Stereochemical Course of an Associative Displacement at Tetracoordinate Sulfur(IV) in a Sulfurane of Known Absolute Configuration. A Proposed System of Nomenclature for Optically Active Pentacoordinate Species[1]

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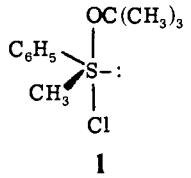
Abstract: The first optically active sulfurane, (+)-1-chloro-3,3-dimethyl-1-phenyl[3*H*-2,1-benzoxathiole] (**4**), is synthesized with known absolute configuration, in 95% optical purity by treatment of (*S*)-2-(2-hydroxy-2-propyl)-1-phenylsulfinylbenzene (**5**) with acetyl chloride at −78 °C. A convention for the designation of absolute configuration in pentacoordinate species is proposed. Racemic **4** is thermally stable at room temperature and does not react rapidly with atmospheric water. Evidence for the covalent nature of the S–Cl bond is discussed. Reaction of **4** with water in the presence of diisopropylethylamine or *N,N*-dimethylaniline is rapid to give **5** with retention of configuration about sulfur. Competitive kinetics studies were performed on the hydrolyses of chlorosulfurane **4** and five of its substituted analogues. An associative nucleophilic displacement at sulfur, proceeding through an octahedral sulfur anion transition state, is suggested to explain the positive ρ values determined for substitution in either of the aryl rings of **4**.

Tetracoordinate, tetracovalent sulfur compounds (sulfuranes) containing halogen ligands have been reported both as intermediates and as stable compounds. Fluorosulfuranes are sufficiently stable that many examples have been isolated and studied.[2] Sulfur tetrafluoride and its substituted analogues containing three S–F bonds are useful fluorinating agents for replacing oxygen with fluorine in organic compounds.[2c,d] Oxidation of sulfides by trifluoromethyl hypofluorite, CH_3OF, has been shown[2e] to be a facile method for the preparation of difluorosulfuranes. Perfluoroalkyl sulfur difluorides show a remarkable resistance to hydrolysis.[2f,g]

The chlorosulfuranes, in contrast, are much less stable. Several have been observed as reaction intermediates without isolation.[3a-d] Those which have been isolated[3e-h] have usually been found to be readily hydrolyzed and thermally unstable[4] at room temperature. The crystal structure[3f] of the unstable (above −20 °C) adduct of chlorine to *bis*(*p*-chlorophenyl) sulfide shows trigonal-bipyramidal geometry and covalent bonding about sulfur.

Sulfides are readily oxidized by alkyl hypochlorites[3a,d] to alkoxychlorosulfuranes. Johnson and Rigau[3a] have observed (by NMR) alkoxychlorosulfurane **1** in the oxidation of methyl phenyl sulfide with *tert*-butyl hypochlorite at −46 °C. Alkoxybromosulfurane **2** prepared by Perozzi and Martin[3e] was



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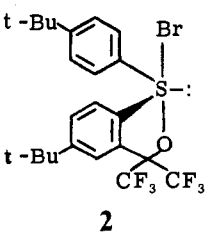

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found to be thermally stable. The covalent character of the sulfur–halogen bond was suggested by available evidence for **1** and **2** but one of the goals of the present work was to provide a wider range of evidence for the covalency of such species.

Experimental Section

General. Chemical shifts for protons are reported on the δ scale, ppm downfield from tetramethylsilane (Me_4Si) internal standard; for fluorine in ppm upfield from fluorotrichloromethane; and for carbon in ppm downfield from Me_4Si. Melting points were obtained on a micro hotstage and Buchi melting point apparatus and are uncorrected. The ^1H and ^{19}P NMR integral ratios are rounded to the nearest whole number of nuclei. Elemental analyses were within 0.4% of the theoretical values for all new compounds.

All solvents were distilled from P_2O_5 or passed through a column of Brinkmann basic alumina (activated at 150 °C for 24 h).

2-(2-Hydroxy-2-propyl)-1-phenylthiobenzene (3). Thionyl chloride (50 ml) and 2-(phenylthio)benzoic acid (10 g, 43.5 mmol) were boiled for 1 h. Excess $SOCl_2$ was distilled and the residue poured into a solution of 150 ml of methanol and 20 ml of pyridine. Ether was added, and the solution was extracted with 10% HCl, 10% NaOH, and H_2O, then dried, and the solvent removed to give the crude ester. This was dried and used without further purification.

To the ester, in ether, was added an ether solution of methyl magnesium bromide (excess, 45 ml of a 2.6 M solution). After 2 h stirring, the mixture was poured into 200 ml of saturated NH_4Cl, the organic layer was washed with water and dried, and the ether was removed to give a yellow oil. Distillation through a short column (145 °C, 2 mm) gave 9.04 g (85%) of **3**: ^1H NMR ($CDCl_3$) δ 1.68 (s, 6, CH_3), 3.40 (broad s, 1, OH), 7.18 (m, 8), 7.48 (m, 1); infrared ($CHCl_3$) 3465 (m, broad, OH), 3079 (s), 1580 (m), 1476 (s), 1439 (m), 1432 (m), 1170 (m), 948 (m), 793 (m), 691 cm^{-1} (m); mass spectrum (70 eV) *m/e* (rel intensity) 244 (85, $M^{\cdot+}$), 229 (51, $M^{\cdot+} - CH_3$), 226 (39, $M^{\cdot+} - H_2O$), 211 (4, $M^{\cdot+} - H_2O$, CH_3), 151 (100), 149 (65). Anal. ($C_{15}H_{16}OS$) C, H.

2-(2-Hydroxy-2-propyl)-1-phenylsulfinylbenzene (5). A chloroform solution of 2-(2-hydroxy-2-propyl)-1-phenylthiobenzene (4.16 g, 17.03 mmol) was treated with *tert*-butyl hypochlorite (1.85 g, 17.03 mmol) and after 10 min was extracted with 10% NaOH. The solution was dried ($MgSO_4$) and the solvent removed to yield a yellow solid which on recrystallization from $CHCl_3$–ether gave 4.13 g (93%) of white **5**: mp 162.5–163.5 °C; ^1H nmr)cdcl$_3$) δ 1.33 (s, 3, CH_3), 1.68 (s, 3, CH_3), 7.13–7.69 (m, 8), 8.23 (m, 1, H, ortho to S in the disubstituted ring); IR ($CHCl_3$) 3360 (w, OH), 3000 (s), 1477 (m), 1445 (m), 1369 (w), 1019 (s), 698 cm^{-1} (m); mass spectrum (70 eV) *m/e* (rel intensity) 260 (8.8, $M^{\cdot+}$), 245 (100, $M^{\cdot+} - CH$), 243 (23, $M^{\cdot+} - OH$), 167 (27), 151 (24), 149 (40), 77 (23). Anal. ($C_{15}H_{16}O_2S$) C, H, S.

2-(4-Methylphenylthio)-5-methylphenyl Methyl Ketone. To 4,4′-dimethyldiphenyl sulfide (4.0 g, 11.8 mmol) in 80 ml of dry CCl_4, $AlCl_3$ (3.14 g, 26.6 mmol) was added. Acetyl chloride (1.66 g, 26.5mol) was then added at 8 °C over a 15-min period.

The mixture was stirred for 30 min and then poured into 400 ml of 6 N HCl. The organic layer was separated and dried ($MgSO_4$), and the solvent was removed to give a brown oil. Crystallization from ether gave 1.3 g (44.5%) of the sulfide-ketone: mp 121.5–122.5 °C; ^1H NMR ($CDCl_3$) δ 2.33 (s, 3), 2.36 (s, 3), 2.62 (s, 3, $COCH_3$), 6.93 (m,

7); IR ($CHCl_3$) 3025 (m), 1668 (s), 1462 (s), 1227 (broad, m) 8.4 cm^{-1} (m); mass spectrum (70 eV) *m/e* (rel intensity) 256 (100, $M^{\cdot+}$), 241 (76, $M^{\cdot+} - CH$) 165 (17), 151 (38). Anal. ($C_{16}H_{16}OS$) C, H.

2-(2-Hydroxy-2-propyl)-4-methyl-1-(4-methylphenylsulfinyl)benzene. An ether solution of 2-(4-methylphenylthio)-5-methylphenyl methyl ketone (3.08 g, 12 mmol) was added to CH_8MgBr (13.9 ml of a 2.6 M solution 26 mmol) in 200 ml of ether at a rate to sustain boiling. After 20 min, aqueous NH_4Cl was slowly added. The ether layer was separated, washed with water, and dried ($MgSO_4$). Removal of the solvent gave 2-(2-hydroxy-2-propyl)-4-methyl-1-(4-methylphenylthio)benzene as a yellow oil: ^1H NMR ($CDCl_3$) δ 1.70 (s, 6, CH_3), 2.28 (s, 3), 2.31 (s, 3), 3.47 (broad, s, 1, OH), 6.83–7.56 (m, 6), 7.73 (m, 1).

To a $CHCl_3$ solution of this yellow oil was added *tert*-butyl hypochlorite (1.30 g, 12.0 mmol). After stirring 10 min, the solution was extracted with 10% NaOH and water and then dried ($MgSO_4$). Removal of solvent gave a yellow amorphous solid which on recrystallization from chloroform–hexane gave 2.29 g (66%) of the sulfoxide-alcohol: mp 168–169 °C; ^1H NMR ($CDCl_3$, 100 MHz) δ 1.32 (s, 3), 166 (s, 3), 2.26 (s, 3) 2.32 (s, 3), 7.13 (m, 4), 7.45 (d, 2, J = 9.0 Hz, H ortho to S in the disubstituted ring), 8.08 (d, 1, J = 8.0 Hz, H ortho to S in the trisubstituted ring); IR ($CHCl_3$) 3358 (broad, w), 2999 (s), 1600 (w), 1249 (w), 1047 (m), 1025 (s), 1017 (s), 798 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 288 (9.6, $M^{\cdot+}$), 273 (89, $M^{\cdot+} - CH_3$), 271 (27, $M^{\cdot+} - OH$), 181 (92), 163 (100), 91 (62), 43 (75). Anal. ($C_{17}H_{20}O_2S$) C, H.

4-Chloro-2-(2-hydroxy-2-propyl)-1-phenylsulfinylbenzene. The published method[5] was used to prepare 5-chloro-2-phenylthiobenzoic acid, mp 164–166 °C (lit.[5] 166–167 °C). This acid (29.41 g, 0.111 mol) was boiled in thionyl chloride for 1 h, and the thionyl chloride was removed. The acid chloride was poured into 800 ml of methanol and 50 ml of pyridine. Addition of 1 l. of water and extraction with ether gave the crude ester.

An ether solution of the crude ester was added to methyl magnesium bromide (76.62 ml of a 2.9 M solution) in ether at a rate sufficient to sustain boiling. The mixture was allowed to stir 1 h after addition and then the complex was destroyed with excess NH_4Cl. The ether solution was washed with 10% HCl, 5% NaOH, and water and dried. The ether was removed to give 26.1 g (84%) of crude 4-chloro-2-(2-hydroxy-2-propyl)-1-phenylthiobenzene as a yellow liquid: ^1H NMR ($CDCl_3$) δ 1.69 (s, 6, CH_3), 3.48 (broad, s, 1), 7.12 (m, 7) 7.51 (m, 1). To a stirred CH_2Cl_2 solution of this crude sulfide (8.23 g, 29.4 mmol) was added *tert*-butyl hypochlorite (3.33 ml, 29.4 mmol). After 1 h stirring the solution was extracted with 5% NaOH and the solvent removed to give a brown oil. This was twice crystallized from chloroform–ether to give 5.37 g (62%) of the sulfoxide-alcohol: mp 158–160 °C; ^1H NMR (CDCl, 100 MHz) δ 1.20 (s, 3, CH_3), 1.68 (s, 3, CH_3), 3.59 (broad, s, 1, OH), 7.16 (1, d, J = 2.1 Hz, H ortho to the alkyl group in the trisubstituted ring), 7.32 (m, 4), 7.57 (m, 2, H ortho to sulfur in monosubstituted ring), 8.16 (d, 1, J = 8.7 Hz); IR ($CHCl_3$) 3338 (broad, m), 3007 (s), 1583 (w), 1444 (m), 1243 (w), 1045 (m), 1019 (s), 695 cm^{-1} (m); mass spectrum (70 eV) *m/e* (rel intensity 294 (5.8, $M^{\cdot+}$ for ^{35}Cl), 296 (2.3, $M^{\cdot+}$ for ^{37}Cl), 279 (91, $M^{\cdot+} - CH$ for ^{35}Cl), 281 (39, $M^{\cdot+} - CH$ for ^{37}Cl), 183 (5), 148 (43), 43 (100.00). Anal. ($C_{15}H_{15}ClO_2S$) C, H, Cl, S.

