Reactions of Some New Diaryldialkoxyspirosulfuranes. The Barrier to Cuneal Inversion of Configuration at Sulfuranyl Sulfur in Diastereomeric Spirosulfuranes[1,2]

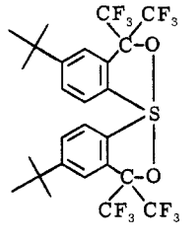
L. J. Adzima and J. C. Martin*

Department of Chemistry, School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

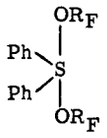
Received April 25, 1977

The syntheses of diaryldialkoxyspirosulfuranes **8**, **11**, **15**, and **17** are reported, including the first example of a pair of diastereomeric spirosulfuranes (**17a** and **17b**) which may be interconverted by cuneal inversion at sulfur(IV). Hydrolyses of these compounds are compared with each other and with those of related species. The most studied of these sulfuranes, 3,3,3′,3′-tetramethyl-1,1′-spiro[3*H*-2,1-benzoxathiole] (**8**), undergoes a wide variety of reactions, including reactions with hydrogen halides to form halosulfuranes and with strong acids to form alkoxysulfonium salts. For both classes of products, ^{1}H NMR spectra show evidence for an intramolecular degenerate ligand-exchange process. Low-temperature ^{1}H NMR studies on one of these adducts confirms this interpretation. The pyrolytic fragmentation reactions of **8**, **11**, and **15** show facile dehydration for **8** and intramolecular disproportionation for **11** and reveal a great thermal stability for **15**. The reactivity (and basicity) of these spirosulfuranes is decreased by increasing electronegativity of apical ligands. The configurational stability of **17** has been determined by measuring the rate of isomerization of *exo*-**17a** to *endo*-**17b**. The rate constant ($k_1 = 3 \times 10^{-6}$ s^{-1}) for this process at 84 °C corresponds to a lower limit of $\Delta G^*_{84°C} = 30$ kcal mol^{-1} for cuneal inversion of configuration (inversion through a planar transition state) at sulfuranyl sulfur. Possible alternative interconversion mechanisms are discussed.

The number of reported examples of spirosulfuranes has grown rapidly.[2-9] However, there have been relatively few reports concerning the reactions of these new compounds.[4,6,9] Martin and Perozzi report[6] that bicyclic spirosulfuranes are much less reactive than acyclic sulfuranes, with monocyclic sulfuranes showing intermediate reactivities. For example, spirosulfurane **1** is reported to be completely inert toward acid or base hydrolysis and unreactive toward a number of reagents, whereas its acyclic analogue **2** is extremely reactive.[6]

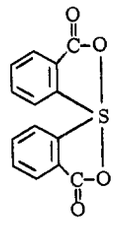


1

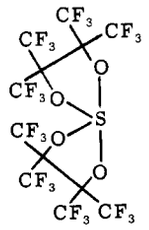


2, (OR_F = $OC(CF_3)_2Ph$)

Kalman and Kapovits[4] reported only one reaction (hydrolysis) for spirosulfurane **3**. Some reactions of tetrakis(alkoxysulfurane)[3] **4** and several spirotris(alkoxysulfuranes) have been reported.[9]



3



4

In the past few years, considerable interest has centered around the determination of inversion barriers of sulfonium salts.[10-14] Only recently has this interest been extended to sulfuranes[9a,15,16] and selenuranes.[17]

We report here the synthesis and reactions of several new spirobicyclic sulfuranes. The results are compared and contrasted with those for previously reported sulfuranes, with the goal of evaluating the influences of changes in electronegativity of apical ligands and of *gem*-dialkyl substitution on the stability of spirosulfuranes. We also describe the isolation of a pair of diastereomeric sulfuranes with a chiral center at the sulfuranyl sulfur and a determination of the barrier to interconversion of the two by a process involving, at least formally, inversion at sulfur.

Experimental Section

General. Proton chemical shifts are reported on the δ scale, ppm downfield from tetramethylsilane internal standard; fluorine chemical shifts are reported on the ϕ scale, ppm upfield from fluorotrichloromethane internal standard. The ^{1}H NMR and ^{19}F NMR integral ratios are uncorrected.

Solvents and Reagents. Chloroform-*d* and methylene chloride were dried by passage through a column of Woelm basic alumina (activated at 150 °C for 24 h). Ether and tetrahydrofuran (THF) were dried by several additions of sodium wire over several days until further additions caused no further hydrogen evolution. Pyridine-d_5 was obtained in sealed ampules from Merck.

2,2′-Dicarboxydiphenyl Sulfide Diethyl Ester (5). 2,2′-Dicarboxydiphenyl sulfide[18] (4.77 g, 17.4 mmol) and 20 mL of thionyl chloride were combined and boiled overnight. Excess thionyl chloride was removed by high vacuum. The residue was dissolved in 50 mL of benzene and added to a solution of 10 mL of absolute ethanol and 20 mL of pyridine. After 5 min the solvents were removed by vacuum. The residue was dissolved in ether, and the ether solution was extracted with dilute aqueous HCl, dilute aqueous NaOH, and water. The ether solution was dried ($MgSO_4$) and the solvent removed, leaving 4.27 g (74.2%) of diester **5**: mp 64.5–65.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.30 (t, 6, CH_3), 4.35 (q, 4, CH_2), 7.12–7.67 (m, 6, Ar**H**), 7.80–8.17 (m, 2, Ar**H**); mass spectrum (70 eV) *m/e* (rel intensity) 330 (100, M$^+$·), 239 (19.0), 213 (69.2), 184 (25.6), 137 (10.8), 136 (19.3), 29 (17.4).

Bis[2-(1-hydroxy-1-methylethyl)phenyl] Sulfide (6). Diethyl ester **5** (20.0 g, 0.061 mol) was dissolved in 100 mL of dry ether and added dropwise with stirring to 100 mL of 2.9 M CH_3MgBr (0.29 mol) in ether. After 2 h of boiling the solution was added to a dilute HCl–ice mixture. The ether layer was extracted with dilute aqueous KOH and water and dried (Na_2SO_4), and solvent was removed, leaving a light yellow oil, which upon trituration with pentane gave a light-yellow solid. The solid was recrystallized from ether–pentane to give 15.93 g (87.2%) of white crystalline product: mp 113.5–114.5 °C; IR ($CHCl_3$) 3465 (m, br, OH), 3000 (s), 1466 (s), 1430 (s), 1384 (s), 1364 (s), 1165 (s), 1036 (m), 947 (s), 855 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 1.76 (s, 12, CH_3), 3.37 (s, 2, OH), 7.00–7.63 (m, 8, Ar**H**); mass spectrum (70 eV) *m/e* (rel intensity) 302 (14.1, M$^+$·), 284 (3.0, M$^+$· – H_2O), 266 (10.9, M$^+$· – $2H_2O$), 251 (42.6, M$^+$· – $2H_2O$ and CH_3), 227 (15.5), 211 (16.5), 149 (100), 134 (58.1), 115 (33.7), 77 (27.3).

Anal. ($C_{18}H_{22}O_2S$) C, H, S.

1-Chloro-1-[2-(1-hydroxy-1-methylethyl)phenyl]-3,3-dimethyl[3*H*-2,1-benzoxathiole] (7). *tert*-Butyl hypochlorite (1.08 g, 10.0 mmol, 1.13 mL) was added slowly by syringe to a stirred solution of diol **6** (3.01 g, 10.0 mmol) in 50 mL of ether at 0 °C. After 15

min the white precipitate was filtered and washed with ether to give 2.94 g (87%) of 7. This material was recrystallized from CH_2Cl_2–hexane: mp 174.5–177 °C; IR ($CHCl_3$) 3390 (w, br, OH), 2968 (s), 1475 (m), 1443 (m), 1391 (w), 1372 (m), 1302 (w), 1245 (m), 1185 (w), 1152 (m), 1129 (w), 840 (s), 793 (m), 675 cm^{-1} (m); ^1H NMR (CD_2Cl_2) δ 1.86 (s, 6, CH_3), 1.94 (s, 6, CH_3), 7.34–7.75 (m, 6, ArH), 8.20 (br s, 2, ArH, protons ortho to S); mass spectrum (70 eV) *m/e* (rel intensity) no molecular ion, 300 (0.4, $M^+ \cdot$ – HCl), 285 (100, $M^+ \cdot$ – HCl and CH_3), 167 (20.6), 149 (14.1), 91 (10.3), 43 (18.3).

Anal. ($C_{18}H_{21}ClO_2S$) C, H, Cl, S.

3,3,3′,3′-Tetramethyl-1,1′-spiro[3*H*-2,1-benzoxathiole] (8). A sample of 4.08 g (12.1 mmol) of chlorosulfurane **7** was added to a mixture of ether and dilute aqueous KOH in a separatory funnel and shaken until no solid remained. The layers were separated, the ether layer was dried (Na_2SO_4), and the solvent was removed. The white solid remaining was recrystallized from ether–pentane to give 2.98 g (82%) of sulfurane **8**: mp 155–155.5 °C; IR (CCl_4) 2972 (s), 1467 (m), 1443 (s), 1376 (m), 1358 (s), 1287 (m), 1253 (m), 1160 (s), 1032 (m), 956 (s), 882 (s), 628 (s), 540 cm^{-1} (m); ^1H NMR (CD_2Cl_2) δ 1.53 (s, 6, CH_3), 1.63 (s, 6, CH_3), 7.10–7.58 (m, 6, ArH), 8.24–8.42 (m, 2, ArH, protons ortho to S); mass spectrum (70 eV) *m/e* (rel intensity) 300 (0.9, $M^+ \cdot$), 285 (100, $M^+ \cdot$ – CH_3), 167 (22.8), 149 (13.0), 135 (9.9), 43 (18.3).

Anal. ($C_{18}H_{20}O_2S$) C, H, S.

Bis[2-(hydroxymethyl)phenyl] Sulfide (9). Diester **5** (23.48 g, 0.071 mol), in 150 mL of dry ether, was added dropwise to a suspension of $LiAlH_4$ (5 g, 0.13 mol, excess) in 300 mL of dry ether under N_2. After 2 h of boiling, the mixture was carefully added to a dilute aqueous HCl–ice mixture. The ether layer was separated 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–hexane to give 17.13 g (98%) of diol **9**: mp 109–110 °C; IR ($CHCl_3$) 3630 (m, OH), 2940 (s), 1740 (w), 1470 (m), 1446 (m), 1389 (w), 1032 (m), 1010 (m), 795 (m), 670 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 2.10 (s, 2, OH), 4.76 (s, 4, CH_2), 7.05–7.64 (m, 8, ArH); mass spectrum (70 eV) *m/e* (rel intensity) 246 (100, $M^+ \cdot$), 228 (91.0, $M^+ \cdot$ – H_2O), 213 (61.0), 197 (52.9), 195 (94.6), 184 (31.3), 165 (33.8), 136 (52.5), 91 (47.8), 77 (67.3).

Anal. ($C_{14}H_{14}O_2S$) C, H, S.

1-Chloro-1-(2-hydroxymethyl)phenyl[3*H*-2,1-benzoxathiole] (10). *tert*-Butyl hypochlorite (0.55 g, 5.06 mmol, 0.547 mL) was added by syringe to a stirred solution of diol **9** (1.245 g, 5.06 mmol) in 30 mL of dry THF at 0 °C. After 15 min of stirring the precipitate was filtered, washed with ether, and dried (vacuum) to give 1.01 g (71%) of chlorosulfurane **10**: mp 90–92 °C; IR (KBr) 3430 (s, br, OH), 3140–2800 (s), 1464 (m), 1446 (m), 1218 (m), 1205 (m), 1032 (m), 931 (s), 769 (s), 730 (m), 548 cm^{-1} (m); mass spectrum (70 eV) *m/e* (rel intensity) no molecular ion, 244 (23.4, $M^+ \cdot$ – HCl), 243 (100, $M^+ \cdot$ – HCl and H), 215 (50.6), 197 (96.5), 184 (44.1), 137 (91.8), 109 (47.2), 91 (27.3), 77 (32.9).

Anal. ($C_{14}H_{13}ClO_2S$) C, H, Cl, S.

