Diaryltetraoxypersulfuranes:[1] Preparation, Characterization, and Reactions

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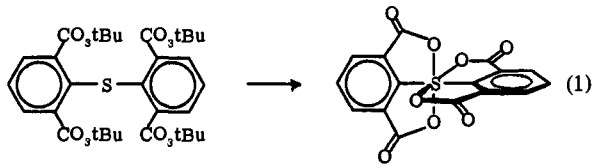
Abstract: Diarylbis(acyloxy)dialkoxypersulfurane **7**, the first example of a hexacoordinate organosulfur(VI) derivative lacking fluorine ligands, a sulfone bisketal, was synthesized by treatment of sulfide diol diacid **6** with pyridine and *tert*-butyl hypochlorite at 0 °C. Persulfurane **7** is stable in crystalline form and unreactive toward atmospheric moisture. It rapidly decomposes at room temperature in ordinary chloroform to give isomeric sulfone diacid diolefin **9** and more slowly in dry pyridine to give a 1:1 mixture of **9** and another isomer, sulfone lactone **10**. Persulfurane **7** reacts with 2 equiv of $LiAlH_4$ to give sulfurane oxide diol **12** (50%), sulfide tetraol **13** (20%), and other unidentified products. Possible mechanisms for the acid-catalyzed fragmentation of **7** to **9** and the $LiAlH_4$ reduction of **7** to **12** and **13** are proposed and discussed. The syntheses of unsymmetrical sulfuranes **31a** and **31b** and sulfurane oxide diol **20** are also reported. Treatment of **20** with KH and then with trifluoroacetic anhydride gives a compound which is postulated to have the structure of a diaryltetraalkoxypersulfurane, **21**, as evidenced by ^1H NMR and field desorption mass spectrometry. Rapid interconversions of topological isomers of **20** and its dipotassium salt **45** are proposed to be responsible for the observed features of their variable-temperature ^1H NMR spectra. Symmetrical persulfurane **21** was found to be less acid sensitive than **7**, in that it undergoes fragmentation very slowly in solution.

Introduction

Hexacoordinate, hexavalent sulfur compounds, called persulfuranes by Musher,[2] belong to the class of hypervalent molecules which we would call 12-S-6 species.[3] Unlike that of sulfuranes, the tetracoordinate 10-S-4 species, the chemistry of persulfuranes is hardly known. Sulfur hexafluoride and its derivatives are perhaps the most commonly known persulfuranes. The perfluoropersulfurane is very stable and inert. Its hydrolysis by water vapor is not observed up to 500 °C, and it does not react with halogens, HCl, NH_3, molten KOH, or silver at red heat.[4] The low reactivity, particularly toward hydrolysis, which contrasts with the very high reactivity of SF_4, is presumably due to a combination of factors including relatively high S–F bond strength (ca. 72 kcal)[5] and the facts that sulfur is both coordinately saturated and sterically hindered, augmented in the case of SF_6 by the lack of polarity of the molecule. Kinetic factors and not thermodynamic factors are responsible for the inertness of SF_6 and for the high reactivity of SF_4, since the average bond energy of SF_4 (ca. 78 kcal) is slightly higher than that of SF_6.[5]

Stable derivatives of SF_6 in which one or two fluorine ligands have been replaced with aryl, vinyl, ethynyl, or perfluoroalkyl groups have been known[6] for many years. The first persulfuranes with two simple alkyl or aryl ligands and four fluorines bound to sulfur were only recently prepared and found to be stable at −78 °C, by Denney et al.[7] In general, warming solutions of these materials to room temperature leads to extensive decomposition to form unidentified products. Reported persulfuranes include only the mono- and disubstituted derivatives of SF_6—persulfuranes bearing no fluorine ligands have never been prepared and characterized. It has been reported[8] that decomposition of tetraperester **1** gave a compound for which structure **2**, a persulfurane, was proposed (eq 1). Evidence for its structure was, however, incomplete. Here we report the synthesis and reactions of the first persulfurane lacking fluorine ligands.



1 **2**

Experimental Section

General Remarks. Proton NMR chemical shifts are reported on the δ scale, ppm downfield from tetramethylsilane internal standard. Melting points were determined on a micro hotstage and are uncorrected. 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 carbon tetrachloride were washed with concentrated H_2SO_4, water, and then 10% $NaHCO_3$ before being distilled from P_2O_5. Pyridine was distilled from CaO and stored over KOH pellets.

Bis[2,6-dicarboxy-4-(1,1-dimethylethyl)phenyl] Sulfide (3). To 2-mercapto-5-*tert*-butylisophthalic acid[13] (33 g, 0.13 mol) and powdered NaOH (26 g, 0.65 mol) in 250 mL of dimethylformamide (DMF) was added copper–bronze powder (ca. 2 g), 2-bromo-5-*tert*-butylisophthalic acid[13] (39.1 g, 0.13 mol), and 400 mL of DMF. The mixture was boiled for 14 h, cooled, and filtered. The residue was dissolved in 800 mL of water, warmed, and filtered. The warm filtrate was added to 500 mL of hot 10% HCl. The yellow precipitate was filtered, washed with water, air-dried, and recrystallized from acetone–water to give yellow crystals of **3** (46.9 g, 0.091 mol, 70%): mp 310–311.5 °C; IR (KBr) 3540 (s), 1700 (s) cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 10.7–9.2 (br, 4, OH), 7.62 (s, 4, ArH), 1.28 (s, 8, $C(CH_3)_3$); mass spectrum (70 eV) *m/e* (relative intensity) 474 (0.18, M^+·), 446 (2.97, M^+· − CO), 222 (7.49), 207 (100), 179 (46.32). Anal. ($C_{24}H_{26}O_8S$): C, H, S.

Bis[2-(1-hydroxy-1-methylethyl)-4-(1,1-dimethylethyl)-6-carbethoxyphenyl] Sulfide (5). Tetraacid **3** (24.7 g, 0.052 mol) in 150 mL of $SOCl_2$ was boiled until the solid was dissolved. Excess $SOCl_2$ was removed under vacuum, leaving a yellow, crystalline acid chloride. This was dissolved in 150 mL of absolute ethanol with 20 mL of pyridine, and the mixture was boiled for 1 h. Ether was added to dissolve the tetraester, leaving the pyridinium hydrochloride as an insoluble solid. The suspension was quickly filtered. The filtrate was washed with water and dried

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(Na_2SO_4), and the solvent was removed to give a brownish oil, tetraester **4** (29.0 g, 0.049 mol, 95%). The oil, in 200 mL of ether, was slowly added to 8 equiv of CH_3MgBr in ether (140 mL of 2.9 M, 0.40 mol). After 3 h of boiling, the solution was poured into dilute aqueous HCl and the aqueous layer was extracted with ether. The combined ether solutions were dried (Na_2SO_4), the solvent was removed, and the product was recrystallized from ethanol–water to give pale yellow crystals of **5** (22.9 g, 0.041 mol, 78.4%): mp 154–156 °C; IR ($CHCl_3$) 3520 (m), 1725 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.63 (d, 2, ArH), 7.32 (d, 2, ArH), 4.63 (br, 2, OH), 3.80 and 3.34 (ABX_3 pattern, 4, J_{AB} = 10.8 Hz, J_{AX} = 7.2 Hz, OCH_2CH_3), 1.83 (s, 6, $OCCH_3$), 1.78 (s, 6, $OCCH_3$), 1.32 (s, 18, $C(CH_3)_3$), 1.02 (t, 6, J_{AX} = 7.2 Hz, OCH_2CH_3). Anal. ($C_{32}H_{46}O_6S$): C, H, S.

Bis[2-(1-hydroxy-1-methylethyl)-4-(1,1-dimethylethyl)-6-carboxyphenyl] Sulfide (6). Diester diol **5** (10.4 g, 18.6 mmol) in a mixture of ethanol (360 mL) and 15% aqueous KOH (300 mL) was heated by a steam bath overnight. The solution was then concentrated under vacuum, diluted with water, and slowly poured into warm 10% HCl. The pinkish precipitate was filtered, washed with chloroform, and recrystallized from acetone–water to give pale yellow crystals of **6** (7.5 g, 14.9 mmol, 80%): mp 268–270 °C dec; IR (Nujol) 3450 (m), 1718 (s) cm^{-1}; ^1H NMR (pyridine-d_5) δ 8.11 (d, 2, ArH), 7.92 (d, 2, ArH), 2.22 (s, 3, CH_3), 2.16 (s, 3, CH_3), 1.13 (s, 18, $C(CH_3)_3$); mass spectrum (10 eV) *m/e* (relative intensity) 502 (100, $M^{+\cdot}$), 500 (16.30, $M^{+\cdot} - 2H$), 484 (12.7, $M^{+\cdot} - H_2O$), 409 (24.48). Anal. ($C_{28}H_{38}O_6S$): C, H, S.

