Relative Reactivities of Acyclic, Cyclic, and Spirobicyclic Sulfuranes and Sulfurane Oxides[1]

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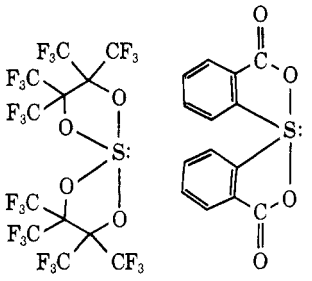
Abstract: The greatly decreased reactivity of cyclic or, more especially, of spirobicyclic diaryldialkoxysulfuranes is probed in studies involving the isolation and characterization of a number of five-membered ring cyclic analogs of previously reported acyclic sulfuranes. The first reported ketal analog of a sulfone, spirodiaryldialkoxysulfurane oxide **9** is, like the spirosulfurane (**3**) from which it is prepared by oxidation with RuO_4 or N_2O_4, inert toward boiling aqueous alkali or acid. In contrast, acyclic sulfurane oxide **21**, or its ionic equivalent, postulated to be an intermediate in the reaction between diphenyl sulfoxide, chlorine, and KOR_F (where R_F is the hexafluoro-2-phenyl-2-propyl group) is very reactive. The observed products, ethers **23** and **24**, are postulated to result from a reaction involving an O-alkylated diphenyl sulfone intermediate which generates a very good leaving group, diphenyl sulfone, in a reaction leading to a carbonium ion or its equivalent. The reduced reactivity of the cyclic or spirosulfuranes or sulfurane oxides relative to their acyclic analogs in hydrolysis reactions is thought to result from the fact that they react by a pathway involving a change from trigonal bipyramidal to tetrahedral geometry. This represents the converse of the change in geometry which has been postulated to be responsible for the great increase in reactivity reflected in hydrolyses of cyclic phosphate or sulfite esters.

The pronounced lack of reactivity of spirosulfuranes has been pointed out in several recent papers.[2-4] Spirosulfuranes **1**, **2**, and **3**[2-4] are reported to be relatively stable toward hydrolysis. For instance, sulfurane **2** is hydrolyzed[3] to the corresponding sulfoxide only after it has been boiled for 30 min in a 9:1 acetone–water mixture. In a preliminary report sulfurane **3** was reported[4] to be stable to boiling aqueous acid or base. This contrasts with the extreme ease with which acyclic sulfurane **4** is hydrolyzed.[5] Acyclic sulfurane **5** is also reported[6] to be a hygroscopic solid which hydrolyzes to phenol and diphenyl sulfite.



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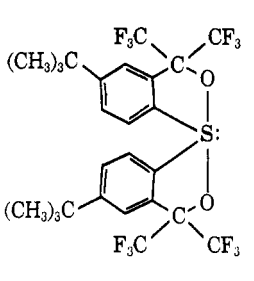

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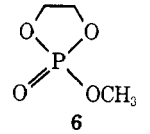
A closely analogous though inverted order of reactivities is observed for cyclic phosphate ester **6** and its acyclic analog trimethyl phosphate. Westheimer, *et al.*,[7] report that the base hydrolysis of **6** is 10^6 times faster than that for trimethyl phosphate. Similar rate enhancements for cyclic *vs.* acyclic phosphonium salts have been reported by Cremer, *et al.*,[8] and Aksnes and Bergesen.[9] The same type of effect is seen in the hydrolyses of aromatic sulfates[10a] and sulfites,[10b] *e.g.*, **7** and its sulfate analog. A study of five-membered cyclic sulfuranes and spirosulfuranes was undertaken to determine the approximate rates of hydrolysis relative to the acyclic sulfuranes.



