11] After being stirred 30 s, the reaction mixture was filtered. The solvent was removed from the filtrate at the rotary evaporator, leaving a pale yellow solid, which was recrystallized from CH_2Cl_2–diethyl ether at 0 °C to give 0.022 g (56%) of a white solid, mp 134–5 °C, dec. Anal. Calcd for $C_{16}H_{14}N_2O_2S$: C 64.41%, H 4.73%, N 9.39%, S 10.74%. Found: C 64.46%, H 4.96%, N 9.39%, S 11.12%. ^{1}H-NMR (CD_2Cl_2): 7.61 (m, 2H), 7.39 (m, 3H), 4.68 (d, J = 18 Hz, 1H), 4.10 (d, J = 18 Hz, 1H). ^{13}C-NMR (CD_2Cl_2): 148.20 (C=N), 130.50, 129.22, 126.53, 46.84 (CH_2). EI-MS (*m/e*, (rel abund)): 298 (M, 2.38), 117 (52.06), 104 (71.24), 103 (100.00), 102 (30.96), 77 (91.76), 76 (55.91), 51 (39.43). IR ($CHCl_3$; cm^{-1}): 3000(w), 1604(w), 1590(w), 1560(w), 1498(m), 1448(m), 1394(m), 1343(s), 1330(w), 945(vs, br), 880(w).

Crystal Structure of 1. Slow evaporation of a benzene solution of **1** afforded colorless needles. A crystal, 0.20 × 0.20 × 0.60 mm, was chosen. Monoclinic, space group $C2/c$, a = 17.281(4) Å, b = 13.380(3) Å, c = 8.442(2) Å, β = 94.18(2)°, Z = 4. Nicolet R3m/v diffractometer, Mo Kα (λ = 0.71073 Å), $\theta/2\theta$ scans, 3.0° < 2θ < 50.0°, 2 standard reflections measured every 50 reflections. 1863 reflections collected (1718 independent) of which 1130 were considered observed ($F > 6\sigma(F)$). The structure was solved by Patterson methods using the SHELX-TL PLUS system of programs; the remaining atoms were located from difference maps following refinement of partial models. Data-to-parameter ratio 9:1, goodness of fit 0.92, largest Δ/σ = 0.072, largest difference peak = −0.23 e/Å^3. R = 3.68%, R_w = 5.51%.

2-(2-Carboxyphenylthio)acetophenone, 7.[12] A mixture of 0.500 g (2.51 mmol) 2-bromoacetophenone, 0.387 g (2.51 mmol) thiosalicylic acid, 0.331 g (5.02 mmol) 85% KOH and 15 mL abs. EtOH was refluxed 2 h under nitrogen. The mixture was allowed to cool to room temperature and poured into a mixture of 10% HCl and ice. The orange solid which precipitated was collected and recrystallized from $CHCl_3$–heptane to give 0.273 g (39.9%) colorless needles, mp 180–2 °C (lit.[12] 180 °C). Anal. Calcd for $C_{15}H_{12}O_3S$: C 66.16%, H 4.44%, S 11.77%. Found: C 66.05%, H 4.60%, S 11.78%. ^{1}H-NMR (DMSO-d_6): 7.1–8.2 (m, 9H), 4.66 (s, 2H).^{13}C-NMR (acetone-d_6): 195.13 (C=O), 167.76 (COOH), 141.88 (quat.), 136.98 (quat.), 134.36, 133.40, 132.26, 129.64 (two coincident signals), 129.02 (quat.), 127.50, 125.26, 40.03 (CH_2).

2-[(2-Carboxyphenyl)thio]acetophenone Oxime, 8. A mixture of 0.265 g (3.82 mmol) of NH_2OH·HCl, 0.252 g (3.82 mmol) of 85% KOH, 15 mL of H_2O, and 15 mL of abs EtOH was treated with 0.520 g (1.91 mmol) of **7** and refluxed 45 min. The hot reaction mixture was poured into 500 mL of slightly acidic water. This was cooled in an ice bath, whereupon a pale yellow solid precipitated. The solid was recrystallized from EtOAc, giving 0.351 g (63.9%) colorless needles, mp 166.5–167 °C, dec. Anal. Calcd for $C_{15}H_{13}NO_3S$: C 62.70%, H 4.56%, N 4.87%, S 11.16%. Found: C 62.57%, H 4.61%, N 4.91%, S 11.23%.^{1}H-NMR (DMSO-d_6): 7.21–7.99 (m, 9H), 4.29 (s, 2H). ^{13}C-NMR (DMSO-d_6): 167.17 (COOH), 151.73 (C=N), 140.87, 134.79, 132.30, 130.75, 128.82, 128.27, 127.80, 125.70, 123.94, 25.23 (CH_2).