Bis[5-(1,1-dimethylethyl)-3-(1-hydroxy-1-methylethyl)benzoato(3–)-C^2,O^1,O^3](*OC*-6-22′)sulfur (Persulfurane 7). To a stirred and cooled (0 °C) suspension of diacid diol **6** (0.67 g, 1.33 mmol) in 45 mL of CCl_4 with pyridine (0.21 mL, 2.66 mmol) was added *tert*-butyl hypochlorite (0.45 mL, 3.99 mmol). After 1 min, another portion of *tert*-butyl hypochlorite (0.3 mL, 2.66 mmol) was added. After 30 min, the suspension was filtered to give white powdery **7** (0.6 g, 1.2 mmol, 90%), which was used for the reactions described below without further purification. Recrystallization from ether–pentane or THF–pentane afforded white crystals of **7**: mp 166–172 °C dec; IR (CH_2Cl_2) 2950 (m), 1712 (s), 1366 (m), 1319 (m), 1236 (s), 1185 (s), 1121 (s), 1059 (m), 863 (s) cm^{-1}; ^1H 220-MHz NMR (CD_2Cl_2, −30 °C) δ 8.113 (d, 2, ArH), 7.710 (d, 2, ArH), 1.791 (s, 6, $OCCH_3$), 1.707 (s, 6, $OCCH_3$), 1.450 (s, 18, $C(CH_3)_3$); mass spectrum (field desorption) *m/e* (estimated relative intensity) 498 (100, $M^{+\cdot}$), 496 (65, $M^{+\cdot} - 2H$), 480 (70, $M^{+\cdot} - H_2O$), 434 (100). Anal. ($C_{28}H_{34}O_6S$): C, H, S.

Addition of a drop of optically active 2,2,2-trifluoro-1-phenylethanol[10] to the NMR sample of **7** in CD_2Cl_2 at −30 °C resolved the methyl singlet at δ 1.707 and the *tert*-butyl singlet each into two singlets. Upon gradual warming of the solution to room temperature, signals of the fragmentation product, sulfone diacid olefin **9**, increased while those of the persulfurane were decreasing.

Fragmentation of Persulfurane 7 in $CHCl_3$. A solution of persulfurane **7** (100 mg, 0.2 mmol) in undried chloroform (2 mL) was allowed to stand 2 h at room temperature. Crystals formed in the $CHCl_3$ solution were recrystallized from ether–pentane to give a white solid, fragmentation product **9** (80 mg, 0.16 mmol, 80%): mp 168–172 °C dec; IR (CH_2Cl_2) 3550–2400 (br, m), 2950 (m), 1745 (s), 1704 (s), 1589 (m), 1319 (s), 1170 (s), 1132 (s) cm^{-1}; ^1H NMR (acetone-d_6) δ 7.41 (d, 2, ArH), 7.20 (d, 2, ArH), 4.87 (m, 2, olefinic CH), 4.31 (br s, 2, olefinic CH), 1.64 (s, 6, CH_3 at olefinic carbon), 1.35 (s, 18, $C(CH_3)_3$); mass spectrum (10 eV) *m/e* (relative intensity) 498 (1.71, $M^{+\cdot}$), 480 (18.99, $M^{+\cdot} - H_2O$), 466 (100, $M^{+\cdot} - H_2O$ and CH_2), 451 (53.64), 434 (21.24), 406 (74.16), 391 (18.69). Anal. ($C_{28}H_{34}O_6S$): C, H, S.

Fragmentation of Persulfurane 7 in Dry Pyridine. Persulfurane **7** (200 mg, 0.4 mmol) in ca. 10 mL of dry pyridine was allowed to stand for 8–10 days at room temperature. The solvent was removed under vacuum, leaving an oily residue. The residue was dissolved in ether, washed with aqueous HCl and with water, and dried (Na_2SO_4). Evaporation of solvent gave a white crystalline solid, which was a 1:1 mixture of sulfone diacid diolefin **9** and lactone sulfone **10** (by NMR). The compounds were separated by preparative TLC (silica gel) using 1:1 (v/v) ether–THF as eluant. The first band was extracted with ether to give a white crystalline solid. Recrystallization from ether–pentane afforded white crystals of **10** (60 mg, 0.12 mmol, 30%): mp 271.5–273.5 °C dec; IR ($CHCl_3$) 3300–2500 (br, m), 1736 (s), 1707 (s), 1318 (s), 1252 (s), 1167 (s), 1131 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.53 (d, 1, ArH), 7.39 (s, 2, ArH), 7.33 (d, 1, ArH), 5.2 (m, 1, olefinic CH), 5.01 (s, 1, olefinic CH), 2.27 (s, 3, CH_3 at olefinic carbon), 2.22 (s, 3, $OCCH_3$), 2.10 (s, 3, $OCCH_3$), 1.32 (s, 9, $C(CH_3)_3$), 1.30 (s, 9, $C(CH_3)_3$); mass spectrum (10 eV) *m/e* (relative intensity) 498 (45.35, $M^{+\cdot}$), 480 (15.25, $M^{+\cdot} - H_2O$), 465 (100). Anal. ($C_{28}H_{34}O_6S$): C, H, S.

Methyl Ester of Lactone Sulfone 10. To an ether solution of **10** (41 mg, 0.082 mmol) was added a slight excess of CH_2N_2 in ether. After 15 min, excess CH_2N_2 was destroyed by adding a drop of acetic acid to the solution and the solvent was then removed. The white solid remaining was recrystallized from ether–pentane to give the white crystalline methyl ester of **10** (22 mg, 0.043 mmol, 53%): mp 262–263 °C; IR ($CHCl_3$) 1730 (s), 1314 (s), 1249 (s), 1126 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.60 (d, 1, ArH), 7.42 (m, 3, ArH), 5.22 (s, 1, olefinic CH), 5.07 (s, 1, olefinic CH), 3.44 (s, 3, $COOCH_3$), 2.27 (slightly br s, 6, CH_3), 2.12 (s, 3, CH_3), 1.32 (s, 18, $C(CH_3)_3$). Anal. ($C_{29}H_{36}O_6S$): C, H.

Ethyl Ester of Lactone Sulfone 10. To a stirred solution of sulfone diester **11** (421 mg, 0.735 mmol) in 50 mL of THF was added *n*-butyllithium in hexane (0.35 mL of 2.1 M, 0.735 mmol). After 6 h, excess CH_3I (ca. 0.5 mL) was added and the solvent was then removed. The yellowish residue was dissolved in ether, washed with aqueous HCl and with water, and dried (Na_2SO_4). The solvent was removed to give a white crystalline solid, ethyl ester of lactone sulfone **10** (223 mg, 0.425 mmol, 57.8%): mp 256–258 °C; IR ($CHCl_3$) 1730 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.59 (d, 1, ArH), 7.37–7.5 (m, 3, ArH), 5.23 (m, 1, olefinic CH), 5.07 (br s, 1, olefinic CH), 4.35–3.6 (m, 2, OCH_2CH_3), 2.26 (s, 6, $OCCH_3$), 2.11 (s, 3, CH_3 at olefinic carbon), 1.37 (s, 9, $C(CH_3)_3$), 1.35 (s, 9, $C(CH_3)_3$), 0.73 (t, 3, OCH_2CH_3). Anal. ($C_{30}H_{38}O_6S$): C, H, S.

2-(1-Hydroxy-1-methylethyl)-6-carboxydiphenyl Sulfide (43). 2-(Phenylthio)isophthalic acid[8] (12 g, 43.7 mmol) was converted to the corresponding diethyl ester by the procedure described for **4**. The diester in 30 mL of ether was added dropwise to a solution of CH_3MgBr in ether (45.2 mL of 2.9 M, 131.1 mmol). After 1 h of boiling, the solution was poured into a dilute aqueous HCl–ice mixture and the aqueous layer was extracted with ether. The combined ether solutions were dried (Na_2SO_4), and the solvent was removed. The resulting oil in 150 mL of a 2:1 (v/v) mixture of ethanol and 20% aqueous KOH was warmed for 14 h. The solution was diluted with water and acidified with dilute HCl. The white precipitate was filtered and recrystallized from acetone–water to give pale yellow crystals of **43** (10.1 g, 35.9 mmol, 82.2%): mp 148–150 °C; IR (Nujol) 3200–2400 (br, m), 1698 (s) cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 12.6 (br, 1, *COOH*), 8.05–6.73 (m, 8, ArH), 5.1 (br, 1, OH), 1.56 (s, 6, CH_3). Anal. ($C_{16}H_{16}O_3S$): C, H, S.