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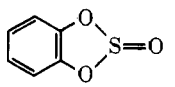

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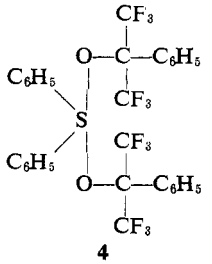
Sulfur oxytetrafluoride, a halosulfurane oxide, is available by oxidation of sulfur tetrafluoride with nitrogen oxides[11] or by oxygen in the presence of nitrogen dioxide at high temperatures or by the reaction of thionyl fluoride (SOF_2) with elemental fluorine.[12-14] More recently, the sulfurane oxides **8a–c** have been ob-



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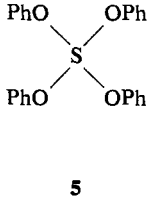

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(1) Paper XII in a series on Sulfuranes. For paper XI in this series, see E. F. Perozzi, J. C. Martin, and I. C. Paul, *J. Amer. Chem. Soc.*, **96**, 578 (1974). Abstracted in part from the Ph.D. Thesis of E. F. P., University of Illinois, 1974.

(2) M. Allan, A. F. Janzen, and C. J. Willis, *Can. J. Chem.*, **46**, 3671 (1968).

(3) (a) I. Kapovits and A. Kálmán, *Chem. Commun.*, 649 (1971); (b) A. Kálmán, K. Sasvári, and I. Kapovits, *Acta Crystallogr., Sect. B*, **29**, 355 (1973).

(4) E. F. Perozzi and J. C. Martin, *J. Amer. Chem. Soc.*, **94**, 5519 (1972).

(5) (a) J. C. Martin and R. J. Arhart, *J. Amer. Chem. Soc.*, **93**, 2341 (1971); (b) R. J. Arhart and J. C. Martin, *ibid.*, **94**, 4997 (1972).

(6) J. I. Darragh and D. W. A. Sharp, *Angew. Chem., Int. Ed. Engl.*, **9**, 73 (1970).

(7) A. Eberhard and F. H. Westheimer, *J. Amer. Chem. Soc.*, **87**, 253 (1965).

(8) S. E. Cremer, B. C. Trivedi, and F. L. Weitl, *J. Org. Chem.*, **36**, 3226 (1971).

(9) G. Aksnes and K. Bergesen, *Acta Chem. Scand.*, **19**, 931 (1965).

(10) (a) E. T. Kaiser, I. R. Katz, and T. F. Wulfers, *J. Amer. Chem. Soc.*, **87**, 3781 (1965); (b) P. B. D. de la Mare, J. G. Tillett, and H. F. van Woerden, *Chem. Ind. (London)*, 1533 (1961); *J. Chem. Soc.*, 4888 (1962).

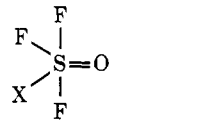
(11) W. C. Smith and V. A. Engelhardt, *J. Amer. Chem. Soc.*, **82**, 3838 (1960).

(12) W. Kwasnik, F.I.A.T. Review of German Science (1936–1946), Inorganic Chemistry, Vol. 1, 1948.

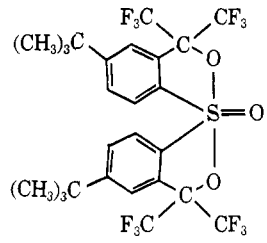
(13) H. Jonas, *Z. Anorg. Allg. Chem.*, **265**, 273 (1951).

(14) F. B. Dudley, G. H. Cady, and D. F. Eggers, Jr., *J. Amer. Chem. Soc.*, **78**, 1553 (1956).

tained[15] by appropriate reactions of OSF_4. Fluorination of perfluoroalkyl sulfoxides has also been reported to lead to analogs of **8**.[16] Treatment of spirosulfurane **3** with ruthenium tetroxide gave[4] spirosulfurane oxide **9**.



