of lactone sulfone **11**, involves only eight-membered-ring inversion; inversion of sulfonyl sulfur is an unlikely and unnecessary component of this process (Scheme II).

The room-temperature ^{1}H NMR of **11** shows absorptions postulated to be averages for two conformations whose interconversion occurs via low activation energy processes involving primarily changes in conformation of the three-atom bridge (**11a** ⇄ **11b** or **11c** ⇄ **11d**). Conformers **11a** and **11c** (and also **11b** and **11d**) are enantiomeric. Since **11a** and **11b** are interconverted at ambient temperatures, the two enantiomeric equilibrating systems give rise to only two methyl peaks in the NMR spectrum. At the coalescence temperature the NMR observation is explained by postulating a process of ring inversion of the eight-membered ring, involving a rotation about the sulfur-aryl bond (**11a** ⇄ **11d** and **11b** ⇄ **11c**). The latter process, a ring inversion involving the one-atom (sulfur) bridge, which interconverts the two enantiomeric systems, occurs with a higher activation energy (19.4 kcal mol^{-1}).

Conclusion

We have shown here that diaryl sulfides, having each benzene ring doubly ortho substituted, show the effects of a high level of steric interference. Isomerization of the possible conformers resulting from restricted internal motions, via the "gear-clashing" pathways, requires a high activation energy. The conformational interconversions are further slowed for the corresponding sulfones, an effect which may reflect the additional transition-state steric effects of the two sulfonyl oxygen atoms.

Explanations for our observations on sulfones may be complicated by the possibility in some conformations of attractive interactions between the nucleophilic oxygen atoms of the ortho-substituents and the electrophilic sulfonyl sulfur. Evidence for such interactions will be discussed in a later paper, including chemical evidence and evidence adduced from an X-ray structure determination for sulfone **7**.

Acknowledgment. This research is supported in part by a grant from the National Science Foundation (CHE-790592). We are grateful to Mr. W. Stevenson for the NMR line-shape analysis calculation.

Registry No. 3, 62558-12-7; **4**, 62558-13-8; **5**, 75893-97-9; **6**, 78480-10-1; **7**, 78479-63-7; **8**, 78480-11-2; **9**, 78479-64-8; **10**, 78480-12-3; **11**, 75893-86-6.

Ketalization of Dihydroxy Sulfones (8-S-4 Species) by Cyclodehydration To Form Spirobicyclic Oxysulfurane Oxides (10-S-5 Species)[1]

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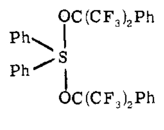
Received September 19, 1980

Dihydroxy sulfones **6** and **7** react with the dehydrating agent $\mathrm{Ph_2S(OC(CF_3)_2Ph)_2}$ (**1**) to give sulfurane oxides **8** and **9**, respectively. These reactions are thought to be the first examples of the direct ketalization of sulfones by dehydration. A possible mechanism for this ketalization is proposed, and related evidence is discussed. The crystal and molecular structures of **6** are solved by X-ray crystallographic techniques (R = 0.079), and reveal a distorted tetrahedral geometry about sulfur, large steric interactions between the ortho substituents, and short interatomic distances consistent with an attractive electronic interaction between the electrophilic sulfonyl sulfur and the nucleophilic hydroxylic oxygens of **6**.

The number of reported oxysulfuranes has grown rapidly[2] since the preparation of the first isolable acyclic dialkoxysulfurane **1**[2i] and spirosulfurane **2**[2j] were published



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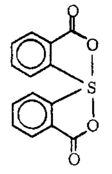


2

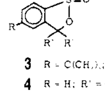
in 1971. The synthesis of **1** involves the oxidative addition of two apical oxygen ligands to a sulfur(II) atom, a process which can be represented in eq 1. The cyclodehydration

$$\mathrm{R_2S} + 2\,{}^{-}\mathrm{OR'} \xrightarrow{[\mathrm{O}]} \mathrm{R_2S(OR')_2} \tag{1}$$

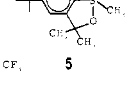
of a dihydroxy sulfoxide to give a dioxysulfurane is a special case of eq 2. The two routes shown in eq 1 and 2 are usually used to prepare other oxysulfuranes.

$$\mathrm{R_2S{=}O} + 2\mathrm{HOR'} \xrightarrow{-\mathrm{H_2O}} \mathrm{R_2S(OR')_2} \tag{2}$$

In contrast to oxysulfuranes, only a few oxysulfurane oxides such as **3**,[3] **4**,[4] and **5**[5] have been reported. These



3 R = C(CH$_3$)$_3$; R' = CF$_3$
4 R = H; R' = CH$_3$



5

sulfurane oxides were synthesized by direct oxidation of their parent sulfuranes. Pathways such as those shown

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[1] The designations of 10-S-5 and 8-S-4 are part of the N-X-L nomenclature system. See: Perkins, C.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753.

[2] (a) Mir, Q.-C.; Babb, D. B.; Shreeve, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 3961. (b) Wilson, G. E.; Belkind, B. A. *Ibid.* **1978**, *100*, 8124. (c) Huszthy, P.; Kopovits, I.; Kucsman, A. *Tetrahedron Lett.* **1978**, 1853. (d) Hodges, K. C.; Schomburg, D.; Weiss, J.-V.; Schmutzler, R. *J. Am. Chem. Soc.* **1977**, *99*, 6096. (e) Kitazume, T.; Shreeve, J. M. *Ibid.* **1977**, *99*, 4194. (f) Adzima, L. J.; Martin, J. C. *J. Org. Chem.* **1977**, *42*, 4006. (g) Adzima, L. J.; Duesler, E. N.; Martin, J. C. *Ibid.* **1977**, *42*, 4001. (h) Martin, J. C.; Perozzi, E. F. *Science* **1976**, *191*, 154. (i) Martin, J. C.; Arhart, R. J. *J. Am. Chem. Soc.* **1971**, *93*, 2341. (j) Kapovits, I.; Kálmán, A. *Chem. Commum.* **1971**, 649.

[3] (a) Perozzi, E. F.; Martin, J. C. *J. Am. Chem. Soc.* **1972**, *94*, 5519. (b) Martin, J. C.; Perozzi, E. F. *Ibid.* **1974**, *96*, 3155.

[4] Adzima, L. J.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 1657.

[5] Lau, P. H. W.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 5490.

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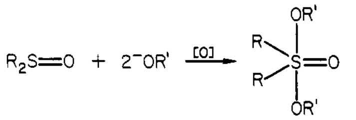
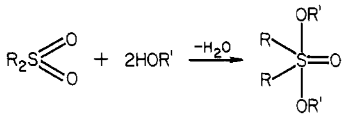
in eq 3 and 4, leading to oxysulfurane oxides, have not been reported.[6]



$$R_2S{=}O + 2\,^{-}OR' \xrightarrow{[O]} R_2S(=O)(OR')_2 \quad (3)$$



$$R_2SO_2 + 2HOR' \xrightarrow{-H_2O} R_2S(=O)(OR')_2 \quad (4)$$

Here we report the cyclodehydration of 8-S-4 species (sulfones) to give 10-S-5 species (sulfurane oxides), a process represented by eq 4.