Spiro(5-oxo-1,2-benzoxathiole-2,2′-4′-phenyl-3′*H*-1′,2′,5′-oxathiazoline), 9. The bicarbonate method described above for the preparation of **1** was used here: $NaHCO_3$ 0.100 g (1.56 mmol), oxime-acid **8** 0.050 g (0.17 mmol), 50 mL of dry $CHCl_3$, *tert*-butyl hypochlorite 18.5 μL (0.17 mmol). The reaction mixture was stirred 2 min before filtering. A white solid resulted from removal of solvent. Recrystallization at 0 °C from CH_2Cl_2/ether gave 0.047 g (94%) of **9**. ^{1}H NMR ($CDCl_3$): 8.23 (m, 1H), 7.99 (m, 1H), 7.79 (m, 2H), 7.59 (m, 2H), 7.43 (m, 3H), 5.61 (d, J = 18 Hz, 1H), 4.44 (d, J = 18 Hz, 1H). ^{13}C NMR ($CDCl_3$): 167.73, 152.31, 135.49, 133.74, 131.63, 129.75, 129.20, 128.52, 127.40, 126.78, 58.77. IR ($CHCl_3$): 3020(m),

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2952(m), 1676(s), 1600(w), 1443(w), 1393(w), 1344(w), 1290(m), 1260(s), 1095(s), 1015(s), 805(s). CI-MS (*m/e*, (rel abund)): 286(68), 270(25), 169(50), 120(25), 104(100), 75(24).

2,2′-Thiobis(isobutyrophenone), 4c.[9] A stirred suspension of 8.902 g (0.114 mol) of Na_2S, made anhydrous by heating $Na_2S{\cdot}9H_2O$ 24 h at 140 °C under vacuum, in 150 mL dry DMF was treated in one portion with 34.543 g (0.152 mol) 2-bromoisobutyrophenone in 75 mL of dry DMF. After being stirred at room temperature 2 h, the reaction mixture was poured into water, precipitating the product. After recrystallization from methanol, 21.62 g (87.1%) of **4c** was obtained as colorless plates, mp 98–99 °C (lit.[9] 103–104 °C). ^{1}H NMR ($CDCl_3$): 1.66 (s, 6H, CH_3), 7.2–7.5, 8.1–8.3 (m, 5H, arom). ^{13}C NMR ($CDCl_3$): 200.74 (C=O), 136.05 (quat.), 131.76, 129.89, 127.75, 54.46 (quat.), 28.14.

2,2′-Thiobis(isobutyrophenone) Bis-oxime, 13.[13] In a 100 mL round-bottom flask, 1.006 g (3.08 mmol) of **4c**, 1.012 g (14.5 mmol) of $NH_2OH{\cdot}HCl$, 5.0 mL of pyridine, and 5.0 mL of absolute ethanol was refluxed 2 h. After cooling, the solvent was removed at the rotary evaporator, leaving a green semisolid. Recrystallization from cyclohexene gave 0.547 g (50.0%) colorless plates, mp 173–176 °C. ^{1}H NMR ($CDCl_3$): 8.43 (s, 2H, OH), 7.37–7.48 (m, 10H, arom), 1.58 (s, 6H, CH_3). ^{13}C NMR (DMSO-d_6): 159.79 (C=N), 133.62, 128.89, 127.29, 127.12, 52.14 (C–S), 28.58 (CH_3). IR (KBr): 3555(s), 3299(s), 3058(w), 3018(w), 2968(m), 2921(w), 1691(w), 1440(m), 1379(s), 1365(w), 1327(s), 1118(vs), 1016(s), 950(vs), 936(vs), 699(vs), 647(m). CI-MS (*m/e* (rel abund)): 357(38), 196(100), 178(32), 163(39), 162(100), 148(43), 144(35), 143(36).

2-Chloroisobutyrophenone, 10. Chlorine was bubbled through a solution of 51.48 g (347.3 mmol) of isobutyrophenone in 100 mL of $CHCl_3$ at room temperature until a yellow color persisted, approximately 2 h. Solvent was removed at the rotary evaporator. The resulting liquid showed no evidence of dichlorinated product (^{1}H NMR ($CDCl_3$): 7.2–8.1 (m, 5H, arom), 1.84 (s, 6H, CH_3)) and was used directly in the synthesis of **11**.

2-Mercaptoisobutyrophenone, 11.[14] Hydrogen sulfide was bubbled into a solution of 2.06 g (89.8 mmol) of sodium in 30 mL of methanol at −20 °C for 5 min. A solution of 10.32 g (56.5 mmol) of 2-chloroisobutyrophenone in ether and methanol was added in one portion. Stirring and bubbling of H_2S was continued at −20 °C for 4 h, during which time a yellow precipitate formed. The entire reaction mixture was added to water. The resulting oil layer was collected, the aqueous layer was extracted 3× with ether, and the combined organic phases were dried over Na_2SO_4. Filtration and removal of solvent gave a material sufficiently pure for use in the synthesis of **4b**. ^{1}H NMR ($CDCl_3$): 7.1–8.1 (m, 5H, arom), 2.28 (s, 1H, SH), 1.66 (s, 6H, CH_3).

2,2-Dimethyl-1,5-diphenyl-3-thia-1,5-pentanedione, 4b.[12] A solution of 2.88 g (16 mmol) of **11**, 4.00 g (20 mmol) of 2-bromoacetophenone, 2.630 g (19 mmol) of $KHCO_3$, 50 mL of ethanol, and 15 mL of H_2O was refluxed under nitrogen 3 h. The resulting green solution was poured over 100 mL of ice-water. The precipitate was collected by filtration and the filtrate reduced in volume to afford a second crop. Recrystallization from methanol gave 2.42 g (51%) of colorless plates, mp 77–79 °C. ^{1}H NMR ($CDCl_3$): 7.25–8.15 (m, 10H, arom), 4.00 (s, 2H, CH_2), 1.66 (s, 6H, CH_3) ^{13}C NMR ($CDCl_3$): 200.74, 194.57, 136.93, 135.55, 133.47, 131.60, 129.09, 128.58, 128.40, 127.97, 51.37 (C–S), 37.37 (SCH_2), 26.40 (CH_3).