8a, $X = N(CH_3)_2$
b, $X = N(C_2H_5)_2$
c, $X = OPh$



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Sulfurane oxide intermediates have often been proposed in nucleophilic displacement on sulfur involving a temporary expansion of the valence octet. Ingold and Jessop[17] proposed such an expansion to account for the alkaline cleavage products of diphenyl sulfone. Douglass, *et al.*,[18] carried out the chlorination of methylsulfinyl chloride in acetic acid and concluded from the products (methylsulfonyl chloride, acetyl chloride, and HCl) that a dichlorosulfurane oxide intermediate was involved. Sulfurane oxide intermediates or transition states have been proposed in the hydrolyses of sulfonyl sulfones[19] and of phenyltoluenesulfonate.[20] Bunnett and Bassett[21] in studying the cleavage of 2,4-dinitrophenyl-*p*-toluenesulfonate with piperidine suggest a related transition state to rationalize their results.

Experimental Section

Proton and carbon-13 chemical shifts are reported on the δ scale, ppm downfield from tetramethylsilane internal standard; fluorine chemical shifts are in ppm upfield from fluorotrichloromethane internal standard. The ^1H and ^{19}F nmr integral ratios are rounded to the nearest whole number of nuclei.

Solvents and Reagents. Chloroform-*d* and fluorotrichloromethane were dried by passage through a column of Woelm Neutral Alumina. Ether was dried by several additions of sodium wire over several days until further additions caused no further hydrogen evolution. Carbon tetrachloride was dried by distillation from phosphorus pentoxide followed by storage over molecular sieves. Hexafluoro-2-phenyl-2-propanol (R_FOH) was prepared by the published procedure,[22a] as was 1,4-endoxocyclohexane.[22b]

Hexafluoro-2-(*p*-*tert*-butylphenyl)-2-propanol. *tert*-Butylbenzene (101 g, 0.754 mol) was mixed with 0.5 g of anhydrous aluminum chloride in 100 ml of dry carbon tetrachloride with cooling to maintain 20°. When hexafluoroacetone, bubbled through the solution, was not consumed an additional 0.5 g of $AlCl_3$ was added to start the reaction. Over a 45-min period 126 g (0.759 mol) of the ketone was added. The cold reaction mixture was stirred for 0.5 hr, warmed to room temperature, stirred for 1 hr, and then quenched by addition of 20 ml of water. The organic phase was dried ($MgSO_4$) and the solvent was removed to give an oil, which was distilled through a vacuum-jacketed, tantalum wire packed column. The first two fractions (bp 30.5–32° (1.2 mm) and 32–39° (1.0 mm)) were largely R_FOH by nmr analysis. The final fractions (bp 39–75° (1.7 mm) and bp 75–78° (1.7 mm)) solidified on standing at −78° to yield 79.1 g (35%) of crude crystalline product. Washing this with cold petroleum ether left 30.5 g of pure material, mp 49.5–51.5°.

Anal. Calcd for $C_{13}H_{14}F_6O$: C, 52.01; H, 4.70. Found: C, 52.20; H, 4.62.

Concentration of the mother liquors from the above wash yielded an additional 33.3 g, mp 40–51°, which was recrystallized from petroleum ether to yield 22.5 g, mp 48.5–51.5°. Total yield of pure material was 53.0 g (24.4%); ^1H nmr ($CDCl_3$) δ 1.32 (s, 9, *tert*-butyl), 3.43 (s, broad, 1, OH), 7.32 and 7.54 (AB pattern, 4, J_{AB} = 9.5 Hz); ^{19}F nmr ($CDCl_3$) singlet 76.1 ppm upfield from $CFCl_3$.

Potassium Hexafluoro-2-(*p*-*tert*-butylphenyl)-2-propoxide. To potassium metal (8.45 g, 0.217 g-atom), suspended as small chunks in 300 ml of dry ether under nitrogen, was added dropwise 50.0 g (0.167 mol) of hexafluoro-2-(*p*-*tert*-butylphenyl)-2-propanol in 80 ml of ether. After 24 hr at room temperature, filtration, followed by evaporation of the solvent, gave an almost quantitative yield of the alkoxide: ^1H nmr (CCl_4) δ 1.31 (s, 9, *tert*-butyl protons), 7.26 and 7.53 (AB pattern, 4, J_{AB} = 8.5 Hz); ^{19}F nmr (ether) singlet at 76.3 ppm upfield from $CFCl_3$.