4-Chloro-1-[2-(2-hydroxy-2-propyl)phenylsulfinyl]benzene. To CH_3MgBr (25 ml of a 2.9 M solution) in 400 ml of ether was added methyl 2-(4-chlorophenylthio)benzoate (15.0 g, 53.81 mmol) at a rate sufficient to sustain boiling. The mixture was stirred for 30 min and then aqueous NH_4Cl was slowly added. The ether solution was separated, washed with 10% HCl, 10% NaOH, and H_2O and dried ($MgSO_4$). Removal of the solvent gave a yellow oil which on distillation [bp 150 °C (0.3 mm)] through a short column gave 11.90 g (79%) of 4-chloro-1-[2-(2-hydroxy-2-propyl)phenylsulfinyl]benzene: ^1H NMR ($CDCl_3$) δ 1.70 (s, 6), 1.34 (s, broad, 1, OH), 6.97–7.23 (m, 7), 7.48 (m, 1); mass spectrum (70 eV) *m/e* (rel intensity) 278 (43, $M^{\cdot+}$ for ^{35}Cl), 280 (15, $M^{\cdot+}$ for ^{37}Cl), 263 (27, $M^{\cdot+} - CH_3$), 210 (25).

To a chloroform solution of this sulfide-alcohol (6.62 g, 23.74 mmol) was added *tert*-butyl hypochlorite (2.58 g, 23.74 mmol). After 10 min stirring the solution was extracted with 10% NaOH and H_2O and dried ($MgSO_4$). Removal of the solvent gave a yellow solid which after two recrystallizations from chloroform–hexane gave 3.97 g (58%) of the sulfoxide-alcohol: mp 169–171 °C; ^1H NMR ($CDCl_3$, 220 MHz) δ 1.34 (s, 3, CH_3), 1.70 (s, 3, CH_3), 3.01 (broad, s, 1, OH), 7.25 (m, 3), 7.40 (m, 2, H para to S and para to the alkyl group in the disubstituted ring), 7.75 (d, 2, J = 8.5 Hz), 8.20 (m, 1, H ortho to S in the alkyl substituted ring); IR ($CHCl_3$) 3351 (w) 3002 (m), 1478 (m), 1391 (w), 1367 (w), 1093 (m), 1011 (s), 842 cm^{-1} (m); mass spectrum (70 eV) *m/e* (rel intensity) 294 (11, $M^{\cdot+}$ for ^{35}Cl), 296 (4, $M^{\cdot+}$ for ^{37}Cl), 279 (94, $M^{\cdot+} - CH_3$), 167 (64), 151 (63), 149 (100), 43 (67). Anal. ($C_{15}H_{15}ClO_2S$) C, H, S.

2-(2-Bromo-5-nitrophenyl)-2-propyl Acetate. To an ether (150 ml) solution of 2-(2-bromophenyl)propan-2-ol[6] (30 g, 139.5 mmol) and pyridine (30 ml), acetyl chloride (30 ml) was slowly added. After 10 min stirring the mixture was extracted with water and twice with 10% HCl and dried, and the solvent was removed. The resulting oil was dissolved in acetic anhydride (10 ml). This was added to a stirred solution of acetic anhydride (157 ml), 90% nitric acid (17.4 ml), and sulfuric acid (0.5 ml) at 0 °C. After 30 min at 0 °C, the solution was poured into crushed ice and stirred for an additional 30 min. This mixture was extracted with ether, and the ether solution was washed with water. Addition of pentane with cooling caused crystallization. Recrystallization from ether–pentane gave 14.3 g (34%) of the desired product: mp 136–139 °C; ^1H NMR ($CDCl_3$, 100 MHz) δ 1.88 (s, 6, CH_3), 2.06 (s, 3, $OCOCH_3$), 7.72 (d, 1, J = 8.8 Hz, H ortho to Br), 7.93 (d, 1, J = 8.8, 2.6 Hz, H para to alkyl group), 8.28 (d, 1, J = 2.6 Hz, H ortho to alkyl group); IR ($CHCl_3$) 2993 (w), 1740 (s), 1532 (s), 1351 (s), 1257 (s), 1153 (m), 1122 cm^{-1} (m); mass spectrum (70 eV) *m/e* (rel intensity) 222 (48, $M^{\cdot+} - Br$), 214 (14), 180 (83), 43 (100). Anal. ($C_{11}H_{12}BrNO_4$) C, H, N, Br.

A sample of this acetate was oxidized by boiling in 6 N HNO_3 to give 2-bromo-5-nitrobenzoic acid, mp 176–179 °C (lit.[7] 178–180 °C).

2-(2-Hydroxy-2-propyl)-4-nitro-1-phenylsulfinylbenzene. Thiophenol (0.802 g, 7.28 mmol) and 2-(2-bromo-5-nitrophenyl)-2-propyl acetate (2.00 g, 6.62 mmol) were dissolved in 95% ethanol (10 ml) and treated with NaOH (0.291 g, 7.28 mmol) and H_2O (3 ml) by boiling under N_2 for 2 h. Water and ether were added, the ether phase was separated and dried, and the solvent was removed to give a yellow oil, 2-(2-hydroxy-2-propyl)-4-nitrophenylthiobenzene: ^1H NMR ($CDCl_3$) δ 1.83 (s, 6, CH_3), 2.74 (broad s, 1, OH), 7.12 (d, 1, J = 9.0 Hz, H ortho to S on the trisubstituted ring), 7.45 (s, 5), 7.88 (dd, 1, J = 9.0, 2.3 Hz, H para to alkyl group), 8.41 (d, 1, J = 2.3 Hz, H ortho to alkyl group); IR ($CHCl_3$) 3551 (m), 1520 (s), 1438 (s), 1121 (m), 1019 (m), 915 cm^{-1} (m).

To a stirred $CHCl_3$ solution of 2-(2-hydroxy-2-propyl)-4-nitrophenylthiobenzene (1.51 g, 5.43 mmol) was added *tert*-butyl hypochlorite (6.15 ml, 5.43 mmol). After 10 min the solution was extracted with 10% NaOH and water, the $CHCl_3$ solution was dried ($MgSO_4$), and the solvent was removed to give an orange paste. This was recrystallized three times from chloroform–hexane to give 621 mg (37%) of the sulfoxide: mp 183–185 °C; ^1H NMR ($CDCl_3$, 100 MHz) δ 1.25 (s, 3, CH_3), 1.73 (s, 3, CH_3), 3.03 (broad, s, 1, OH), 7.29 (m, 3), 7.60 (m, 2), 8.02 (d, 1, J = 2.2 Hz, H ortho to the alkyl group on the trisubstituted ring), 8.20 (dd, 1, J = 2.2, 8.9 Hz, H para to the alkyl group on the trisubstituted ring), 8.49 (d, 1, J = 8.9 Hz, H ortho to S on the trisubstituted ring); IR ($CHCl_3$) 3144 (broad, s), 3007 (m), 1533 (s), 1350 (s) 1024 (m), 907 cm^{-1} (w); mass spectrum (70 eV) *m/e* (rel intensity) 305 ($M^{\cdot+}$, 13), 290 ($M^{\cdot+} - CH_3$, 100), 288 (27), 194 (52), 49 (82). Anal. ($C_{15}H_{15}NO_4S$) C, H, N.

2-(2-Hydroxy-2-propyl)benzenethiol. Methyl thiosalicylate (10 g, 59.45 mmol) in 100 ml of ether was added dropwise to a stirred ether (300 ml) solution of CH_3MgBr (61.5 ml of a 2.9 M ether solution), and this mixture was refluxed for 30 min. To this cold solution, 50 ml of saturated ammonium chloride was slowly added. The ether layer was separated, extracted with water, and dried ($MgSO_4$). Removal of the ether gave an oil which was twice recrystallized from hexane–ether to give 8.33 g (83%) of the desired alcohol: mp 45–46 °C; ^1H NMR ($CDCl_3$) δ 1.67 (s, 6, CH_3), 2.48 (broad, s, 1, disappears with D_2O shake), 4.07 (broad, s, 1, disappears with D_2O shake), 6.91–7.39 (m, 4); IR ($CHCl_3$) 3595 (s), 3480 (braod, w), 3012 (s), 2982 (s), 1470 (s), 1367 (s), 1242 (w), 855 cm^{-1} (w); mass spectrum (70 eV) *m/e* (rel intensity) 168 (16, $M^{\cdot+}$), 151 (16, $M^{\cdot+} - OH$), 150 (100, $M^{\cdot+} - HO$) 135 (6.0, $M^{\cdot+} - HO, CH$). Anal. ($C_9H_{12}OS$) C, H, S.

1-[2-(2-Hydroxy-2-propyl)phenylthiol]-4-nitrobenzene. A solution of 2-(2-hydroxy-2-propyl)benzenethiol (3.0 g, 17.83 mmol) and 4-chloronitrobenzene (2.81 g, 17.83 mmol) in 50 ml of 95% ethanol was heated under a nitrogen atmosphere with NaOH (0.72 g, 17.83 mmol) and 10 ml of water for 90 min. Ether and water were added, and the organic layer was separated and dried ($MgSO_4$). Removal of the ether gave a brown solid which after two recrystallizations from $CHCl_3$ gave

1.86 g (36%) of the sulfide-alcohol: mp 117–118 °C; ^{1}H NMR ($CDCl_3$) δ 1.71 (s, 6, CH_3), 4.02 (s, 1, OH, disappears with D_2O shake), 7.02–7.82 (m, 6), 8.04 (d, 2, J = 9.0 Hz, H ortho to NO_2); IR ($CHCl_3$) 3510 (broad, w), 3019 (w), 1580 (s), 1523 (s), 1340 (s), 1111 (m), 1088 (m), 854 cm^{-1} (s); mass spectrum (70 eV) *m/e* (rel intensity) 289 (51, M·$^+$), 274 (100, M·$^+$ − CH_3), 210 (43), 151 (27), 149 (34), 134 (14). Anal. ($C_{15}H_{15}NO_3S$) C, H, N, S.

1-[2-(2-Hydroxy-2-propyl)phenylsulfinyl]-4-nitrobenzene. To a stirred $CHCl_3$ solution of 1-[2-(2-hydroxy-2-propyl)phenylthio]-4-nitrobenzene (1.12 g, 3.89 mmol) was slowly added *tert*-butyl hypochlorite (0.44 ml, 3.89 mmol). After 10 min the solution was extracted with 10% NaOH and water. The $CHCl_3$ solution was dried ($MgSO_4$) and the solvent removed to give an oil. Two recrystallizations from pentane–ether gave 1.04 g (88%) of the sulfoxide-alcohol: mp 158–159 °C; ^{1}H NMR ($CDCl_3$) δ 1.47 (s, 3, CH_3), 1.73 (s, 3, CH_3), 3.24 (broad s, 1, OH, disappears with D_2O shake), 7.34 (m, 3, 8.01 (m, 5); IR ($CHCl_3$) 3380 (w, broad), 3015 (m), 1608 (m), 1533 (s), 1350 (s), 1014 (m), 855 cm^{-1} (s); mass spectrum (70 eV) *m/e* (rel intensity) 305 (5, M·$^+$), 290 (100, M·$^+$ − CH_3), 167 (18), 151 (34), 149 (39), 43 (40). Anal. ($C_{15}H_{15}NO_4S$) C, H, N.