2,2-Dimethyl-1,5-diphenyl-3-thia-1,5-pentanedione Bis-oxime, 12. The procedure used to prepare **13** was used here. Recrystallization from ethanol/H_2O gave a 90% yield, mp 172–175 °C. Anal. Calcd for $C_{18}H_{20}N_2O_2S$: C 65.83%, H 6.14%, N 8.53%, S 9.76%. Found: C 65.75%, H 6.18%, N 8.53%, S 9.82%.^{1}H NMR ($CDCl_3$): 7.0–7.7 (m, 10H, arom), 4.11 (s, 2H, CH_2), 1.53 (s, 6H, CH_3).

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Scheme 1

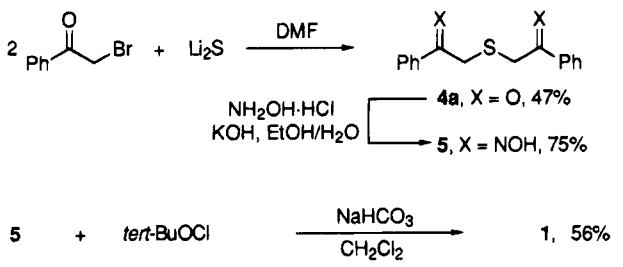


Table 1. Atomic coordinates (× 10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3)

	x	*y*	*z*	*U* (eq)[a]
S	0	5537(1)	2500	57(1)
O	767(1)	5595(2)	1091(3)	69(1)
N	1256(1)	6418(2)	1320(3)	57(1)
C(1)	603(1)	6379(2)	3712(3)	47(1)
C(2)	1178(1)	6826(2)	2679(3)	41(1)
C(3)	1646(1)	7711(2)	3173(2)	39(1)
C(4)	1503(1)	8231(2)	4530(3)	51(1)
C(5)	1933(2)	9070(2)	4985(3)	63(1)
C(6)	2516(2)	9396(2)	4104(4)	64(1)
C(7)	2671(2)	8884(2)	2766(4)	68(1)
C(8)	2245(2)	8043(2)	2290(3)	59(1)
C(9)	310(2)	7563(3)	−2006(4)	90(2)
C(10)	632(2)	8417(4)	−1460(4)	102(2)
C(11)	322(3)	9312(3)	−1970(5)	109(2)

[a] Equivalent isotropic *U* is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

2,2′-Spirobi(4-(4-bromophenyl)-3*H*-1,2,5-oxathiazoline), 6. The procedure used to prepare **4c** was used to synthesize 2,2′-thiobis(4-bromoacetophenone), 78%, mp 142–142.5 °C. ^{1}H NMR (acetone-d_6): 8.00, 7.90, 7.76, 7.66 (AB quartet, 8H, arom), 4.10 (s, 4H, CH_2). This was converted to the bis-oxime following the procedure used to prepare **13**: 71%, mp 176–177.5 °C. ^{1}H NMR (acetone-d_6): 7.70, 7.60, 7.55, 7.45 (AB quartet, 8H, arom), 4.02 (s, 4H, CH_2). EI-MS (*m/e* (rel abund)): 458 (<1), 247(16), 245(18), 199(21), 184(57), 183(100), 182(61), 181(85), 157(27), 155(27), 149(44), 102(92), 76(34), 75(44). Sulfurane **6** was synthesized from the bis-oxime according to the method used to prepare **1**, 53%, mp 140–141 °C dec. ^{1}H NMR ($CDCl_3$): 7.54, 7.52, 7.50, 7.48 (AB quartet, 8H, arom), 4.66, 4.62, 4.04, 4.00 (AB quartet, 4H, CH_2).

Pyridinium Oximate 15. Bis-oxime **13** (0.054 g, 0.15 mmol) was dissolved in the minimum volume (*ca.* 0.5 mL) of dry pyridine, and 17 μL (0.15 mmol) of *tert*-butyl hypochlorite was added. The precipitate which formed was filtered and washed with CH_2Cl_2. The solid was soluble in water and DMSO. mp 141–4 °C. ^{1}H NMR (DMSO-d_6): 11.57 (s, 0.7 H), 9.29 (d, 2H, J = 6.4 Hz), 8.65 (t, 1H, J = 7.8 Hz), 8.17 (t, 2H, J = 7.2 Hz), 7.36 (m, 3H), 6.94 (m, 2H), 1.99 (s, 6H). HRMS 161.0834961 (calcd for $C_{10}H_{11}NO$, 161.0840641).

Results

Sulfurane **1** was synthesized as shown in Scheme 1. The oximate sulfurane 2,2′-spirobi(4-(4-bromophenyl)-3*H*-1,2,5-oxathiazoline) (**6**) was synthesized by the same route beginning with *p*-bromophenacyl bromide.