Potassium Perfluoro-*tert*-butoxide. To perfluoro-*tert*-butyl alcohol (PCR, Inc., 4.81 g, 0.0204 mol) magnetically stirred in 20 ml of dry ether was added 0.86 g (0.220 g-atom) of fine shavings of potassium metal over a 1.5-hr period. Then 0.27 g (0.00693 g-atom) of potassium metal was added and the mixture was stirred overnight and filtered. Evaporation of the filtrate gave 5.34 g (95.6%) of the potassium alkoxide.

2-(1,1,1,3,3,3-Hexafluoro-2-hydroxy-2-propyl)-4,4′-di-*tert*-butylphenyl Sulfide (11). To 4,4′-di-*tert*-butyldiphenyl sulfide (60.0 g, 0.201 mol)[23] in 90 ml of dry carbon tetrachloride, aluminum chloride (6.32 g, 0.0473 mol) was added. Hexafluoroacetone (21.0 ml, 33.6 g, 0.202 mol) was bubbled into the magnetically stirred mixture at 65°. After 4.75 hr reflux became slow but an nmr spectrum indicated the presence of starting material, suggesting that volatile ketone had escaped through the condenser; so more hexafluoroacetone (10.0 ml, 16.0 g, 0.0964 mol) and aluminum chloride (4.25 g, 0.0318 mol) were added at this point. After the mixture had been heated for 2 hr, water (20 ml) was added and the reaction mixture was filtered. Chromatography on alumina, eluting with petroleum ether and ether, gave 65.6 g (70.5% yield) of crude alcohol. One fraction (17.1 g) was recrystallized twice from petroleum ether to give 7.98 g of pure alcohol, mp 60.5–62°. This fraction was dissolved in petroleum ether and treated with potassium metal to yield 9.42 g of the alkoxide. The remaining fractions were dissolved in petroleum ether and treated with potassium metal (*ca.* 20 g) to yield an additional 21.54 g of the alkoxide (overall, 30.7%). Data for the alcohol: ^1H nmr (CCl_4) δ 1.32 and 1.36 (2 singlets, 18, *tert*-butyl hydrogens), 7.26 (m, 4, protons on disubstituted phenyl ring), 7.41 (broad, s, 2, protons ortho to sulfur and ortho to *tert*-butyl in the trisubstituted phenyl ring), 7.81 (broad s, 1, proton ortho to the fluoroalkyl grop), 7.98 (broad, 2, disappears with D_2O shake, −OH); ^{19}F nmr (CCl_4) 75.0 (s, 6, ratio of ^1H to ^{19}F determined by addition of CF_3CH_2OH); ir (KBr) 3420 (w, broad), 3230 (s, broad, OH), 2971 (s), 1483 (w), 1399 (w), 1240 (s, 5 or 6 strong peaks), 1151 (s), 1141 (s), 1118 (m), 971 (s), 950 (m), 832 (m), 741 (m), 718 (w); mass spectrum (70 eV) *m/e* (rel intensity) 464 (66.59, $M\cdot^+$), 449 (84.71, $M\cdot^+ - CH_3$), 217 (13.67), 189 (13.30), 181 (14.52), 169 (16.05), 131 (18.43), 119 (25.25), 69 (100.00, $^+CF_3$), 57 (24.11, $^+C(CH_3)_3$).

Anal. Calcd for $C_{23}H_{26}F_6OS$: C, 59.47; H, 5.64; S, 6.90. Found: C, 59.60; H, 5.70; S, 6.76.