1,1′-Spiro[3*H*-2,1-benzoxathiole] (11). Method A. Triethylamine (1.89 g, 18.7 mmol) was added to a stirred suspension of 5.29 g (18.7 mmol) of chlorosulfurane **10** in 250 mL of dry ether in an inert atmosphere box. After stirring for 5 days at 25 °C, the mixture was filtered and the filtrate was cooled to −78 °C. After 3 h the deposited crystals were filtered and washed with ether to give 1.18 g (26%) of sulfurane **11**: mp 158–161 °C (sealed tube); IR ($CHCl_3$) 3015 (s), 2853 (m), 1470 (m), 1452 (m), 1258 (w), 1141 (s), 652 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 5.100 and 5.195 (AB pattern, 4, CH_2, J = 14 Hz), 7.14–7.50 (m, 6, ArH), 7.95–8.14 (m, 2, ArH, protons ortho to S); mass spectrum (70 eV) *m/e* (rel intensity) 244 (30.4, $M^+ \cdot$), 243 (100, $M^+ \cdot$ – H), 226 (22.7, $M^+ \cdot$ – H_2O), 215 (48.1), 197 (99.1, $M^+ \cdot$ – CH_3O_2), 184 (28.9), 165 (23.0), 237 (82.0), 109 (39.1), 91 (20.9), 77 (27.9).

Anal. ($C_{14}H_{12}O_2S$) C, H, S.

Method B. About 1 g (~0.025 mol) of potassium hydride was added to a mixture of 3.88 g (0.0138 mol) of chlorosulfurane **10** in 150 mL of dry THF in an inert atmosphere box. Hydrogen evolution occurred, and after 1 h the mixture was filtered. The solvent was removed leaving yellowish crystalline 11, 2.33 g (69%).

2-Bromo-2′-carboxydiphenyl Sulfide. 2-Bromothiophenol[19] (28.7 g, 0.152 mol) and 2-iodobenzoic acid (37.7 g, 0.152 mol) were dissolved in 300 mL of water containing about 20 g of potassium hydroxide and 0.5 g of copper bronze. The solution was boiled 8 h and filtered while hot. After cooling to 25 °C, the solution was acidified with concentrated HCl. The precipitate was filtered, washed with water and air dried to give 45.0 g (95.8%) of the acid: mp 184–185 °C; IR (KBr) 3440 (s, OH), 3000 (s, br), 1682 (s, C=O), 1587 (w), 1560 (w), 1462 (m), 1416 (m), 1312 (m), 1290 (m), 1270 (s), 1258 (s), 1149 (m), 1056 (m), 1040 (m), 1020 (m), 750 cm^{-1} (s); ^1H NMR (Me_2SO-d_6) δ 6.60–6.83 (m, 1, ArH), 7.10–8.10 (m, 7, ArH), 13.1 (br s, 1, OH); mass spectrum (70 eV) *m/e* (rel intensity) 310 (71.4, $M^+ \cdot$ ^{81}Br), 308 (69.6, $M^+ \cdot$ ^{79}Br) 229 (45.6, $M^+ \cdot$ – Br), 212 (10.2, $M^+ \cdot$ – Br and OH), 185 (22.6), 184 (55.2), 183 (20.8), 139 (22.2), 137 (100), 136 (32.0), 108 (20.4), 69 (12.7).

Anal. ($C_{13}H_9BrO_2S$) C, H, Br, S.

2-Bromo-2′-carboxydiphenyl Sulfide Ethyl Ester (12). 2-Bromo-2′-carboxydiphenyl sulfide (34 g, 0.11 mol) was dissolved in excess thionyl chloride and refluxed for 5.5 h. The excess $SOCl_2$ was removed in vacuum, leaving a red solid. The solid acid chloride was dissolved in benzene and added to a solution of EtOH and pyridine. After a few minutes of swirling, the mixture was stripped of solvent and the residue was dissolved in ether and extracted with dilute aqueous HCl, dilute aqueous NaOH, and water. The ether layer was dried ($MgSO_4$) and ether removed, leaving an amber oil which crystallized after 1 day: 32.3 g (87%); mp 59–63 °C; ^1H NMR ($CDCl_3$) δ 1.30 (t, 3, CH_3), 4.37 (q, 2, CH_2), 6.75–7.15 (m, 8, ArH); mass spectrum (70 eV) *m/e* (rel intensity) 338 (82.3, M^+.^{81}Br), 336 (79.1, M^+.^{79}Br), 293 (9.8, M^+.^{81}Br – OEt), 291 (10.5, M^+.^{79}Br – OEt) 257 (32.3, $M^+ \cdot$ – Br) 229 (100), 212 (70.8, $M^+ \cdot$ – OEt and Br), 184 (84.8), 139 (32.6), 137 (32.7), 108 (21.9).

Anal. ($C_{15}H_{13}BrO_2S$) C, H, Br, S.

2-Bromo-2′-(1-hydroxy-1-methylethyl)diphenyl Sulfide (13). Ester **12** (15.8 g, 0.047 mol) was dissolved in 150 mL of dry ether and added dropwise to a stirred solution of 50 mL of 2.86 M CH_3MgBr in ether (0.14 mol) to maintain gentle reflux. After this addition, the solution was stirred for 30 min at room temperature, and then quenched with saturated aqueous NH_4Cl. The ether layer was extracted with aqueous HCl and water and dried ($MgSO_4$), and ether was removed to give 13.7 g (90.4%) of **13** as a light yellow viscous oil: IR (neat) 3450 (s, OH), 3100–2900 (s), 1580 (s), 1450 (s), 1360 (s), 1250 (s), 1170 (s), 1140 (s), 1110 (s), 1050 (s), 1043 (s), 1023 (s), 955 (s), 860 (s), 755 (s), 710 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.71 (s, 6, CH_3), 3.36 (br s, 1, OH), 6.76–7.83 (m, 8, ArH); mass spectrum (70 eV) *m/e* (rel intensity) 324 (63.4, M^+.^{81}Br), 322 (63.9, M^+.^{79}Br), 309 (50.6, M^+.–^{81}Br – CH_3), 307 (50.0, M^+.^{79}Br – CH_3), 228 (29.0, $M^+ \cdot$ – Br and CH_3), 213 (27.8, $M^+ \cdot$ – Br and $2CH_3$), 210 (42.8), 185 (11.3), 184 (22.3), 151 (100), 149 (12.6), 108 (15.6), 59 (17.2), 43 (63.1).

Anal. ($C_{15}H_{15}BrOS$), C, H, Br, S.

2-(1-Hydroxy-1-methylethyl)-2′-(1-hydroxy-1-trifluoromethyl-2,2,2-trifluoroethyl)diphenyl Sulfide (14). Bromo alcohol **13** (4.52 g, 13.98 mmol), in 150 mL of dry ether in a flask equipped with a dry ice condenser, was cooled to 0 °C, 15 mL of *n*-butyllithium in hexane (ca. 2.1 M, 31.5 mmol, slight excess) was added by syringe, and the solution was stirred for 0.5 h at 25 °C. Hexafluoroacetone was bubbled in (7 mL, 9.8 g, excess), and the mixture was stirred for 10 min and added to a saturated NH_4Cl ice–water solution. Ether was added and the mixture was shaken. The ether layer was washed with water and dried ($MgSO_4$) and solvent was removed, leaving 6.25 g of red oil. The oil was chromatographed on a column of silica gel (50-cm long, 4.5-cm diameter) using chloroform as eluent. The fraction containing diol **14** (2.18 g) was rechromatographed on another silica gel column (26 × 3 cm) using 1:1 ether–hexane as eluent and again on a 2-in. column of silica gel containing activated charcoal with 1:1 ether–hexane: 1.844 g (32.1%) of light yellow solid; mp 99.5–103 °C; IR ($CHCl_3$) 3600 (w, free OH), 3250 (m, hydrogen bonded OH), 3000 (w), 1472 (w), 1437 (w), 1387 (w), 1370 (w), 1300–1170 (four or five strong bands, CF_3 stretch), 1152 (m), 1114 (m), 1040 (w), 965 (m), 952 (m), 931 (m), 715 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 1.78 (s, 6, CH_3), 2.76 (s, 1, disappears with D_2O shake, OH), 6.90–7.66 (m, 7, ArH), 7.80 (br, 1, ArH, proton ortho to carbon bearing $2CF_3$), 7.92 (s, 1, disappears with D_2O shake, OH); ^{19}F NMR ($CDCl_3$) ϕ 74.52 (s, 6, CF_3); mass spectrum (70 eV) *m/e* (rel intensity) 410 (46.6, $M^+ \cdot$), 395 (32.7 $M^+ \cdot$ – CH_3), 377 (6.4, $M^+ \cdot$ – CH_3 and H_2), 210 (20.0), 151 (49.0), 149 (27.3), 128 (9.4), 59 (10.4), 43 (100).

Anal. ($C_{18}H_{16}F_6O_2S$) C, H, F, S.

Another method used to prepare **14** using activated magnesium[20] resulted in purer material, but yields were quite variable.

3,3-Bis(trifluoromethyl)-3′,3′-dimethyl-1,1′-spiro[3*H*-2,1-benzoxathiole] (15). Diol **14** (1.70 g, 4.1 mmol) was dissolved in 50 mL of ether and cooled to 0 °C. *tert*-Butyl hypochlorite (0.45 g, 0.47 mL, 4.1 mmol) was added dropwise with stirring. A very small amount of white precipitate was noted. After 1 h, the ether solution was extracted with dilute aqueous NaOH and dried ($MgSO_4$), and solvent was removed to give a white solid. The crude product was recrystallized from CH_2Cl_2–ether–hexane to give 1.1 g (65.6%) of white, crystalline sulfurane **15**: mp 167.5–168.5 °C; IR ($CDCl_3$) 3000 (w), 1470 (w), 1448 (w), 1296 (m), 1267 (m), 1210 (s), 1167 (m), 1150 (s), 1131 (m), 1054 (w), 970 (m), 954 (m), 877 (w), 660 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.65 (s, 3, CH_3), 1.83 (s, 3, CH_3), 7.23–8.00 (m, 6, ArH), 8.27–8.67 (m, 2, ArH, protons ortho to S); mass spectrum (70 eV) *m/e*

(rel intensity) 408 (0.5, $M^{+}\cdot$), 393 (100, $M^{+}\cdot - CH_3$), 339 (16.2, $M^{+}\cdot - CF_3$), 213 (6.0), 212 (4.9), 205 (8.6), 184 (7.2), 151 (12.7), 149 (11.4), 91 (12.3), 43 (23.7).

Anal. ($C_{18}H_{14}F_6O_2S$) C, H, F, S.

2-(1-Hydroxy-1-methylethyl)-2′-(1-hydroxy-1-methylpropyl)diphenyl Sulfide (16). Bromo alcohol **13** (10.7 g, 33.1 mmol) in 200 mL of dry ether was cooled to 0 °C and 45 mL of *n*-butyllithium in hexane (ca. 2.1 M, 94.5 mmol, excess) was added by syringe. After stirring the mixture at 25 °C for 0.75 h, methyl ethyl ketone (10 mL, excess) was added. The mixture was stirred for 15 min and added to a saturated NH_4Cl ice–water solution. An ether extract was washed with water and dried ($MgSO_4$), and solvent was removed to give 15.04 g of yellow liquid. This was chromatographed on a column of silica gel (96-cm long by 3-cm diameter) using chloroform as eluent. The fraction of diol **16** (4.38 g) was treated with activated charcoal and passed through a short column of silica gel containing some activated charcoal to give a light yellow oil: 4.02 g (38.4%); ^1H NMR ($CDCl_3$) δ 0.85 (t, 3, CH_2CH_3), 1.73 (s, 3, CH_3), 1.78 (s, 6, CH_3), 2.00 (m, 2, CH_2), 3.45 (br s, 2, OH, disappears with D_2O shake), 7.10–7.45 (m, 6, ArH), 7.45–7.80 (m, 2, ArH); mass spectrum (70 eV) *m/e* (rel intensity) 316 (6.7, $M^{+}\cdot$), 283 (1.0, $M^{+}\cdot - H_2O$ and CH_3), 269 (4.6, $M^{+}\cdot - H_2O$ and CH_2CH_3), 251 (2.4), 227 (6.9), 211 (4.0), 155 (6.4), 151 (12.4), 127 (10.3), 115 (30.0), 57 (100), 43 (53.6).

Anal. ($C_{19}H_{24}O_2S$) C, H, S.