2-(1,1,1,3,3,3-Hexafluoro-2-hydroxy-2-propyl)-4-methyl-1-(4-methylphenylthio)benzene. To 4,4′-dimethyldiphenyl sulfide (75.0 g, 0.35 mol) in 400 ml of dry CCl_4 was added $AlCl_3$ (12.64 g, 0.0946 mol). Hexafluoroacetone (36.4 ml, 0.35 mol) was distilled into the stirred mixture at 0 °C. After 3 h, refluxing of the volatile ketone had ceased. An NMR spectrum showed the presence of starting material (ca. 25%). More hexafluoroacetone (19 ml, 0.18 mol) and aluminum chloride (3.16 g, 0.0236 mol) were added, and the mixture was stirred for 2 h. To the mixture was added 300 ml of water, and the mixture was filtered. The CCl_4 solution was separated and dried ($MgSO_4$). Removal of the solvent gave a purple oil. The oil was dissolved in 800 ml of pentane and the solution cooled. A solid precipitate was recrystallized twice from pentane to yield 43 g (32.3%) of pure sulfide-alcohol: mp 66–66.5 °C; H NMR (CCl_4) δ 2.31 and 2.43 (2 s, 3 each, $ArCH_3$), 7.70 (m, 5), 7.34 (d, 1, J = 8.1 Hz, H ortho to S in the trisubstituted ring), 7.50 (broad s, 1, H ortho to the fluoroalkyl group), 7.99 (broad s, disappears with D_2O shake, OH); ^{19}F NMR (CCl_4) 74.7; IR (CCl_4) 3455 (m, broad, OH, 2920 (w), 1240 (s, 4 strong peaks), 1175 (m), 970 (m), 810 cm^{-1} (m); mass spectrum (70 eV) *m/e* (rel intensity) 380 (95, M·$^+$), 219 (100), 150 (16), 123 (9.5), 91 (12). Anal. ($C_{17}H_{14}F_6OS$) C, H, S.

2-(1,1,1,3,3,3-Hexafluoro-2-hydroxy-2-propyl)-4-methyl-1-(4-methylphenylsulfinyl)benzene. To 2-(1,1,1,3,3,3-hexafluoro-2-hydroxy-2-propyl)-4-methyl-10(4-methylphenylsulfinyl)benzene (1.62 g, 4.26 mmol) in 30 ml of CCl_4 was added *tert*-butyl hypochlorite (0.46 g, 4.26 mmol). This solution was stirred for 0.5 h and the solvent removed to give a white solid. This was recrystallized twice from ether to yield 1.30 g (76.7%) of the sulfoxide-alcohol: mp 202–203 °C; ^{1}H NMR (CCl_4) δ 2.32 and 2.46 (2 singlets, 3 each, CH_3), 7.02–7.06 (m, 7), 8.17 (d, 1, J = 8.0 Hz, H ortho to S in the trisubstituted ring); ^{19}F NMR ($CDCl_3$) 75.2 (broad s); IR (Nujol) 1250 (s, 3 or 4 strong peaks), 1160 (s), 970 (s), 830 (m), 752 (m), 705 cm^{-1} (m); mass spectrum (70 eV) *m/e* (rel intensity) 396 (10, M·$^+$), 380 (19), 219 (100), 139 (46), 107 (39), 91 (39). Anal. ($C_{17}H_{14}F_6O_2S$) C, H, S.

General Synthesis of Chlorosulfuranes: 1-Chloro-3,3-bis(trifluoromethyl-5-methyl-1-(4-methylphenyl)[3*H*-2,1-benzoxathiole] (14). To 2-(1,1,1,3,3,3-hexafluoro-2-hydroxy-2-propyl)-4-methyl-1-(4-methylphenylsulfinyl)benzene (1 g, 2.4 mmol) was added to 20 ml of $CHCl_3$, and the suspension was stirred. Acetyl chloride (2 ml, excess) was added to the mixture, which became homogeneous after 10 min. The solvent and excess acetyl chloride were removed in vacuo to give 1.03 g (99%) of **14**: mp 165–167 °C (sealed tube); ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3, CH_3), 2.68 (s, 3, CH_3), 7.28 (m, 4, tolyl aromatic CH), 7.60 (broad s, 1, H ortho to fluoroalkyl group), 7.73 (d, 1, J = 9.0 Hz, H meta to S in the fused ring), 9.14 (d, 1, J = 9.0 Hz, ortho to S in the fused ring); ^{19}F NMR ($CDCl_3$) 74.6 (q, 3, J = 9.4 Hz), 76.4 (q, 3, J = 9.4 Hz); IR ($CHCl_3$) 3000 (w), 1250 (s, 4 strong peaks), 1110 (m), 970 (m), 790 cm^{-1} (m); mass spectrum (70 eV) *m/e* (rel intensity (414 (0.98, M·$^+$ for ^{35}Cl), 416 (0.28, M·$^+$ for ^{37}Cl), 380 (45, M·$^+$ − Cl), 379 (94, M·$^+$ − HCl), 345 (1.7, M·$^+$ − CF_3), 241 (100), 219 (83), 197 (35). Anal. ($C_{17}H_{13}ClF_6OS$) C, H.

Chlorosulfurane **14** was formed in similar yields by treatment of 2-(1,1,1,3,3,3-hexafluoro-2-hydroxy-2-propyl)-4-methyl-1-(4-methylphenylthio)benzene with 1 equiv of *tert*-butyl hypochlorite under strictly anhydrous conditions, or by bubbling HCl through a $CHCl_3$ solution of the sulfoxide-alcohol. Chlorosulfurane **14** is readily hydrolyzed to regenerate the sulfoxide alcohol from which it was made.

1-Chloro-3,3-dimethyl-1-phenyl[3*H*-2,1-benzoxathiole] (4). A $CHCl_3$ solution of 2-(2-hydroxy-2-propyl)-1-phenylsulfinylbenzene (2.60 g, 10.0 mmol) when treated by the general method gave 2.80 g (100%) of sulfurane **4**: mp 125–126 °C; ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 3, CH_3 cis to the phenyl), 1.68 (s, 3, CH_3 trans to the phenyl), 7.44 (s, 6), 7.70 (m, 2), 9.33 (m, 1, H ortho to S in the fused ring); ^{13}C NMR ($CDCl_3$), 28.544 (CH_3), 30.370 (CH_3), 99.106 (quaternary aliphatic), 122.911 (CH), 127.763 (2 identical CH), 128.563 (aromatic CH_3CC), 129.762 (2 identical CH), 130.789 (CH), 132.103 (CH), 133.187 (CH), 134.786 (CH), 141.408 (quaternary aromatic), 146.946 (quaternary aromatic); IR ($CHCl_3$) 2980 (s), 1448 (m), 1240 (m), 1150 (m), 833 cm^{-1} (s); mass spectrum (field desorption) *m/e* 278 (minor, M·$^+$), 243 (major, M·$^+$ − Cl). Anal. ($C_{15}H_{15}ClOS$) C, H, Cl, S.

1-Chloro-3,3-dimethyl-5-methyl-1-(4-methylphenyl)[3*H*-2,1-benzoxathiole] (6a). A $CHCl_3$ solution of 2-(2-hydroxy-2-propyl)-4-methyl-1-(4-methylphenylsulfinyl)benzene (2.04 g, 8.93 mmol), when treated by the general method gave 2.71 (99%) of pure sulfurane **6a**: mp 125–127 °C; ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 3, CH_3 cis to the aryl), 1.68 (s, 3, CH_3 trans to the aryl), 2.35 (s, 3, $ArCH_3$), 2.55 (s, 3, $ArCH_3$), 7.02–7.60 (m, 7), 9.18 (d, 1, J = 8.0 Hz, H ortho to S on the fused ring); IR ($CHCl_3$) 2969 (s), 1595 (w), 1131 (w), 1068 (w), 818 (s), 793 cm^{-1} (m). Anal. ($C_{17}H_{19}ClOS$) C, H.

1,5-Dichloro-3,3-dimethyl-1-phenyl[3*H*-2,1-benzoxathiole] (6b). A $CHCl_3$ solution of 4-chloro-2-(2-hydroxy-2-propyl)-1-phenylsulfinylbenzene (4.11 g, 13.94 mmol) when treated by the general method gave 4.39 g (101%) of sulfurane **6b**: mp 132–133 °C; ^{1}H NMR ($CDCl_3$) δ 1.24 (s, 3, CH_3 cis to the phenyl), 1.68 (s, 3, CH_3 trans to the phenyl), 7.28 (d, 1, J = 1.8 Hz, H ortho to the alkyl group in the fused ring), 7.38 (s, 5, phenyl CH), 7.60 (d of d, 1, J = 1.8, 8.5 Hz, H para to the alkyl group on the fused ring), 9.34 (d, 1, J = 8.5 Hz, H ortho to S on the fused ring); IR ($CHCl_3$) 2890 (s), 1568 (m), 1445 (s), 1280 (s), 1152 (s), 1000 (w), 852 cm^{-1} (m). Anal. ($C_{15}H_{14}Cl_2OS$) C, H, S.

1-Chloro-1-(4-chlorophenyl)-3,3-dimethyl[3*H*-2,1-benzoxathiole] (6c). A $CHCl_3$ solution of 3-chloro-1-[2-(2-hydroxy-2-propyl)phenylsulfinyl]benzene (2.66 g, 9.02 mmol) when treated by the general method gave sulfurane **6c**, contaminated with acetic acid. Recrystallization from chloroform–hexane gave 2.56 (91%) of sulfurane **6c**: mp 129–131 °C; ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 3, CH_3 cis to the aryl ring), 1.68 (s, 3, CH_3 trans to the aryl ring), 7.34 (s, 5), 7.71 (m, 2), 9.29 (m, 1, H ortho to S on the fused ring); IR ($CHCl_3$) 3349 (broad, m), 3000 (m), 1478 (m), 1092 (m), 1011 (s), 824 cm^{-1} (w). Anal. ($C_{15}H_{14}Cl_2OS$) C, H, S.

1-Chloro-3,3-dimethyl-1-phenyl-5-nitro[3*H*-2,1-benzoxathiole (6d). A $CHCl_3$ solution of 2-(2-hydroxy-2-propyl)-4-nitro-1-phenylsulfinylbenzene (85.3 mg, 0.28 mmol) when treated by the general method gave 81.8 mg (100%) of sulfurane **6d**: mp 126–128 °C; ^{1}H NMR δ 1.27 (s, 3, CH_3 cis to the phenyl), 1.76 (s, 3, CH_3 trans to the phenyl), 7.47 (s, 5), 8.19 (d, 1, J = 2.4, 8.6 Hz, H para to the alkyl group on the fused ring), 9.31 (d, 1, J = 8.6 Hz, H ortho to S on the fused ring); IR ($CHCl_3$) 2980 (s), 1544 (s), 1447 (m), 1352 (s), 1279 (m), 835 cm^{-1} (s). Anal. ($C_{15}H_{14}ClNO_3S$) C, H, N.