A crystal of **1** suitable for X-ray diffraction was obtained by slow evaporation of a benzene solution, and the results of an X-ray crystal structure determination[37] are presented in Tables 1 and 2 and Figure 2. The crystal contained a benzene of crystallization, which is not shown in Figure 2. Both the sulfurane and benzene lie on a crystallographic two-fold axis. Atoms numbered in Tables 1 and 2 with an "A" are equivalent by virtue of the symmetry axis to atoms having the same number sans the "A" suffix. The benzene is disordered between two orientations: one in which the axis bisects C–C bonds,

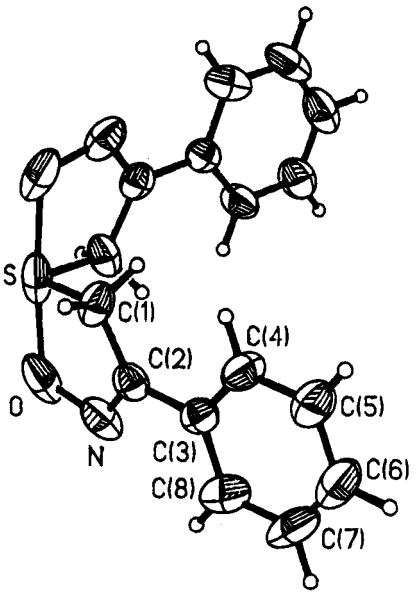


Figure 2. Crystal structure of oximate sulfurane **1**, showing crystallographic numbering system. A benzene of crystallization is not shown.

Table 2. Geometric Parameters for 1 (Å, deg)

	Bond Length		
S–O	1.846(2)	S-C(1)	1.802(2)
O–N	1.394(3)	N–C(2)	1.286(3)
C(1)–C(2)	1.495(3)	C(2)–C(3)	1.477(3)
C(3)–C(4)	1.378(3)	C(3)–C(8)	1.391(3)
C(4)–C(5)	1.384(4)	C(5)–C(6)	1.366(4)
C(6)–C(7)	1.365(4)	C(7)–C(8)	1.388(4)
C(9)–C(10)	1.339(6)	C(9)–C(9A)	1.308(7)
C(10)–C(11)	1.368(7)	C(11)–C(11A)	1.377(8)
	Bond Angle		
O–S–C(1)	85.8(1)	O–S–OA	175.2(1)
C(1)–S–OA	91.1(1)	C(1)–S–C(1A)	102.6(1)
S–O–N	113.6(1)	O–N–C(2)	111.0(2)
S–C(1)–C(2)	107.5(2)	N–C(2)–C(1)	117.9(2)
N–C(2)–C(3)	120.0(2)	C(1)–C(2)–C(3)	122.1(2)
C(2)–C(3)–C(4)	120.8(2)	C(2)–C(3)–C(8)	121.2(2)
C(4)–C(3)–C(8)	118.0(2)	C(3)–C(4)–C(5)	121.0(2)
C(4)–C(5)–C(6)	120.7(3)	C(5)–C(6)–C(7)	119.2(3)
C(6)–C(7)–C(8)	121.0(3)	C(3)–C(8)–C(7)	120.2(2)
C(10)–C(9)–C(9A)	121.4(2)	C(9)–C(10)–C(11)	119.6(3)
C(10)–C(11)–C(11A)	119.0(2)		

about 75% occupancy, and another in which the axis passes through opposite carbons of the ring, about 25% occupancy. A lower R was achieved, however, by treating the benzene as nondisordered. The final $R = 0.0368$, $R_w = 0.0551$. Other details of the crystallographic data collection and solution are given in the Experimental Section

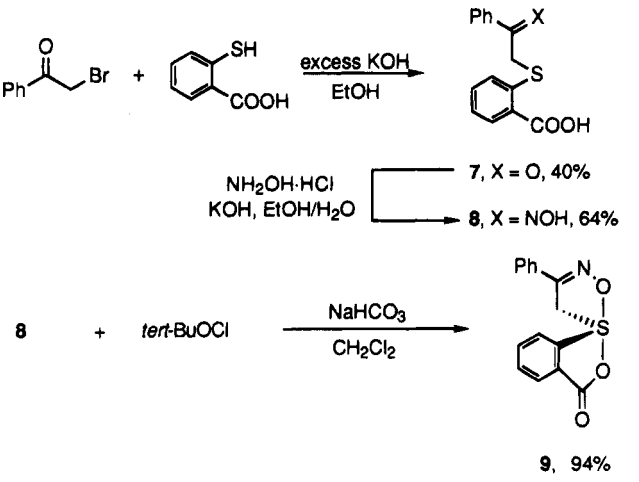
Oximate sulfurane **9** was synthesized by the route shown in Scheme 2.

The planned routes to sulfuranes **2** and **3** are shown in Schemes 3 and 4 respectively. Each of these pathways failed to give the desired sulfurane.

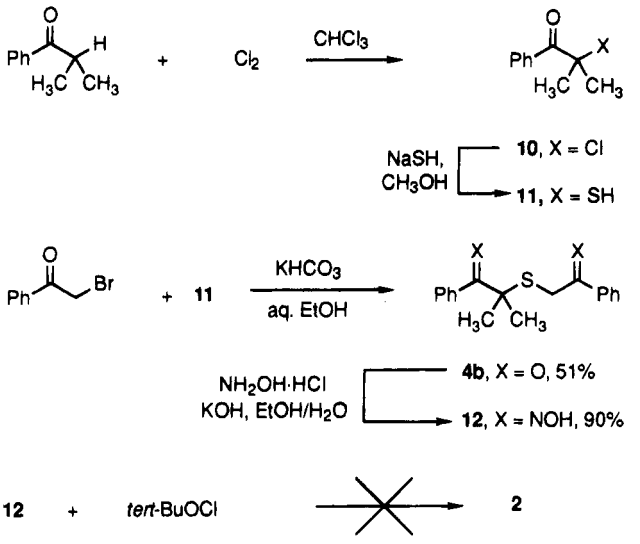
Discussion

Bis-oxime **5**, the precursor to oximate sulfurane **1**, may exist in three possible forms, isomeric about the C=N bonds. Of these, presumably only the *ZZ* isomer, with both OHs trans to the phenyls, is able to close to the desired sulfurane, assuming no isomerization of C=N bonds during sulfurane formation. The ^{1}H-NMR spectrum of **5** ($CDCl_3$ solvent) shows a large singlet at 3.97 ppm and two small singlets of equal intensity at 3.92 and