The Exo and Endo Isomers of 3,3,3′-Trimethyl-3′-ethyl-1,1′-spiro[3*H*-2,1-benzoxathiole] (17a, 17b). *tert*-Butyl hypochlorite (1.36 mL, 1.30 g, 12.0 mmol) was added by syringe to a solution of diol **16** (3.79 g, 11.98 mmol) in 200 mL of dry ether at 25 °C. A yellow precipitate was filtered and washed with ether. The yellow solid was suspended in 75 mL of ether and shaken with dilute aqueous NaOH until the solid dissolved. The ether layer was separated and dried ($MgSO_4$) and solvent was evaporated leaving a light yellow oil which slowly solidified after a few days. Analysis by ^1H NMR showed a 50:50 mixture of exo and endo isomers of sulfurane **17** (2.64 g, 70.1%). All attempts to recrystallize this material failed. Analysis by TLC showed some impurities, so a sample of 2.23 g of the mixture was chromatographed on a column of 117 g of Woelm neutral alumina, activity grade 1, using 1:1 (v/v) ether–hexane. The first fraction (0.36 g) was a 83/17 mixture of exo and endo isomers. A sample of this mixture (280 mg) was recrystallized from hexane at −20 °C. A total of 211 mg of an 89/11 mixture of exo and endo isomers was isolated: mp 83–85 °C; IR (CCl_4) 3118 (w), 3065 (w), 2975 (s), 2925 (m), 1466 (m), 1441 (m), 1375 (m), 1365 (w), 1356 (m), 1286 (w), 1251 (w), 1159 (s), 1030 (m), 961 (m), 920 (m), 882 (m), 624 cm^{-1} (s); ^1H NMR (220 MHz, pyridine-d_5) **17a** (exo), δ 0.794 (t, 3, CH_2CH_3, J = 7.3 Hz), 1.606 (s, 3, *exo*-CH_3), 1.682 (s, 6, *endo*-CH_3), 1.72–2.05 (m, 2, CH_2CH_3), 7.11–7.57 (m, 6, ArH), 8.55–8.73 (m, 2, ArH, protons ortho to S); **17b** (endo), δ 1.138 (t, 3, CH_2CH_3, J = 7.3 Hz), 1.522 (s, 3, *exo*-CH_3 on same carbon as C_2H_5), 1.606 (s, 3, other *exo*-CH_3), 1.70 (s, 3, *endo*-CH_3), other peaks were obscured by those of the major isomer; mass spectrum (70 eV) *m/e* (rel intensity), no molecular ion, 299 (30.3 $M^{+}\cdot - CH_3$), 285 (100, $M^{+}\cdot - CH_2CH_3$), 167 (25.1), 151 (11.8), 149 (10.0), 135 (11.6), 91 (9.3).

Anal. ($C_{19}H_{22}O_2S$) C, H, S.

Further elution with 1:1 (v/v) ether–hexane failed to give any more product. Elution with methanol was necessary to obtain the remaining material (1.77 g). ^1H NMR analysis of this material in $CDCl_3$ showed it to be 50% sulfurane (79% exo, 21% endo) and 50% sulfoxide diol. Hydrolysis had occurred on the column and partial cyclodehydration of the diol in $CDCl_3$.

Interactions of Spirosulfuranes 8 and 15 with Optically Active Solvent. To a solution of 19.4 mg (0.065 mmol) of sulfurane **8** in 0.5 mL of carbon tetrachloride (0.13 M) was added 45.0 mg (0.255 mmol, 0.51 M) of L(−)-2,2,2-trifluoro-1-phenylethanol.[21] The 220-MHz ^1H NMR spectrum showed four resolved methyl singlets at δ 1.460, 1.486, 1.572, and 1.596. Also, the two protons ortho to sulfur, which are normally seen as one doublet, were resolved into two doublets (δ 8.12, 8.19) in the presence of the chiral solvent. To a solution of 25.7 mg (0.063 mmol) of sulfurane **15** in 0.5 mL of carbon tetrachloride (0.126 M) was added 45.9 mg (0.261 mmol, 0.52 M) of L(−)-2,2,2-trifluoro-1-phenylethanol.[21] The 220-MHz ^1H NMR spectrum showed four resolved methyl singlets at δ 1.568, 1.592, 1.760, and 1.774.

Hydrolysis of Sulfurane 8 to Sulfoxide Diol 18. Sulfurane **8** (1.01 g, 3.37 mmol) was boiled in 11 mL of 10:1 methanol–water solution for 2 h. The solvent was removed in vacuum leaving a clear semisolid which was dissolved in ether. Evaporation of the ether afforded 0.953 g (89%) of crystalline sulfoxide diol **18**: mp 139–144 °C; IR ($CHCl_3$) 3380 (m, OH), 3000 (s), 1472 (w), 1437 (w), 1388 (w), 1370 (m), 1245 (w), 1184 (w), 1110 (w), 1056 (w), 998 (m), 965 (m), 588 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 1.38 (s, 6, CH_3), 1.70 (s, 6, CH_3), 4.78 (br s, 2, OH), 7.01–7.75 (m, 8, ArH); mass spectrum (70 eV) *m/e* (rel intensity) 318 (6.0, $M^{+}\cdot$), 303 (10.1, $M^{+}\cdot - CH_3$), 300 (0.3, $M^{+}\cdot - H_2O$), 285 (100, $M^{+}\cdot - H_2O$ and CH_3), 167 (27.8), 151 (21.9), 149 (54.4), 135 (22.2), 91 (14.0), 43 (37.3).

Anal. ($C_{18}H_{22}O_3S$) C, H, S.

Sulfurane **18** (47 mg, 0.156 mmol) was dissolved in 0.5 mL of dry $CDCl_3$ to which was added 10 μL (0.55 mmol) of deuterium oxide. After 7.5 h at 25 °C less than 5% hydrolysis to **18** was noted. After 13 days at 25 °C, 25% hydrolysis to **18** had occurred.

Hydrolysis of Dibenzyloxysulfurane 11. To a solution of sulfurane **11** (36.3 mg, 0.149 mmol) in 0.5 mL of dry chloroform-*d* was added 10 μL (0.55 mmol) of deuterium oxide. ^1H NMR analysis showed that **11** was 94% hydrolyzed to sulfoxide diol **19** after 3.6 h at 25 °C and that hydrolysis was essentially complete after 7.1 h at 25 °C.

Bis[2-(hydroxymethyl)phenyl] Sulfoxide (19). A solution of 2.32 g of 85% *m*-chloroperbenzoic acid (MCPBA) (11.4 mmol) in 50 mL of $CHCl_3$ was added dropwise to a solution of sulfide diol **9** (2.81 g, 11.4 mmol) in 150 mL of $CHCl_3$ at 0 °C. After stirring at 25 °C for 36 h the $CHCl_3$ solution was extracted with aqueous $NaHCO_3$ and dried (Na_2SO_4), and solvent was removed to afford a light yellow oil which crystallized after 10 min leaving 2.1 g (70%) of sulfoxide **19**: mp 128–129 °C; IR (KBr) 3280 (s br, OH), 3065 (s), 2930 (s), 1470 (s), 1455 (s), 1444 (s), 1370 (s), 1217 (m), 1202 (s), 1166 (m), 1067 (m), 1050 (s), 1041 (s), 1031 (s), 994 (s), 820 (m), 766 (s), 608 (m), 542 (s), 529 (m), 454 cm^{-1} (m); ^1H NMR (CF_3COOH) δ 5.75 (s, 4, CH_2), 7.46–8.04 (m, 8, ArH); mass spectrum (70 eV) *m/e* (rel intensity), no molecular ion, 244 (3.8 $M^{+}\cdot - H_2O$), 197 (100), 165 (13.3), 138 (18.0), 137 (19.9), 109 (24.6), 91 (8.9), 77 (48.5).

Anal. ($C_{14}H_{14}O_3S$) C, H, S.

Attempted Hydrolysis of Spirosulfurane 15. Method A. A sample of spirosulfurane **15** (166 mg, 0.41 mmol) was added to 5 mL of 10% aqueous methanol and boiled for 4.75 h. Upon cooling, crystals of **15** (134 mg, 72.3%) were deposited.

Method B. Spirosulfurane **15** (149 mg, 0.36 mmol) was dissolved in 1 mL of tetrahydrofuran-d_8 containing 10 μL of water. Boiling for 0.5 h caused no change in the ^1H NMR spectrum. Concentrated HCl (10 μL) was added and the solution was boiled 1 h more. No change in the ^1H NMR spectrum was noted. Addition of 0.85 mL of 50% aqueous KOH rendered the solution basic. Boiling of this solution for 1 h caused no change in the ^1H NMR spectrum.

Reactions of Sulfurane 8 with Acids. (a) Hydrochloric Acid. Sulfurane **8** (0.702 g, 2.34 mmol), in 20 mL of CH_2Cl_2, was shaken with 10 mL of concentrated aqueous HCl. The organic layer was dried ($MgSO_4$) and solvent was removed. The product was recrystallized from CH_2Cl_2–hexane to give 0.60 g (76.5%) of chlorosulfurane **7**: mp 173.5–176 °C.

(b) Hydrobromic Acid. A comparable experiment using 16% aqueous HBr gave 72.8% of bromosulfurane **21**: mp 169.5–170.5 °C; IR ($CHCl_3$) 3400 (w), 2960 (s, br), 1472 (m), 1441 (m), 1389 (m), 1370 (m), 1239 (m), 1150 (m), 1125 (m), 835 (s), 665 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.97 (s, 6, CH_3), 2.05 (s, 6, CH_3), 7.45–8.00 (m, 6, ArH), 8.00–8.41 (m, 2, ArH, protons ortho to S).

Anal. ($C_{18}H_{21}BrO_2S$) C, H, Br, S.

(c) Fluoroboric Acid. A comparable procedure using 25% aqueous fluoroboric acid gave, after recrystallization from CH_2Cl_2–hexane, 81.6% of sulfonium salt **22a**: mp 197–199 °C; IR ($CHCl_3$) 3350 (m, OH), 3040 (m), 2990 (m), 1475 (m), 1445 (m), 1370 (m), 1150 (m), 1055 (s, B–F stretch), 835 (s), 670 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 1.87 (s, 6, CH_3), 2.01 (s, 6, CH_3), 6.67 (br s, 1, OH), 7.38–7.90 (m, 6, ArH), 7.90–8.30 (m, 2, ArH, protons ortho to S).

Anal. ($C_{18}H_{21}BF_4O_2S$) C, H, S.

(d) *d*-10-Camphorsulfonic Acid. Methylene chloride solutions of **8** (1.84 g, 6.13 mmol) and *d*-10-camphorsulfonic acid (1.42 g, 6.13 mmol) were combined and stirred for 15 min. Solvent removal left a thick clear oil which crystallized after 9 days. Recrystallization from CH_2Cl_2–ether–hexane gave 2.2 g (68%) of sulfonium salt **22c**: mp 166–168 °C; IR ($CHCl_3$) 3020 (s), 1746 (s), 1448 (w), 1375 (w), 1320–1100 (s), 1038 (s), 843 (s), 675 cm^{-1} (m).

Anal. ($C_{28}H_{36}O_6S_2$) C, H, S.

After two recrystallizations, the material was checked for any change in the optical activity compared to the unrecrystallized material. No change was detectable.

(e) Trifluoromethanesulfonic (Triflic) Acid. Triflic acid (0.50 g, 3.33 mmol, 0.294 mL), added by syringe to a solution of sulfurane **8** (1.0 g, 3.33 mmol) in 90 mL of ether at 0 °C, immediately gave a white precipitate. After overnight stirring at 25 °C, the solid was filtered, washed with ether, and air dried to give 1.486 g (99%) of sulfonium salt **22b**: mp 166–169 °C; IR ($CHCl_3$) 3130 (m), 3020 (m), 1376 (m), 1300 (s), 1253 (s), 1180 (s), 1033 (s), 839 (s), 640 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.70–2.20 (singlet and broad singlet overlapping, 12, CH_3),

7.30–7.90 (m, 8, ArH), 8.25 (br s, 1, OH); mass spectrum (70 eV) *m/e* (rel intensity) no molecular ion, 302 (3.7), 301 (1.3, $M^{+\cdot}$ – OTf), 285 (100, $M^{+\cdot}$ – HOTf and CH_3), 265 (39.5), 249 (27.2, 167 (24.4), 149 (64.0), 115 (25.5), 91 (20.7), 77 (12.2), 69 (82.1).

Anal. ($C_{19}H_{21}F_3O_5S_2$) C, H, S.

(f) Acetic Acid. TO SULFURANE — (121 mg, 0.403 mmol), in 0.5 mL of dry $CDCl_3$, was added 23 μL (24.2 mg, 0.403 mmol) of glacial acetic acid. No changes in the ^1H NMR spectrum of **8** were noted after 20 h at 25 °C.

Low-Temperature ^1H NMR Studies on Chlorosulfurane 7. Low-temperature 100-MHz ^1H NMR studies on chlorosulfurane **7** were carried out in CD_2Cl_2 solution from 28 to −95 °C. At 28 °C, six aromatic protons were seen as a multiplet at δ 7.34–7.75 and the two ortho protons to sulfur were seen as a broad singlet at δ 8.20. On cooling, continued broadening of the peak at δ 8.20 occurred. At −95 °C, one ortho proton was seen as a doublet at δ 8.55 and the other became a part of the aromatic multiplet (δ 7.3–8.2) which integrated for seven protons. A new singlet was observed at δ 10.33 which is assigned to the hydroxyl proton, hydrogen bonded to the chlorine atom. The methyl groups of **7** at 28 °C were seen as two singlets. On cooling, one of them broadened more rapidly than the other one. At −95 °C only a single broad peak at δ 1.92 was seen whose width at half-height was 0.5 ppm. Throughout the study, the sample remained homogeneous.