2,2-Dimethyl-6-oxo-8-phenyl-2*H*,6*H*-[1,2]thioxolo[4,5,1-*hi*]benzthioxole (31a). To a suspension of sulfide **43** (0.5 g, 1.73 mmol) in 50 mL of chloroform and pyridine (0.15 mL, 1.82 mmol) was added *tert*-butyl hypochlorite (0.21 mL, 1.82 mmol). After 15 min, the solution was washed twice with ice water and dried (Na_2SO_4), and the solvent was removed. The white solid (0.45 g) was recrystallized from $CHCl_3$ to give crystals of **31a** (0.42 g, 1.47 mmol, 85%): mp 206–207 °C; IR ($CHCl_3$) 2940 (m), 1639 (s), 1346 (s), 1316 (s), 1279 (s), 1168 (m), 1088 (m), 962 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.23 (d, 1, J = 7.5 Hz, Ar*H* ortho to the carboxy group), 7.92 (t, 1, J = 7.5 Hz, ArH), 7.53 (d, 1, J = 7.5 Hz, ArH), 7.5–7.27 (m, 5, ArH), 1.70 (s, 3, CH_3), 1.38 (s, 3, CH_3); mass spectrum (70 eV) *m/e* (relative intensity) 286 ($M^{+\cdot}$, not observed), 271 (7.81, $M^{+\cdot} - CH_3$), 184 (19.93, $M^{+\cdot} - CO_2$ and OC_3H_6), 151 (21.22). Anal. ($C_{16}H_{14}O_3S$): C, H, S.

2,2-Dimethyl-4-(1,1-dimethylethyl)-6-oxo-8-phenyl-2*H*,6*H*-[1,2]thioxolo[4,5,1-*hi*]benzthioxole (31b). Sulfurane **31b** was prepared by the procedure described for **31a** from 2-(1-hydroxy-1-methylethyl)-4-*tert*-butyl-6-carboxydiphenyl sulfide, the *tert*-butyl-substituted analogue of **43**, in 80% yield: mp 240–242 °C; IR ($CHCl_3$) 1645 (s) cm^{-1}; ^1H 220-MHz NMR ($CDCl_3$) δ 8.30 (d, 1, ArH), 7.50 (d, 1, ArH), 7.48–7.32 (m, 5, ArH), 1.717 (s, 3, CH_3), 1.461 (s, 9, $C(CH_3)_3$), 1.406 (s, 3, CH_3). Anal. ($C_{20}H_{22}O_3S$): C, H, S.

2-(1-Hydroxy-1-methylethyl)-4-*tert*-butyl-6-carboxydiphenyl sulfide was prepared by the procedure described for **43** from 2-phenylthio-5-*tert*-butylisophthalic acid. This sulfide diacid was synthesized by the procedure described for **3** from 2-bromo-5-*tert*-butylisophthalic acid[13] and thiophenol.

Reaction of Persulfurane 7 with $LiAlH_4$. To a stirred suspension of persulfurane **7** (304 mg, 0.61 mmol) in 50 mL of ether was added powdered $LiAlH_4$ (46 mg, 1.21 mmol). After 21 h, the solution was added to 10% aqueous NaOH and the aqueous layer was extracted with ether. The aqueous alkaline solution, together with some insoluble particles, was then acidified with dilute aqueous HCl and extracted with ether. The combined ether solutions were dried (Na_2SO_4), and the solvent was removed, leaving 230 mg of white crystalline solid, a mixture of compounds as observed by NMR. The mixture was separated into five bands by preparative TLC (silica gel) by using ether as eluant. The second band was extracted with ether to give a white solid (ca. 90 mg). Recrystallization from ether–pentane afforded white crystals of sulfurane oxide **12**. From the mother liquor, crystals of sulfide tetraol **13** were isolated. Sulfide tetraol **13** was present to the extent of ca. 20% (by NMR) in the initial mixture. The residue, after evaporation of solvent from the mother liquor, was identified as a mixture of sulfurane oxide **12** and its fragmentation product, **14**. The sulfurane oxide was about 40–50% (by NMR) of the reaction product.

The identities of these compounds were confirmed by comparing the ^1H NMR spectra with those of authentic samples.

Bis[2-(1-hydroxy-1-methylethyl)-4-(1,1-dimethylethyl)-6-(hydroxymethyl)phenyl] Sulfide (13). Diester diol **5** (4 g, 7.16 mmol) in 20 mL of ether was boiled for 10 h with a suspension of $LiAlH_4$ (0.65 g, 18 mmol, excess) in 50 mL of ether. The solution was poured into a dilute aqueous HCl–ice mixture, and the aqueous layer was extracted with ether. The combined ether solutions were dried (Na_2SO_4), the solvent was removed, and the product was recrystallized from ether–pentane to give crystals of tetraol sulfide **13** (2.52 g, 5.30 mmol, 74%): mp 138–140 °C; IR ($CHCl_3$) 3640 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.47 (d, 2, ArH), 7.30 (d, 2, ArH), 4.32 and 3.82 (AB pattern, 4, J = 13.5 Hz, CH_2OH), 2.62 (br, 4, OH), 1.83 (s, 6, $OCCH_3$), 1.74 (s, 6, $OCCH_3$), 1.29 (s, 18, $C(CH_3)_3$); mass spectrum (10 eV) m/e (relative intensity) 474 (100, $M^{+\cdot}$), 456 (1.51, $M^{+\cdot} - H_2O$), 438 (9.9, $M^{+\cdot} - 2H_2O$), 420 (23.65, $M^{+\cdot} - 3H_2O$), 407 (25.52). Anal. ($C_{28}H_{42}O_4S$): C, H, S.

Reaction of Unsymmetrical Sulfurane 31a with $LiAlH_4$. To a stirred solution of sulfurane **31a** (194 mg, 0.677 mmol) in 30 mL of ether was added powdered $LiAlH_4$ (26 mg, 0.68 mmol). After 21 h, the solution was added to dilute aqueous HCl and the aqueous layer was extracted with ether. The combined ether solutions were dried (Na_2SO_4), and the solvent was removed to give 160 mg of white solid, which was shown by NMR to be a 2:1 mixture of sulfide hydroxy acid **43** and sulfide diol **44**.

An authentic sample of sulfide diol **44** was prepared by methods described below.

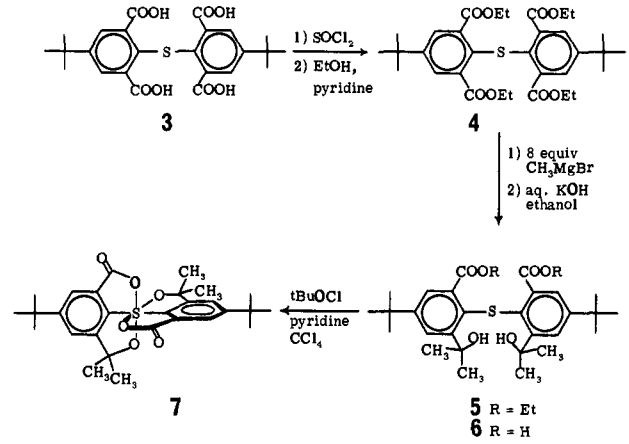
To a stirred suspension of sulfide hydroxy acid **43** (400 mg, 1.39 mmol) was added excess CH_2N_2 in ether carefully until the evolution of N_2 subsided. A few drops of acetic acid was added to destroy the excess CH_2N_2 in the solution. Solvent was removed, leaving an oil, the methyl ester of **43**. A solution of the ester in ether was slowly added to a suspension of $LiAlH_4$ (105 mg, 2.79 mmol) in ether. After 14 h of boiling, the solution was added to dilute aqueous HCl. The ether layer was separated and dried (Na_2SO_4), and the solvent was removed. The solid was recrystallized from ether–pentane to give white crystals of sulfide diol **44** (288 mg, 1.05 mmol, 75.7%): mp 110.5–111.5 °C; ^1H NMR ($CDCl_3$) δ 7.7–6.87 (m, 8, ArH), 4.66 (s, 2, CH_2OH), 4.05 (br s, 1, OH), 1.92 (br, 1, OH), 1.72 (s, 6, CH_3). Anal. ($C_{16}H_{18}O_2S$): C, H, S.