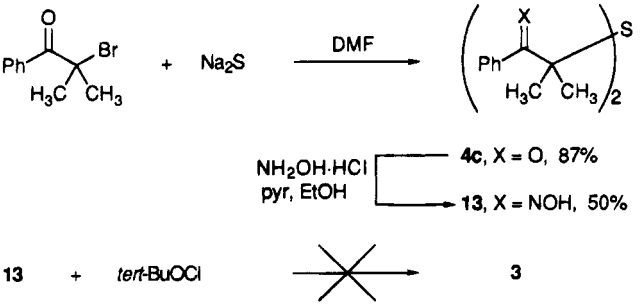
Scheme 2



Scheme 3



Scheme 4



3.69 ppm. In DMSO-d_6, OH signals at 11.61, 11.58, and 11.05 ppm are in evidence. Previous NMR studies of oxime geometrical isomerism in phenacyl systems[15,16] support the assignment of the 3.92 and 3.69 ppm peaks to the *EZ* isomer of **5**, and the 3.97 ppm signal to the *ZZ* isomer. Consistent with this, the large singlet at 11.61 ppm (DMSO-d_6) is due to the *ZZ* isomer, and the 11.58 and 11.05 ppm singlets are due to the *EZ* isomer. No signals attributable to the *EE* isomer were detected. By careful integration of the CH_2 signals, the isomeric

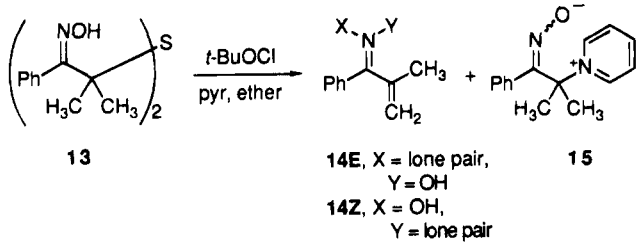
(15) Moehrle, H.; Wehefritz, B. Steigel, A. *Tetrahedron* **1987**, *43*, 2255–2260.
(16) Rouillard, M.; Girault, Y.; Decouzon, M.; Azzaro, M. *Org. Magn. Reson.* **1983**, *21*, 357–360.

composition of **5** was calculated; yields of **1** are reported based on the amount of *ZZ* isomer present.

Sulfurane **6**, the analogue of **1** having *para* bromines, was prepared to facilitate crystallographic structure determination. However, a suitable crystal of **1** was obtained before a suitable crystal of **6** could be grown. A thorough discussion of the structure of **1** appears at the end of this section.

The synthesis of **1** by the usual[17-21] method, *viz. tert*-butyl hypochlorite and pyridine, was inefficient in our hands. We found that replacing pyridine with a rapidly stirred suspension of dry, powdered $NaHCO_3$ resulted in improved yields in reactions on a small scale.

In view of the success encountered in the synthesis of **1**, **6**, and **9**, it was surprising to find that **2** and **3** could not be made by the same method. On the other hand, **2** and **3** might merely be too crowded to exist. In these cases, treatment of the bis-oxime with *tert*-butyl hypochlorite proceeded briskly, but gave products which were not the desired sulfuranes. Treatment of tetramethyl bis-oxime **13** with 1 equiv each of pyridine and *tert*-BuOCl in ether solvent, followed by immediate removal of solvent, gave a residue exhibiting no ^1H NMR peaks ascribable to **3**, but showing peaks in the 4.8–5.5 ppm region. The olefins giving rise to these signals were identified as **14E** (5.46 (m, 1H), 5.03 (m, 1H), and 2.05 (m, 3H) ppm) and **14Z** (5.34 (m, 1H), 4.88 (m, 1H), and 2.06 (m, 3H) ppm), which are formed in the ratio 2.2:1, respectively. Zwitterionic compound **15** is also formed. The structures of compounds **14Z**, **14E**, and **15** were confirmed by an alternate synthesis. Namely, the reaction of α-bromoisobutyrophenone with 2 equiv of $NH_2OH{\cdot}HCl$ in refluxing 1:1 EtOH:pyridine gave **14E** and **14Z** in a ratio of about 1 to 2. When the solvent was ethanol instead of 1:1 EtOH:pyridine in the α-bromoisobutyrophenone reaction, the ratio of **14E** to **14Z** was about 2 to 1.