Reaction of Chlorosulfurane 7 with Diazasulfurane 24. Samples of **7** (97.5 mg, 0.29 mmol) and **24** (103.5 g, 0.29 mmol) were dissolved in ca. 1.5 mL of dry $CDCl_3$ at 25 °C. Subsequent ^1H NMR analysis showed the presence of sulfurane **8** and chloroazasulfurane **23**.

Reaction of Sulfurane 8 with Methyl Fluorosulfonate. Methyl fluorosulfonate (0.565 g, 4.95 mmol, 0.4 mL) was added by a syringe to a solution of sulfurane **8** (0.909 g, 3.03 mmol) in 80 mL of ether. After stirring at 25 °C for 11 h the precipitate was filtered, washed with ether, and air dried. A yield of 0.924 g (74%) of monocyclic sulfonium fluorosulfonate **25** was obtained: mp 153–154 °C; IR ($CHCl_3$) 3040 (s), 1469 (m), 1450 (m), 1395 (m), 1377 (m), 1293 (s), 1152 (m), 1134 (m), 1073 (s), 1057 (m), 942 (m), 840 (s), 588 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.78 (s, 3, CH_3), 1.87 (s, 3, CH_3), 1.98 (s, 3, CH_3), 2.17 (s, 3, CH_3), 3.73 (s, 3, OCH_3), 7.30–8.05 (m, 8, ArH); mass spectrum (70 eV) *m/e* (rel intensity) no molecular ion, 315 (1.2, $M^{+\cdot}$ – O_3SF), 314 (6.1, $M^{+\cdot}$ – HO_3SF), 265 (89.2), 211 (22.7), 165 (14.0), 149 (100), 134 (45.6), 115 (47.9), 91 (43.3), 77 (19.6).

Anal. ($C_{19}H_{23}FO_5S_2$) C, H, S.

Reactions of Spirosulfurane 8 and 15 with Acetyl Chloride. To a sample of sulfurane **8** (346.5 mg, 1.15 mmol) dissolved in 1 mL of dry $CDCl_3$ was added 82 μL (1.15 mmol) of acetyl chloride. The reaction was complete within 3.5 h at 25 °C (^1H NMR). The chlorosulfurane **26** was crystallized from a $CDCl_3$–CH_2Cl_2–ether–hexane solvent mixture: 344.7 mg (79%); mp 129–132 °C; IR ($CHCl_3$) 3380 (w, OH, slight hydrolysis), 2960 (s), 1742 (s, C=O), 1470 (m), 1443 (m), 1288 (m), 1370 (s), 1243 (s), 1150 (s), 1120 (s), 1018 (m), 935 (m), 836 (s), 666 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.23 (s, 3, CH_3), 1.73 (s, 3, CH_3), 2.06 (s, 3, CH_3), 2.20 (s, 3, acetyl CH_3), 2.26 (s, 3, CH_3), 6.73 (d, 1, ArH, J = 8 Hz), 7.13 (m, 1, ArH), 7.45–8.00 (m, 5, ArH), 9.54 (d, 1, proton ortho to S on the fused ring, J = 8 Hz).

Anal. ($C_{20}H_{23}ClO_3S$) C, H, Cl, S.

To a sample of sulfurane **18** (78.5 mg, 0.192 mmol) dissolved in 1 mL of dry $CDCl_3$ was added 14 μL (0.197 mmol) of acetyl chloride. After 21.5 h at 25 °C, ^1H NMR analysis showed that no reaction had taken place.

Attempted Reaction of Spirosulfurane 8 and Benzoyl Fluoride. Sulfurane **8** (190.7 mg, 0.634 mmol) and benzoyl fluoride (78.9 mg, 0.635 mmol) were combined in 1.1 mL of dry $CDCl_3$ at 25 °C. After 80 h no change in the ^1H NMR spectrum was evident. After 19 days at 25 °C a few small peaks in the aliphatic region were seen (7% of total aliphatic integral). A catalytic amount of BF_3 was added, but even after 24 h at 25 °C no further change in the ^1H NMR spectrum was noted.

Reduction of Sulfurane 8 to Sulfide Diol 6. (a) With Lithium Aluminum Hydride. Sulfurane **8** (1.065 g, 3.54 mmol), in 25 mL of dry THF, was added dropwise to a solution of excess $LiAlH_4$ in 25 mL of THF under N_2. The solution was boiled for 2 h and added to an ice–water mixture. The THF was removed in vacuum and the aqueous layer was extracted with ether three times. The ether layer was dried ($MgSO_4$) and solvent was removed to give sulfide diol **6**, an oil which crystallized after 24 h: 0.98 g (91.5%).

(b) With Hydriodic Acid. Sulfurane **8** (1.13 g, 3.76 mmol), in 20 mL of methylene chloride, was shaken with 30 mL of 19% aqueous HI. Almost immediately the mixture became very dark red (I_2). The CH_2Cl_2 layer was extracted with aqueous sodium thiosulfate and dried ($MgSO_4$), and solvent was removed, which left a solid mixture of sulfide diol **6** (68%) and sulfurane **8** (32%) (^1H NMR analysis).

Interaction of Spirosulfuranes with Eu(fod)$_3$.[22] (a) Sulfurane 8 (22.2 mg, 0.074 mmol) in 1.0 mL of CCl_4 (0.074 M) was examined by ^1H NMR before and after successive additions of $Eu(fod)_3$ until the concentration of $Eu(fod)_3$ reached 0.073 M. Relative concentrations were determined through comparison of the integrals of the *tert*-butyl groups of $Eu(fod)_3$ and the methyl resonances of sulfurane **8**. The *exo*-methyls (δ 1.51) shift rapidly downfield (82.4 ppm/M), with a linear dependence of $Eu(fod)_3$ concentration, with much peak broadening. The *endo*-methyls shift downfield more slowly (32.4 ppm/M) with less peak broadening. At a $Eu(fod)_3$ concentration of 0.026 M, the aromatic protons were resolved into two triplets at δ 7.24 and 7.58 and two doublets at δ 7.87 and 9.06. The doublet at δ 9.06 represents the two protons ortho to sulfur.

In a parallel experiment at a higher initial concentration of **8** (0.26 M), at concentrations of $Eu(fod)_3$ up to 0.22 M significantly smaller concentration dependence of chemical shifts were seen for the *exo*-methyls (23.0 ppm/M) and the *endo*-methyls (9.3 ppm/M), evidence for a large formation constant for the $Eu(fod)_3$ complex. In this experiment, the protons ortho to sulfur shifted downfield at a rate of 7.1 ppm/M.

(b) Sulfurane 15 (30.1 mg, 0.074 mmol) in 1.0 mL of CCl_4 (0.074 M) was examined in the same way with increments of $Eu(fod)_3$ up to a concentration of 0.069 M. The interaction of **15** with $Eu(fod)_3$ is much weaker than with sulfurane **8**, as evidenced by smaller downfield shifts for the methyl singlets at δ 1.60 (3.92 ppm/M) and 1.76 (.378 ppm/M) as $Eu(fod)_3$ concentration was increased.

(c) Diastereomeric Sulfuranes 17 (40.8 mg, 0.13 mmol, 86/14 mixture of **17a** and **17b**) in 0.5 mL of CCl_4 (0.26 M total) was examined as above at $Eu(fod)_3$ concentrations up to 0.193 M. Downfield shifts for the *exo*-methyl at δ 1.51 (36.1 ppm/M) and the two *endo*-methyls at δ 1.60 (14.5 and 5.5 ppm/M) were assigned to the major isomer (**17a**), along with the peak for the two ortho protons of **17a**, at δ 8.31 (10.7 and 2.7 ppm/M).

The ortho protons of **17b** were located between the ortho protons of **17a**. The peaks were too indistinct after broadening by $Eu(fod)_3$ to allow a similar study to be performed for the minor isomer **17b**.

Interaction of Sulfurane 8 Simultaneously with Chiral Alcohol and Eu(fod)$_3$. Sulfurane **8** (30 mg, 0.10 mmol) and (*S*)-(+)-2,2,2-trifluoro-9-(anthryl)ethanol[23] (82.5 mg, 0.30 mmol) in 0.5 mL of CCl_4 (0.2 M in **8**, 0.6 M in carbinol) was examined as above with incremental addition of $Eu(fod)_3$ to a final concentration of 0.16 M. Initially, only one of the methyl peaks split into two peaks (δ 1.18, 1.34) and during addition of $Eu(fod)_3$ the peak (δ 1.23) that was unsplit broadened and moved rapidly downfield. Hence, this peak was assigned to the *exo*-methyls by comparing the results of the interaction of **8** with $Eu(fod)_3$ only. The other singlet that was split into two singlets moved downfield more slowly. The separation of the two singlets stayed nearly the same. Only when the molar ratio reached about 0.53 did a small change occur.

Pyrolyses of Spirosulfuranes 8, 11, and 15. Sulfurane **8** (0.695 g, 2.31 mm) was heated to 205 °C for 20 min leaving an amber oil. This oil was dissolved in CH_2Cl_2, the solution was dried ($MgSO_4$), and solvent was removed to give 0.464 g (71.3%) of sulfoxide–diolefin **27**: IR (neat) 3040–2900 (s), 1825 (w), 1640 (s), 1585 (s), 1465 (s), 1425 (s), 1370 (s), 1300 (m), 1245 (m), 1160 (w), 1110 (s), 1065 (s), 1030 (s), 907 (s), 765 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.90 (m, 6, CH_3), 5.01 (m, 2, vinyl CH), 5.16 (m, 2, vinyl CH), 7.00–7.90 (m, 8, ArH); mass spectrum (70 eV) *m/e* (rel intensity) 282 (0.9, $M^{+\cdot}$), 266 (25.5), 265 (64.4), 264 (11.5), 251 (16.4), 249 (20.4), 234 (15.2), 210 (15.5), 151 (23.0), 149 (100), 147 (30.4), 134 (39.2), 115 (34.9), 91 (28.2), 77 (12.7).

Anal. ($C_{18}H_{18}OS$) C, H, S.

Spirosulfurane **11** (138.7 mg, 0.57 mmol) was heated to 180 °C for 10 min. Analysis by ^1H NMR showed that fragmentation to *o*-arylthiobenzaldehyde **28** was 90% complete. Chromatography on a short column of silica gel (5 g) with chloroform gave 83 mg (60%) of sulfide **28** as a light yellow oil: IR ($CHCl_3$) 3620 (w, OH), 2860 (w, aldehyde CH), 2755 (w, aldehyde CH), 1697 (s, C=O); ^1H NMR ($CDCl_3$) δ 2.36 (br s, 1, OH), 4.72 (s, 2, CH_2), 6.70–6.95 (m, 1, ArH), 7.10–7.65 (m, 6, ArH), 7.70–7.90 (m, 1, ArH), 10.24 (s, 1, aldehyde CH); mass spectrum (70 eV) *m/e* (rel intensity) 244 (4.9, $M^{+\cdot}$), 226 (5.7, $M^{+\cdot}$ – H_2O), 197 (31.3, $M^{+\cdot}$ – CH_3O_2), 85 (66.4), 83 (100), 47 (20.4). After 3 days, ^1H NMR analysis showed that a new compound was forming, possibly the dibenzyl ether. Also, infrared analysis showed another carbonyl absorption at 1681 cm^{-1}.

Two samples (76 mg and 36.3 mg) of spirosulfurane **15** were heated to 205 °C for 20 min and to 295 °C for 10 min, respectively. ^1H NMR analysis showed that no reaction had occurred in either procedure. Another sample (23 mg), heated to 355 °C for 15 min, gave a nearly

black product whose ^1H NMR in $CDCl_3$ showed that the sulfurane was completely gone. There were characteristic peaks for the 2-propenyl group and other unidentified peaks were seen. The ^{19}F NMR showed no quartets but showed a series of singlets or doublets near ϕ 74.7. No products were isolated from this reaction.

Reaction of Sulfide Diols with 2 Equiv of *m*-Chloroperbenzoic Acid. (a) Sulfide Diol 6. A solution of MCPBA (1.40 g of 85% peracid, 6.90 mmol of peracid) in 15 mL of chloroform was added dropwise to a cooled solution of sulfide diol **6** (1.04 g, 3.45 mmol) in 25 mL of $CHCl_3$. After stirring for 3 days at 25 °C, the solution was twice extracted with aqueous Na_2HCO_3 and dried (Na_2SO_4), and solvent was removed leaving 1.09 g (95%) of sulfone **29** which was recrystallized from CH_2Cl_2–hexane: mp 165.5–167 °C; IR ($CHCl_3$) 3480 (s, OH), 3000 (s), 1435 (w), 1367 (m), 1290 (s), 1151 (s), 1134 (s), 1115 (s), 966 (m), 599 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.70 (s, 12, CH_3), 4.40 (br s, 2, OH), 7.10–7.93 (m, 8, ArH); mass spectrum (70 eV) *m/e* (rel intensity) no molecular ion, 302 (12.1), 301 (54.8, $M^+ \cdot - H_2O$ and CH_3), 283 (1.2, $M^+ \cdot - 2H_2O$ and CH_3), 259 (12.1), 237 (17.7), 183 (100), 134 (21.1), 115 (27.8), 91 (82.3), 77 (31.7).