1-Chloro-3,3-dimethyl-1-(4-nitrophenyl)[3*H*-2,1-benzoxathiole] (6e). A $CHCl_3$ solution of 1-[2-hydroxy-2-propyl)phenylsulfinyl]-4-nitrobenzene (3.22 g, 10.54 mmol) when treated by the general method gave 3.41 g (100%) of pure sulfurane **6e**: mp 110–112 °C; ^{1}H NMR ($CDCl_3$) δ 1.19 (s, 3, CH_3 cis to the aryl ring), 1.70 (s, 3, CH_3 trans to the aryl ring), 7.27–7.99 (m, 5), 8.19 (d, 2, J = 9.5 Hz, H ortho to NO_2), 9.20 (m, 1, H ortho to S in the fused ring); IR ($CHCl_3$) 3375 (broad, m), 1533 (s), 1349 (s), 1014 (broad, m), 855 cm^{-1} (s). Anal. ($C_{15}H_{14}ClNO_3S$) C, H, N.

2-(2-Hydroxy-2-propyl)-1-methylsulfinylbenzene. Thionyl chloride (35 ml) and 2-(methylthio)benzoic acid (19.4 g, 115.3 mmol) were mixed, and the solution was refluxed for 1 h. The $SOCl_2$ was removed in vacuo, and the residue was poured into 750 ml of methanol and 30 ml of pyridine. Addition of water and ether extraction gave the crude ester. The ester solution was added to methyl magnesium bromide (90 ml of a 2.9 M solution) in ether at a rate sufficient to sustain reflux and then stirred for 1 h before adding aqueous NH_4Cl. The ether solution was separated, washed with water, and dried, and the solvent was removed. Distillation, bp 108 °C at ca. 0.1 mm (lit.[8] bp 95 °C at 0.1 mm), gave 11.83 g (56%) of the sulfide-alcohol: ^{1}H NMR

($CDCl_3$) δ 1.68 (s, 6, CH_3), 2.48 (s, 3, SCH_3), 7.02–7.48 (m, 4); IR ($CHCl_3$) 3444 (broad, m), 3019 (s), 1438 (s), 1172 (m), 1051 (w), 954 cm^{-1} (m). Anal. ($C_{10}H_{14}OS$) C, H, S.

1-Chloro-3,3-dimethyl-1-methyl[3*H*-2,1-benzoxathiole] (7). To a stirred ether solution of 2-(2-methylthiophenyl)propan-2-ol (1.03 g, 5.67 mmol) was added *tert*-butyl hypochlorite (0.62 g, 5.67 mmol). The resulting precipitate was collected and washed with ether to give 1.13 g (92%) of the sulfurane: mp 107–109 °C; ^1H NMR ($CDCl_3$) δ 1.77 (s, 3), 1.87 (s, 3), 3.76 (s, 3, SCH_3), 7.32 (m, 1, H ortho to alkyl group), 7.72 (m, 2), 9.2 (m, 1, H ortho to S); IR ($CHCl_3$) 2970 (s), 1472 (w), 1444 (m), 1373 (m), 1298 (m), 1244 (broad, m), 1151 (m), 838 cm^{-1} (s). Anal. ($C_{10}H_{13}ClOS$) C, H, Cl, S.

A solution of chlorosulfurane 7 (36.9 mg, 0.17 mmol) in 0.6 ml of chloroform was placed in an NMR tube and cooled to 0 °C. Trifluoromethane sulfonic acid (15.1 μl, 0.17 mmol) was added by syringe. An NMR spectrum of **12** was obtained at probe temperature: NMR ($CDCl_3$) δ 1.86 (s, 3), 1.96 (s, 3), 3.45 (s, 3, SCH_3), 7.46–7.94 (m, 3), 8.32 (m, 1, H ortho to S).

2-(2-Hydroxy-2-propyl)methylsulfinylbenzene. A $CHCl_3$ solution of sulfurane 7 (0.526 g, 2.4 mmol) was extracted with 10% NaOH and dried ($MgSO_4$), and the solvent was removed to give 0.466 g (97%) of the sulfoxide-alcohol: mp 94–96 °C; ^1H NMR ($CDCl_3$) δ 1.65 (s, 6, CH_3), 2.78 (s, 3, SCH_3), 7.38 (m, 3), 8.19 (m, 1, H ortho to S); IR ($CHCl_3$) 3335 (broad m), 2985, (s), 1368 (w), 1055 (m), 1018 (s), 960 cm^{-1} (m); mass spectrum (70 eV) *m/e* (rel intensity) 198 (H, $M\cdot^+$), 183 (63, $M\cdot^+ - CH_3$), 182 (72), 167 (100), 149 (100), 134 (41). Anal. ($C_{10}H_{14}O_2S$) C, H.

(*S*)-2-(2-Hydroxy-2-propyl)-1-phenylsulfinylbenzene (5). To magnesium (1.04 g, 42.8 mg-atom) in 100 ml of THF, ethylene dibromide (1.04 g, 42.8 mmol) was added at a rate to maintain reflux under a nitrogen atmosphere. After the mixture was stirred overnight, potassium metal (3.0 g, 76.8 mg-atom) and potassium iodide (3.19 g, 19.2 mmol) were added, and the mixture was refluxed for 2.5 h. The dark suspension of Rieke[10a] magnesium was allowed to cool to room temperature.

The flask was fitted with an additional funnel containing 2-(2-bromophenyl)-propan-2-ol and 50 ml of dry THF. To the alcohol solution was added ethyl magnesium chloride (6.46 ml of a 2.96 M solution). Only slight warming was noted. This solution was added dropwise to the stirred magnesium suspension, and this mixture was stirred for 90 min.

To this stirred mixture was added 25 ml of a THF solution of menthyl-(*S*)-benzenesulfinate (5.38 g, 1.92 mmol) which had been prepared by the literature[10b] method, mp 50–51 °C (lit.[10b] 50–51 °C), $[\alpha]^{23}D$ −202°, acetone (lit.[10b] $[\alpha]^{23}D$ − 206°, acetone). After 30 min, the reaction mixture was hydrolyzed with saturated aqueous ammonium chloride. Ether (300 ml) was added, and the organic layer was separated, washed with water, and dried, and the solvent was removed to give a yellow oil. The product was crystallized from ether and then twice recrystallized from pentane–ether to give 3.2 g (64%) of (*S*)-2-(2-hydroxy-2-propyl)phenylsulfinylbenzene: mp 124–125 °C (softens, 85 °C); $[\alpha]^{23}D$ −140.1° (*c* 4.0, methanol); ^1H NMR ($CDCl_3$) δ 1.35 (s, 3, CH_3), 1.68 (s, 3, CH_3), 3.13 (broad, s, OH), 7.14–7.75 (m, 8), 8.20 (m, 1, H ortho to S on the disubstituted ring); IR ($CHCl_3$) 3360 (w, OH), 3000 (s), 1477 (m), 1444 (m), 1369 (w), 1018 (s), 698 cm^{-1} (m); mass spectrum (70 eV) *m/e* (rel intensity) 260 (7.1, $M\cdot^+$), 245 (100, $M\cdot^+ - CH$), 243 (23, $M\cdot^+ - OH$), 167 (41), 151 (29), 149 (58), 77 (34); CD (THF, 23°) λ 231 ($[\theta] = -9.4 \times 10^{+4}$), λ 269 ($[\theta] = -1.8 \times 10^{+4}$). Anal. ($C_{15}H_{16}O_2S$) C, H, S.

(*S*)-(+)-1-Chloro-3,3-dimethyl-1-phenyl[3*H*-2,1-benzoxathiole] (4). A mixture of (*S*)-2-(2-hydroxy-2-propyl)phenylsulfinylbenzene (2.37 g, 0.91 mmol) was stirred in ether at room temperature, and acetyl chloride (3 ml, excess) was added. Removal of the solvent in vacuo gave 2.53 g (100%) of the optically active sulfurane, mp 110–112 °C (softens at 101 °C); $[\alpha]^{23}D$ +72.1° (*c* 8.1, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 1.27 (s, 3, CH_3 cis to the phenyl), 1.69 (s, 3, CH_3 trans to the phenyl), 7.44 (s, 6), 7.72 (m, 2), 9.36 (m, 1, H ortho to S on the fused ring); IR ($CHCl_3$) 2969 (s), 1448 (s), 1243 (m), 1153 (m), 831 cm^{-1} (s). Anal. ($C_{15}H_{15}ClOS$) C, H, Cl, S.

The reaction was repeated with addition of the acetyl chloride being done at −78 °C, to give 100% yield of the chlorosulfurane, mp 103–104 °C, $[\alpha]^{23}D$ +253.4° (*c* 8.2 CH_2Cl_2).

1-(3,3-Dimethyl-1-phenyl[3*H*-2,1-benzoxathiolyl]) Tetrafluoroborate (10). To a stirred nitromethane solution of chlorosulfurane **4** (1 g, 3.59 mmol) was added a nitromethane solution of silver tetrafluoroborate (0.51 g, 3.59 mmol). The silver chloride which formed was filtered and the solvent removed to leave a brown oil. Recrystallization twice from ethyl acetate gave 0.652 g (55%) of the crystalline salt: mp 120–121 °C; ^1H NMR ($CDCl_3$) δ 1.70 (s, 3, CH_3), 1.82 (s, 3, CH_3), 7.47–7.90 (m, 8), 8.10 (broadened d, 1, J = 7.5 Hz, H ortho to S in the fused ring); ^{13}C NMR ($CDCl_3$) 29.683 (CH_3), 30.256 (CH_3), 106.698 (quaternary aliphatic), 123.456 (CH), 131.018 (2 identical CH), 132.302 (CH), 133.273 (quaternary aromatic), 135.842 (CH), 137.155 (CH), 145.204 (quaternary aromatic); IR ($CHCl_3$) 3040 (w), 1448 (m), 1228 (m), 1070 (broad, s), 832 (s), 796, 675 cm^{-1} (m). Anal. ($C_{15}H_{15}BF_4OS$) C, H, S.

The trifluoromethanesulfonate salt was prepared in solution by addition of trifluoromethanesulfonic acid (14.1 μl, 0.159 mmol) to a $CDCl_3$ solution of chlorosulfurane **4** (44.4 mg, 0.159 mmol): ^1H NMR ($CDCl_3$) δ 1.68 (s, 3), 1.83 (s, 3), 7.41–7.93 (m, 8), 8.15 (broadened d, 1, J = 7.9 Hz).

1-Chloro-1-methyl[3*H*-2,1-benzoxathiol] (9). A sample of 2-methylsulfinylbenzyl alcohol[11] was treated with excess acetyl chloride in $CDCl_3$. The ^1H NMR spectrum of the sulfurane was obtained after ca. 30 min at room temperature; ^1H NMR ($CDCl_3$), δ 3.62 (s, 3, SCH_3), 5.82 (broadened s, 2, CH_2O, 7.67 (m, 3), 9.17 (m, 1, H ortho to S).

Enantiomeric Purity of (*S*)-3 and (*S*)-5. A sample (14.8 mg) of (*S*)-sulfoxide **5** ($[\alpha]^{23}D$ −140.1°) was dissolved in 1 ml of a 0.18 M $CDCl_3$ solution of (*S*)-(+)-1-(10-methyl-9-anthryl-2,2,2-trifluoroethanol.[19] The upfield methyl group showed peaks (−5°) at δ 1.09 and 1.16, for the *R* and *S* isomers, respectively, with an integral ratio of 2:98.

A sample (16.0 mg) of partially resolved (*S*)-chlorosulfurane **4** ($[\alpha]^{23}D$ +72.1°) was dissolved in 1 ml of a 0.18 M $CDCl_3$ solution of (*S*)-(+)-1-(10-methyl-9-anthryl)-2,2,2-trifluoroethanol. The downfield methyl group showed absorptions (−10°) at δ 1.20 and 1.29, for the *R* and *S* enantiomers, respectively, with an integral ratio of 36.5:63.5.

Hydrolysis of (*S*)-Chlorosulfurane 4. A sample of (*S*)-chlorosulfurane 4 ($[\alpha]^{23}D$ +72.1°, methylene chloride) was dissolved in $CHCl_3$ and extracted with 5% NaOH. Removal of the solvent gave (*S*)-2-(2-hydroxy-2-propyl)phenylsulfinylbenzene, $[\alpha]^{23}D$ −35.0° (*c* 4.2, methanol).