Experimental Section

General Methods. Proton NMR chemical shifts are reported on the δ scale (parts per million downfield from tetramethylsilane as an internal standard). Melting points were determined on a micro hot stage. Elemental analyses of new compounds are within 0.4% of theoretical values, unless otherwise noted.

Solvent and Reagents. Ether, tetrahydrofuran (THF), and pentane were dried and stored over sodium wire. Chloroform and carbon tetrachloride were washed with concentrated H_2SO_4, water, and then 10% aqueous $NaHCO_3$ before being distilled from P_2O_5.

7,7′-Bis(hydroxymethyl)-5,5′-bis(1,1-dimethylethyl)-3,3,3′,3′-tetramethyl-1,1′-spirobi[3*H*-2,1-benzoxathiole] (17a). Method A. A solution of *m*-chloroperbenzoic acid (98 mg of 85% peracid, 0.57 mmol) in $CHCl_3$ was quickly added in one portion to a stirred solution of sulfide tetraol **15a** (0.27 g, 0.57 mmol) in $CHCl_3$. After 30 min, the solution was extracted with aqueous $NaHCO_3$ and dried (Na_2SO_4), and the solvent was removed. The remaining solid was recrystallized from ether to give a crystalline **17a**: 0.23 g, (0.46 mmol, 80%); mp 174.5–175.5 °C; IR ($CHCl_3$) 3367 (m, OH), 2950 (s), 1595 (w), 1364 (m), 1161 (m), 1019 (m), 969 (m), 882 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.34 (d, 2, Ar H), 7.27 (d, 2, Ar H), 4.55 and 4.08 (AB pattern, 4, J_{AB} = 11 Hz, CH_2OH), 1.67 (s, 6, $OCCH_3$), 1.63 (s, 6, $OCCH_3$), 1.36 (s, 18, $C(CH_3)_3$); mass spectrum (10 eV), *m/e* (relative intensity) 472 (12.02, M$^+$), 457 (100, M$^{+\cdot}$ − H_2O and CH_3), 439 (10.27), 269 (24.58), 251 (23.52), 204 (42.14). Anal. ($C_{28}H_{40}O_4S$) C, H, S.

Method B. To a solution of sulfide tetraol **15a** (1 g, 0.211 mmol) in 80 mL of ether was added *tert*-butyl hypochlorite (0.24 mL, 0.211 mmol) at 0 °C. After 30 min, the white precipitate formed was collected and washed several times with ether to give pure chlorosulfurane **18**: 0.935 g (0.184 mmol, 87.2%); mp 143–145 °C; ^{1}H NMR ($CDCl_3$) δ 7.61 (br, 1, Ar H), 7.39 (br, 2, Ar H), 7.18 (br, 1, Ar H), 4.87 (br, 3, OH), 4.2 and 3.8 (AB pattern, 4, OCH_2), 1.93 (s, 3, $OCCH_3$), 1.75 (s, 3, $OCCH_3$), 1.68 (s, 3, $OCCH_3$), 1.62 (s, 3, $OCCH_3$), 1.41 (s, 9, $C(CH_3)_3$), 1.35 (s, 9, $C(CH_3)_3$). Anal. ($C_{28}H_{41}O_4SCl$) C, H, Cl, S.

Powdered KH (ca. 60 mg, slightly excess) was added to a stirred solution of chlorosulfurane **18** (448 mg, 0.88 mmol) in ca. 100 mL of THF. After 22 h, the solution was filtered, the solvent was removed to leave a white solid, which was recrystallized from ether–pentane to give crystalline **17a** (291 mg, 0.62 mmol, 70%).

7,7′-Bis(hydroxymethyl)-5,5′-bis(1,1-dimethylethyl)-3,3,3′,3′-tetramethyl-1,1′-spirobi[3*H*-2,1-benzoxathiole] 1-Oxide (9). A solution of MCPBA (118 mg of 85% peracid, 0.583 mmol) in $CHCl_3$ was added to a solution of sulfurane diol **17a** (275 mg, 0.583 mmol) in $CHCl_3$. After 1 h, the solution was extracted with aqueous $NaHCO_3$ and dried (Na_2SO_4), and the solvent was removed under vacuum. The remaining solid was recrystallized from ether–pentane to give crystals of **9**: 214 mg (0.438 mmol, 75.2%); mp 130–136 °C; IR ($CHCl_3$) 3500 (m), 2900 (s), 1370 (m), 1260 (m), 1140 (m), 1075 (m), 925 (s), 913 (s), 866 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.43 (d, 2, Ar H), 7.06 (d, 2, Ar H), 5.20 and 4.60 (AB pattern, 4, J_{AB} = 12 Hz, CH_2OH), 3.5 (br, 2, OH), 1.73 (s, 6, $OCCH_3$), 1.54 (s, 6, $OCCH_3$), 1.35 (s, 18, $C(CH_3)_3$); in dry solvent, the AB pattern at δ 5.20 and 4.60 appears as broad peaks due to coupling with the hydroxy protons; mass spectrum (10 eV), *m/e* (relative intensity) 488 (1.89, M$^{+\cdot}$), 473 (4.96, M$^{+\cdot}$ − CH_3), 455 (26.98, M$^{+\cdot}$ − CH_3 and H_2O), 437 (10.15, M$^{+\cdot}$ − CH_3 and $2H_2O$), 422 (14.49), 409 (14.46), 404 (13.49), 388 (21.48), 373 (31.88), 331 (24.66), 317 (15.69). Anal. ($C_{28}H_{40}O_5S$) C, H. S.

Fragmentation Product of Sulfurane Oxide Diol 9, Sulfone Olefin 11. Several drops of chloroform saturated with HCl were added to a solution of sulfurane oxide diol **9** (60 mg) in $CHCl_3$. After 30 min, the solvent was removed to give a crystalline solid, **11**: 60 mg (100%); IR ($CHCl_3$) 3448 (m), 1592 (m), 1362 (m), 1258 (s), 1157 (m), 1115 (s), 1017 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.50 (d, 1, Ar H), 7.47 (d, 1, Ar H), 7.45 (d, 1, Ar H), 7.42 (d, 1, Ar H), 4.98 (br m, 1, olefinic CH), 4.62 (br, 1, olefinic CH), 4.81 and 4.47 (AB pattern, 2, J_{AB} = 13.5 Hz, CH_2OH), 4.55 and 4.37 (AB pattern, 2, J_{AB} = 13.5 Hz, CH_2OH), 3.48 (br, 3, OH), 1.87 (s, 3, $C{=}CCH_3$), 1.73 (s, 6, $OCCH_3$), 1.35 (s, 18, $C(CH_3)_3$). Anal. ($C_{28}H_{40}O_5S$) C, H.