Anal. ($C_{18}H_{22}O_4S$) C, H, S.

(b) Sulfide Diol 9. A solution of 1.97 g of 85% MCPBA (9.76 mmol peracid) in 50 mL of $CHCl_3$ was added dropwise to a solution of sulfide diol **9** (1.28 g, 4.88 mmol) in 150 mL of $CHCl_3$ at 0 °C. After stirring at 25 °C for 12 h the solution was extracted with aqueous $NaHCO_3$ and dried ($MgSO_4$), and solvent was removed to give a clear oil which crystallized upon addition of ether. Filtration yielded 0.81 g of sulfone **30** and removal of the ether in the filtrate yielded 0.27 g of sulfone. Total yield of **30** was 1.08 g (80%): mp 109–115 °C; IR (KBr) 3541 (s), 1476 (w), 1453 (w), 1398 (m), 1304 (s), 1227 (w), 1193 (m), 1159 (s), 1133 (m), 1082 (m), 1038 (s), 977 (w), 955 (w), 775 (s), 731 (s), 614 (s), 593 (m), 568 cm^{-1} (s); mass spectrum (70 eV) *m/e* (rel intensity) no molecular ion, 260 (5.5, $M^+ \cdot - H_2O$), 231 (13.8), 213 (82.7), 195 (100), 165 (41.8), 137 (23.0), 91 (36.8), 77 (69.0).

Anal. ($C_{14}H_{14}O_4S$) C, H, S.

(c) Sulfide Diol 14. *m*-Chloroperbenzoic acid (319 mg of 85% peracid, 1.57 mmol) in 10 mL of CH_2Cl_2 was added within 15 s to a cooled (0 °C) solution of diol **14** (320 mg, 0.78 mmol) in 15 mL of CH_2Cl_2. The solution was stirred for 14 h at 25 °C followed by extraction with aqueous $NaHCO_3$. After separating the organic layer and drying ($MgSO_4$), the solvent was removed, leaving 311 mg (86%) of white solid, sulfoxide-ene-ol **31.** Two unidentified minor peaks (14% of total methyl group of **31**) were also seen, perhaps attributable to sulfone diol **35** or sulfurane **15.**

Rate of Isomerization of 17. An 89/11 mixture of sulfurane **17a** and **17b** (29.1 mg, 0.093 mmol) in 0.5 mL of pyridine-d_5 was sealed in an NMR sample tube. The rate of isomerization to the equilibrium mixture (exo/endo::78/22) was followed by 220-MHz ^1H NMR by integration of the ethyl triplets of each isomer. The isomerization was followed for about three half-lives. The data were fit to a first-order least-squares plot (R = 0.987) to give a first-order rate constant $k_1 = 3 \times 10^{-6}$ s^{-1}. This corresponds to a free energy of activation of 30 kcal/mol.

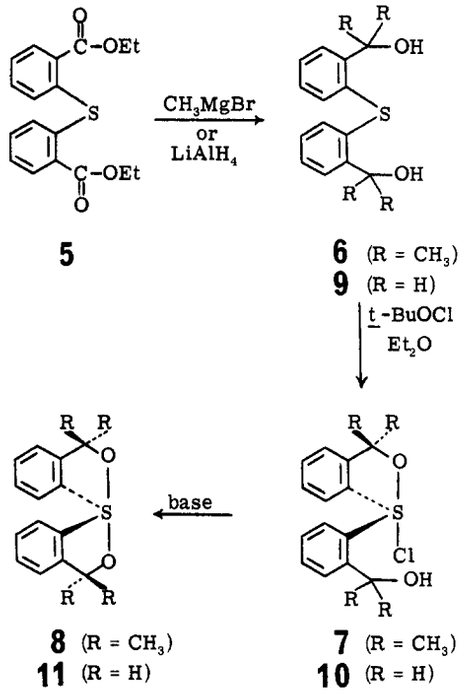
A 50/50 mixture of **17a** and **17b** in pyridine-d_5 was heated to 84 °C for a few days. Subsequent ^1H NMR analysis confirmed the earlier quoted equilibrium composition (78/22) with approach from the opposite direction.

Results

Synthesis. Spirosulfurane **8**, prepared by the method shown in Scheme I, is a white, crystalline material whose ^1H NMR spectrum (CD_2Cl_2) shows diastereotopic methyl singlets at δ 1.53 and 1.63. The 220-MHz spectrum of a carbon tetrachloride solution of **8** containing L(−)-2,2,2-trifluoro-1-phenylethanol[21] shows four resolved methyl singlets, consistent with the expected trigonal bipyramidal geometry about chiral sulfur. The two aromatic protons ortho to sulfur show a low-field chemical shift (δ 8.24–8.42 in CD_2Cl_2) characteristic of sulfuranes and selenuranes of this type.[9b,17]

Spirodibenzyloxysulfurane **11** was synthesized by a related method (Scheme I). Final ring closure of **10** to form **11** required use of triethylamine in dry ether or potassium hydride in dry tetrahydrofuran because of the reactivity of **11** toward water. Crystalline **11** can, however, be handled in air without hydrolysis from atmospheric moisture. The 220-MHz ^1H NMR spectrum of **11** shows an AB pattern at δ 5.100 and 5.195 (J = 14 Hz) for the diastereotopic benzyl hydrogens. Also seen

Scheme I



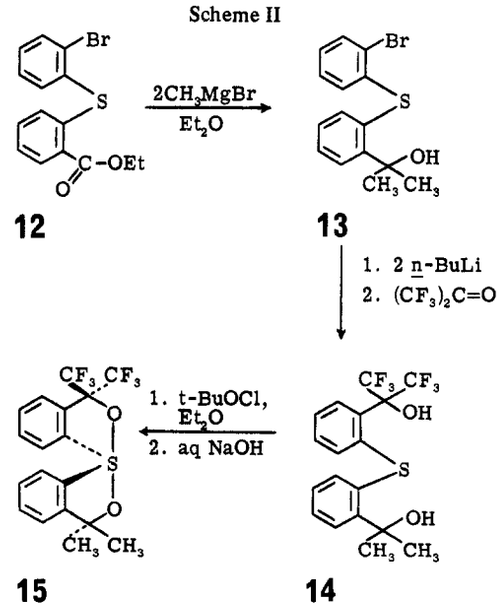
5 **6** (R = CH_3) **9** (R = H) **8** (R = CH_3) **11** (R = H) **7** (R = CH_3) **10** (R = H)

is the characteristic downfield shift of the two aromatic protons ortho to sulfur at δ 7.95–8.14.

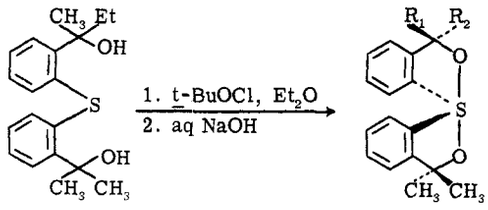
Unsymmetrical spirosulfurane **15** was prepared by oxidation of sulfide diol **14** by the same procedure used for sulfurane **8** (Scheme II). The ^1H NMR spectrum of **15** in $CDCl_3$ shows two diastereotopic methyl singlets at δ 1.65 and 1.83. The two protons ortho to sulfur are seen at δ 8.27–8.67. The ^{19}F NMR shows two quartets at ϕ 74.15 and 77.06 (J_{FF} = 9.2 Hz) which correspond to the diastereotopic trifluoromethyl groups. The chiral nature of **15** is demonstrated by the observation of four methyl singlets for the enantiomers of **15** in a 220-MHz spectrum of **15** in a chiral medium.[21] It should be pointed out that the hydrochloride of **15,** presumed to be an intermediate in its synthesis, loses HCl too rapidly to permit isolation.

Diastereomeric spirosulfuranes **17a** and **17b** were formed in almost equal amounts upon applying the standard procedure to **16.** Column chromatography on neutral alumina followed by one recrystallization gave an 89/11 mixture of isomers **17a** and **17b.** The 220-MHz ^1H NMR of the mixture in

Scheme II



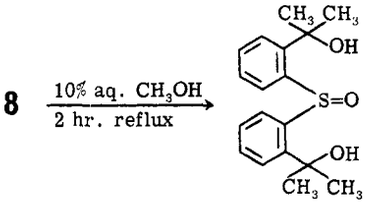
12 **13** **15** **14**



16 **17a** $R_1 = CH_3$; R_2 = Et
17b R_1 = Et; $R_2 = CH_3$

pyridine-d_5 shows *exo*- (**17a**) and *endo*- (**17b**) ethyl triplets at δ 0.794 and 1.606. These assignments are based in part on an examination of molecular models which places the *endo*-ethyl group in the deshielded region of the cis aromatic rings and in part on the expectation that the thermodynamically favored isomer would be that with the more bulky ethyl group in the less hindered exo position (**17a**). More substantial evidence for the assignments by the interaction of $Eu(fod)_3$ with **17** will be discussed later.

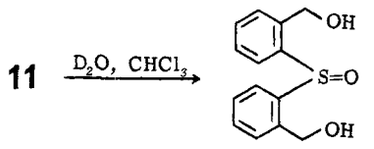
Hydrolysis. Sulfurane **8** can be handled in air and is not easily hydrolyzed. It is hydrolyzed to sulfoxide diol **18** upon boiling for 2 h in 10% aqeuous methanol. The ^1H NMR spectrum of **18** in $CDCl_3$ shows diastereotopic methyl singlets at



18

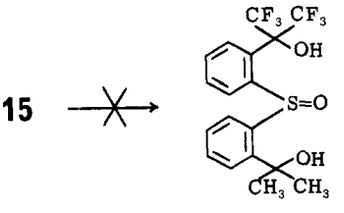
δ 1.38 and 1.70. Similar spectroscopic evidence shows that **18** slowly loses water to re-form spirosulfurane **8** in $CDCl_3$. After 5 days at 25 °C, reversion to **8** had occurred to the extent of 63%, starting with pure **18**.

Sulfurane **11** is more easily hydrolyzed than is **8**. The addition of D_2O to a chloroform solution of **11** resulted in 94% hydrolysis to sulfoxide diol **19** after 3.6 h at 25 °C. An alter-



19

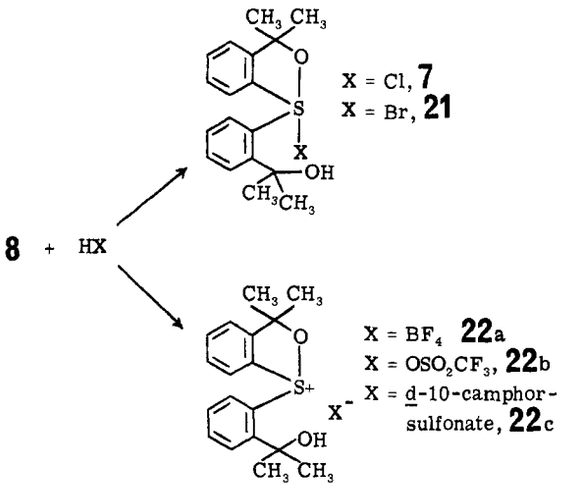
native route to **19** is by oxidation of **9** with *m*-chloroperbenzoic acid (MCPBA). A parallel hydrolysis experiment using sulfurane **8** showed only 25% hydrolysis after 13 days at 25 °C. Unsymmetrical sulfurane **15** failed to hydrolyze to sulfoxide diol **20** even under stringent conditions such as boiling it in



20

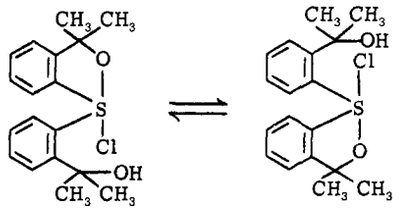
10% aqueous methanol for 4.75 h or using acidic or basic solutions.

Reactions and Interactions. Sulfurane **8** reacts with strong acids (HCl, HBr, HBF_4, CF_3SO_3H, *d*-10-camphorsulfonic acid) to form halosulfuranes or sulfonium salts. All of



these monocyclic compounds are isolable and can be handled in air without hydrolysis. They are insoluble in ether but are quite soluble in methylene chloride or chloroform. Repeated recrystallizations of *d*-10-camphorsulfonate **22c** failed to resolve the two diastereomers.