A sample of (*S*)-**4** was similarly hydrolyzed in $CHCl_3$ by addition of diisopropylethylamine and water, $[\alpha]^{23}D$ −36.1° (*c* 4.5, methanol).

A sample of (*S*)-**4** was dissolved in 95:5 chloroform–nitromethane and stirred with excess silver tetrafluoroborate. The solution was filtered, extracted with 5% NaOH, and the solvent removed to give (*S*)-2-(2-hydroxy-2-propyl)phenylsulfinylbenzene, $[\alpha]^{23}D$ −34.2° (*c* 4.3, methanol).

Equilibrium Constant for Equation 1. Hydrogen chloride gas was passed through acetone at 0 °C. To 1.0 ml of the resulting solution was added sulfoxide **5** (21.3 mg, 0.082 mmol). Conversion to sulfurane **4** was quickly complete (NMR). Water (120 μl) was added until **5** was detected in the NMR spectrum. The areas of the methyl peaks for **4** (2.1) and **5** (1.0) were determined. The solution was added to water and titrated with 0.1 N NaOH to a phenolphthalein end point (0.82 M in HCl at equilibrium). The equilibrium constant for eq 1 is ca. 15.

Competitive Kinetics. A $CHCl_3$ solution of approximately 1 equiv of each of two sulfoxides was treated with excess acetyl chloride for 10 min and then the solvent, acetic acid and excess acetyl chloride were removed in vacuo. This process was repeated. The mixture was dissolved in $CDCl_3$, 1 equiv of either *N,N*-dimethylaniline or diisopropylethylamine was added. Water, ca. 1 equiv, was slowly added to the rapidly stirred solution at 4 °C. The relative concentrations of sulfuranes and sulfoxides were determined from NMR peak areas.

Sulfurane **6d** reacted too rapidly to measure relative to **6b**. The relative rate was determined with **6b** twice as concentrated as **6d**.

One equivalent each of chlorosulfurane **14** and sulfoxide alcohol **5** were dissolved in $CDCl_3$. No reaction was detected by NMR after 30 min at 4 °C.

Racemization of 4. A CH_2Cl_2 solution of (*S*)-(+)-**4** with α_{obsd} = +9.2 racemized within 3 h at room temperature. Two ml of the original solution was diluted with 1 ml of CH_2Cl_2 saturated with HCl. Racemization was complete within 5 min.

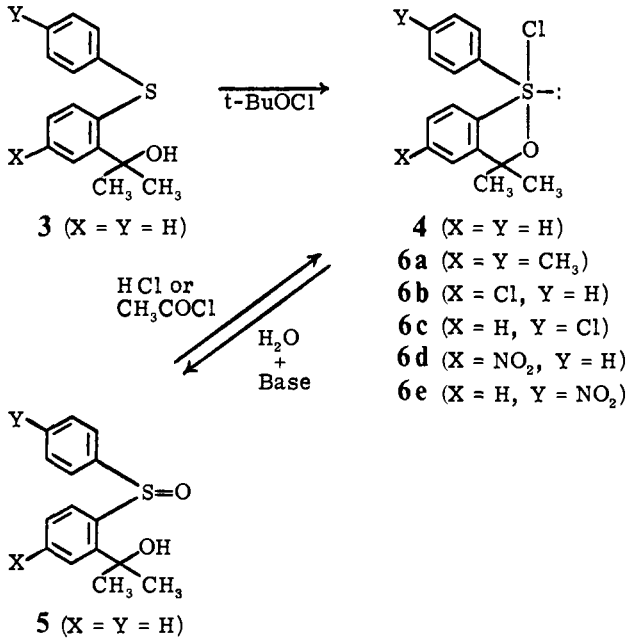
A solution of (*S*)-(+)-**4** (α_{obsd} = +21.67°) in a 98:2 mixture of methylene chloride and 2,6-lutidine racemized with an initial rate constant of ca. 10^{-6} s^{-1} at 22 °C.

Chlorosulfurane **4** (62.3 mg, 0.22 mmol) was dissolved in 0.5 ml

of CH_2Cl_2. To this solution was added 2,6-di-*tert*-butylphenol (46.1 mg, 0.22 mmol). After 24 h the NMR spectrum was identical with that of a mixture of **4** and the phenol. No sulfide-alcohol **3** was detected.

Results and Discussion

Synthesis. Following literature precedents[3a,d] for the oxidation of sulfides with hypochlorites, we have found the treatment of sulfide-alcohol **3** with 1 equiv of *tert*-butyl hypochlorite to give a quantitative yield of chlorosulfurane **4** rapidly at room temperature.



3 (X = Y = H)

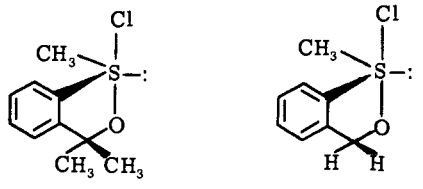
4 (X = Y = H)
6a (X = Y = CH_3)
6b (X = Cl, Y = H)
6c (X = H, Y = Cl)
6d (X = NO_2, Y = H)
6e (X = H, Y = NO_2)

5 (X = Y = H)

A chloroform solution (ca. 1 M) of **4** is not perceptibly (NMR) hydrolyzed upon addition of 1 equiv of water. Addition of 1 equiv of diisopropylethylamine or *N,N*-dimethylaniline with the water causes immediate and complete conversion of **4** to sulfoxide-alcohol **5**. As a precursor to **4**, sulfoxide **5**, being highly crystalline, is much more readily purified than the liquid sulfide **3**. The conversion of **3** to **5** can be carried out in one vessel by addition of *tert*-butyl hypochlorite to a $CHCl_3$ solution of **3**, followed by extraction with 10% NaOH. Addition of ether with cooling causes crystallization of pure **5**.

Sulfoxide-alcohol **5** is readily cyclized to sulfurane **4** by acetyl chloride or gaseous HCl. The five analogues (**6a–e**) of **4** are readily prepared in a similar manner.

Compound **4** is more stable thermally and hydrolytically than any other reported chlorosulfurane.[12] Two melting-cooling cycles (mp 125–126 °C) cause only slight decomposition (ca. 1 °C lowering in melting point). Less than 15% hydrolysis is detected by NMR after overnight exposure of crystalline **4** to air. The *S*-methyl analogue **7** is prepared by

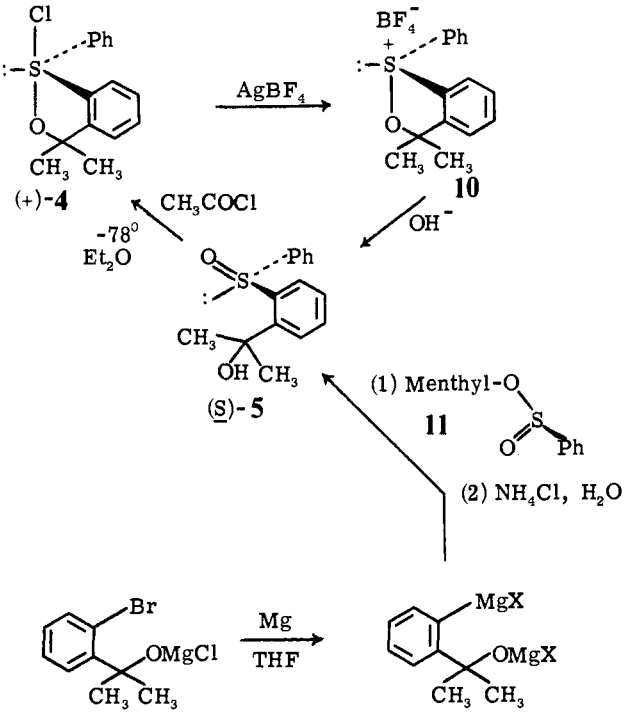


7 **8**

oxidation of the corresponding sulfide-alcohol with *tert*-butyl hypochlorite. It is also thermally stable at room temperature. Sulfurane **8**, with a methylene bridge was observed (NMR) in $CDCl_3$ solution at room temperature but was not isolated.

We have synthesized optically active **4**, the first optically active sulfurane, and have determined its absolute configuration. The synthesis uses the general method of Andersen[13] for formation of optically active sulfoxide-alcohol **5**. This is readily cyclized to the sulfurane by treatment with acetyl chloride, retaining a high degree of optical purity.

In order to protect the alcohol during Grignard formation, salt **9** was formed by adding ethyl magnesium chloride to a solution of 2-(2-bromophenyl)propan-2-ol in dry tetrahydrofuran (THF). Formation of the Grignard reagent[14,15] and reaction with menthyl-(*S*)-benzenesulfinate (**11**) followed by



(+)-**4** **10** (S)-**5**

9

workup with aqueous ammonium chloride gives (*S*)-**5** in 65% yield ($[\alpha]^{23}D$ −140.1°, methanol). Mislow[16] has shown the reaction of Grignard reagents with certain sulfinate esters to proceed with inversion. If this reaction proceeds in an analogous manner, this establishes an absolute configuration of *S* for the sulfoxide-alcohol. The circular dichroism (CD) spectrum of (*S*)-**5**, showing transitions at λ 231 nm ($[\alpha] = -9.4 \times 10^{+4}$) and λ 269 nm ($[\alpha] = -1.8 \times 10^{+4}$), is in excellent agreement with those reported for other ortho substituted diarylsulfoxides with the *S* configuration.[17]

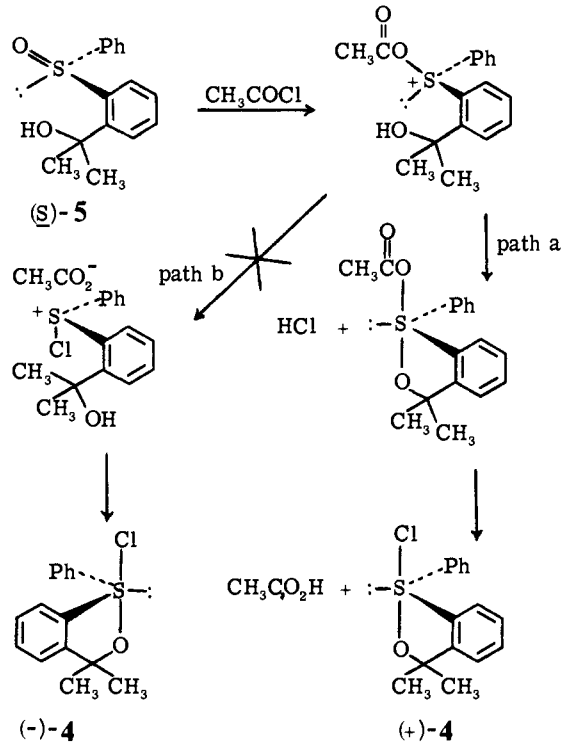
The enantiomeric purity of (*S*)-**5** was determined by the method of Pirkle[18] using 0.18 M $CDCl_3$ solution of (*S*)-(+)-1-(10-methyl-9-anthryl)-2,2,2-trifluoroethanol[19] to provide the chiral medium in which the methyl signals for enantiomers of **5** were resolved. An enantiomeric purity of 96% was determined from integrals of the upfield methyl signals at δ 1.09 and 1.16 for the *R* and *S* enantiomers, respectively.

Reaction of (*S*)-**5** in ether at room temperature gives complete conversion to a mixture of enantiomers of sulfurane **4** ($[\alpha]^{23}D$ +72.1°, methylene chloride). The enantiomeric purity, determined by the method used for (*S*)-sulfoxide **5**, was 27%. When the reaction is repeated at −78 °C, the optical purity is greatly increased ($[\alpha]^{23}D$ +253.4, methylene chloride). Based on the purity determination for the sample obtained at room temperature, this material is 95% optically pure (we have assumed optical and enantiomeric purities to be identical).