Bis[2-(1-hydroxy-1-methylethyl)-4-(1,1-dimethylethyl)-6-(carbethoxy)phenyl] Sulfoxide (17). *m*-Chloroperbenzoic acid (MCPBA) (114 mg, 0.66 mmol) in 5 mL of CH_2Cl_2 was quickly added in one portion to a stirred solution of sulfide diester diol **5** (367 mg, 0.66 mmol) in 350 mL of CH_2Cl_2. After ca. 30 s, the solution was quenched with aqueous $NaHCO_3$. The CH_2Cl_2 layer was dried (Na_2SO_4), and the solvent was removed to give a yellow solid, **17** (340 mg, 0.59 mmol, 90%). Slow evaporation of solvent from a solution of this solid in pentane afforded brown crystals of **17** (200 mg, 0.35 mmol, 53%): mp 153–154 °C; IR ($CHCl_3$) 3401 (m), 2941 (s), 1715 (s), 1692 (s), 1592 (m), 1466 (m), 1369 (s), 1312 (s), 1241 (w), 1212 (s), 1195 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.52 (d, 1, ArH), 7.47 (d, 1, ArH), 7.28 (d, 1, ArH), 6.98 (d, 1, ArH), 5.46 (s, 1, OH), 5.20 (s, 1, OH), 3.98 and 3.80 (ABX_3 pattern, 2, J_{AB} = 10.5 Hz, J_{AX} = 7.05 Hz, OCH_2CH_3), 3.70 and 3.17 (ABX_3 pattern, 2, J_{AB} = 10.5 Hz, J_{AX} = 7.05 Hz, OCH_2CH_3), 1.74 (s, 6, $OCCH_3$), 1.71 (s, 3, $OCCH_3$), 1.58 (s, 3, $OCCH_3$), 1.32 (s, 9, $C(CH_3)_3$), 1.28 (s, 9, $C(CH_3)_3$), 1.07 (t, 3, J = 7.05 Hz, OCH_2CH_3), 0.69 (t, 3, J = 7.05 Hz, OCH_2CH_3); mass spectrum (field desorption) m/e (estimated relative intensity) 574 (100, $M^{+\cdot}$), 558 (20, $M^{+\cdot} - O$). Anal. ($C_{32}H_{46}O_7S$): C, H.

7,7′-Dicarbethoxy-5,5′-bis(1,1-dimethylethyl)-3,3,3′,3′-tetramethyl-1,1′-spiro[3*H*-2,1-benzoxathiole] (18). A solution of MCPBA (85 mg, 0.49 mmol) in 5 mL of $CHCl_3$ was added to a stirred solution of diester diol sulfide **5** (274 mg, 0.49 mmol) in 30 mL of $CHCl_3$. After 18 h, the solution was washed with aqueous $NaHCO_3$ and dried (Na_2SO_4), and the solvent was removed. The remaining solid was recrystallized from pentane to give crystals of **18** (220 mg, 0.40 mmol, 80%): mp 189.5–191.5 °C; IR ($CHCl_3$) 2959 (m), 1718 (s), 1470 (m), 1370 (m), 1330 (m), 1261 (s), 1148 (m), 1026 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.49 (d, 2, ArH), 7.10 (d, 2, ArH), 4.4 (q, 4, J = 7.2 Hz, OCH_2CH_3), 1.45 (t, 6, J = 7.2 Hz, OCH_2CH_3), 1.33 (s, 24, $C(CH_3)_3$ and $OCCH_3$), 1.07 (s, 6, $OCCH_3$); mass spectrum (10 eV) m/e (relative intensity) 556 (0.28, $M^{+\cdot}$), 541 (100, $M^{+\cdot} - CH_3$), 511 (364, $M^{+\cdot} - OC_2H_5$). Anal. ($C_{32}H_{44}O_6S$): C, H, S.

7,7′-Dicarbethoxy-5,5′-bis(1,1-dimethylethyl)-3,3,3′,3′-tetramethyl-1,1′-spiro[3*H*-2,1-benzoxathiole] 1-Oxide (19). A solution of MCPBA (233 mg, 1.35 mmol, excess) in CH_2Cl_2 was added to a stirred solution of sulfurane diester **18** (500 mg, 0.9 mmol) in 50 mL of CH_2Cl_2. After 5 h, the solution was washed with dilute aqueous NaOH and with water and dried (Na_2SO_4), and the solvent was removed. The remaining solid was recrystallized from ether–pentane to give crystals of **19** (450 mg, 0.78 mmol, 86%): mp 156–158 °C; IR (CH_2Cl_2) 2950 (m), 1730 (s), 1216.5 (s), 1138 (s), 1080 (m), 918 (s), 869 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.53 (d, 2, ArH), 7.18 (d, 2, ArH), 4.42 and 4.26 (ABX_3 pattern, 4, J_{AB} = 10.5 Hz, J_{AX} = 7.05 Hz, OCH_2CH_3), 1.67 (s, 6, $OCCH_3$), 1.48 (s, 6, $OCCH_3$), 1.34 (t, 6, J = 7.05 Hz, OCH_2CH_3), 1.32 (s, 18, $C(CH_3)_3$); mass spectrum (70 eV) m/e (relative intensity) 572 (0.26, $M^{+\cdot}$), 526 (5.09, $M^{+\cdot} - O$ and $2CH_3$), 416 (12.65), 326 (8.48). Anal. ($C_{32}H_{44}O_7S$): C, H, S.

Scheme I



7,7′-Bis(1-hydroxy-1-methylethyl)-5,5′-bis(1,1-dimethylethyl)-3,3,3′,3′-tetramethyl-1,1′-spiro[3*H*-2,1-benzoxathiole] 1-Oxide (20). To a stirred solution of sulfurane oxide diester **19** (532 mg, 0.93 mg, 0.93 mmol) in 120 mL of ether was added a solution of CH_3MgBr (1.5 mL of 3 M) in 10 mL of ether. After 3 h, the suspension was added to a saturated NH_4Cl solution and the aqueous layer was extracted with ether. The combined ether solutions were dried (Na_2SO_4), and the solvent was removed to give a mixture of products (by NMR). The mixture was separated by preparative TLC (silica gel) using 1:1 (v/v) ether–pentane as eluant. The first band (R_f = 0.63) was extracted with ether to give a solid. Recrystallization from ether–pentane afforded white crystals of **20** (125 mg, 0.23 mmol, 24.7%): mp 174–176 °C; IR ($CHCl_3$) 3390 (m), cm^{-1}; ^1H 220-MHz NMR ($CDCl_3$) δ 7.386 (d, 2, ArH), 6.955 (d, 2, ArH), 5.307 (s, 2, OH), 1.727 (s, 6, CH_3), 1.705 (s, 12, CH_3), 1.545 (s, 6, CH_3), 1.348 (s, 18, $C(CH_3)_3$); mass spectrum (field desorption) m/e (estimated relative intensity) 544 (100, $M^{+\cdot}$), 528 (18.9, $M^{+\cdot} - O$), 526 (16.2, $M^{+\cdot} - H_2O$). Anal. ($C_{32}H_{48}O_5S$): C, H.

1,3-Bis(1-hydroxy-1-methylethyl)-5-(1,1-dimethylethyl)benzene (**22**) was the major undesired product in this reaction. Pure **22** was obtained by recrystallization from CH_2Cl_2–pentane: mp 129.5–130.5 °C; ^1H NMR ($CDCl_3$) δ 7.4 (s, 3, ArH), 1.76 (br s, 2, OH), 1.65 (s, 12, CH_3), 1.37 (s, 9, $C(CH_3)_3$); mass spectrum (10 eV) m/e (relative intensity) 250 (15.0, $M^{+\cdot}$), 235 (100, $M^{+\cdot} - CH_3$), 217 (10.89, $M^{+\cdot} - CH_3$ and H_2O). Anal. ($C_{16}H_{26}O_2$): C, H.

Other products, such as methyl sulfide **23**[13] and sultine **24**[13] were identified by ^1H NMR spectra.

Symmetrical Persulfurane 21. To a stirred solution of sulfurane oxide diol **20** (53 mg, 0.097 mmol) in 2 mL of THF was added excess powdered KH. After 18 h, the brownish solution was filtered and the solvent was removed under vacuum, leaving a brown residue. This was dissolved in 5 mL of ether and freshly distilled trifluoroacetic anhydride (20 μL, 0.14 mmol) was added. After 5 h, the solution was filtered and the solvent was removed under vacuum to give a solid, which was shown by NMR to be a mixture of compounds. The mixture was separated by preparative TLC (silica gel) using 1:1 (v/v) ether–pentane as eluant. The first band (R_f = 0.71) was extracted with ether to give a white solid (10 mg, 0.019 mmol, 19.6%), persulfurane **21**: ^1H 220-MHz NMR ($CDCl_3$) δ 7.240 (s, 4, ArH), 1.571 (s, 24, CH_3), 1.389 (s, 18, $C(CH_3)_3$); mass spectrum (field desorption) m/e (estimated relative intensity) 526 (58, $M^{+\cdot}$), 510 (100, $M^{+\cdot} - CH_4$).

The second band (R_f = 0.53) was extracted with ether to give the starting material, sulfurane oxide diol **20** (17 mg, 0.031 mmol, 32.2%). Compounds isolated from several other bands were not identified.

Results

Synthesis. Diarylbis(acyloxy)dialkoxypersulfurane **7**, the first example of a hexacoordinate (12-S-6) organosulfur derivative lacking fluorine ligands, was prepared by the method shown in Scheme I.