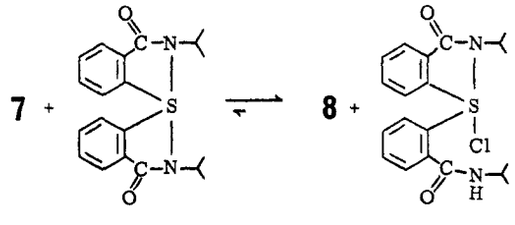
A rapid degenerate intramolecular ligand exchange, interconverting **7a** and **7b,** was first suspected upon examining its



7a **7b**

^1H NMR spectrum. Because of the chirality about sulfur, a total of four methyl singlets would be expected. However, the 100-MHz ^1H NMR spectrum of **7** at 28 °C in CD_2Cl_2 showed only two methyl singlets at δ 1.86 and 1.94. It was also observed that peaks for the two protons ortho to sulfur at δ 8.20 were broadened, unlike the usual sharp peaks seen for ortho protons in sulfuranes and selenuranes.[9b,17] On stepwise cooling, the peak at δ 8.20 was further broadened and then sharpened at −95 °C to show peaks for one ortho proton as a doublet at δ 8.55 and the other as a part of the unresolved aromatic multiplet. Also, a new peak appeared at δ 10.33, as a singlet, which is assigned to the hydroxyl proton, strongly hydrogen-bonded to the chlorine atom. The −95 °C temperature was not sufficiently low to resolve the four methyl singlets expected for **7**. At this temperature, which was the lowest permitted by solubility characteristics of **7**, the methyl region showed a single broad peak.

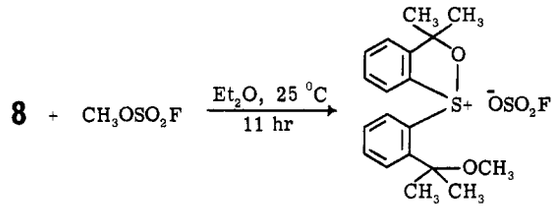
A similar downfield shift is seen for the amide NH proton (δ 11.60) in chloroazasulfurane **23.**[18] Failure to see evidence for the intramolecular ligand exchange in **23** may result from the greater basicity of diazasulfurane **24** compared to **8.** This order of basicities was demonstrated by combining **24** and chlorosulfurane **7** in dry $CDCl_3$ to give sulfurane **8** and chloroazasulfurane **23.** The ^1H NMR spectra for bromosulfurane **21** and sulfonium salts **22a–c** also show evidence for an in-



24 **23**

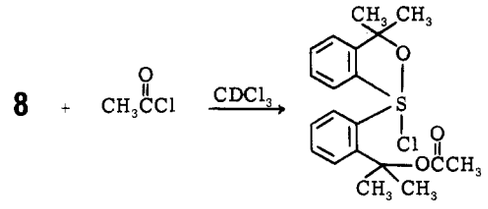
tramolecular exchange process similar to the one seen for **7**. No evidence was seen for reaction of **8** with the weaker acetic acid.

Spirosulfurane **8** reacts with methyl fluorosulfonate at 25 °C to methylate one of the apical oxygens to give **25**. This



25

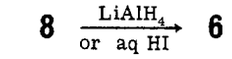
compound provides a model for the low-temperature ^{1}H NMR spectrum for protonated analogues **21** and **22**, since it cannot show the degenerate intramolecular ligand exchange postulated for the protonated species. It shows four resolved methyl singlets as anticipated. A similar model compound which cannot undergo the degenerate exchange is provided by acetylation of **8**, using acetyl chloride to give **26**, which also



26

shows four methyl singlets. The less nucleophilic fluorinated analogue, sulfurane **15**, does not react with acetyl chloride under these conditions. Treatment of sulfurane **8** with benzoyl fluoride gave no reaction after 80 h at 25 °C.

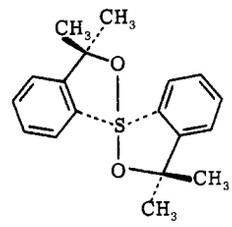
Sulfurane **8** is reduced to sulfide diol **6** with lithium aluminum hydride or by treatment of a methylene chloride solution with aqueous hydriodic acid.



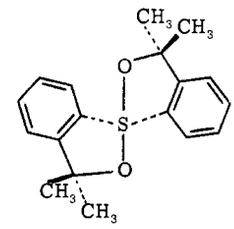
Successive additions of Eu(fod)$_3$[22] to a carbon tetrachloride solution of **8** caused the two methyl singlets at δ 1.51 and 1.59 to move downfield, the peak at δ 1.51 more rapidly than the peak at δ 1.59. Plots of the chemical shift of each singlet vs. the concentration of Eu(fod)$_3$ are nearly linear with slopes of 82.4 and 32.4 ppm/M for the peaks initially at δ 1.51 and 1.59. The complexation of Eu(fod)$_3$ with the less basic sulfurane **15** is much weaker. Similar plots of chemical shift vs. Eu(fod)$_3$ concentrations are nearly linear with slopes of 3.92 and 3.78 ppm/M for the peaks initially at δ 1.60 and 1.76. The aromatic protons in **8** also shift downfield and are eventually completely resolved into two doublets and two triplets. In **15**, the aromatic protons shift less and never become completely resolved.

Pirkle and Sikkenga[24] have used Eu(fod)$_3$ to indicate relative stabilities of diastereomeric solvates. In the presence of chiral arylperfluoroalkylcarbinols, the ^{1}H NMR spectra of sulfoxide enantiomers are nonequivalent. The addition of Eu(fod)$_3$ alters the magnitude of the nonequivalence. The detailed dependence of the nonequivalence on concentration of Eu(fod)$_3$ was related to energies of solvation of the sulfoxide enantiomers by the chiral alcohol.

Since sulfurane enantiomers **8a** and **8b** interact with chiral carbinols to give nonequivalent ^{1}H NMR spectra and since sulfurane **8** also interacts strongly with Eu(fod)$_3$, Pirkle's method was applied to determine the relative solvation energies of **8a** and **8b** with a chiral alcohol. In the absence of Eu(fod)$_3$, sulfurane **8** (0.2 M) and (*S*)-2,2,2-trifluoro(9-anthryl)ethanol (0.6 M) interact in CCl_4 such that one of the



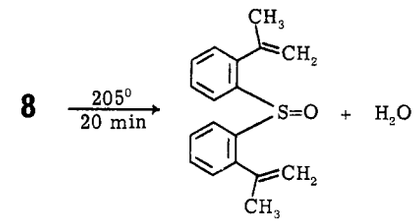
8a



8b

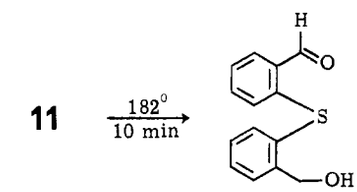
diastereotopic methyl singlets seen for the racemic mixture in achiral media is resolved into two singlets at δ 1.18 and 1.34. The other methyl singlet at δ 1.23 is not resolved. Successive additions of Eu(fod)$_3$ cause the peaks to move progressively downfield. The change in the magnitude of the chemical shift of the two resolved singlets was monitored with each addition of Eu(fod)$_3$. Except for the change from no Eu(fod)$_3$ to the first increment of Eu(fod)$_3$, there was very little change in the magnitude of nonequivalence of the resolved methyl singlets as more Eu(fod)$_3$ was added. This suggests that the energies of the interaction of sulfurane enantiomers with chiral alcohol are nearly the same.

Sulfurane **8**, when heated to 205 °C for 20 min, loses 1 equiv of water and forms sulfoxide diene **27**. In comparison, Reich[17]



27

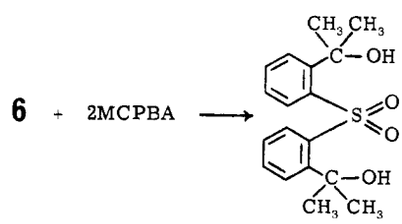
has reported that the selenium analogue of **8** decomposes at its melting point (123 °C), but is stable in solution to at least 200 °C. Pyrolysis of sulfurane **11**, which cannot give such a dehydration, at 182 °C gives sulfide **28**, with disproportiona-



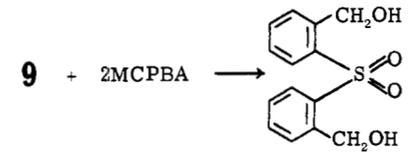
28

tion of the apical alkoxy ligands. Sulfurane **15** fails to pyrolyze when heated to 205 °C for 20 min or at 295 °C for 10 min. When **15** was heated to 355 °C for 15 min, the ^{1}H NMR spectrum of the nearly black sample showed that **15** was completely gone. There were characteristic peaks for the 2-propenyl group as a minor product and other unidentified peaks were seen. The ^{19}F NMR spectrum showed no quartets but showed a series of singlets or doublets at about ϕ 75. No products were isolated from this reaction.

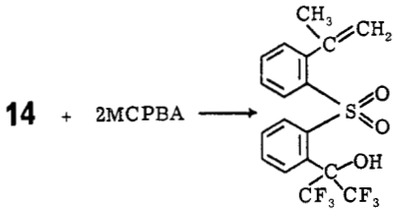
The oxidation of sulfide diol **6** with 2 equiv of MCPBA gives sulfone diol **29**. In a parallel reaction, sulfide diol **9** is oxidized



29



30



31

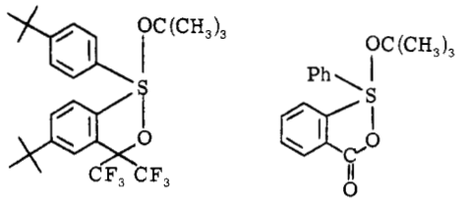
to give sulfone diol **30**. In contrast, oxidation of sulfide diol **14** gives sulfone-ene-ol **31** in greater than 86% yield. Some minor peaks in the ^1H NMR spectrum of the product may be due to the corresponding sulfone diol or sulfurane.

Interconversion of 17a and 17b. The barrier for interconversion of diastereomers **17a** and **17b** was determined in pyridine-d_5 solution at 84 °C. An equilibrium ratio **17a/17b** of 78/22 was determined by heating a 89/11 mixture of diastereomers at 84 °C for a few days. The same ratio was reached from the opposite direction, starting with a 50/50 sample of diastereomers. The rate of approach to equilibrium of a mixture of **17** initially 89/11 (exo/endo) was followed by 220-MHz ^1H NMR integral comparisons of the resolved ethyl triplets of **17a** and **17b**. The resulting rate constant ($k_1 = 3 \times 10^{-6}$ s^{-1}) corresponds to a free energy of activation (at 84 °C) of 30 kcal mol^{-1}. No decomposition of **17** was observed during this experiment.

Discussion

Sulfurane Reactivity. The remarkable unreactivity of spirosulfurane **1** toward water has been mainly attributed to the "five-membered ring effect".[6] Westheimer has shown that five-membered-ring phosphate esters hydrolyze a million times faster than their acyclic analogues.[25] Much of this acceleration results from the relief of strain which accompanies a change from a tetrahedral ground state to a trigonal bipyramidal (TBP) transition state. A similar but smaller accelerating effect seen in the hydrolysis of cyclic sulfites[26] has been attributed primarily to "entropy strain" factors favoring approach to a TBP transition state. For cyclic sulfuranes the inverse transformation of a "trigonal bipyrimidal" ground state to a "tetrahedral" transition state results in an increase in ring strain, which is reflected in the failure of **1** to hydrolyze. Other factors cited[6] as possible contributors to the low reactivity of **1** relative to its acyclic analogue include (a) retardation of the ionization of apical ligands by the electron-withdrawing effect of the fluoroalkyl substituents ortho to sulfur and (b) the minimization of possible repulsive interactions between the π-donor equatorial ligands and the apical three-center four-electron bond which is a consequence of the geometry of the spiro system.

Acyclic sulfurane **2** rapidly converts *tert*-butyl alcohol to isobutylene, even at −60 °C, by a route believed to involve a very unstable intermediate *tert*-butoxy sulfurane formed by a ligand-exchange reaction.[27] The fact that two monocyclic *tert*-butoxy sulfuranes **32** and **33** have been isolated[6,28] illustrates the great stabilizing effect of a single five-membered ring. The addition of a second five-membered ring as in sulfurane **8** adds sufficient stability that the tertiary alkoxy ligands do not give elimination reactions except at elevated temperatures.