The absolute configuration of (+)-**4** is confirmed as that shown. Racemic **4** reacts readily with silver tetrafluoroborate to give the corresponding alkoxysulfonium salt. Reaction of

(+)-**4** with silver tetrafluoroborate followed by extraction with 5% sodium hydroxide gives (*S*)-sulfoxide **5**. The silver assisted ionization initiates a dissociative route for displacement via sulfonium salt **10.** If this ionization can be considered to proceed with retention of configuration at sulfur and the further reaction with hydroxyl ion is considered to proceed by the stereochemical route demonstrated earlier for the basic hydrolysis of acyclic alkoxysulfonium salts[20,21] (with inversion at sulfur), the stereochemical relationship between **5** and **4** and the absolute configuration of (+)-**4** is established as that shown.

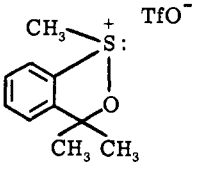
The stereochemical relationship of (*S*)-sulfoxide **5** and (+)-sulfurane **4** suggests that path a is followed in the reaction of (*S*)-**5** with acetyl chloride at −78 °C. At elevated temperatures path b, or some other pathway leading to inverted product, becomes competitive, perhaps a pathway involving ionization of the tertiary acetate which could be formed by acetylation of the alcohol function of **5.** Closely analogous ring closures have been suggested by others.[22-24] For example, the rate of oxygen exchange of simple diarylsulfoxides in acidic media is identical with that of racemization.[24-26] In contrast, the rate of oxygen exchange is about 10^4 times faster than racemization for 2-phenylsulfinylbenzoic acid. Neighboring group participation in formation of a five-membered ring has been suggested[22] to explain the rate difference.



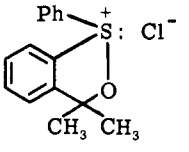
Covalent Nature of the S–Cl Bond. The geminal methyl groups of chlorosulfurane **4** provide ^{1}H NMR evidence for the covalent nature of the S–Cl bond. The chemical shifts are dramatically affected by a change from tetrahedral to trigonal-bipyramidal geometry about sulfur. While cyclic oxysulfonium tetrafluoroborate **10** absorbs at δ 1.70 and 1.82 for the geminal methyl groups, chlorosulfurane **4** absorbs at δ 1.26 and 1.68. These differences are readily explained if we assume a structure for **4** related to those found[27,28] for acyclic and spirodialkoxysulfuranes. Models show that as the geometry about sulfur changes from tetrahedral (**10**) to trigonal bipyramidal (**4**), one methyl group is forced into the shielded region over the face of the nonfused phenyl ring, while the other methyl is held in the deshielding region of the fused ring. This is in agreement with both the large upfield shift of one methyl group in **4** and the larger difference of chemical shifts between the methyl groups of **4** ($\Delta\delta$ = 25.2 Hz) relative to **10** ($\Delta\delta$ = 7.2 Hz). Similarly large values of $\Delta\delta$ for the geminal methyl groups are seen for other sulfuranes in which the chlorine of **4** has been replaced by azido (28.2 Hz), acetoxy (33.0 Hz), OR_F (40.1 Hz), cyano (36.0 Hz), and methoxy (34.5 Hz).[29] Changing counterions in the ionic sulfonium species **10** from tetrafluoroborate to triflate, however, causes negligible change in the NMR spectrum.

The dissimilarity of **4** and **10** is also reflected in the difference in chemical shift of the protons ortho to sulfur in the fused phenyl rings. The absorption for **4** is some 1.13 ppm downfield from that for **10,** the largest shift for any of the sulfuranes observed. A similar downfield shift for protons ortho to sulfur in an acyclic chlorosulfurane has been reported by Johnson and Rigau.[3a] In the oxidation of thioanisole with *tert*-butyl hypochlorite, the tetracovalent species **1** was proposed on the basis of NMR comparisons. While **1** absorbs at δ 8.25, the sulfonium tetrafluoroborate analogue exhibits absorption upfield at δ 8.05. Similar downfield shifts have been observed for dichlorosulfuranes.[30] The furthest downfield peak in chlorosulfurane **4** (δ 9.33) is distinctly downfield from that found[3a] for **1.** While there is relatively free rotation in **1,** rotation is restricted in **4** by its cyclic nature. The ortho proton in the fused ring of **4** is forced into the region near the S–Cl bond and its chemical shift strongly reflects the anisotropic deshielding effects of the S–Cl bond. The large downfield shift for **4** relative to **1** is in agreement with this.

A large downfield shift for the SCH_3 group of **1** (δ 3.78) relative to the analogous tetrafluoroborate salt (δ 3.42) was also observed by Johnson and Rigau.[3a] We have isolated the cyclic analogues **7** and **12.** Sulfonium triflate **12** exhibits a peak at δ 3.45, while chloride **7** absorbs at δ 3.76, closely parallel to the acyclic analogues.[3a] The proton ortho to sulfur in **7** shows a large downfield shift similar to that observed for **12.** In contrast to the large $\Delta\delta$ (25 Hz) for the geminal methyl groups in **4, 7** has $\Delta\delta$ = 10 Hz. This confirms our analysis, which suggests that the large difference in chemical shifts in **4** is in part a result of the ring-current shielding by the freely rotating phenyl ring, since **7** lacks such a ring.



12



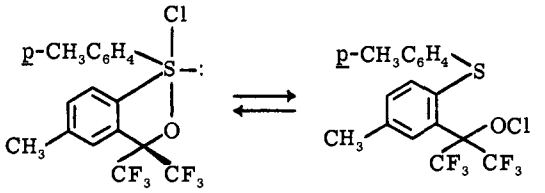
13

A rapid equilibrium between sulfonium salt (**13**) and the sulfurane could explain the NMR spectrum of **4.** If this equilibrium were important, an increase in chloride ion concentration would be expected to force the equilibrium toward the sulfurane. This should be reflected in an increase in $\Delta\delta$ for the geminal methyl groups of **4** and in the downfield chemical shift of the proton ortho to sulfur on the fused ring. Spectra obtained on an 0.83 M $CDCl_3$ solution of **4** with tetraethylammonium chloride at three concentrations (0, 0.78, and 2.25 M) showed negligible changes in $\Delta\delta$ for the *gem*-dimethyl signals (25.2, 25.0, 25.4 Hz) or in the chemical shift of the ortho proton (9.33, 9.30, and 9.28 ppm). We therefore conclude that the equilibrium lies far toward covalent chlorosulfurane.

Evidence for covalency in chlorosulfurane **4** is seen in the ^{13}C NMR spectra of **4** and **10** in the downfield chemical shift of the aliphatic quaternary carbon of more than 7 ppm on going from covalent **4** to ionic **10** and in the gross upfield shift (8–12 ppm) seen for one of the two quaternary aromatic carbons attached to sulfur.

An important datum indicating a covalent structure for **4** is the presence of a molecular ion in its field desorption mass

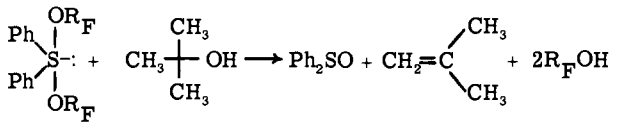
spectrum. The molecular ion is a minor peak with $M\cdot^+ - Cl$ as the base peak. Loss of a chlorine atom from the radical cation of **4** to give a very stable sulfonium species probably has a negligible energy barrier and is facile even using field desorption methods. No molecular ion is observed in the 70 eV electron bombardment spectrum. The fluorinated analogue **14** does exhibit a molecular ion in its 70 eV spectrum (1% of



14

base) and also a $M\cdot^+ - CF$ peak (1.7% of base). Loss of a chlorine atom would give a sulfonium species which would be expected to be less stable than the ion resulting from **4**, because of substitution with trifluoromethyl groups. A small molecular ion is also observed[3e] in the spectrum of bromosulfurane **2**. As suggested by Martin and Perozzi[3e] for **2**, a rearrangement of **4** or **14** to their hypochlorite isomers could possibly explain the occurrence of molecular ions. Evidence presented later in this paper will show that, for **4** at least, such an isomerization, if it occurs at all, is slow.

Hydrolysis of Chlorosulfuranes. Studies[31] of substituent effects on the reaction of dialkoxysulfurane **15** with *tert*-butyl



15, $R_F = Ph(CF_3)_2C$

alcohol favor a dissociative mechanism via a sulfonium type transition state. Hydrolysis of **15** is very rapid, presumably also by a dissociative mechanism via the alkoxysulfonium ion.

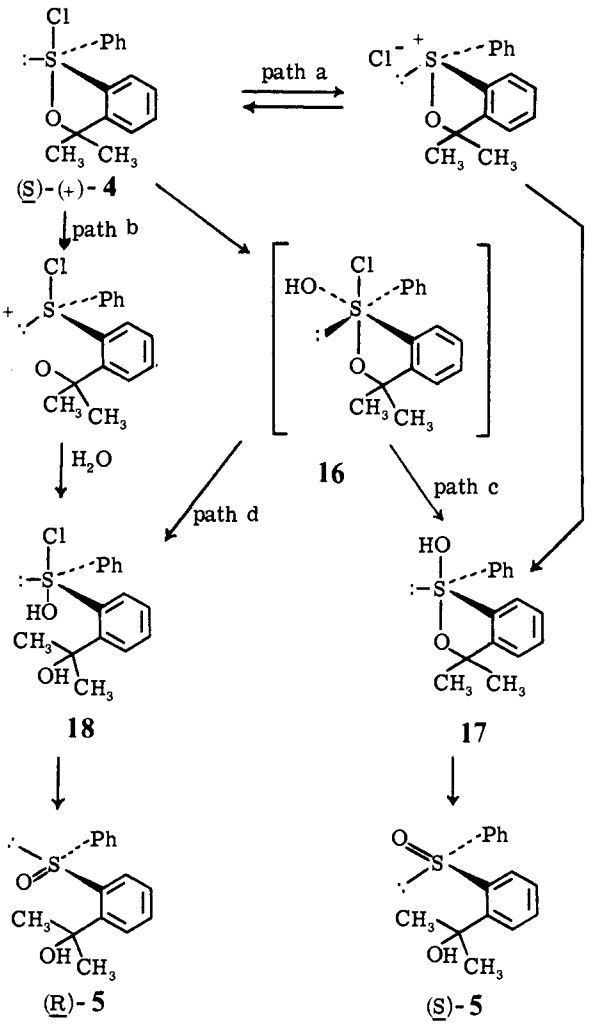
The equilibrium between sulfoxide **5** and sulfurane **4** (eq 1)

$$5 + HCl \overset{K_{eq}}{\rightleftharpoons} 4 + H_2O \qquad (1)$$

strongly favors the chlorosulfurane. In acetone the equilibrium constant K_{eq} is ca. 15. The equilibrium for the fluoroalkyl analogue **14** lies toward the sulfoxide and **14**, unlike **4**, is quickly hydrolyzed in moist air. The great difference in equilibrium behavior between **4** and **14** initiated our interest in the differences in the rates of hydrolysis. Partial hydrolysis of a mixture of **4** and **14** in $CDCl_3$ in the presence of 1 equiv of *N,N*-dimethylaniline shows exclusive reaction with the fluorinated derivative **14**; no detection of sulfoxide **5** is noted until destruction of chlorosulfurane **14** is complete. This result is not compatible with a mechanism involving initial loss of chloride ion in a dissociative[32] manner (path a of Scheme I) since such an ionization would be expected to be slowed by the inductive effect of the CF_3 groups relative to the pictured CH_3 analogue. Although initial scission of the S-O bond (path b of Scheme I) is compatible with this increase in rate for the CF_3 analogue, such a pathway can be eliminated by stereochemical evidence presented later in this paper.