Diester diol **5**, a key intermediate in the synthesis of **7**, was the only product isolated (in 80% yield) from the reaction of tetraester

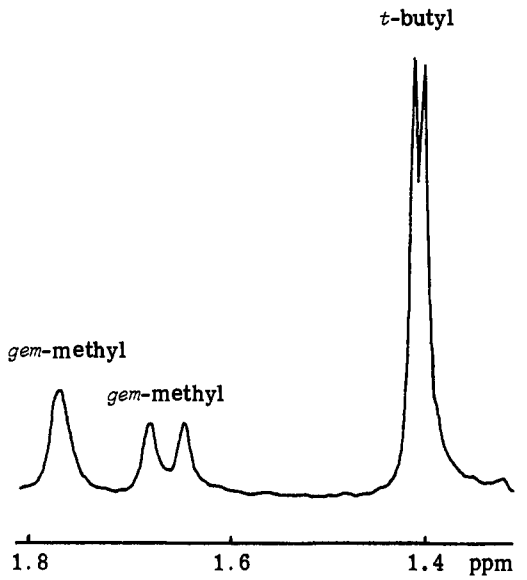
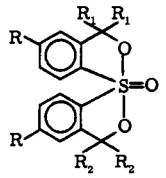


Figure 1. Expanded ^1H NMR (220-MHz) spectrum of persulfurane **7** in CD_2Cl_2 (−30 °C) in the presence of optically active 2,2,2-trifluoro-1-phenylethanol showing the geminal methyls and *tert*-butyl signals. The methyl singlet at δ 1.707 and the *tert*-butyl singlet are each resolved into two singlets.

4 with CH_3MgBr. Under conditions with a still larger excess of CH_3MgBr or longer reaction time, however, the reaction gives other products. Treatment of **6** with pyridine and *tert*-butyl hypochlorite at 0 °C gives **7** in high yield. By analogy to the spirobicyclic sulfurane oxide **8a**, the first reported[9] monoketal

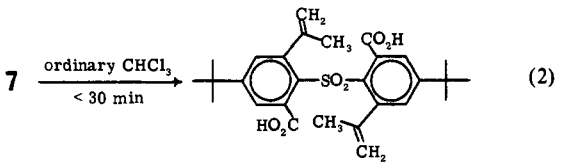


8a R = $C(CH_3)_3$; $R_1 = R_2 = CF_3$

8b R = H; $R_1 = R_2 = CH_3$

analogue of a sulfone, persulfurane **7**, is considered to be the first bisketal analogue of a sulfone. The ^1H NMR spectrum of **7** shows two peaks at δ 1.791 and 1.707, which clearly indicate the diastereotopic nature of the two geminal methyl groups on the five-membered heterocyclic ring, as expected from the pictured octahedral structure of **7**. The chirality of persulfurane **7** was evidenced by the addition of optically active 2,2,2-trifluoro-1-phenylethanol[10] to a CD_2Cl_2 solution of **7** (−30 °C) in the 220-MHz NMR spectrum. The methyl singlet at δ 1.707 and the *tert*-butyl singlet were each resolved into two singlets (Figure 1).

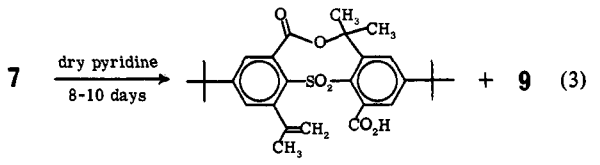
Fragmentation. Crystalline persulfurane **7** is thermally stable and unreactive toward atmospheric moisture. It decomposes completely at room temperature, however, in ordinary chloroform (<30 min) to give the isomeric sulfone diacid diolefin **9** (eq 2),



(2)

9

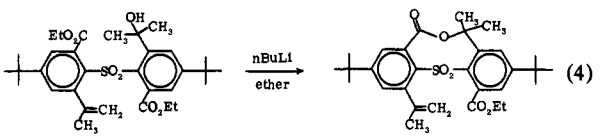
or in dry pyridine (8–10 days) to give a 1:1 mixture of **9** and an isomer, sulfone lactone **10** (eq 3). The amount of **10** which is formed apparently depends on the dryness of the solvent. When a few drops of water were added to a pyridine solution of **7**, the rate of fragmentation was greatly enhanced (complete reaction



(3)

10

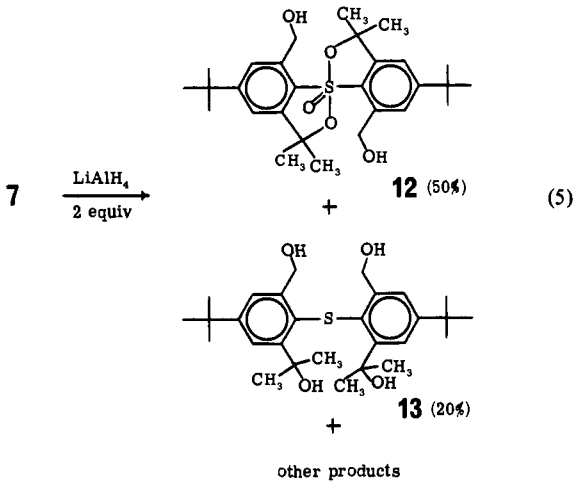
within minutes at room temperature), and only **9** was isolated. Compound **10** is stable and unreactive toward aqueous HCl in solution. Its ^1H NMR spectrum shows two nonequivalent geminal methyls, which coalesce at 91.5 °C (90 MHz) in 5:1 (v/v) Ph_2O–$CDCl_3$ solvent. Two carbonyl stretching frequencies, 1707 and 1736 cm^{-1}, are seen in **10**, together with a broad hydroxy absorption at 3000–2500 cm^{-1}. Reaction with diazomethane gives the methyl ester of **10**, which has only one carbonyl stretching frequency at 1730 cm^{-1} and no hydroxy absorption. Authentic ethyl ester of **10** was prepared by treatment of sulfone diester **11** with 1 equiv of *n*-BuLi (eq 4). This ethyl ester of **10** also has only one carbonyl stretching frequency at 1730 cm^{-1}. Except for the methoxy and ethoxy resonances, these two esters of **10** show all peaks within 0.01 ppm of each other in the ^1H NMR spectra.



(4)

11 ethyl ester of **10**

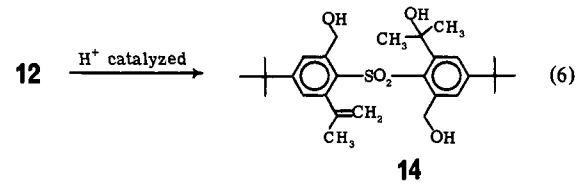
Reaction with $LiAlH_4$. Persulfurane **7** reacts with $LiAlH_4$ in ether to give sulfurane oxide diol **12**,[11] sulfide tetraol **13**, and other unidentified products (eq 5). Sulfurane oxide **12**, the major



(5)

other products

product of the reaction, undergoes fragmentation to form the isomeric sulfone **14** (eq 6). Unlike its analogue, sulfurane oxide



(6)

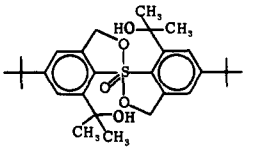
14

8b,[12] **12** is stable to mild acid such as benzoic acid and in ordinary

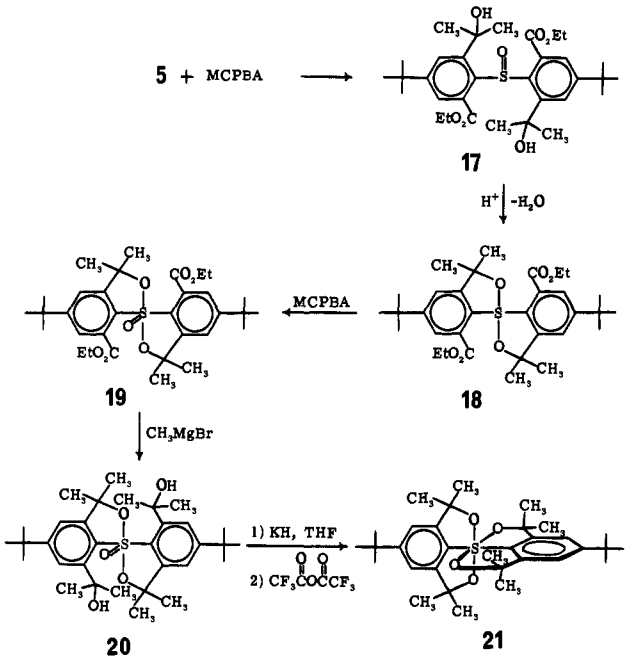
(9) (a) Perozzi, E. F.; Martin, J. C. *J. Am. Chem. Soc.* **1972**, *96*, 5519. (b) Martin, J. C.; Perozzi, E. F. *Ibid.* **1974**, *96*, 3155.

(10) (a) Pirkle, W. H.; Muntz, R. L.; Paul, I. C. *J. Am. Chem. Soc.* **1971**, *93*, 2817. (b) Pirkle, W. H.; Sikkenga, D. L. *J. Org. Chem.* **1975**, *40*, 3430.

(11) We prefer the structure for sulfurane oxide diol **12** which is pictured. An alternative structure of **12**, shown below, which is also consistent with the IR and ^1H NMR spectral data, cannot be ruled out.