7,7′-Bis(acetoxymethyl)-5,5′-bis(1,1-dimethylethyl)-3,3,3′,3′-tetramethyl-1,1′-spirobi[3*H*-2,1-benzoxathiole] (19). Acetic anhydride (0.2 mL, 20.4 mmol) and a solution of sulfurane diol **17a** (100 mg, 0.212 mmol) in 10 mL of $CHCl_3$ was stirred for 2 days, and the solvent was removed under vacuum to give a powdery solid (114 mg, 100%), which was recrystallized from ether–pentane to give crystals of **19**: 91 mg (0.17 mmol, 80%); mp 177.5–179 °C; IR ($CHCl_3$) 2967 (s), 1730 (s), 1383 (s), 1370 (s), 1250 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.35 (d, 2, Ar H), 7.23 (d, 2, Ar H), 5.42 and 5.2 (AB pattern, 4, J_{AB} = 13.2 Hz, $OCOCH_2$), 1.65 (s, 6, $OCCH_3$), 1.57 (s, 6, $OCCH_3$), 1.48 (s, 6, CH_3COO), 1.34 (s, 18, $C(CH_3)_3$); mass spectrum (10 eV), *m/e* (relative intensity) 556 (5.86, M$^{+\cdot}$), 541 (29.72, M$^{+\cdot}$ − CH_3, 513 (2.19, M$^{+\cdot}$ − CH_3CO), 496 (4.08), 311 (25.59). Anal. ($C_{32}H_{44}O_6S$) C, H, S.

7,7′-Bis(acetoxymethyl)-5,5′-bis(1,1-dimethylethyl)-3,3,3′,3′-tetramethyl-1,1′-spirobi[3*H*-2,1-benzoxathiole] 1-Oxide (20). A solution of MCPBA (8.8 mg of 85% peracid, 0.43 mmol) in $CHCl_3$ was added to a solution of sulfurane **19** (25 mg, 0.43 mmol) in $CHCl_3$. After 10 min, the solution was washed with aqueous NaHCO and dried (Na_2SO_4) and the solvent was removed to leave a solid, which was recrystallized to give crystals of **20**: 18.5 mg (0.32 mmol, 75%); mp 103–104 °C; IR ($CHCl_3$) 1736 (s), 1260 (s), 1136 (s), 1105 (s), 912 (s), 860 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.48 (d, 2, Ar H), 7.08 (d, 2, Ar H), 5.66 and 5.52 (AB pattern, 4, J_{AB} = 13.8 Hz, $OCOCH_2$), 2.17 (s, 6, CH_3COO), 1.75 (s, 6, $OCCH_3$), 1.54 (s, 6, $OCCH_3$), 1.33 (s, 18, $C(CH_3)_3$). Anal. ($C_{32}H_{44}O_7S$) C, H.

Reaction of Sulfone Diol 6 with Acyclic Sulfurane 1. The dehydrating agent sulfurane **1** (ca. 500 mg, 0.75 mmol, excess) was added to a stirred solution of sulfone diol **6** (150 mg, 0.253 mmol) in ca. 50 mL of CCl_4 in a N_2 glovebox. After 16 h, the solution was extracted with 10% aqueous NaOH and dried (Na_2SO_4), and the solvent was removed under vacuum to leave an oil, which was a mixture of diphenyl sulfoxide, sulfurane oxide diester **8** (ca. 70%), and other products (ca. 30%), as observed by ^{1}H NMR. These were separated by preparative TLC (silica gel) with 1:1 (v/v) ether–pentane as eluant. The weak band, close to the solvent front, contained only trace amount of an unidentified oily material. The second band was extracted with ether to give ca. 30 mg of white crystalline sulfone diolefin diester **12**, which was recrystallized from ether–pentane: mp 166–168 °C; IR (CCl_4) 1733 (s), 1328 (s), 1252 (s), 1214 (m), 1198 (s), 1148 (s), 1028 (br s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.28 (d, 2, Ar H), 7.07 (d, 2, Ar H), 4.90 (br m, 2, olefinic CH), 4.38 (q, 4, J = 7.2 Hz, OCH_2CH_3), 4.34 (br, 2, olefinic CH), 1.60 (s, 3, $C{=}CCH_3$), 1.38 (t, 6, J = 7.2 Hz, OCH_2CH_3), 1.30 (s, 18, $C(CH_3)_3$). Anal. ($C_{32}H_{42}O_6S$) C, H.

The third band was extracted with ether to give ca. 70 mg of crystalline sulfone diester hydroxy olefin **10**, which was recrystallized from ether–pentane: mp 191.5–193.5 °C; IR ($CHCl_3$) 3534 (w), 1724 (s), 1311 (s), 1255 (s), 1136 (s), 1024 (m) cm^{-1}; ^{1}H NMR (220 MHz, $CDCl_3$) δ 7.305 (d, 2, Ar H) 7.262 (d, 1, Ar H), 7.120 (d, 1, Ar H), 4.852 (br, 1, olefinic CH), 4.462 (br, 1, olefinic CH), 4.412 (q, 2, J = 7.2 Hz, OCH_2CH_3), 4.396 and 4.342 (ABX_3 pattern, 2, J_{AB} = 11 Hz, J_{AX} = 7.2 Hz, OCH_2CH_3), 3.892 (s, 1, OH), 1.678 (s, 3, $C{=}CCH_3$), 1.560 (s, 3, $OCCH_3$), 1.404 (t, 3, J = 7.2 Hz, OCH_2CH_3), 1.360 (t, 3, J = 7.2 Hz, OCH_2CH_3), 1.324 and 1.292 (2 s, 21, $C(CH_3)_3$ and $OCCH_3$); mass spectrum (field desorption), *m/e* (estimated relative intensity) 572 (100, M$^{+\cdot}$), 554 (13, M$^{+\cdot}$ − H_2O). Anal. ($C_{32}H_{44}O_7S$) C, H, S.

The material, presumably diphenyl sulfoxide, in the remaining band was not isolated. Sulfurane oxide diester **8** in the original product mixture was identified by comparing its ^1H NMR spectrum with that of an authentic sample.

Reaction of Sulfone Tetraol 7 with Acyclic Sulfurane 1. To a stirred solution of sulfone tetraol 7 (120 mg, 0.237 mmol) in ca. 10 mL of ether was added acyclic sulfurane 1 (ca. 160 mg, 0.238 mmol) in a N_2 glovebox. After 30 min, the solution was washed with aqueous $NaHCO_3$ and dried (Na_2SO_4), and the solvent was removed under vacuum to give a solid, which was a mixture of diphenyl sulfoxide, sulfurane oxide diol 9 (ca. 40%), and other products as observed by ^1H NMR. The mixture was separated by preparative TLC (silica gel) with 1:1:1 (v/v/v) ether–$CHCl_3$–pentane as eluant. The slowest moving band (R_f 0.11) was extracted with $CHCl_3$ to give a solid, which was recrystallized from ether–pentane to give crystals of sulfurane oxide diol 9 (by melting point and ^1H NMR).