A more extensive study of substituent effects was undertaken. Relative reactivities were determined for the six aryl-substituted chlorosulfuranes listed in Table I. The relative rate constants for hydrolysis of **4** and **6a–e** yield positive ρ values ($\rho_X = 2.0$, $\rho_Y = 0.3$) for substitution in each aryl ring. Figure 1 is a Hammett plot for the hydrolysis of these six chlorosulfuranes. We propose the operation of an associative[32] mechanism involving the development of negative charge on sulfur in a transition state resembling **16**. Known analogues of **16** include the SF_5^- species reported by Christe[33a] and Muetterties.[33b] Vibrational studies[33a] of SF_5^- indicate it to possess C_{4v} symmetry. Similar sulfur anions have been suggested in NMR ligand exchange studies.[34,35] Archie and Westheimer[36] have reported kinetic evidence indicating an associative mechanism for the basic hydrolysis of pentaaryloxyphosphoranes involving hexacoordinated phosphorus. Hexacoordinate phosphorus compounds are well known.[37,38] Ramirez[38] and Schmutzler[39] have shown that pentaalkoxyphosphoranes readily add pyridine or trimethylphosphine to give stable adducts of this type.

Scheme I



The associative mechanism we have proposed could involve two stereochemically distinct intermediates: hydroxysulfurane **17** (path c of Scheme I), which would lead to sulfoxide-alcohol **5** with the same absolute configuration (*S*) as seen for hydrolysis of salt **10**, and chlorohydroxysulfurane **18** (path d of Scheme I) which would yield sulfoxide-alcohol of opposite configuration, *R*. Hydrolysis of (*S*)-**4** (using a sample of 27% enantiomeric purity) with 1 equiv of water in the presence of diisopropylethylamine gave (*S*)-**5** (25% optically pure), a result compatible with reaction via path c.

There are 24 stereoisomers (12 pairs of enantiomers) of the general octahedral structure **16**. The observed retention of configuration about sulfur during hydrolysis makes two pairs of enantiomers, those with Cl and OH trans seem unlikely intermediates.

Substituents on the fused ring of **4** show a markedly greater influence on the rate of hydrolysis compared with the freely

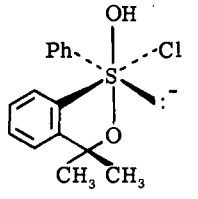
Table I. Relative Rates of Hydrolysis for Chlorosulfuranes **4** and **6a–e** at 4 °C

X	Y	Compd[a,b]	k_{rel}	$\sigma_X + 0.15\sigma_Y$
H	H	**4**[c]	1.0	0
CH_3	CH_3	**6a**[c]	0.3	−0.20
Cl	H	**6b**[c]	2.8	0.23
H	Cl	**6c**[c]	1.2	0.035
NO_2	H	**6d**[d,e]	26.0	0.78
H	NO_2	**6e**[c]	1.6	0.12

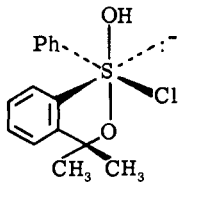
[a] CDCl solvent. [b] Ca. 0.1 M sulfurane. [c] Ca. 0.1 M diisopropylethylamine. [d] Ca. 0.05 M sulfurane. [e] Ca. 0.05 M *N,N*-dimethylaniline as base.

rotating ring ($\rho_X = 2.0$, $\rho_Y = 0.3$). The fused ring is held coplanar with the O-S-Cl bond, a conformation which would maximize π delocalization of the electron pair in **16**. Correlation of relative rates with σ^- for the fused ring ($\rho^- = 1.2$, $R^2 = 0.934$) were, however, distinctly worse than that with σ ($\rho = 2.0$, $R^2 = 0.985$), suggesting that differences in capacity for π delocalization do not form the basis for an explanation for the differences in ρ values between the aryl rings. Centers of high electron density in the transition state may be on the more electronegative oxygen and chlorine atoms. Inductive stabilization of transition state negative charge on the trans oxygen by way of the fused ring of **16c** provides a pathway for operation of a substituent effect which is unavailable to the free ring. This may be reflected in the difference in ρ values for the two aryl rings. The large ρ differences may also indicate a difference in capacity for stabilization by the aryl groups because of different cis-trans relationships relative to the electron pair in the transition state. Structures for the transition state with both aryl groups cis to the electron pair might not be expected to show such differences.

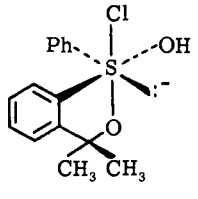
The principle of least motion ("those elementary reactions will be favored that involve the least change in atomic position and electronic configuration" [40]) might lead one to favor transition states similar to structures **16a–d**. Structures **16c** and **16d** result from attack by hydroxide ion on the least



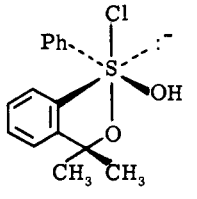
16a



16b



16c



16d

crowded face of **4** and for this reason have perhaps rather more claim to consideration than other isomeric possible structures. None of the structures can be rigorously ruled out.

Racemization. The small degree of racemization observed to accompany hydrolysis (ca. 9%) is compatible with the postulated operation of the mechanism of path c (Scheme I) since solutions of (*S*)-chlorosulfurane **4** are found to racemize slowly

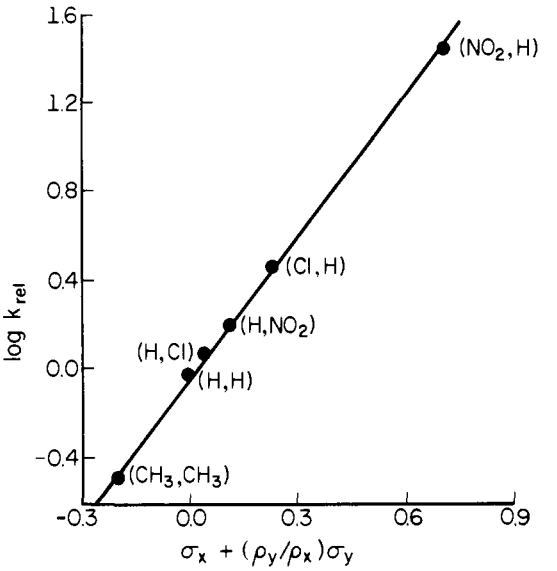
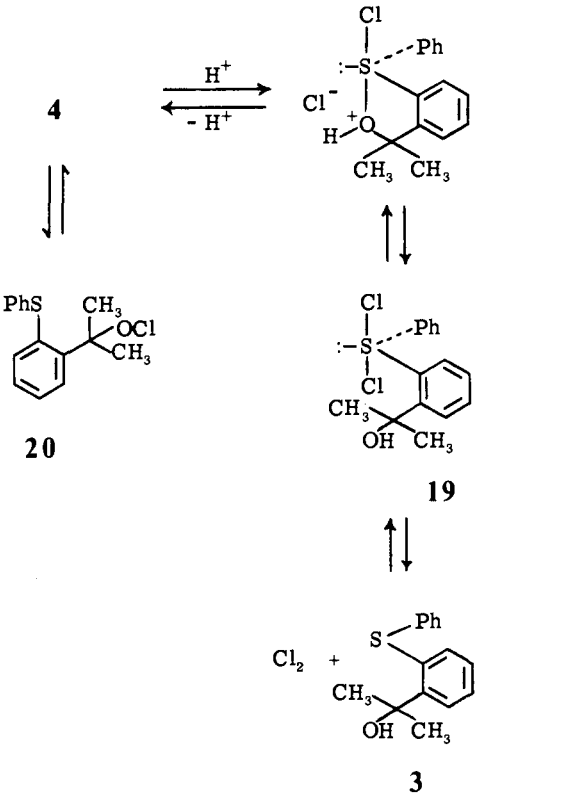


Figure 1. Hammett plot for the base-catalyzed hydrolyses of chlorosulfuranes **4** and **6a–e** ($\rho_X = 2.0$, $\rho_Y = 0.3$).

Scheme II



on standing. Addition of HCl causes very rapid racemization. Two possible pathways for this racemization are shown (Scheme II) which involve initial protonation of oxygen. Equilibration with achiral sulfide **3** or dichlorosulfurane **19** leads, of course, to racemic chlorosulfurane. Direct equilibration with **3** and chlorine can be shown to be unlikely. Although a sample of (*S*)-**4** is racemized within 3 h in CH_2Cl_2, no sulfide **3** was formed after 24 h (by NMR) in a similar reaction in which 2,6-di-*tert*-butylphenol was added to scavenge chlorine. If chlorine scavenging were complete, the rates for loss of optical activity and for sulfide formation would be equal. Since no sulfide is detected, we favor the routes for racemization via **19** or **20** rather than via **3**.

Addition of 2,6-lutidine to a solution of (*S*)-**4** caused a large retardation of racemization. An initial rate constant of ca. 10^{-6}

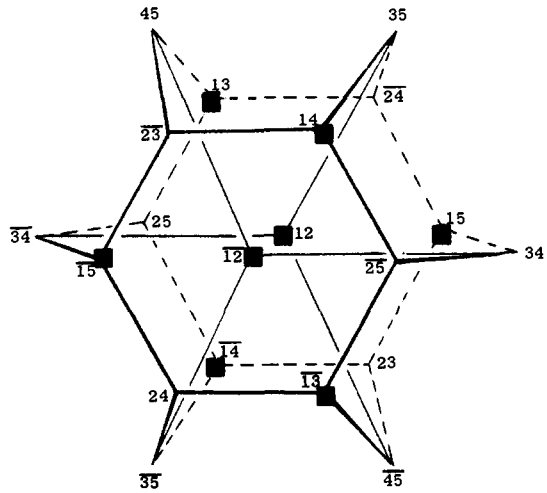


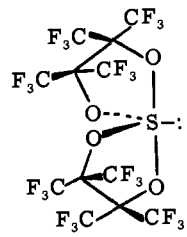
Figure 2. A Desargues-Levi graph (after Mislow, ref 56). The two numerals at each vertex represent the identity of the two apical substituents of the TBP isomer represented by that vertex. Two enantiomers are differentiated by a bar over one pair of numerals (e.g., 34 and $\overline{34}$). The lines connecting neighboring vertices represent Berry pseudorotation (BPR) processes. Vertices representing high-energy species with apical electron pairs are marked by ■. Discussion in the text applying this graph to a description of the stereochemistry of **4** assigns the index numeral 1 to the sulfur lone pair of electrons, 2 to the phenyl ligand, 3 to the chloro ligand, 4 to the alkoxy ligand, and 5 to the substituted aryl ligand.

s^{-1} was observed. This value is very crude since impurities were present and since we have found a very small amount of 1-phenylsulfinyl-2-(2-propenyl)benzene to be formed under these conditions. The estimate of 10^{-6} s^{-1} is therefore to be considered no more than an upper limit to rate. A crude minimum value of $\Delta G^*_{23} = 25$ kcal/mol can be set for the uncatalyzed racemization, whether it occurs by way of an equilibrium with hypochlorite **20**, by intramolecular ligand permutation process of the type usually called pseudorotation, or by inversion via a conformation involving a planar disposition of the four ligands about sulfur.

Designation of Absolute Configuration. (+)-Sulfurane **4** is one of the few examples of an optically active trigonal bipyramidal (TBP) molecule and the only example for which experiments pointing to a specific absolute configuration have been performed. Other reported examples[41-44] include a selenurane, which was partially resolved by Lindgren,[41] and a pentaarylphosphorane prepared by Hellwinkel.[42] Wolf[43,44] has resolved several phosphoranes with chiral ligands. Although nomenclature systems[45,46] describing stereochemistry have been constructed for discussions of pseudorotation processes, we would propose to designate absolute configuration for trigonal-bipyramidal (TBP) or square-pyramidal (SP) molecules of known absolute configuration by an extension of the Cahn, Ingold, Prelog (CIP) *R-S* nomenclature system[47] used for tetrahedral species.