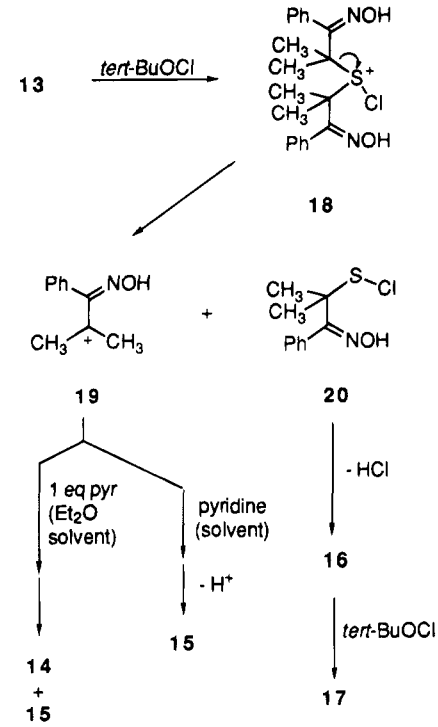


13 — 14E, X = lone pair, Y = OH; 14Z, X = OH, Y = lone pair — 15

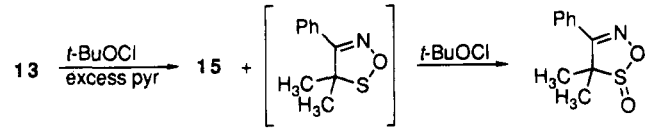
Other conditions were tried in the reaction of **13** with *tert*-BuOCl. When the reaction of **13** with *tert*-BuOCl was carried out in the presence of rapidly stirred powdered $NaHCO_3$ in place of pyridine, only **14Z** formed. This **14Z**, after inorganic solids were removed by filtration, isomerized to a 3.5:1 mixture of **14E**:**14Z** over the course of seven days in $CDCl_3$ solvent. Thus **14Z** is the kinetic and **14E** the thermodynamic product in this reaction.

The reaction of **13** with *tert*-BuOCl proceeded slightly differently in pyridine solvent. Product **15** precipitated immediately and was removed by filtration. The supernatant was shown by mass spectrometry to contain

Scheme 5



sultine **17**. This product may arise from *in situ* oxidation of sultene **16** by *tert*-BuOCl. Astrologes and Martin[22] have reported the reaction of a sultene with water producing a sultine and a disulfide. We have been unable to detect the corresponding disulfide which would be formed were **17** to arise from the reaction of **16** with water.



16 — 17

A mechanism which rationalizes these results is shown in Scheme 5. The key step here is the fragmentation of chlorosulfonium ion **18**. Such an ion is presumably an intermediate whenever *tert*-BuOCl/pyridine is used to synthesize a sulfurane.[21] That the fragmentation occurs in this case and not in all the many other cases is presumably the result of formation here of the relatively stable tertiary carbocation **19**. (Such fragmentation of a halosulfonium ion is not novel.[23] According to Wilson,[23a] "Carbon–sulfur bond cleavage is a major pathway of halosulfonium ion reaction....When the α-carbon can support a positive charge, the cleavage reaction is favored." An example[24] which is quite reminiscent of the

(17) Astrologes, G. W.; Martin, J. C. *J. Am. Chem. Soc.* **1976**, *98*, 2895–2900.
(18) Livant, P.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 5761–5767.
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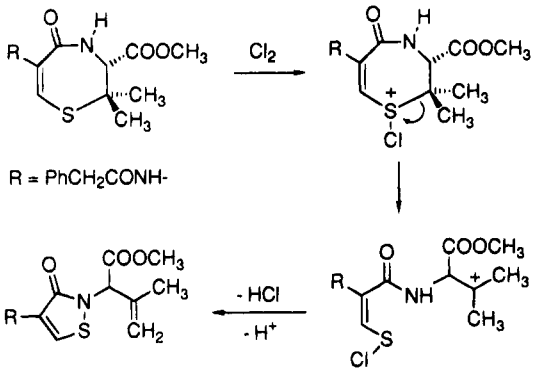
(22) Astrologes, G. W.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 4390–4400.
(23) (a) For a review, see Wilson, G. E., Jr. *Tetrahedron* **1982**, *38*, 2597–2625. Several more recent references are (b) Lee, W. S.; Nam, K. D.; Hahn, H.-G.; Mah, H. D. *J. Heterocycl. Chem.* **1993**, *30*, 1105–1109. (c) Lee, W. S.; Park, O. S.; Choi, J. K.; Nam, K. D. *J. Org. Chem.* **1987**, *52*, 5374–5377. (d) Yamamoto, K.; Yamazaki, S.; Murata, I.; Fukazawa, Y. *J. Org. Chem.* **1987**, *52*, 5239–5243. (e) Caputo, R.; Ferreri, C.; Palumbo, G.; Capozzi, G. *Tetrahedron* **1986**, *42*, 2369–2376. (f) King, J. F.; Rathore, R. *Tetrahedron Lett.* **1989**, *30*, 2763–2766. (g) Somoza, C.; Mascaretti, O. A. *Tetrahedron* **1988**, *44*, 7007–7012.
(24) (a) Leonard, N. J.; Wilson, G. E., Jr. *Tetrahedron Lett.* **1964**, 23, 1471–1475. (b) Leonard, N. J.; Wilson, G. E., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 5307–5316.

transformation **18** → **19** + **20** is shown below.) Thus, we proffer a *caveat* concerning the "traditional" method of sulfurane synthesis: *when the initially formed chlorosulfonium ion can cleave to a relatively stable cation,*



it will do so rather than close to the sulfurane and the method will fail. Since "Martin-type" sulfuranes all have phenyls adjacent to sulfur, cleavage to a phenyl cation is clearly disfavored and the method always works. However, the limitation uncovered in this work should be borne in mind. In keeping with this idea, our attempts to synthesize **2** failed in the way our attempts to synthesize **3** failed: fragmentation products such as **15** were detected.