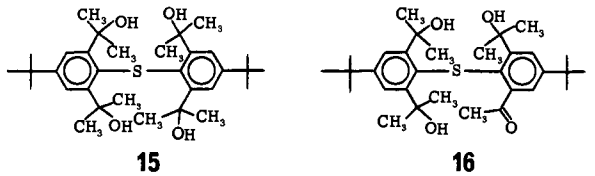


Scheme II



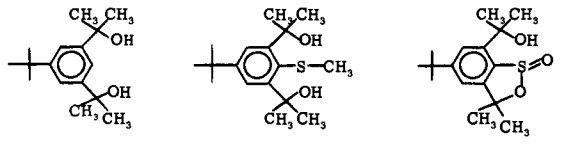
chloroform. A sample of **12** in $CHCl_3$ reacts completely within minutes at room temperature when a drop of chloroform saturated with HCl or a drop of trifluoroacetic acid is added.

Synthesis of Another Persulfurane. As mentioned earlier, reaction of tetraester **4** with a large excess of CH_3MgBr gives some products in addition to the desired diester diol **5**. Sulfide tetraol **15**, however, is not observed. Neither was any of **15** observed in



experiments using CH_3Li. In all cases, the most highly methylated product isolated was keto triol **16**. Pure **16** would not react further to give **15**. We had expected that sulfide tetraol **15** produced in this way would be a precursor of a symmetrical tetraalkoxypersulfurane. Although we were frustrated in the direct preparation of diaryltetraalkoxypersulfurane **21** via **15** produced in this way, the less direct method shown in Scheme II provides a successful route to **21**.

Sulfoxide diester diol **17** undergoes cyclodehydration under the acidic reaction condition to give sulfurane **18**. Further oxidation of sulfurane **18** gives sulfurane oxide diester **19**, a compound analogous to **12**, which is stable in ordinary chloroform and to mild acid such as benzoic acid. A sample of **19** in $CHCl_3$, however, reacts completely within minutes to give sulfone diester **11** when a drop of chloroform saturated with HCl or a drop of trifluoroacetic acid is added. The precursor of **21**, sulfurane oxide diol **20**, was synthesized via the reaction of **19** with CH_3MgBr. Other observed products such as diol **22**, methyl sulfide **23**,[13] and sultine **24**[13] can be explained by postulating attack of the methyl Grignard reagent at the sulfur atom.



(12) Adzima, L. J.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 1657.
(13) (a) Lau, P. H. W.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 5490. (b) Lau, P. H. W. Ph.D. Thesis, University of Illinois, 1979.

Treatment of **20** with KH in THF and then with trifluoroacetic anhydride gave a compound postulated to be persulfurane **21**. A sharp singlet at δ 1.57 in its 220-MHz spectrum clearly indicates the symmetrical nature of the two geminal methyl groups on the five-membered heterocyclic ring, as expected from the pictured structure of **21**. The field desorption mass spectrum shows a sizable molecular ion peak at m/e 526 and a prominent fragmentation peak at m/e 510 corresponding to a loss of a CH_4 fragment. Because of low quantity and its high solubility in most solvents, attempts to recrystallize persulfurane **21** for elemental analyses have not yet been successful. Persulfurane **21** is stable in ordinary chloroform for hours. In one case, however, **21** was found to have decomposed in solution after 2 weeks, to give unidentified products as evidenced by ^1H NMR.

^1H NMR Observations on 20 and Its Dipotassium Salt (45). The ^1H NMR spectrum of sulfurane oxide diol **20** at room temperature in 3:1 (v/v) Me_2SO-d_6–$CDCl_3$ solvent showed three methyl singlets corresponding to the four nonequivalent methyl groups, with two of them accidentally having the same chemical shift. At 124 °C, the three singlets were coalesced into a slightly broad singlet, which was narrowed at higher temperature. Meanwhile, the two aromatic doublets at δ 7.5 and 7.1 were broadened. Studies at higher temperature were prevented by the fact that rather rapid decomposition of **20** was observed at temperatures above 135 °C. From the coalescence temperature and the largest chemical shift differences for the methyl peaks (12.6 Hz), a $\Delta G^{\ddagger}$ of ca. 20.8 kcal mol^{-1} was calculated by using the Gutowsky–Holm equation.[14] Cooling the sample to room temperature reproduced the original spectrum of **20**, together with some peaks of the decomposition product.

Sulfurane oxide diol **20** reacts with KH in THF to give a solid, which is postulated to be the dipotassium salt of **20** (**45**). Although its ^1H NMR spectrum might be expected to be similar to that of **20**, the 220-MHz spectrum of this sulfurane oxide alkoxide at room temperature in THF-d_8 showed two broad peaks at δ 7.23 and 1.56, corresponding to the aromatic protons and the four nonequivalent methyl groups, respectively. On stepwise cooling, the peaks were further broadened and then resolved into several broad peaks at −50 °C, the lowest temperature available to us on this instrument. The −50 °C temperature was not sufficiently low to resolve the broad peaks into well-defined peaks. From the separation of the broad methyl peaks (ca. 32.5 Hz) and the estimated coalescence temperature, 0 °C, an approximate $\Delta G^{\ddagger}$ of 13.6 kcal mol^{-1} was calculated.[14] No decomposition of this dipotassium salt of **20** (**45**) was observed during this experiment.

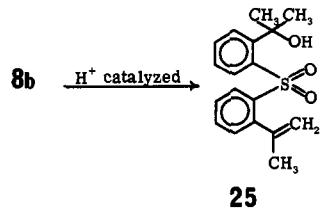
Discussion

Persulfurane **7**, the first isolated 12-S-6 species bearing no fluorine ligands, is stable indefinitely at room temperature and unreactive toward atmospheric moisture. Its surprisingly low reactivity suggests the importance of the stabilizing five-membered ring effect and of the Thorpe–Ingold effect,[15] which has been well documented in the chemistry of phosphoranes,[16] sulfuranes,[9] and iodinanes.[17]

The rapid decomposition of persulfurane **7** in ordinary chloroform to give sulfone diacid diolefin **9** is analogous to the acid-catalyzed fragmentation of spirosulfurane oxide **8b** to give **25** (eq 7)[12] fragmentation deriving its driving force from the formation of the stable sulfonyl functional group.

The bond dissociation energy of the S=O bond of diphenyl sulfoxide is 91.7 kcal mol^{-1},[18] and the energy of the second S=O bond added on going from a sulfoxide to a sulfone is an even larger

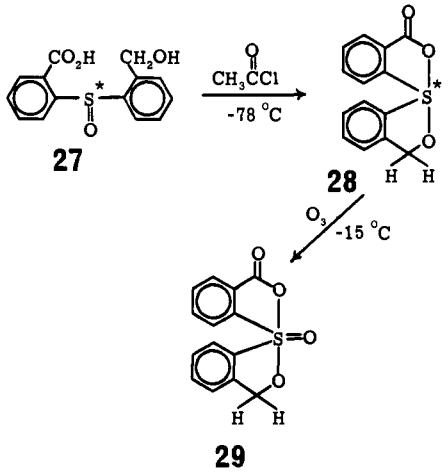
(14) (a) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228. (b) Pople, J. A.; Schneider, W. G.; Bernstein, H. J. "High Resolution Nuclear Magnetic Resonance"; McGraw-Hill: New York, 1959; p 223. (c) Drago, R. S. "Physical Methods in Inorganic Chemistry"; Van Nostrand-Reinhold: Princeton, N.J., 1965; pp 281–285.
(15) (a) Beesley, R. M.; Ingold, C. K.; Thorpe, J. F. *J. Chem. Soc.* **1915**, *107*, 1080. (b) Ingold, C. K. *Ibid.* **1921**, 305.
(16) Westheimer, F. H. *Acc. Chem. Res.* **1968**, *1*, 70.
(17) Amey, R. L.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 5294.
(18) Sanderson, R. T. "Chemical Bonds in Organic Compounds"; Sun and Sand Publishing Co.: Tempe, Ariz., 1976.



(7)

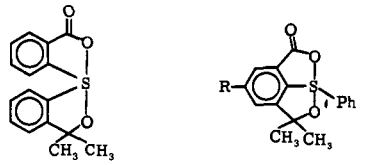
106.6 kcal mol^{-1}.[18] The strong tendency for **8b** to fragment to give **25**, when a suitable pathway is available, is therefore not surprising. In the case of persulfurane **7**, fragmentation is catalyzed by a trace of HCl present in ordinary chloroform. A possible stepwise pathway for this acid-catalyzed fragmentation is shown in Scheme III.