Attempt to Synthesize Tetraoxypersulfurane 38 (Reaction of 6 with *sec*-Butyllithium). To a stirred solution of 6 (227 mg, 0.384 mmol) in ca. 30 mL of ether was added *sec*-butyllithium in cyclohexane (0.6 mL of 1.4 M, 0.84 mmol) at −78 °C. After ca. 3 min, CH_3I (ca. 0.5 mL) was added. After 10 min, the solvent was removed to leave a yellowish residue, which was redissolved in ether and filtered. Removal of solvent gave a mixture (200.8 mg) of 6 (ca. 20%) and a new compound (ca. 80%), as observed by ^1H NMR. Recrystallization from ether afforded some crystals of the new compound, which were still contaminated with 6: ^1H NMR ($CDCl_3$) δ 7.70 (d, 1, Ar H), 7.62 (d, 1, Ar H), 7.52 (d, 1, Ar H, 7.43 (d, 1, Ar H), 4.71 (s, 1, OH), 4.3–3.6 (m, 2, OCH_2CH_3), 2.25 (s, 3, CH_3), 2.17 (s, 3, CH_3), 1.82 (s, 3, CH_3), 1.37 (s, 9, $C(CH_3)_3$), 1.35 (s, 9, $C(CH_3)_3$); IR ($CHCl_3$) 3500 (m, OH), 1727 (s, C=O), 1321 (s), 1124 (s) cm^{-1}. On the basis of the ^1H NMR and IR spectra, which are very similar to those of sulfone lactone 14,[12,13] sulfone lactone 13 was postulated to be the structure of this new compound. Attempts to obtain a pure sample of this compound by fractional crystallization and preparative TLC failed.

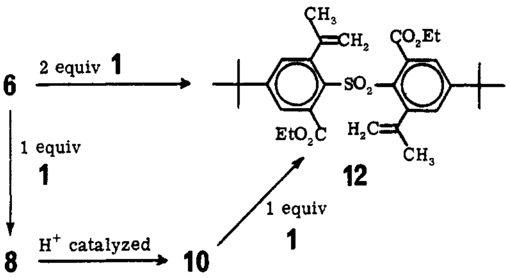
X-ray Crystallography of Sulfone Diol 6. Crystals of 6 were grown by slowly evaporating a solution of 6 in methanol–water.

Crystal data for 6: $C_{32}H_{46}O_8S$, mol wt 590.8, trigonal, $a = b = 9.971$ (2) Å, $c = 28.304$ (4) Å, $\gamma = 120.0°$, $V = 2437$ Å^3, $\rho_c = 1.21$ g/cm^3, μ(Cu Kα) = 12.5 cm^{-1}, $F(000) = 954$, systematic absences for $00l$, $l \neq 3n$, with Laue symmetry $\bar{3}$. The absences and Laue symmetry are consistent with the space group $P3_1$ and its enantiomorph $P3_2$. The cell dimensions were obtained by a least-squares fit to the automatically centered settings for 15 reflections measured on a Syntex $P2_1$ diffractometer equipped with a graphite monochromator, λ(Cu Kα) = 1.5418 Å.

Solution and Refinement of the Structure of 6. A crystal with dimensions ca. 0.5 × 0.3 × 0.3 mm was used for data collection. The data were collected in the 2θ–θ scan mode. The variable-scan option was used (2–15 °C/min) with total background time/scan time set at 0.25. Three reflections were monitored every 57 reflections. Examination of these reflections showed no sign of crystal deterioration. The hkl and $hk\bar{l}$ octants were collected out to $2\theta = 130°$. Of the 3027 unique reflections collected, 2710 were observed by using a 2σ criterion based on counting statistics. The data were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by direct methods in $P3_2$ by using programs supplied by Syntex.[7] All the nonhydrogen atoms were located except for the tertiary butyl groups which were placed such that there are two positions each partially occupied and roughly displaced 60° from each other. The electron density distribution suggest a 2:1 occupancy ratio for the sites, and as a consequence the occupancies of the major and minor sites were fixed at $^2/_3$ and $^1/_3$, respectively.[8] A difference map showed all the ring hydrogens and a few of the methylene hydrogens. Reasonable positions for the hydroxyl hydrogens were found by taking a difference map near the oxygens. Since the electron densities of these hydroxyl hydrogens corresponded to only one-fifth of an ideal hydrogen atom, these positions were not included in the final structure factor calculation but were included in the stereodrawings.

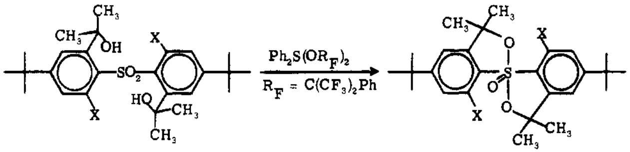
Scheme I



The positions and isotropic thermal parameters of the ring hydrogens were allowed to vary. Hydrogens of the disordered *tert*-butyl groups were not included in the refinements, and the positions of all other hydrogens were calculated and not allowed to vary. These fixed hydrogens were assigned fixed isotropic thermal parameters equal to the last isotropic value of their parent carbon atom. All nonhydrogen atoms, except the disordered *tert*-butyl groups, were allowed to vary in their positional and anisotropic thermal parameters. The positions of both sets of the *tert*-butyl groups were allowed to vary, but they were given isotropic thermal parameters.[9] Final full-matrix least-squares refinement converged to values for R and R_w of 0.079 and 0.104.[10] The final value of $[\sum(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, where m is the number of observations and n is the number of variables, was 3.27. The scattering curves were taken from the analytical expression used in the literature.[11a] Anomalous dispersion correction for S was also included.[11b] The final difference map was clean; no peak greater than 51% of an ideal hydrogen atom was present. The final values of the atomic coordinates of 6 are given in Table I (see paragraph at the end of the paper regarding supplementary material).

Results

Cyclodehydration of Dihydroxysulfuranes. The syntheses and ^1H NMR studies of conformational equilibria of dihydroxy sulfones 6 and 7 have been reported.[12]



6 X = CO$_2$Et

7 X = CH$_2$OH

8 X = CO$_2$Et

9 X = CH$_2$OH

Both 6 and 7 react with acyclic sulfurane 1, to give sulfurane oxides 8[13] (ca. 70%) and 9 (ca. 40%), respectively, as observed by ^1H NMR. Separation of sulfurane oxide 8 from the reaction mixture by preparative TLC, however, resulted in the complete fragmentation of 8 to form isomeric sulfone olefin 10.[13] Sulfurane oxide 9, which undergoes fragmentation to form 11,[13] was isolated in this way in small quantity. A small amount of sulfone diolefin 12 was also isolated in the reaction of 6 with 1. Diolefin

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(6) (a) Pathways, analogous to that shown in eq 3, leading to diaryl- and bis(perfluoroalkyl)difluorosulfurane oxides from oxidative addition of fluorine ligands to sulfoxides have, however, been reported. See: Sauer, D. T.; Shreeve, J. M. *Z. Anorg. Allg. Chem.* **1971**, *385*, 113. Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 880. (b) Attempts to introduce alkoxy ligands to form sulfurane oxides were unsuccessful. See ref 3b.

(7) The structure was solved by a version of the MULTAN program (Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr.*, **Sect. A 1971**, *A27*, 368) that has been incorporated into the SYNTEX EXTL system, based on the Data General ECLIPSE computer. All crystallographic calculations were carried out on this program.

(8) The minor sites for the disordered *tert*-butyl groups are designated by the suffix A: C(12A), C(13A).

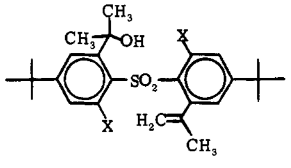
(9) The model was tested in the space group $P3_212$ and $P3_121$.

(10) $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$.