Oximate as an Axial Ligand. Compounds **1**, **6**, and **9** represent the first examples of a 10-S-4 species having an oximate axial ligand. Therefore it is of interest to compare this new ligand to other axial ligands. One way to do this is to examine the axial S–O bond length of **1** and of other symmetrical dioxasulfuranes. Chart 1 pictures nine sulfuranes which fit this description; their axial S–O bond lengths are collected in Table 3. All are 10-S-4 [$(CO)_2$] species save **26** (10-S-4 [CO_3]) and **28** (10-S-4 [O_4]), so these two may not be directly comparable. The 1.846(2) Å S–O bond of **1** seems to resemble most closely the 1.83 Å S–O bond of **21** which has a carboxylate axial ligand, and the 1.839(2) Å S–O bond of **24** which also has a carboxylate axial ligand. Therefore, S–O bond length comparison leads to the suggestion that oximate is a little less apicophilic than carboxylate.

Another way to assess the apicophilicity of an axial ligand (L) is to measure the C=O stretching frequency (ν^{CO}) of a carboxylate ligand in a sulfurane in which carboxylate and L are termini of the axial three-center four-electron bond.[18] The ν^{CO} in these cases spans a wide range: from 1740 cm^{-1} for L = Cl to 1640 cm^{-1} for L = O*t*-Bu. Oximate sulfurane **9** exhibits ν^{CO} of 1676 cm^{-1}. This value falls between 1647 cm^{-1} for **30** and 1708 cm^{-1} for **31**.[18] Sulfurane **21** exhibits ν^{CO} at 1724 cm^{-1}.[18] This comparison suggests that the apicophilicity of oximate more closely resembles that of a hexafluorocumyloxy apical ligand than a carboxylate ligand.

Chart 1

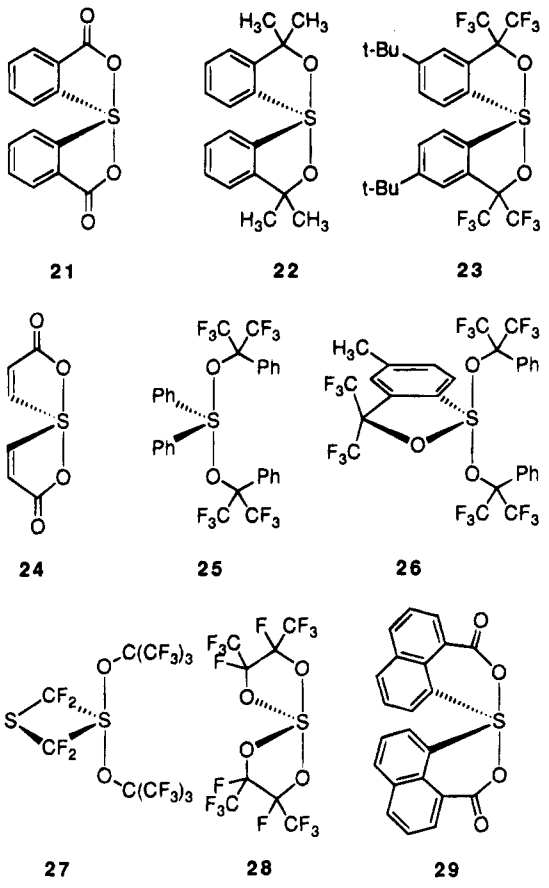
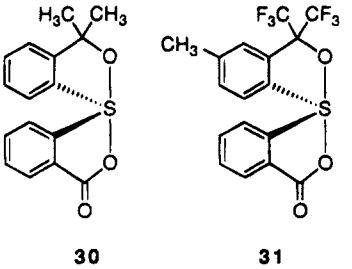


Table 3. Axial Bond Lengths and Equatorial Angles of Symmetric Dioxasulfuranes

sulfurane	S–O (Å)	C–S–C (deg)[a]	ref
21	1.83(1)	107.8	25
22	1.814(2)	112.4(1)	26
	1.787(2)		
23	A: 1.819(5)[b]	A: 108.1(4)[b]	27
	1.832(5)		
	B: 1.816(5)[b]	B: 107.6(3)[b]	
	1.831(5)	–	
24	1.839(2)	105.3(2)	28
25	1.916(4)	104.4(3)	29
	1.889(4)		
26	1.829(10)	–	30
	1.840(10)		
27	1.811(7)	–	31
	1.816(7)		
28	1.754(3)	104.6(2)	32
	1.756(3)		
29	1.870	106.9	21
1	1.846(2)	102.6(1)	this work

[a] Only those C–S–C bonds not part of a cyclic structure are included. [b] Two independent molecules per unit cell.



(25) Kálmán, A.; Sasvári, K.; Kapovits, I. *Acta Crystallogr.* **1973**, *B29*, 355–357.
(26) Lam, W. Y.; Duesler, E. N.; Martin, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 127–135.
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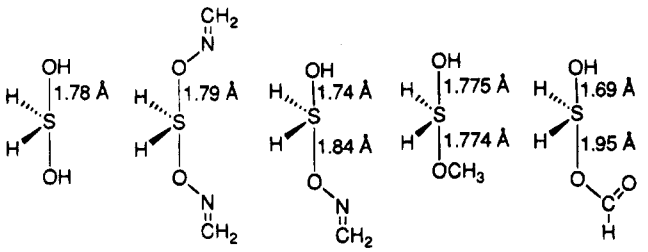
(32) Hodges, K. C.; Schomburg, D.; Weiss, J.-V.; Schmutzler, R. *J. Am. Chem. Soc.* **1977**, *99*, 6096–6097.