The postulated intermediate **26** (R = H), a sulfurane oxide, is also expected to be acid sensitive and to undergo fragmentation as seen for closely analogous sulfurane oxides.[12,13] No evidence is seen in the NMR for intermediacy of **26** (R = H) in the reactions. Sulfurane oxides with apical acyloxy ligands analogous to **26** are not known. The recently reported[19] synthesis of an optically active unsymmetrical sulfurane **28** and its corresponding sulfurane oxide **29** (optically inactive) from the oxidation of **28** with ozone is, in view of our observations, of questionable validity (eq 8). The carbonyl stretching frequency reported for **28**, 1740



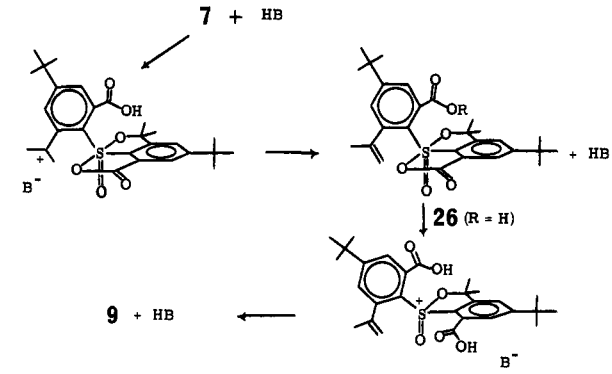
(8)

cm^{-1}, is inconsistent with that seen in closely related unsymmetrical sulfuranes **30**[20] (1647 cm^{-1}), **31a** (1639 cm^{-1}), and **31b** (1645 cm^{-1}). Attempts to oxidize sulfurane **31a** or other sulfuranes with two different apical ligands to the corresponding sulfurane oxides have not been successful in our laboratory.[20,21]

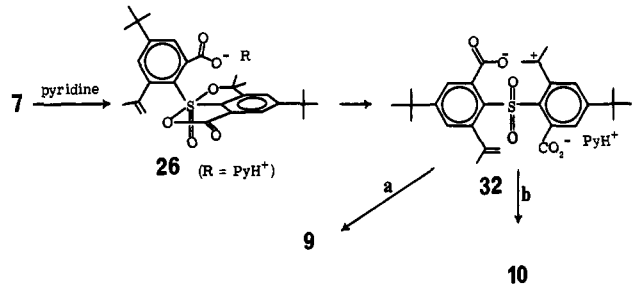


The slow fragmentation of **7** in dry pyridine probably follows a pathway similar to that shown in Scheme III. Dissociation of the first hypervalent O–S–O bond in this basic medium (Scheme IV) would give a sulfurane oxide intermediate (**26**, R = pyH$^+$), having a carboxylate anion substituent at the unbridged aryl ring. Further fragmentation of this intermediate would give a sulfone carbocation **32**, which may follow pathway a to give **9** or an alternate pathway b to give sulfone lactone **10**. A decomposition

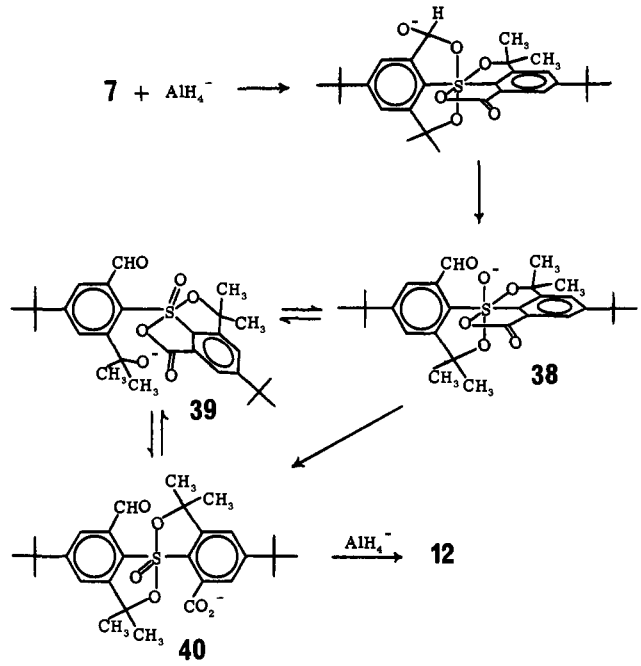
Scheme III



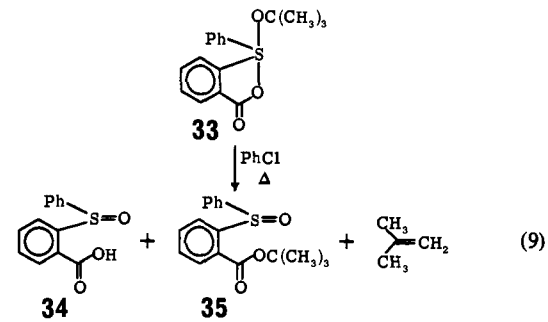
Scheme IV



Scheme V



analogous to that producing sulfone lactone **10** from **7** is reported[20] for sulfurane **33**. Thermolysis of **33** in chlorobenzene gives among other products sulfoxide ester **35** (ca. 45%) by a pathway which could be closely analogous to that leading to **10** (eq 9).



(9)

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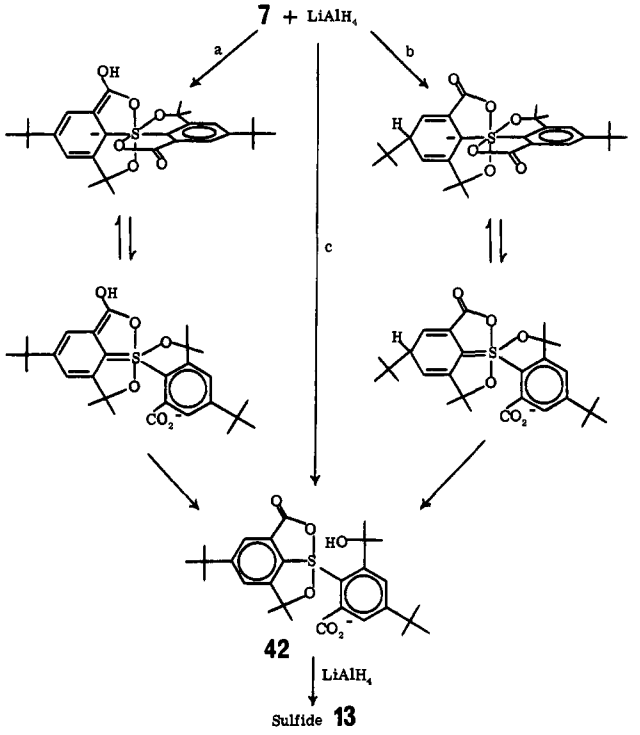
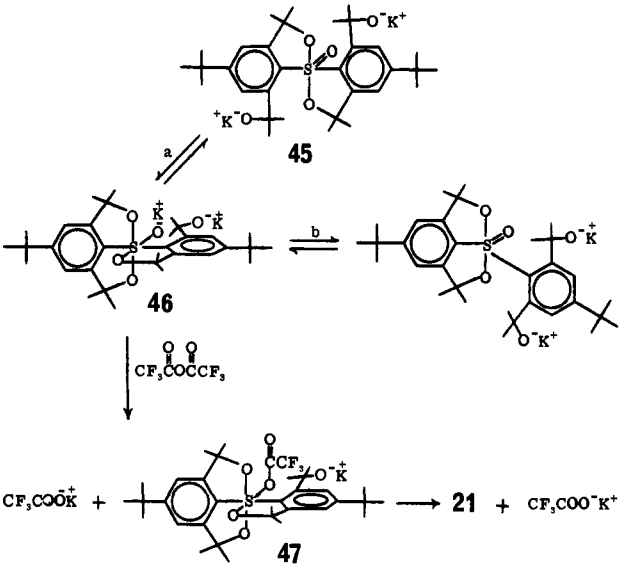
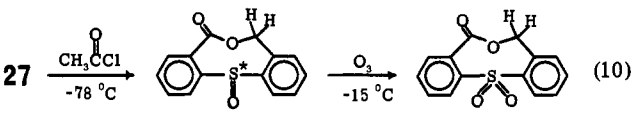
Scheme VI



Scheme VII



The unreactivity of compound **10** toward acid in solution, together with observations of infrared and ^1H NMR spectra, eliminate the possibility of its having the structure of an isomeric sulfurane oxide such as **26**. The formation of this eight-membered-ring lactone suggests an alternative explanation for the observations of Kapovits et al.[19] on the dehydration of their optically active sulfoxide hydroxy acid **27**. Reaction with acetyl chloride could have given the optically active sulfoxide lactone **36**, instead of the postulated sulfurane **28** (eq 10). Compound

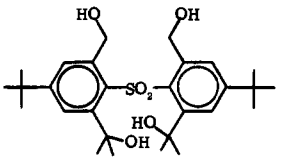


(10)

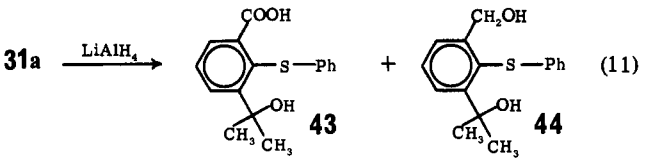
36 would also show an AB pattern for the two diastereotopic methylene protons in the ^1H NMR spectrum, as was reported for the postulated sulfurane structure **28**. The reported carbonyl stretching frequency, 1740 cm^{-1}, is closer to that expected for lactone **36** than for **28**. Oxidation of **36** with ozone would give the optically inactive sulfone lactone **37**, in keeping with the optical inactivity of the material which was posulated[19] to have the sulfurane oxide structure **29**. The reported ^1H NMR observation would also be in accord with that which would be seen for sulfone lactone **37**. An AB pattern was observed in the NMR spectrum at −70 °C, demonstrating the magnetic nonequivalence of the methylene protons. Coalescence of this AB resonance occurred at −49 °C, and a sharp singlet corresponding to the methylene protons was observed at room temperature. This NMR observation on **37** would be analogous to that for our sulfone lactone **10**. Coalescence of the two nonequivalent geminal methyl singlets is, in our interpretation, the result of a rapid ring conformational isomerization process of **10**. We will discuss these processes in a later paper.