(11) (a) "International Tables for X-ray Crystallography"; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99–102; (b) pp 148–150.

(12) Lam, W. Y.; Martin, J. C. *J. Org. Chem.*, preceding paper in this issue.

(13) Lam, W. Y.; Martin, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 120.



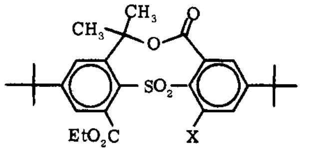
10 X = CO_2Et

11 X = CH_2OH

12 might arise from dehydration of **6** by sulfurane **1** or from dehydration of **10** by **1** (Scheme I).

Attempted thermal dehydration of **6** and **7** under vacuum to give sulfurane oxides **8** and **9** failed. Heating **6** at 140 °C for 2 days gave no reaction. Heating **7** at 100 °C for 14 h resulted in its decomposition to unidentified products. Reaction of sulfone tetraol **7** with acetic anhydride also failed to give sulfurane oxide diol **9**.

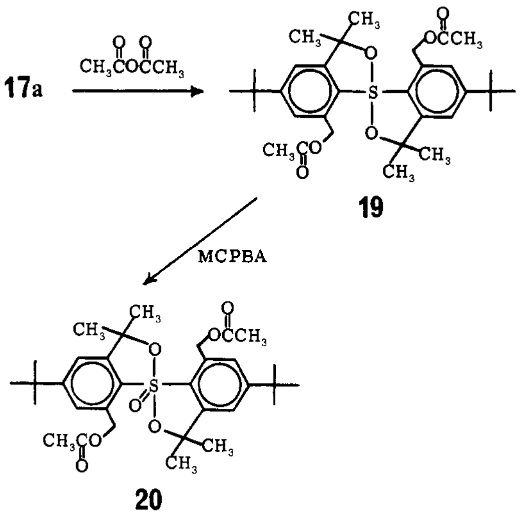
Other Reactions. Treatment of sulfone diester diol **6** with *sec*-butyllithium gave a compound for which structure **13** is proposed. Evidence for its structure was, however, incomplete. An analogous reaction of **10** with *n*-butyllithium to give sulfone lactone **14** has been reported.[13] Treatment of **6** with excess CH_3MgBr in ether gave mostly starting material after 20 h of boiling.



13 X = $C(CH_3)_2OH$

14 X = $C(CH_3){=}CH_2$

Syntheses of Authentic Compounds. The syntheses and some properties of sulfurane oxide diester **8** have been reported.[13] Methods similar to those used earlier for **8** were used to prepare sulfurane oxide diol **9** from sulfide tetraol **15a** (Scheme II). Sulfurane diol **17a** reacts with acetic anhydride to form diacylated sulfurane **19**, which is oxidized with MCPBA to give sulfurane oxide **20**.



X-ray Structure of 6. The crystal structure of sulfone diester diol **6** reveals a distorted tetrahedral geometry about sulfur. The C(1)–S–C(17) angle is 117.9 (4)°, and the O(1)–S–O(2) angle is 118.9 (5)°. The dihedral angle between the two planes containing the phenyl rings is 87.1°, between the planes containing the S, O(1), and O(2) atoms and the S, C(1), and C(17) atoms is 88.4°, between the planes containing the phenyl [C(1)–C(6)] ring and the C(9), O(4), and O(5) atoms is 82.0°, whereas that for the phenyl [C(17)–C(22)] ring and the C(25), O(7), and O(8) atoms is 82.2°. Some intramolecular contact distances between sulfur and alkoxy and carbonyl oxygen atoms are listed in Table II. Figure 1 shows a stereo view of a single molecule and Figure 2 shows a stereoview of the packing on one unit cell.

Scheme II

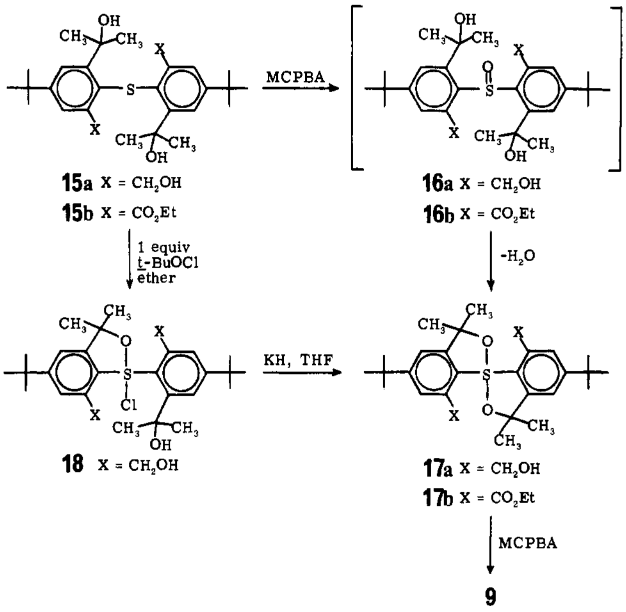
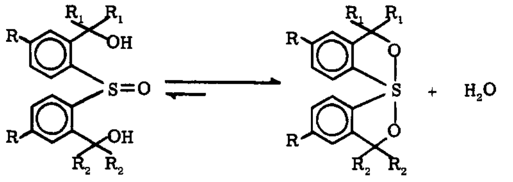


Table II. Intramolecular Contact Distances (Å) of the Sulfur and Oxygen Atoms in 6

O(1)···O(3)	2.892	O(2)···O(6)	2.851
O(1)···O(8)	2.860	O(2)···O(4)	2.806
O(3)···O(8)	3.273	O(6)···O(4)	3.260
S···O(3)	2.913	S···O(6)	2.916
S···O(4)	3.765	S···O(8)	3.783

Discussion

By analogy to dioxysulfurane oxide 10-S-5 species, such as **3**–**5**, the monoketal analogues of 8-S-4 sulfones,[3] dioxysulfuranes (10-S-4) may be considered to be monoketal analogues of sulfoxides (8-S-3). The ketalization of sulfoxide diols **21**,[3] **22**,[4] and **23**[4] to sulfuranes **24**–**26** are rapid processes, and the equilibria in aprotic solvent clearly favor the spirosulfuranes. In fact, sulfoxide diols **21** and **22** have not yet been observed or isolated, and sulfoxide diol **23** slowly loses water to form **26** in chlorform at room temperature. Facile cyclodehydrations to form sulfuranes are also seen in this work. Oxidation of sulfides **15a** and **15b** gives the expected sulfoxides **16a** and **16b**, respectively, which undergo rapid cyclodehydration to give sulfuranes **17a** and **17b**, respectively, under the acidic reaction conditions. Sulfoxide diester diol **16b** is isolable only if the reaction mixture is quenched with aqueous $NaHCO_3$ solution within 30 s.[13] Both the five-membered-ring effect and the Thorpe–Ingold effect are expected[14] to play important roles in the dehydrative ring closures to form these spirosulfuranes. The ketalization of a sulfoxide to an acyclic sulfurane, e.g., diphenyl sulfoxide and hexafluorocumyl alcohol to sulfurane **1** (eq 2, R = Ph, R′ =



21 R = $C(CH_3)_3$; $R_1 = R_2 = CF_3$

22 R = H; $R_1 = CF_3$; $R_2 = CH_3$

23 R = H; $R_1 = R_2 = CH_3$

24 R = $C(CH_3)_3$; $R_1 = R_2 = CF_3$

25 R = H; $R_1 = CF_3$; $R_2 = CH_3$

26 R = H; $R_1 = R_2 = CH_3$

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(14) (a) Beesley, R. M.; Ingold, C. K.; Thorpe, J. F. *J. Chem. Soc.* **1915**, 1080. (b) Ingold, C. K. *Ibid.* **1921**, 305.