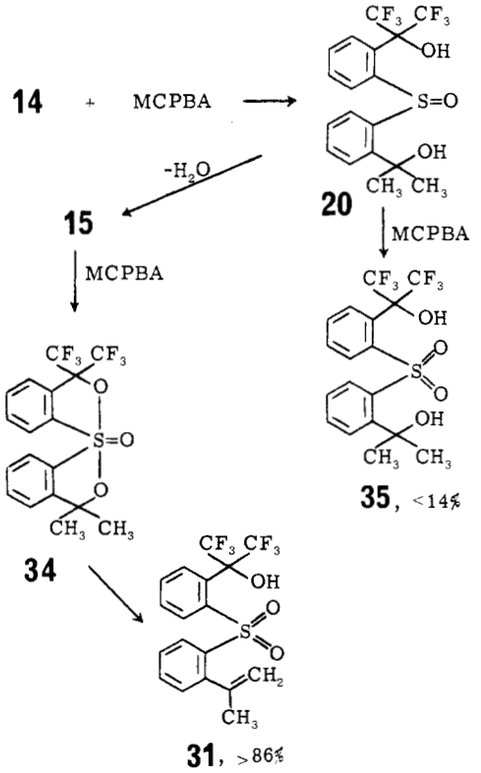


32 33

Not only does sulfurane **1** fail to hydrolyze, but attempts to observe or isolate the corresponding sulfoxide diol also give only **1**. This suggests that the reasons for this failure to hydrolyze **1** are to be found in both kinetic and thermodynamic properties of the molecule. The equilibrium clearly favors the spirosulfurane and cyclodehydration of the sulfoxide diol is a rapid process. Sulfurane **8** is hydrolyzed to sulfoxide diol **18** in protic media, reflecting a lesser thermodynamic stability, relative to the hydrolysis product, than is the case for **1**. Strenuous attempts to hydrolyze unsymmetrical sulfurane **15** fail, suggesting that it is also favored at equilibrium relative to the hydrolysis product. The stabilization of **1** and **15** by the five-membered ring effect is clearly enhanced by the electron-withdrawing inductive effect of the CF_3 substituents. Dehydrative ring closures to form sulfuranes **1**, **8**, and **15** are all favored by the presence in the five-membered rings of *gem*-dialkyl groups. Many examples of facilitated ring closures in systems possessing this structural feature, manifestations of the Thorpe–Ingold effect, have been noted.[29] It is therefore not surprising that the analogous sulfurane lacking this *gem*-dialkyl group, **11**, is less stable toward hydrolysis than is **8**. it is also more rapidly hydrolyzed than **8**.

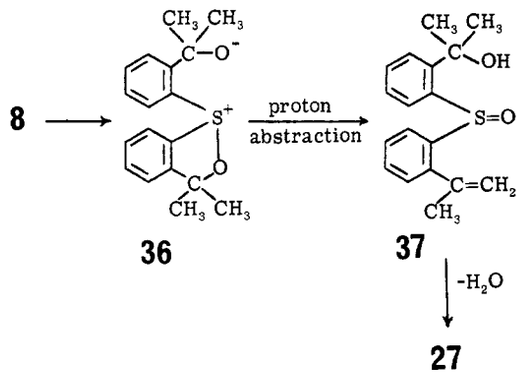
Parallel experiments in which sulfides **6**, **9**, and **14** were each treated with 2 equiv of MCPBA led to further insight into their relative rates of cyclodehydration. For **6** and **9** the corresponding sulfone diols are obtained, but for unsymmetrical sulfide **14** more than 86% of sulfone-ene-ol **31** is obtained. In all three of these oxidations, the first step is expected to be oxidation to give the corresponding sulfoxide diols. In the first two cases, further oxidation simply gives sulfone diols **29** and **30**. However, in the third case (Scheme III), the dehydration

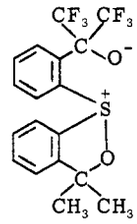
Scheme III



of sulfoxide diol **20** to give sulfurane oxide **34** is faster than further oxidation with MCPBA to form sulfone diol **35**. Fragmentations of sulfurane oxides analogous to that converting **34** to **31** have been reported.[30] These results further suggest a high stability of sulfurane **15** compared to **8**.

The relative thermal stabilities of spirosulfuranes **8**, **11**, and **15** parallel their relative hydrolysis rates. Zwitterion **36**, a possible intermediate in the pyrolysis of **8**, could perhaps abstract a proton to give sulfoxide-ene-ol **37**, and then undergo dehydration to **27**. Similar intermediates have been postulated in the pyrolysis of **4** and in the reaction of **2** with perfluoropinacol.[9a,31] The pyrolysis of **11** may follow a route involving an intermediate similar to **36**. In this case, α-proton abstraction would lead directly to **26**. The two trifluoromethyl groups on **15** render the alkoxide function of the possible intermediate zwitterion **38** much less basic than the analogous





38

alkoxide function in **8** or **11**. This may account in part for the remarkable thermal stability of **15**.

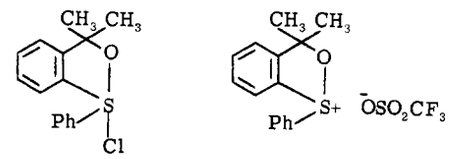
The "five-membered-ring effect" is well established as a major factor that increases the stability of sulfuranes. Hydrolytic equilibria, the rates of hydrolyses and pyrolyses of **8**, **11**, and **15**, and the reactions of the corresponding sulfide diols with *m*-chloroperbenzoic acid suggest another major factor that enhances sulfurane stability, i.e., an increase in the electronegativity of the apical ligand or ligands. The results also show that the "*gem*-dialkyl effect"[29] can also play a role in stabilizing spirosulfuranes.

Basicities of Sulfuranes. Pirkle[21,24] has developed a set of chiral alcohols which are useful in making enantiomers separately observable by NMR. In addition to confirming the chiral nature of our spirosulfuranes, these alcohols have been used to provide information about their relative basicities. Since (−)-2,2,2-trifluoro-1-phenylethanol is moderately acidic, the major type of interaction converting enantiomers into diastereomeric solvates involves hydrogen bonds to basic sites on solute molecules. Racemic spirosulfuranes **8** and **15** both interact with this chiral solvent to allow resolution of the two methyl singlets into two peaks each, with sulfurane **8** interacting with the chiral solvent more strongly than **15**, as evidenced by the magnitude of nonequivalence of enantiomeric methyl peaks. For **8** the differences in chemical shift for each set of peaks was 0.026 and 0.024 ppm, but for **15** these same differences were less (0.024 and 0.017 ppm), even though the concentration of chiral solvent for **15** (0.52 M) was slightly higher than for **8** (0.51 M). Sulfurane **1** shows no nonequivalence in ^{19}F NMR for CF_3 peaks of enantiomers in this chiral medium;[6] thus, the relative order of basicity is **8** > **15** > **1**.

More dramatic evidence for this ordering is found in interactions of these spirosulfuranes with the lanthanide-shift reagent $Eu(fod)_3$,[22] a Lewis acid. Sulfurane **1** is reported[6] to show no chemical-shift changes in the presence of $Eu(fod)_3$, in keeping with the low basicity of **1**. Sulfurane **15** shows a moderately strong interaction with $Eu(fod)_3$, while a very large interaction is seen for **8**. Complexation of $Eu(fod)_3$ with spirosulfuranes might occur at the oxygen or sulfur atoms or both.

Spirosulfurane **8** reacts with strong acids to give halosulfuranes or sulfonium salts; no such reaction occurs for the less basic **1**. The chlorosulfurane of **15**, from the reaction of **14** and *tert*-butyl hypochlorite, was not isolable, losing HCl to generate **15**, reflecting the reduced basicity of **15** relative to **8**. Treatment of **8** with other electrophiles showed it unreactive toward the weaker acid, acetic acid, but reactive toward methyl fluorosulfonate and acetyl chloride. The less nucleophilic sulfurane **15**, however, does not react with acetyl chloride and methylation is very slow.[32] The order of decreasing basicity and nucleophilicity (**8** > **15** > **1**) parallels the increase in number of CF_3 groups on the oxygen apical ligands.

Ligand Exchange. Chlorosulfurane **7** is closely related to previously described[16,33] chlorosulfurane **39**. Strong evidence

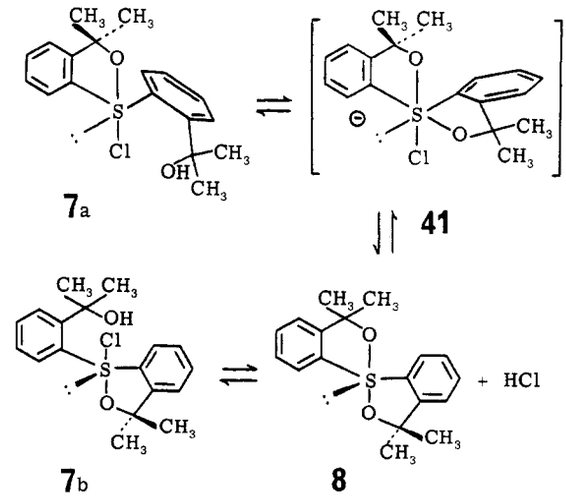


39 **40**

is reported[16] for the covalent nature of the S–Cl bond in **39**, partly through ^1H NMR spectroscopic comparison with the ionic sulfonium triflate **40**. The addition of the alcohol function in **7**, **21**, and **22a–c** provides the opportunity for a facile intramolecular ligand exchange which is fast on the NMR time scale at room temperature. When the exchange is slowed at low temperature, the proton ortho to sulfur on the fused ring in **7** is seen at very low field characteristic[9b] of such protons in, for example, model compound **39**.

An associative mechanism (Scheme IV) similar to the one postulated[16,33] for the hydrolysis of chlorosulfurane **39** may be operating for the exchange reaction of **7**. The failure to detect intramolecular exchange in the more weakly acidic chloroazasulfurane **23** is consistent with this mechanism, since loss of HCl to form the more basic diazasulfurane might be expected to be slower than for the more acidic **7**.

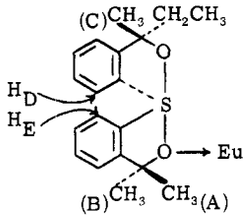
Scheme IV



The Structures of 17a and 17b. The two *endo*-methyl groups of 8 (δ 1.59) are held in the deshielded region of space relative to the cis aromatic ring, causing them to be shifted downfield relative to the *exo*-methyl groups (δ 1.51). This assignment is consistent with the results of the Eu(fod)$_3$ study on 8 in which the singlet at δ 1.51 broadens more and moves downfield faster than the singlet at δ 1.59 as the concentration of Eu(fod)$_3$ increases. If we make the reasonable assumption that Eu(fod)$_3$ interacts with the oxygens and/or sulfur lone pair of 8 from the less hindered direction away from the aryl rings, the *exo*-methyls, being closer to the Eu(fod)$_3$ than the *endo*-methyls, would be expected to move downfield more rapidly.

Tentative ^{1}H NMR assignments for 17 were made on the basis of the expected greater stability of *exo*-ethyl sulfurane **17a** because of the greater steric crowding of the *endo*-ethyl group in **17b.** The ^{1}H NMR spectrum of **17a** shows two methyl singlets at δ 1.51 and 1.60. Successive additions of Eu(fod)$_3$ causes the singlet initially at δ 1.51 (A) to broaden and move rapidly downfield. One of the other two methyl peaks initially at δ 1.60 (B) broadens less and moves downfield more slowly. The other methyl peak initially at δ 1.60 (C) broadens only slightly and moves downfield even more slowly. Plots of chemical shift vs. concentration of Eu(fod)$_3$ were nearly linear with slopes for the three methyl peaks of **17a** of 36.1 (A), 14.5 (B), and 5.5 (C) ppm M^{-1}.

This is consistent with our tentative assignment of structure **17a** (exo) to the major isomer. The *exo*-ethyl group of **17a** might be expected to provide greater steric hindrance to complex formation by Eu(fod)$_3$ at the nearer oxygen, favoring complexation at the oxygen α to the *gem*-dimethyl group as in **42.**

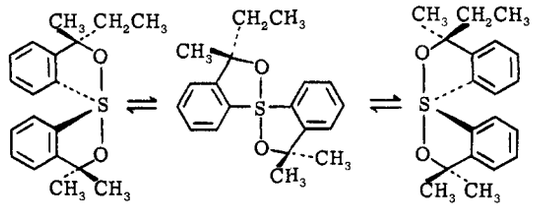


42

The greater proximity of the europium to methyl group A in **42** causes it to move downfield most rapidly, with B, second nearest, second most rapidly. The more distant *endo*-methyl (C) moves downfield most slowly. The chemical shift for A in the absence of Eu(fod)$_3$ (δ 1 51) is identical to the *exo*-methyl peaks in 8 (which also move downfield with addition of Eu(fod)$_3$ more rapidly than do the *endo*-methyl peaks, as expected). These observations are consistent with the idea that the oxygen atoms, rather than the sulfur, provide the primary sites for Eu(fod)$_3$ complex formation in these sulfuranes.