2,2′-Di(1,1,1,3,3,3-hexafluoro-2-hydroxy-2-propyl)-4,4′-di-*tert*-butyldiphenyl Sulfide (10). Bis-*p*-*tert*-butyldiphenyl sulfide[23] (7.00 g, 0.0235 mol) and hexafluoroacetone (6.2 ml, 9.91 g, 0.0597 mol) in 10 ml of dry carbon tetrachloride were vacuum degassed at −196° and heated with 0.8818 g (6.61 mmol) of anhydrous aluminum chloride in a sealed tube at 65° for 1 hr with shaking. Water (10 ml) was added to the cooled red-black mixture, and the mixture was filtered to give 1.83 g (15.9%) of a solid which was recrystallized from ether–petroleum ether to give $HOC(CF_3)_2CH_2C(=CH_2)$-$CH_2C(CF_3)_2OH$ (**12**), mp 126–130°, sublimes (lit.[24] mp 149–150°). The nmr spectrum agrees well with that reported[24] for **12** and the mass spectrum shows a molecular ion at *m/e* 388.

(15) S. P. von Halasz and O. Glemser, *Chem. Ber.*, **103**, 594 (1970); S. P. von Halasz, O. Glemser, and M. F. Feser, *ibid.*, **104**, 1242 (1971).
(16) J. M. Shreeve, *Accounts Chem. Res.*, **6**, 387 (1973).
(17) C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, 708 (1930).
(18) I. B. Douglass, B. S. Farah, and E. G. Thomas, *J. Org. Chem.*, **26**, 1996 (1961).
(19) J. L. Kice and G. J. Kasperek, *J. Amer. Chem. Soc.*, **91**, 5510 (1969).
(20) C. A. Bunton and Y. F. Frei, *J. Chem. Soc.*, 1872 (1951).
(21) J. F. Bunnett and J. Y. Bassett, Jr., *J. Org. Chem.*, **27**, 2345 (1962).
(22) (a) B. S. Farah, E. E. Gilbert, and J. P. Sibilia, *J. Org. Chem.*, **30**, 998 (1965); (b) E. A. Fehnel, S. Goodyear, and J. Berkowitz, *J. Amer. Chem. Soc.*, **73**, 4978 (1951).
(23) V. Franzen, H. J. Schmidt, and C. Mertz, *Chem. Ber.*, **94**, 2942 (1961).
(24) W. H. Urry, J. H. Y. Niu, and L. G. Lundsted, *J. Org. Chem.*, **33**, 2302 (1968).

The filtrate from above was evaporated to give 11.9 g of red–black oil. Upon chromatography on alumina with petroleum ether and ether eluents the later fractions gave 4.0 g (27.0% crude yield) of diol **10**, which was recrystallized twice from petroleum ether to give 1.09 g of white crystals: mp 116–118.5°; ^{1}H nmr ($CDCl_3$) δ 1.32 (s, 18, $C(CH_3)_3$), 6.14 (s, 2, disappears with D_2O shake, OH), 6.99 (d, 2, protons ortho to sulfur, J_{BC} = 8.5 Hz), 7.28 (d of d, 2, protons ortho to *tert*-butyl group, J_{AB} = 2 Hz, J_{BC} = 8.5 Hz), 7.64 (broad s, 2, protons ortho to the fluoroalkyl group); ^{19}F nmr ($CDCl_3$) 75.0 (s, 12); ir (KBr) 3495 (m, broad), 3110 (m, broad), 2978 (s), 1487 (*m*), 1268 (s), 1238 (s), 1213 (s), 1188 (s), 1148 (s), 975 (s), 962 (s), 741 (s); mass spectrum (70 eV) *m/e* (rel intensity) 630 (100.00, $M\cdot^+$), 615 (90.05, $M\cdot^+ - CH_3$), 300 (19.07, $M\cdot^+ - H - (CH_3)_3CC_6H_3C(CF_3)_2OH$), 286 (10.08), 272 (21.41), 57 (62.68); uv (ether) λ_{max} 296 nm (log ϵ 3.70) and 242 (log ϵ 4.08).

Also 3.3 g (30.3% crude yield) of alcohol **11** was isolated from the earlier chromatographic fractions.