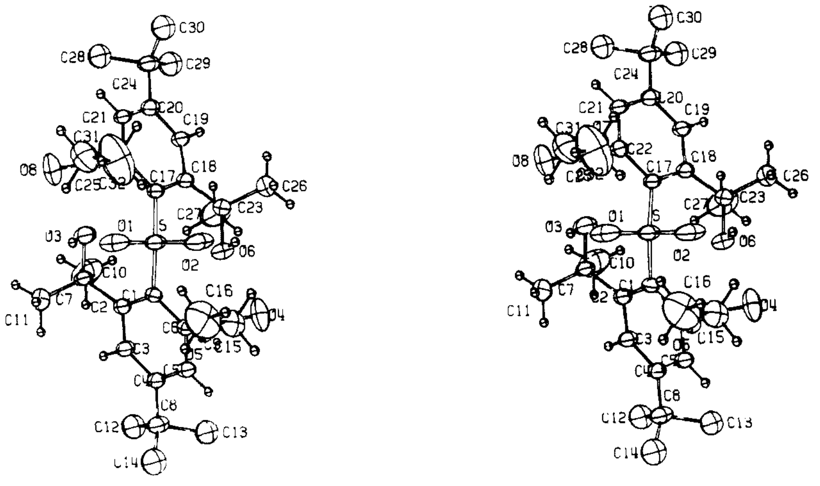


Figure 1. Stereoscopic view of the single molecule of sulfone diester diol **6**.

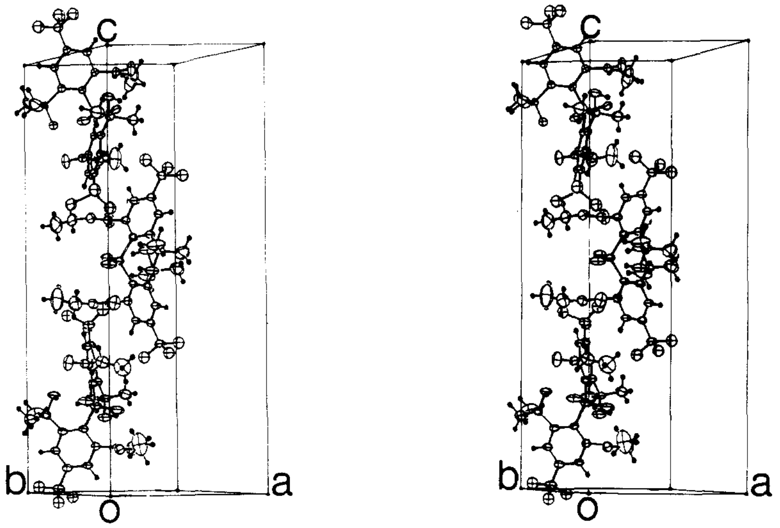
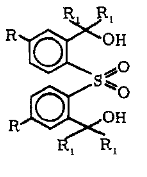


Figure 2. Stereoscopic view of the crystal structure of **6**.

$C(CF_3)_2Ph$), are not known. The equilibrium apparently greatly favors the sulfoxide. Acyclic sulfurane **1** is known[15] to be a strong dehydrating agent. It rapidly converts *tert*-butyl alcohol to isobutylene even at −50 °C.[15]

The ketalization of a sulfone (8-S-4 species) to give a dioxysulfurane oxide (10-S-5 species) is, however, less facile, even though the reaction is superficially similar to that converting dihydroxy sulfoxides to spirosulfuranes. For examples, sulfone diols **27**,[2f] **6**, and **7**, in contrast to sulfoxide diols **23**, **16a**, and **16b**, do not undergo cyclodehydration to form sulfurane oxides **4**, **8**, and **9**, respectively, in acidic media. Sulfone diol **28**, a sulfone judged more likely to undergo ketalization, however, has not been synthesized. There is therefore no test of the prediction that ketalization of this sulfone to sulfurane oxide will occur. The difference in facility of ketalization between dihydroxy sulfoxides and dihydroxy sulfones may be at least partly due to the difference in the S═O bond energies of sulfoxide and sulfone. The bond-dissociation energy of the S═O bond of diphenyl sulfoxide is 91.7 kcal mol^{-1},[16] and the energy of the second S═O bond added on going from a sulfoxide to a sulfone is an even larger 106.6 kcal mol^{-1}.[16] The lesser tendency for dihydroxy sulfones to ketalize to give sulfurane oxides, as compared to the tendency of dihydroxy sulfoxides to lose water to give sulfuranes, is therefore explicable in terms of the greater stability of the sulfonyl function.



27 R = H; $R_1 = CH_3$

28 R = $C(CH_3)_3$; $R_1 = CF_3$

The cyclodehydrations of sulfone diols **6** and **7** by sulfurane **1** to give sulfurane oxides **8** and **9**, respectively, represent the first reported example of ketalization of 8-S-4 species (sulfones) to form 10-S-5 species (sulfurane oxides). A mechanism for this reaction is proposed in Scheme III.

The proposed interconversions and rearrangements among 5- and 6-coordinate species **29** and **30** as well as **31** and **32** have precedents in our work. Similar mechanisms were proposed for conformational interconversions postulated to explain ^1H NMR observations on sulfurane oxide diol **33** and its dipotassium salt.[13]

We initially speculated that compound **6** was indeed the postulated structure **30** (X = CO_2Et), a dihydroxypersulfurane (12-S-6 species) on the basis of the ^1H NMR and IR spectroscopic and chemical evidence. The peak positions for the two diastereotopic methyl peaks in the ^1H

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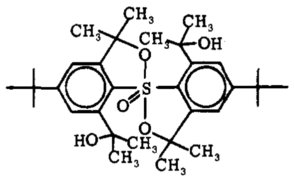
[15] (a) Arhart, R. J.; Martin, J. C. *J. Am. Chem. Soc.* **1972**, *94*, 5003. (b) Kaplan, L. J.; Martin, J. C. *Ibid.* **1973**, *95*, 793.

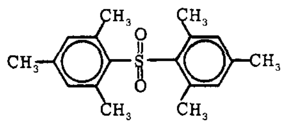
[16] Sanderson, R. T. "Chemical Bonds in Organic Compounds"; Sun and Sand Publishing Co.: Tucson, AZ, 1976.