Ab initio calculations with a 4-31-G(*) basis set have been shown to be useful adjuncts to experimental investigations of the hypervalent bond of sulfuranes.[4] Assessing the apicophilicity of a ligand L can be done by performing a series of three geometry optimizations: for H_2SL_2, H_2SX_2 and H_2SXL, where H is always equatorial. If L is more apicophilic than X, the S–L bond in H_2SXL will be longer than the S–L bond in H_2SL_2 and the S–X bond in H_2SXL will be shorter than the S–X bond in H_2SX_2.[4] The calculated bond lengths of hypothetical sulfuranes **32**–**34** constitute just such a comparison. Clearly the oximate ligand is more apicophilic than OH.



32 **33** **34** **35** **36**

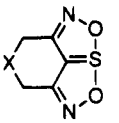
Further, the bond length distortions engendered by putting oximate opposite OH in **34** are greater than those engendered by putting methoxy opposite OH, in **35**, but less than those engendered by putting formate opposite OH, in **36**. Thus, the apicophilicity of oximate falls between that of alkoxy (modeled here by methoxy) and that of carboxylate (modeled here by formate), which is consistent with the conclusion reached by consideration of the IR data. A conformer of **34** in which the C–N–O–S dihedral angle was 0° instead of 180° was found to be higher in energy than **34**.

Structure of Oximate Sulfurane 1. In addition to the S–O bond lengths already mentioned, Table 3 shows the equatorial angles for **21**–**25**, **28**, and **29**. The equatorial angle of **1**, 102.6(1)°, is significantly smaller than those listed in Table 3. It would be unwise to speculate on the cause for this angle compression, but it can be noted that 102.6° is smaller than a typical sulfurane equatorial angle by roughly the same amount that it is larger than a typical sulfonium ion angle. This inherently small equatorial angle would militate against the successful synthesis of **2** and **3**, quite apart from the problem of sulfonium ion cleavage noted. With the X-ray structure of **1** in hand, the question of the possible nonexistence of **2** or **3** for reasons of excessive steric strain can be addressed as follows. To the structure of **1** we substituted for each of the four α-hydrogens a methyl group with standard bond lengths and angles, keeping all other structural parameters constant. This resulted in a hydrogen–hydrogen contact between the inward-pointing methyls of 1.75 Å, well below the sum of van der Waals radii for two hydrogens.[33] However, when various structural parameters were allowed to deviate from their value in **1**, especially when the equatorial angle was allowed to expand, the inward-pointing methyls could successfully avoid each other. A structure with an equatorial angle of 112.8° put the nearest methyl hydrogens a comfortable 2.27 Å apart. As can be seen from Table 3, 112.8° is large for a sulfurane equatorial angle, but not outrageously so. Therefore we conclude **2** and **3** are not prohibited from existing by dint of insurmountable van der Waals repulsions.

A remarkable feature of **1** is how little the C=NO geometry changes on going from oxime to sulfurane oximate ligand. For example, a typical C=N bond length of an oxime (an average of 67 values taken from the Cambridge Structural Database)[34] is 1.281(13) Å. The C=N bond length of **1** is 1.286(3) Å. The average oxime N–O bond length[34] is 1.394(18) Å; that of **1** is 1.394(3) Å. The average oxime C=N–O bond angle[35] is 111.2(15)°; that of **1** is 111.0(2)°.

Since there are only rare instances of sulfuranes with nonfluorinated sp^3 carbon equatorial ligands, it is of interest to examine the S–C equatorial bond length of **1**. The value, 1.802(2) Å, is little different than the value exhibited by a sulfurane with an equatorial phenyl substituent, *viz.* 1.795(17) Å for the average of **21**–**26** and **29**. Insensitivity of C–S bond length to carbon hybridization would appear to be more the rule than the exception: for example, compare the average C_{sp3}–SO_2–C bond length, 1.779(20) Å,[34] and the average C_{Ar}–SO_2–C bond length, 1.763(9) Å.[34]

Finally, several 10-S-3 species with oximate ligands have been the subject of X-ray crystal structure determinations. Although one should not consider 10-S-3 and 10-S-4 species comparable *a priori*, it is nevertheless irresistible to make a comparison of cogent structural parameters. Specifically **37**–**39** were reported by Cam-



37, X = S
38, X = SO
39, X = SO_2

illeri et al.[36] to show very little variation in bond lengths and angles in the fused five-membered rings. The bond lengths and angles averaged over **37**, **38**, and **39**, followed by the corresponding parameter of **1** are: S–O 1.851(16) Å, 1.846(2) Å; N–O 1.344(9) Å, 1.394(3) Å; S–O–N 114.0(3)°, 113.6(1)°; C=N–O 110.5(4)°, 111.0(2)°. The two sets of data are remarkably similar.

Acknowledgment. The authors thank Dr. K. P. Sarathy of Auburn University's NMR Instrumentation Facility for a generous allocation of time. The invaluable suggestions of Dr. Abe Brubaker are warmly acknowledged.

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(37) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.