Added evidence for complexation of Eu(fod)$_3$ at oxygen rather than at sulfur comes from the shifts seen for the downfield protons ortho to sulfur. Both ortho protons of **8** shift downfield with a slope of 7.1 ppm M^{-1}. The two ortho protons of **17a,** initially at δ 8.31, move downfield at different rates (slopes = 10.65 and 2.73 ppm M^{-1}). The ortho proton with a slope of 10.65 is postulated to be H_D, which is nearer the preferred site of complex formation in **42** than is H_E. In the presence of Eu(fod)$_3$, the ortho protons of the minor isomer **17b** are seen as two resolved doublets *between* the two ortho protons of the major isomer **17a.** This is expected for an interaction of Eu(fod)$_3$ with **17b,** whose less obtrusive *endo*-ethyl group provides less basis for steric differentiation between the two basic sites than is the case for the exo isomer **17a.**

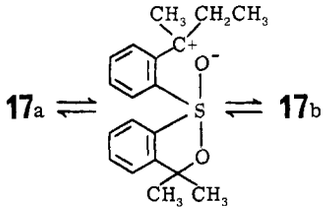
Possible Interconversion Mechanisms. Our kinetic study of the equilibration of mixtures of **17a** and **17b** provides a free energy of activation for whatever process converts **17a** to **17b** of 30 kcal mol^{-1} at 84 °C. One mechanism for this process interconverting wedge-shaped conformers could be called cuneal inversion (by analogy to the pyramidal inversions common for many species with tricoordinated central atoms), inversion through planar transition state **43.** From high-



17a **43** **17b**

temperature ^{19}F NMR of spirosulfurane **1,** Martin, Perozzi, and Paul[15] set a lower limit of 25.3 kcal mol^{-1} for ΔG^* at 200 °C for the comparable cuneal inversion for **1.** The racemization of the optically active (*S*)-**39** may also involve such an inversion, for which a lower limit for ΔG^* of 25 kcal mol^{-1} at 23 °C was determined.[33]

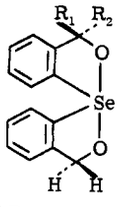
Another possible mechanism for the equilibration of **17a** and **17b** would begin by ionization of one of the apical S–O bonds, followed by pyramidal inversion of the resulting sulfonium ions and then recombination. Inversion barriers for some sulfonium ions have been determined[10-14] to be in the range 25–29 kcal mol^{-1}, very similar to the lower limit obtained for **17.** It should be noted, however, that the sulfonium species in this case has an electronegative alkoxy substituent, a structural feature expected[34] to increase the barrier to pyramidal inversion. The use of pyridine as a medium for this study minimizes the importance of acid-catalyzed ionization to a alkoxysulfonium ion as a mechanism for the isomerization of **17.** It is conceivable that interconversion may be occuring at chiral carbon via inversion through a carbonium ion **44,**



44

although the failure to see any olefin makes this mode extremely unlikely.

Related work by Reich[17] on the configurational stability of selenuranes has established the equilibrium mixture of diastereotopic selenurane **45a** and **45b** to be 74/26 (vs. 78/22 for **17a** and **17b**). In both cases, the more stable isomer has the greater steric bulk located exo to the aryl function.[35] The rate of exo–endo isomerization for **45** showed ΔG^* = 30.9 kcal mol^{-1} at 120 °C, very similar to that for **17.** Reich[17] also reported evidence that trace amounts of water in benzene might catalyze the isomerization. Since this may also be occurring in our system (trace amounts of water in pyridine-d_5), higher



45a R_1 = H; R_2 = CH_3

45b R_1 = CH_3; R_2 = H

barriers for cuneal inversion at sulfur(IV) may be obtainable in systems which are inert toward hydrolysis or with more rigorous exclusion of water.

Conclusion

Additional factors that influence sulfurane stability have been found. An increase in the electronegativity of the apical ligands is reflected in an increase in the stability of sulfuranes. Hydrolyses of spirosulfuranes are slowed by the presence of *gem*-dialkyl groups on the carbon α to the apical atoms, and sulfurane stability is enhanced by this structural feature.

A lower limit of 30 kcal mol^{-1} has been set for $\Delta G^*_{84°C}$ for the cuneal inversion at sulfur(IV), a process that interconverts a pair of diastereomeric spirosulfuranes. This value is the highest yet found for sulfuranyl sulfur but still represents only a lower limit to the value because inversion by another mechanism or catalysis by water, acids, or bases cannot rigorously be ruled out.

Acknowledgment. This research was supported in part by a grant from the National Science Foundation, CHE 75-17742.

Registry No.—**5,** 62220-51-3; **6,** 62750-57-6; **7,** 63743-90-8; **8,** 62750-58-7; **9,** 38059-09-5; **10,** 63743-91-9; **11,** 34400-24-3; **12,** 63743-92-0; **13,** 63743-93-1; **14,** 63743-94-2; **15,** 63731-54-4; **16,** 63743-95-3; **17a,** 63743-96-4; **17b,** 63813-46-7; **18,** 62750-61-2; **19,** 63743-97-5; **21,** 63743-98-6; **22a,** 63744-00-3; **22b,** 63744-01-4; **22c,** 63813-47-8; **24,** 63744-02-5; **25,** 63731-59-9; **26,** 63744-03-6; **27,** 63744-04-7; **28,** 63744-05-8; **29,** 63744-06-9; **30,** 24536-81-0; 2,2′-dicarboxydiphenyl sulfide, 22219-02-9; 2-bromo-2′-carboxydiphenyl sulfide, 20076-94-2; 2-bromothiophenol, 6320-02-1; 2-iodobenzoic acid, 88-67-5; methyl ethyl ketone, 78-93-3; L(−)-2,2,2-trifluoro-1-phenylethanol, 10531-50-7; fluoroboric acid, 14874-70-5; *d*-10-camphorsulfonic acid, 3144-16-9; triflic acid, 1493-13-6; acetyl chloride, 75-36-5; (*S*)-(+)-2,2,2-trifluoro-9-(anthryl)ethanol, 60646-30-2; hexafluoroacetone, 684-16-2.

References and Notes

(1) Paper 34 in a series on sulfuranes. For paper 33 in this series, see: L. J. Adzima, E. N. Duesler, and J. C. Martin, *J. Org. Chem.*, preceding paper in this issue.
(2) A preliminary account of a portion of this work has appeared. See L. J. Adzima and J. C. Martin, *J. Am. Chem. Soc.*, **99,** 1657 (1977).
(3) M. Allan, A. F. Janzen, and C. J. Willis, *Can. J. Chem.*, **46,** 3671 (1968). See also G. E. Wilson, Jr., and B. A. Belkind, *J. Org. Chem.*, **42,** 765 (1977) for a description of another tetraoxysulfurane.
(4) I. Kapovits and A. Kalman, *Chem. Commun.*, 649 (1971).
(5) E. F. Perozzi and J. C. Martin, *J. Am. Chem. Soc.*, **94,** 5519 (1972).
(6) J. C. Martin and E. F. Perozzi, *J. Am. Chem. Soc.*, **96,** 3155 (1974).
(7) J. C. Martin and M. M. Chau, *J. Am. Chem. Soc.*, **96,** 3319 (1974).
(8) G. W. Astrologes and J. C. Martin, *J. Am. Chem. Soc.*, **97,** 6909 (1975).
(9) (a) G. W. Astrologes and J. C. Martin, *J. Am. Chem. Soc.*, **98,** 2895 (1976); (b) G. W. Astrologes and J. C. Martin, *ibid.*, **99,** 4390 (1977).
(10) K. K. Andersen, M. Cinquini, and N. E. Papanikolaou, *J. Org. Chem.*, **35,** 706 (1970).
(11) R. Scartazzini and K. Mislow, *Tetrahedron Lett.*, 2719 (1967).
(12) D. Darwish and G. Tourigny, *J. Am. Chem. Soc.*, **88,** 4303 (1966).
(13) D. Darwish and R. L. Tomilson, *J. Am. Chem. Soc.*, **90,** 5938 (1968).
(14) J. C. Martin and R. J. Basalay, *J. Am. Chem. Soc.*, **95,** 2572 (1973).
(15) E. F. Perozzi, J. C. Martin, and I. C. Paul, *J. Am. Chem. Soc.*, **96,** 6735 (1974).
(16) J. C. Martin and T. M. Balthazor, *J. Am. Chem. Soc.*, **99,** 152 (1977).
(17) H. J. Reich, *J. Am. Chem. Soc.*, **95,** 964 (1973).
(18) L. J. Adzima, C. C. Chiang, I. C. Paul, and J. C. Martin, *J. Am. Chem. Soc.*, in press; see also ref 2.
(19) A. J. Saggiomo, P. N. Craig, and M. Gordon, *J. Org. Chem.*, **23,** 1906 (1958).
(20) R. D. Rieke and S. E. Bales, *J. Am. Chem. Soc.*, **96,** 1775 (1974).
(21) W. H. Pirkle, R. L. Muntz, and I. C. Paul, *J. Am. Chem. Soc.*, **93,** 2817 (1971).
(22) B. Feibush, M. F. Richardson, R. E. Sievers, and C. S. Springer, Jr., *J. Am. Chem. Soc.*, **94,** 6717 (1972).
(23) We thank Dr. Pirkle and Dr. Sikkinga for the sample of chiral alcohol.
(24) W. H. Pirkle and D. L. Sikkenga, *J. Org. Chem.*, **40,** 3430 (1975).
(25) A. Eberhard and F. H. Westheimer, *J. Am. Chem. Soc.*, **87,** 253 (1965). F. H. Westheimer, *Acc. Chem. Res.*, **1,** 70 (1968).
(26) See J. G. Tillett, *Chem. Rev.*, **76,** 747 (1976), and references included therein.
(27) L. J. Kaplan and J. C. Martin, *J. Am. Chem. Soc.*, **95,** 793 (1973).
(28) P. Livant and J. C. Martin, *J. Am. Chem. Soc.*, **98,** 7851 (1976)
(29) E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, N.Y., 1962, p 196 ff.
(30) Fragmentations of this type have been reported.[2]
(31) (a) J. C. Martin and R. J. Arhart, *J. Am. Chem. Soc.*, **93,** 2339 (1971); (b) R. J. Arhart and J. C. Martin, *ibid.*, **94,** 4997 (1972).
(32) Methylation with methyl fluorosulfonate took 12.5 days to complete at 25 °C.
(33) T. M. Balthazor and J. C. Martin, *J. Am. Chem. Soc.*, **97,** 5634 (1975).
(34) K. Mislow, *Trans. N.Y. Acad. Sci.*, **35,** 227 (1973).
(35) It should be noted that the chemical-shift assignments for *exo*- and *endo*-methyl groups of **45** are inverted from those for the sulfuranes of this study, with the *endo*-methyl being found at higher field than the *exo*-methyl of **45.** Differences in geometry between the two systems may provide an explanation.

Synthesis of Methyl-Substituted *trans*- and *cis*-1-Thiadecalins

Peter K. Claus and Friedrich W. Vierhapper*

Organisch-Chemisches Institut, Universität Wien, Austria

and in part Rodney L. Willer

W. R. Kenan, Jr. Laboratories, University of North Carolina, Chapel Hill, North Carolina 27514

Received May 4, 1977

Synthetic procedures for *trans*-1-thiadecalin (**1**), *cis*-1-thiadecalin (**11**), and 15 *trans*- (**2–10**) and *cis*-1-thiadecalins (**12–17**) with methyl substituents in various positions of the heterocyclic or the carbocyclic ring are described.

Interest in the conformational and configurational properties,[1] and in the rearrangement reactions[2] of thiane-1-*N*-arylimides motivated us to synthesize a number of methyl-substituted 1-thiadecalins. Configuration and conformational equilibria of the compounds were established by ^{13}C and ^{1}H NMR spectroscopy;[3] here the synthetic procedures are discussed in some detail. The formulas of the compounds prepared are collected in Schemes I and II; in Table I the compositions of the product mixtures are summarized.

The following procedures were used. **Method A.** Addition of a (methyl)allylmagnesium halide to a (methyl)cyclohexene sulfide[4] and ring closure of the resulting (methyl-substituted) 1-allyl-2-mercaptocyclohexane (Schemes III and IV).

Methods B and C. Cyclization of (methyl substituted) 1-(3′-mercaptopropyl)cyclohexene-1 and (methyl substituted) 3-(3′-mercaptopropyl)cyclohexene-1 (Schemes V and VI).

Method D. Reaction of (methyl substituted) 1-(3′-methylsulfonyloxypropyl)-2-methylsulfonyloxycyclohexane (cis and trans mixtures) with sodium sulfide, in 50% ethanol or in dimethylformamide (Scheme VII).