33

NMR spectrum of **6**[12] are very similar to those for sulfurane oxide diester **8**, and complete coalescence of the two peaks is not seen even up to 140 °C (90 MHz).[12] The peak position for the hydroxy protons is apparently not concentration dependent. The carbonyl stretching frequency in the IR spectrum of **6** (in $CHCl_3$) appears at 1698 cm^{-1}, which is lower than that of sulfone diester diolefin **12** (1724 cm^{-1}) and sulfide diester diol **15b** (1725 cm^{-1}), compounds of similar structures. These observations were explained by postulating a strong hydrogen bonding between carbethoxy oxygens and hydroxy protons in structure **30** (X = CO_2Et). Compound **30** (X = CO_2Et) would be expected to lose water to give sulfurane oxide **8**. The only example of a persulfurane having a hydroxy ligand, SF_5OH, was prepared by Seppelt[17] and found not to be stable above −80 °C. On warming (−60 °C) it decomposes to give $F_4S{=}O$ and HF.

The X-ray structure of **6**, however, clearly reveals a distorted tetrahedral geometry about sulfur, instead of the octahedral structure expected for **30**. The molecule is apparently in a conformation which minimizes interactions between the bulky ortho substituents. The plane containing one phenyl ring is at an angle of 87.1° to that of the other. The great degree of steric interference results in a twisting of the carbethoxy groups from coplanarity with the phenyl rings. The dihedral angles between the planes containing phenyl [C(1)–C(6) and C(17)–C(22)] rings and carboxy [C(9), O(4), O(5); C(25), O(7), O(8)] atoms are 82.0° and 82.2°, respectively. The solid-state IR (KBr disk) spectrum of **6**, however, shows a carbonyl stretching frequency at 1727 cm^{-1}, higher than that for benzoate esters lacking bulky ortho substituents (1719–1724 cm^{-1}).[18] The steric interaction may also be reflected in the large C(1)–S–C(17) angle (117.9 (4)°), which is much larger than the C–S–C angles for some reported diaryl sulfones such as the sterically very hindered **34** (104.5(5)°),[19] or the relatively unhindered **35** (106°)[20] and **36** (104.8 (4)°).[21] It is interesting to note that the C–S–C angle in sulfurane oxide **3** is 117.7 (3)°,[3] very close to that of sulfone **6**. If the intermediate hydroxysulfurane oxide **29** (X = CO_2Et) postulated to be an intermediate in the cyclodehydration indeed exists and its C–S–C angle is comparable to that of **3**, then the change of the C–S–C angle upon going from the "tetrahedral" sulfone **6** to trigonal bipyramidal **29** (X = CO_2Et) would be small. The interactions between the sulfur and the two hydroxy oxygens of **6** are, however, very similar for the two oxygens. The almost identical intramolecular distances between sulfur and the two alcohol oxygen atoms [S···O(3), 2.913 Å; S···O(6), 2.916 Å; Table II] are well within the sum of van der Waals radii of sulfur and oxygen atoms (3.25 Å),[22] consistent with there being significant attractive interactions between the nucleophilic oxygen atoms of the ortho alcohol substituents and the electrophilic sulfonyl sulfur. From these structural data, together with the IR observations, the postulated interconversions among species **6**, **29**, and even **30** (Scheme III) in solution seem to be not entirely impossible. Indeed, the structure of **6**, in which the hydroxy protons seem to be partially transferred to the sulfone oxygen atoms in the intramolecular hydrogen bonded structure **37**, can be viewed as a very distorted form of **30**.



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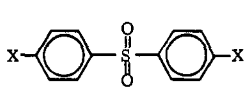
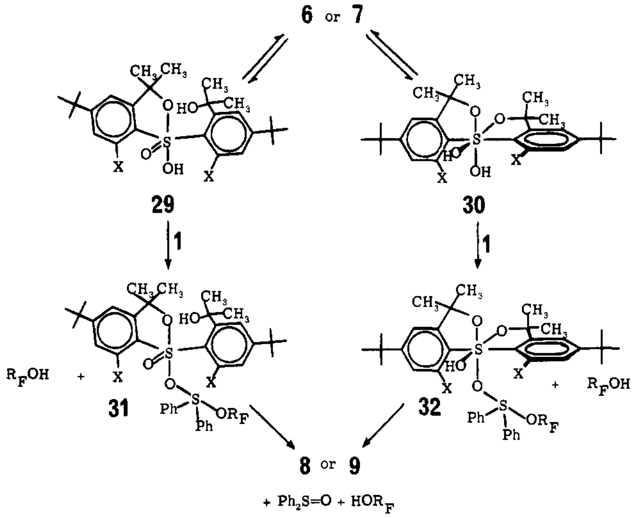
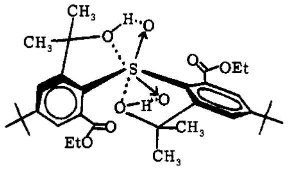


35 X = NH_2

36 X = Cl

Scheme III





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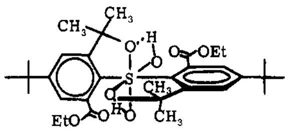
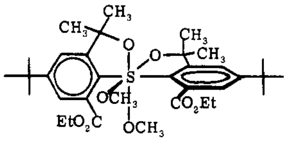


30

Attempts to gain evidence for the intermediacy of **29** and **30** by methylating **6** with methyl iodide, a reaction which would form tetraalkoxypersulfurane **38**, were unsuccessful.



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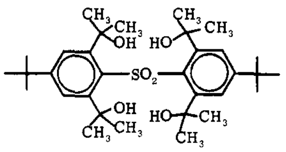
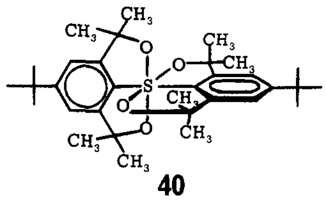


39

An attempt to prepare **39** by reaction of the ester functions in **6** with CH_3MgBr also failed. We speculate that sulfone tetraol **39** would be a desirable precursor to sulfurane oxide **33**,[13] from which tetraalkoxypersulfurane **40**[13] would be



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[17] Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 44.

[18] Bellamy, L. J. "The Infrared Spectra of Complex Organic Molecules", 2nd Ed.; Wiley: New York, 1958; p 207.

[19] Chawdhury, S. A.; Hargreaves, A. *Acta Crystallogr. Sect. B* **1971**, *B27*, 548.

[20] Dickinson, C.; Stewart, J. M.; Ammon, H. L. *J. Chem. Soc., Chem. Common.* **1970**, 920.

[21] Sime, J. G.; Abrahams, S. C. *Acta Crystallogr.* **1960**, *13*, 1.

[22] Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260.

synthesized by cyclodehydration, a process of stepwise ketalization of 8-S-4 species (sulfones) to 10-S-5 species (sulfurane oxides) and then to 12-S-6 species (persulfuranes). The second step in this sequence has already been observed to occur.[13]

Acknowledgment. The research was supported in part by a grant from the National Science Foundation (CHE-7905692). We also acknowledge the assistance of Dr. Eileen N. Duesler, who obtained the X-ray structure.

Registry No. 1, 32133-82-7; 2, 33973-62-5; 6, 78479-63-7; 7, 78479-64-8; 8, 75894-03-0; 9, 75893-96-8; 10, 78479-65-9; 11, 75893-98-0; 12, 75893-89-9; 13, 78479-66-0; 15a, 75893-97-9; 17a, 78479-67-1; 18, 78479-68-2; 19, 78479-69-3; 20, 78479-70-6.