A mechanism for the reaction of persulfurane **7** with $LiAlH_4$ to give sulfurane oxide diol **12** is proposed in Scheme V. Hydride transfer to the carbonyl carbon to give persulfurane anion intermediate **38** or sulfurane oxide **39** is followed by rearrangement to its topological isomer **40**, which is favored because the negative charge is on the carboxyl group. The aldehyde and carboxylate substituents in **40** are subsequently reduced by $LiAlH_4$ to the primary alcohol functional group.

The isolation of sulfide tetraol **13** from the reaction is of particular interest. Experiments have shown that neither sulfurane oxide **12** nor sulfone tetraol **41** reacts with $LiAlH_4$ under similar



conditions to give sulfide tetraol **13**. It is unlikely that direct attack on octahedral sulfur(VI) is to be observed. Possible explanations are shown in Scheme VI. The posulated S_N2'' displacement of path a or path b produces sulfurane **42** which is expected to be readily reduced to the sulfide, with reduction of its carboxylate substituents to hydroxymethylene groups. A third route to the intermediate sulfurane **42** is the direct hydride transfer to an alkoxy oxygen of **7** to give **42** in a single step (path c). Under comparable reaction conditions unsymmetrical sulfurane **31a** gives a mixture of hydroxy acid **43** and diol **44** (eq 11). Sulfide **43** may be formed by hydride transfer to sulfur, a process which is not possible in the case of persulfurane **7**.



(11)

As mentioned earlier, the formation of sulfurane oxide diol **12** from the reaction of persulfurane **7** with $LiAlH_4$ involves the rearrangement of a persulfurane anion intermediate **38** to sulfurane oxide **40** as a key step in the process (Scheme V). The proposed interconversions and rearrangements among 5- and 6-coordinate species **38**–**40** which involve the intramolecular attack at sulfur of an anion substituent, either alkoxide or carboxylate, may provide an explanation for the ^1H NMR observations on sulfurane oxide diol **20** and its dipotassium salt (**45**), as well as a mechanism for persulfurane **21** formation (Scheme VII).

Because of the chirality of sulfur, a total of four methyl singlets might be expected for **45** in its ^1H NMR spectrum. Nevertheless, the room-temperature ^1H NMR spectrum showed only a broad methyl peak, which sharpened at high temperature and was resolved at −50 °C into several broad peaks. This is consistent with rapid interconversion of isomers via pathways such as a and b,

making the four methyl groups magnetically equivalent at higher temperature. Sulfurane oxide diol **20** apparently undergoes similar topological isomerization processes via pathways similar to a and b, though the activation barrier is much higher for **20** than for its dipotassium salt (**45**). Three methyl singlets were seen in the ^{1}H NMR spectrum of **20** at room temperature, and coalescence of the three peaks into a singlet occurred only at 124 °C. This is in accord with the postulate that pathways a and b, Scheme VII, are associative processes, nucleophilic displacements on sulfur by an alkoxy ligand, more rapid for the alkoxide of **45** than for the alcohol oxygen of **20**.

The acylation of **46** to give persulfurane **47** provided a possible precursor to persulfurane **21** (Scheme VII). Unlike unsymmetrical persulfurane **7**, **21** is not very acid sensitive and undergoes fragmentation very slowly in solution under conditions which lead to rapid fragmentation of **7**. The symmetrically substituted three-center, four-electron bonds in persulfurane **21** are less polarized than those of persulfurane **7**.[21] Thus the protonation of the alkoxy ligands in **21** might not be as easy as protonation of the electron-rich acyloxy ligand of **7** (Scheme III). Furthermore, in the case of persulfurane **21**, the dissociation of a hypervalent bond in the first fragmentation step would generate an intermediate sulfurane oxide, which would be more stable to acid-catalyzed fragmentation (Scheme III).

Conclusion

The successful synthesis of persulfurane **7** enables us for the first time to go beyond the limited scope of hexacoordinate sulfur(VI) chemistry involving the chemistry of mono- and disubstituted derivatives of SF_6. The results from the study of persulfurane **7** presented here have already given us a new insight into the syntheses of persulfuranes. The indirect method of cyclodehydration of sulfurane oxide diol **20** to give tetraalkoxypersulfurane **21** is one such example. It also demonstrates the fact that a sulfone bisketal, a 12-S-6 species such as **21**, can be prepared from the monoketal analogue of a sulfone, a 10-S-5 species such as **20**. We have found that sulfone monoketals can be obtained from their corresponding sulfones (8-S-4 species) by cyclodehydration. The chemistry of this ketalization of a sulfone will be reported in a later paper. A single-crystal X-ray structure determination on **7** has been completed. From its structural data, together with that of sulfurane **31a**, we shall learn more of the nature of the hypervalent bonding in persulfuranes and sulfuranes. These will be discussed in the following paper.

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A Comparison of Hypervalent Bond Polarizabilities in Sulfuranes (10-S-4 Species) and Persulfuranes (12-S-6 Species)

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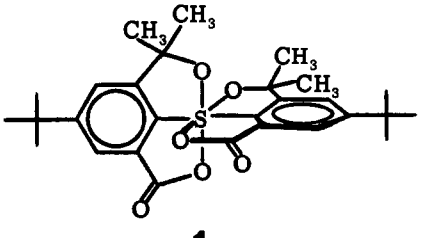
Abstract: The crystal and molecular structures of bis[5-(1,1-dimethylethyl)-3-(1-hydroxy-1-methylethyl)benzoato(3-)-C^2,O^1,O^3](*OC*-6-22′)sulfur (persulfurane **1**), symmetrical spirosulfurane **9**, and unsymmetrical bicyclic sulfurane **10** were solved by X-ray crystallographic techniques. The X-ray structure analysis for **1** (R = 0.203) confirms the approximate octahedral geometry around sulfur previously postulated. From the large difference (0.24 Å) between the S–O bond lengths, we infer a high degree of polarization in the hypervalent O–S–O bonds. The X-ray crystal structure analyses of both **9** (R = 0.059) and **10** (R = 0.063) reveal distorted trigonal-bipyramidal geometry about sulfur, similar to structures previously determined for other spirosulfuranes. The large difference (0.59 Å) between the lengths of the S–O bonds in **10**, 2.248 (2) and 1.662 (2) Å, clearly reflects the highly polarized nature of the hypervalent O–S–O bond, resulting from the difference in electronegativities of the apical ligands. Elements of the structure of bicyclic sulfurane **10** are compared with analogous elements in the structure of **1** and **9** and other spirosulfuranes. The postulated polarization of the hypervalent bonds is also reflected in the chemical shifts of the quaternary carbon in the alkoxy ligands in some unsymmetrically substituted sulfuranes of type **15** and **16**, as well as other model sulfuranes. The peak position for the quaternary carbon in the ^{13}C NMR spectrum is found to be very responsive to the electronic nature of the ligand trans to an alkoxy group. Studies of structural data, carbonyl stretching frequencies, and carbon chemical shifts of the quaternary carbon in the alkoxy ligands agree that the O–S–O hypervalent bonds to sulfur(VI) in persulfurane **1** are less polarizable than the O–S–O hypervalent bond in sulfurane **10**.

Introduction

Before our successful synthesis of a diarylbis(acyloxy)dialkoxypersulfurane, **1**,[1] hexacoordinate sulfur(VI) compounds (12-S-6 species) which had been reported included only sulfur hexafluoride (**2**) and its mono- and disubstituted derivatives, in which one or two fluorine ligands had been replaced with aryl, vinyl, ethynyl, perfluoroalkyl, and alkyl groups and various inorganic ligands.[2] Octahedrally symmetric[3] compound **2** has only a single ^{19}F resonance as expected.[4] Complete structure determinations, by



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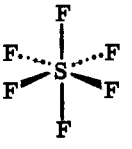

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