It is clear that unsymmetrically substituted pentacoordinate species (including that which we discuss here, if one considers the sulfur lone pair of electrons of **4** a ligand) are not likely to be perfectly trigonal bipyramidal. Distortions from the TBP toward the SP geometry are common in structures of pentacoordinate species which have been studied.[48] Such distortions are evident in the x-ray structures which are available for sulfuranes.[3b,27,28] In fact one does not expect either perfect TBP or perfect SP skeletal geometry if all five ligands are different, as they are in sulfurane **4**. It is clear that in many cases such distortions will make it impossible to develop rational mathematical descriptors of chirality, such as that advanced by Ruch.[49,50] In particular, Ruch has pointed out that square-pyramidal structures (local C_{4v} symmetry) belong to a class of structures which is in principle not susceptible to division into subclasses of "right" or "left" chirality except by arbitrary definition. The TBP geometry, on the other hand, belongs to the class of structures which is so divisible.

Despite these difficulties, it is clearly desirable to have available as an aid in communication a system of nomenclature, however arbitrary, which can be used to designate the sense of chirality in pentacoordinate species. Our approach to this problem must begin by defining the chiral species, **4**, in terms of the appropriate time scale.[51] All conformations rapidly interconverted by permutational isomerism on a time scale short relative to that for racemization may be included within the bounds defined for one enantiomeric species. The demonstration of rapid permutational isomerism for SF_4[52] and for symmetrically substituted spirotetraoxysulfurane **21**,[53] in-



21

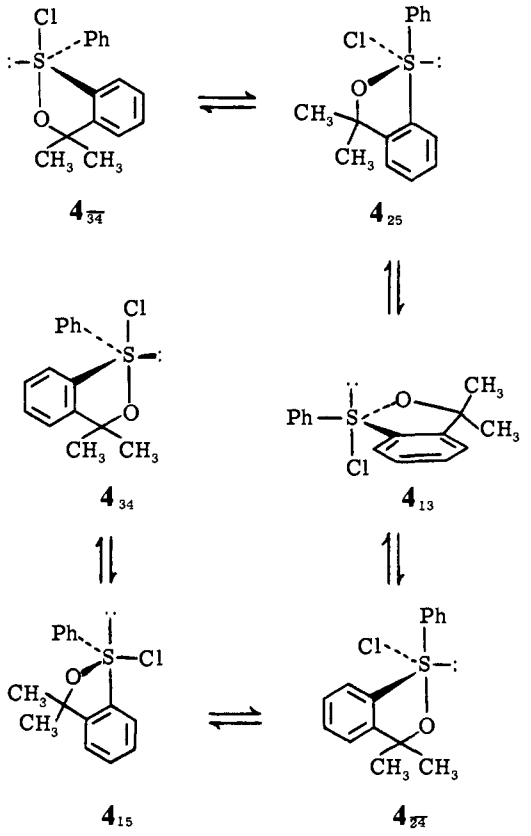
volving pairwise interchange of two apical ligands with two equatorial ligands, suggests that the permutational isomerizations of species such as **4** might profitably be discussed in terms of the Berry pseudorotation (BPR)[53-55] process. In the light of recent[48] suggestions that electronegative ligands in five-membered rings favor SP relative to TBP geometries in phosphoranes, it is interesting that **21**, despite having four equivalent electronegative ligands in two five-membered rings, is not SP in solution but is distorted toward TBP geometry sufficiently to make two types of substituents distinguishable in its low-temperature NMR. When we label these "apical" and "equatorial" we do not mean to suggest perfect collinearity of the "apical" bonds, as in an undistorted TBP, but simply an angle between apical bonds larger than that between equatorial bonds. In such a geometry, as in the geometries which have been established[27,28] for other spirosulfuranes, it is easy to identify the idealized TBP conformation which is nearest in geometry to that of a given molecular species. We will propose a system of nomenclature for pentacoordinate species which is based on the premise that such species can be related systematically to idealized TBP structures, which can in turn be related to chiral tetracoordinate species.

It is convenient to use a graphical method for the systematic visualization of the rearrangement pathways available to a pentacoordinate species such as **4**. Mislow[56] has described a particularly appealing format for what he calls a Desargues-Levi graph appropriate for describing these rearrangements. Each vertex of the graph, shown in Figure 2, represents a single TBP isomer, with a structure specified by index numbers representing the identity of its apical ligands. Any two vertices at opposite extremes of the figure represent enantiomers, which are differentiated from one another by a bar over the numbers representing the apical ligands of one enantiomer (e.g., 34 and $\overline{34}$ are enantiomers). Line segments joining adjacent vertices represent BPR processes. Racemization may be accomplished most directly by following one of the six possible five-step rearrangement pathways which join one vertex to the vertex representing its enantiomer.

Compound **4** has as one of its "ligands" an electron pair. It is reasonable to suppose[57,58] that TBP geometries with apical electron pairs should be of very high energy, perhaps even representing an energy maximum rather than a minimum.[54] Let us represent the electron pair of **4** by the index numeral 1 in Figure 2, the phenyl group by 2, and the aryl ring by 5. The

racemization represented by the interconversion of $\mathbf{4}_{34}$ and $\mathbf{4}_{\overline{34}}$ (where 3 and 4 represent the chloro and alkoxy ligands, the most apicophilic[58] of the ligands of **4**), if it is to occur by one of the pseudorotation processes described by the graph, must go via two high-energy TBP geometries with an apical electron pair (species with index 1n, which are designated by the black squares in Figure 2). We postulate that the racemization of **4** is slow enough to allow its isolation in high enantiomeric purity because of the high energies of these intermediate states (or, more precisely, of transition states with geometries similar to those of the high-energy TBP species with apical electron pairs).[59]

Scheme III



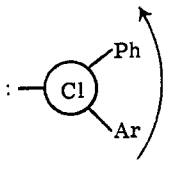
$\mathbf{4}_{\overline{34}}$ $\mathbf{4}_{25}$ $\mathbf{4}_{34}$ $\mathbf{4}_{13}$ $\mathbf{4}_{15}$ $\mathbf{4}_{\overline{24}}$

Scheme III details one of the six possible five-step routes from $\mathbf{4}_{\overline{34}}$ to $\mathbf{4}_{34}$ (the route $\overline{34} \rightarrow 25 \rightarrow 13 \rightarrow \overline{24} \rightarrow 15 \rightarrow 34$ of Figure 2). The conversion of $\mathbf{4}_{\overline{34}}$ (the lowest energy conformer) to the higher energy conformer $\mathbf{4}_{25}$ (with its two apical carbon substituents of much lower apicophilicity[57] than the chlorine and alkoxy ligand of $\mathbf{4}_{34}$) is an ordinary BPR process. While it leads to a product higher in energy than $\mathbf{4}_{34}$ the product does not have the energetically very unfavorable apical electron pair which is a feature of the next species along the reaction pathway, $\mathbf{4}_{13}$. Conformer $\mathbf{4}_{13}$ also has the energetically unfavorable structural feature of a five-membered ring spanning two equatorial positions.[60] One could therefore, reasonably expect $\mathbf{4}_{13}$ to lie near in energy to the transition state for racemization. While $\mathbf{4}_{15}$ lacks the diequatorial ring it does have an apical electron pair and a second apical ligand of low apicophilicity, the aryl group, and is therefore also expected to lie near a high point along the reaction coordinate. Flanked by two high-energy species, $\mathbf{4}_{24}$ might be expected to be converted to the lower energy $\mathbf{4}_{34}$ (or back to $\mathbf{4}_{34}$) with an activation energy which might be appreciable. Conformer $\mathbf{4}_{24}$ and its enantiomer $\mathbf{4}_{\overline{24}}$ would be expected, however, to be considerably higher in energy than conformers $\mathbf{4}_{34}$ and $\mathbf{4}_{\overline{34}}$ as a result of the exchange of apical phenyl in the former for the more apicophilic chlorine in the apical position of the latter. No evidence for the presence of conformer $\mathbf{4}_{24}$ was seen in spectra of **4**.

In the general case the ground-state geometries of the individual members of the family of rapidly interconverting conformers which we wish to differentiate from the enantiomeric family of conformers will not be known in detail nor will we know the geometry of the transition state for racemization. For example, whether the transition state geometry for the racemization of $\mathbf{4}_{34}$ via the pathway of Scheme III resembles $\mathbf{4}_{13}$ or $\mathbf{4}_{15}$ in geometry is not known with certainty. It is therefore, not clear to which of the enantiomeric manifolds of conformers $\mathbf{4}_{\overline{24}}$ belongs.[61] It is clear, however, from what we know of ligand apicophilicities in such compounds that $\mathbf{4}_{34}$ and $\mathbf{4}_{\overline{34}}$ probably represent the most stable of the idealized TBP geometries available to **4** and that the ground-state geometry of an enantiomer of **4** will be recognizable as a distorted form of one of these two TBP geometries (probably distorted toward one of the flanking SP geometries). Evidence has been presented that (+)-**4** isolated here is the species whose manifold of conformers includes $\mathbf{4}_{\overline{34}}$. This level of knowledge about the spatial distribution of ligands in a pentacoordinate species is necessary if the absolute configuration is to be specified. We would propose to choose, as a basis for a name specifying absolute configuration, one of the TBP geometries known to lie within the manifold of conformers for which a name is being considered.[62] It is convenient to choose that conformer expected to be lowest in energy.

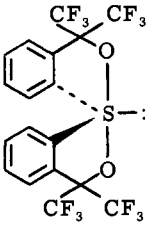
The first step in naming this TBP structure is the specification of apical and equatorial ligands using existing[63] nomenclature rules. The sense of chirality can then be specified by viewing the idealized TBP structure along its apical axis in the orientation which places nearer the viewer that apical substituent which has the higher priority rank in the CIP[47] nomenclature scheme. The priority ranking of the equatorial ligands using the CIP[47] conventions results in an order of decreasing priority which can be recognized by the viewer as being clockwise (*R*) or counterclockwise (*S*).

Application of these conventions to the TBP structure labeled $\mathbf{4}_{34}$ leads to its designation as (*S*)-(+)-**4**.



Ar = $C_6H_4C(CH_3)_2$

(S)-(+)-**4**



(S)-**22**

Among the other types of sulfuranes which might be expected to show high barriers to racemization are spirosulfuranes such as **21**. The extension of our nomenclature convention to this compound, for which an x-ray structure[28] has established a geometry near the TBP ideal, requires only the application of existing rules promulgated[47] for the systems for which the CIP nomenclature conventions were devised. The application of the "near precedes far" convention[47a] for priority ranking of the aryl ligands of **21** leads to the designation *S*-**21** for the pictured isomer.

Conclusion

The racemization of (*S*)-(+)-**4** is strongly catalyzed by HCl. The uncatalyzed racemization, which has an energy barrier (ΔG^*_{23}) of at least 25 kcal/mol, may proceed by a BPR process involving intermediate structures with geometries near TBP with apical electron pairs, by an inversion through a

planar transition state, or by other processes as yet unknown. This value of ΔG^* is at least as large as those found[64] for the inversion of several sulfonium salts (25-29 kcal/mol).

An associative displacement of chloride by attack of hydroxide on (*S*)-(+)-**4** has been shown to proceed with retention of configuration at sulfur.

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(62) Note that even though the actual ground-state geometry may be near SP, a simple distortion of the skeletal framework in the mode of the BPR process (which maintains a C_2 axis through the pivot ligand while opening to 180° the angle between the two bonds joining the more apicophilic pair of trans basal ligands to the central atom in the SP molecule, while closing to 120° the angle between the bonds joining the other two ligands to the central atom) will convert the SP to an idealized TBP geometry.
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