Supplementary Material Available: Listings of the atomic coordinates (Table I), the thermal parameters (Table III), and bond angles and lengths (Tables IV and V) (9 pages). Ordering information is given on any current masthead page.

Apical Ligand Preference and Fluxional Behavior of Some Sulfuranes

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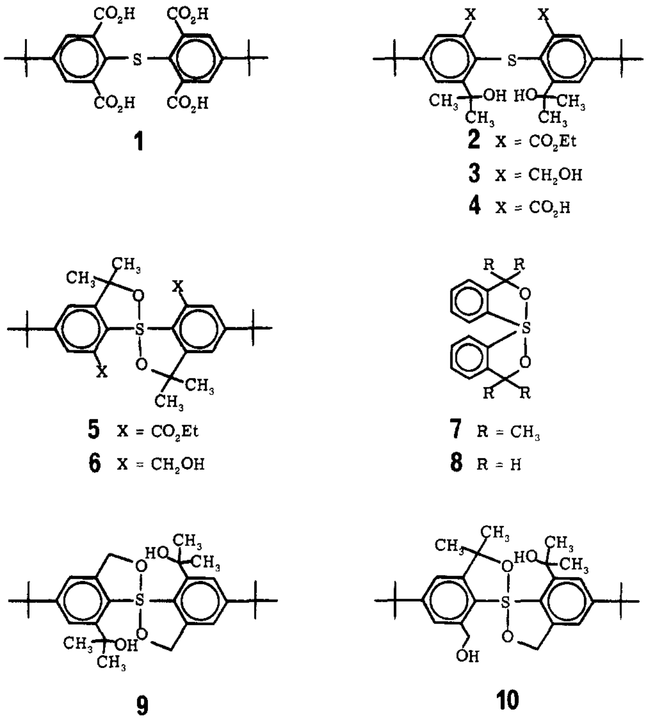
Received September 19, 1980

Sulfides 4, 11, and 12 react with *m*-chloroperbenzoic acid to form apically unsymmetrically substituted sulfuranes 18–20, respectively, instead of the isomeric symmetrically substituted dialkoxysulfuranes. Rapid equilibration ($\Delta G^*_{12\,°C} = 14.7$ kcal mol^{-1}) of isomers of sulfurane 18 is observed and studied by ^{1}H NMR spectroscopy. An associative mechanism for these interconversion processes is proposed. Potassium salts of 18 and 19 are symmetrical dialkoxysulfuranes 21 and 22, respectively. Other reactions involving these sulfuranes are also reported.

In the course of our studies on persulfuranes,[1] a number of completely ortho-substituted diaryl sulfides such at 1–4 (Chart I) were synthesized. Dialkoxysulfuranes 5[1] and 6,[2] analogues of sulfurane 7,[3] were prepared from sulfides 2 and 3, respectively. It is interesting that no evidence is found, in the case of 6, for the presence of isomeric symmetrical sulfurane 9 or unsymmetrical sulfurane 10, even though sulfurane 8, a close analogue of 9, has been synthesized[3] and found to be stable at room temperature. Structure 6 with apical tertiary alkoxy ligands is therefore preferred over 9 with its two primary alkoxy ligands and the unsymmetrical isomer 10. No evidence was seen for intramolecular ligand exchanges between the primary and tertiary alcohol substituents. We report here the conformational preference and fluxional behavior of the sulfurane formed by oxidation from sulfide 4 and related observations on the reactions of other sulfuranes.

Chart I



1

2 X = CO$_2$Et

3 X = CH$_2$OH

4 X = CO$_2$H

5 X = CO$_2$Et

6 X = CH$_2$OH

7 R = CH$_3$

8 R = H

9

10

Experimental Section

General Methods. Proton chemical shifts are reported on the δ scale (parts per million downfield from tetramethylsilane as an internal standard). Melting points were determined on a micro hot stage. Elemental analyses of new compounds are within 0.4% of the theoretical values unless otherwise noted.

Solvents and Reagents. Ether, tetrahydrofuran (THF), and pentane were dried and stored over sodium wire. Chloroform and methylene chloride were washed with concentrated H_2SO_4, water, and then 10% $NaHCO_3$ before being distilled from P_2O_5.

7-(1-Hydroxy-1-methylethyl)-7′-carboxy-5,5′-bis(1,1-dimethylethyl)-3-oxo-3′,3′-dimethyl-1,1′-spirobi[3*H*-2,1-benzoxathiole] (Hydroxy Acid Sulfurane 18). A solution of *m*-chloroperbenzoic acid (1.24 g of 85% peracid, 6.1 mmol) in 40 mL of $CHCl_3$ was added in one portion to a suspension of sulfide diacid diol 4 (3 g, 5.98 mmol) in 80 mL of $CHCl_3$. After 40 min, the solution was filtered, washed with aqueous $NaHCO_3$, and dried (Na_2SO_4), and the solvent was removed to leave a solid, which was recrystallized from ether–CH_2Cl_2 to give 18: 1.7 g (3.41 mmol, 57%); mp 181.5–182.5 °C; IR (CH_2Cl_2) 3546 (m), 1715 (br, s), 1616 (s), 1587 (s) cm^{-1}; ^{1}H 220 MHz NMR ($CDCl_3$, −30 °C) δ 8.04 (br, 1, Ar H), 7.46 (br, 1, Ar H), 7.35 (br, 1, Ar H), 7.18 (br, 1, Ar H), 6.1 (br, 2, OH), 1.93 (s, 3, $OCCH_3$), 1.84 (s, 3, $OCCH_3$), 1.80 (s, 3, $OCCH_3$), 1.65 (s, 3, $OCCH_3$), 1.41 (s, 9, $C(CH_3)_3$), 1.26 (s, 9, $C(CH_3)_3$); ^{1}H NMR (Me_2SO-d_6, 90 °C) δ 7.68 (d, 2, Ar H), 7.52 (d, 2, Ar H), 1.84 (s, 6, $OCCH_3$), 1.71 (s, 6, $OCCH_3$), 1.38 (s, 18, $C(CH_3)_3$); mass spectrum (70 eV), *m/e* (relative intensity) 500 ($M^{+\cdot}$, not observed), 482 (2.85, $M^{+\cdot} - H_2O$), 464 (100, $M^{+\cdot} - 2H_2O$), 449 (31.27, $M^{+\cdot} - 2H_2O$ and CH_3), 431 (25.47, $M^{+\cdot} - 3H_2O$ and CH_3), 405 (10.87, *m/e* 499 − CO_2). Anal. ($C_{28}H_{36}O_6S$) C, H.

Sulfurane 18 was found to be hygroscopic. Crystals of 18 may contain a molecule of water of crystallization, as observed in the

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[1] (a) Lam, W. Y.; Martin, J. C. *J. Am. Chem. Soc.* 1977, *99*, 1659. (b) *Ibid.* 1981, *103*, 120.

[2] Lam, W. Y.; Martin, J. C. *J. Org. Chem.*, preceding paper in this issue.

[3] Adzima, L. J.; Martin, J. C. *J. Org. Chem.* 1977, *42*, 4006.

0022-3263/81/1946-4468$01.25/0