Anal. Calcd for $C_{26}H_{26}F_{12}O_2S$: C, 49.53; H, 4.16; S, 5.09. Found: C, 49.86; H, 4.12; S, 5.18.

Yields for this reaction were highly variable, ranging from 0 to 27% of the diol for various runs. The variable quality of the aluminum chloride is suspected as the cause of some of the observed fluctuations in yield.

Spirosulfurane 3. To diol **10** (0.9658 g, 1.53 mmol) in 20 ml of dry ether in an inert atmosphere box was added 0.1715 g (4.29 mmol, excess) of potassium hydride and hydrogen evolution was noted for *ca.* 15 min. An additional 0.010 g was added and the mixture was stirred for 2 hr. The mixture was filtered and the ether evaporated. The nonvolatile product was redissolved in carbon tetrachloride (15 ml) and 0.246 g (1.53 mmol) of bromine was added with magnetic stirring. The KBr (0.357 g, 98.2%) was removed by filtration and the solvent removed *in vacuo* to give an almost quantitative yield of **3** Recrystallization from petroleum ether at −78° gave white prisms: mp 159–160.5°; ^{1}H nmr (100 MHz, ^{19}F decoupled, CCl_4) δ 1.14 (s, 18, *tert*-butyl protons), 7.668 (d of d, protons para to the fluoroalkyl group, J_{AB} = 9.3 Hz, J_{BC} = 2.0 Hz), 7.665 (d, broad s in absence of decoupling, total area for δ 7.668 and 7.665 = 4, proton ortho to the fluoroalkyl group, J_{BC} = 2.0 Hz), 8.225 (d, 2, protons ortho to sulfur); ^{19}F nmr (CCl_4) two quartets (J_{FF} = 9 Hz) at 73.9 and 77.0 ppm having equal areas; ir ($CHCl_3$) 2965 (w), 1297 (*m*), 1265 (s), 1193 (s), 1122 (m), 1038 (w), 986 (m), 965 (m); mass spectrum (70 eV) *m/e* (rel intensity) 628 (7.43, $M\cdot^+$), 613 (1.27, $M\cdot^+ - CH_3$), 609 (2.25, $M\cdot^+ - F$), 559 (100.00, $M\cdot^+ - CF_3$), 475 (15.73, $M\cdot^+ - CH_3(CF_3)_2$), 57 (21.06, $^+C(CH_3)_3$); uv (ether) λ_{max} 243 nm (log ϵ 4.11) and 229 (log ϵ 4.08).

Anal. Calcd for $C_{26}H_{24}F_{12}O_2S$: C, 49.69; H, 3.85; S, 5.10. Found: C, 50.00; H, 3.82; S, 5.06.

Spirosulfurane Oxide 9. To spirosulfurane **3** (31.6 mg, 5.03 × 10^{-5} mol) in 0.5 ml of carbon tetrachloride was added an excess of a concentrated solution of ruthenium tetroxide[25] (prepared as in ref 25 and dried over P_2O_5) in carbon tetrachloride. Ruthenium dioxide precipitated immediately and the ^{19}F nmr spectrum indicated that reaction was about half completed. Addition of 2 drops of water with shaking resulted in immediate completion of the reaction as indicated by ^{19}F nmr. The excess RuO_4 was quenched with 1 ml of ethanol. The solvent was evaporated and the product was redissolved in ether. Filtration of the mixture to remove the RuO_2 and removal of the solvent *in vacuo* gave 29.1 mg (90%) of the crude product, which was recrystallized from petroleum ether to give white needles, mp 183.5–184°. In other runs it was found that the RuO_2 precipitated as very fine particles, which were removed by passing the reaction mixture through a very short (*ca.* 1 in.) column of alumina: ^{1}H nmr (100 MHz, ^{19}F decoupled, CCl_4) δ 1.39 (s, 18, *tert*-butyl protons), 7.750 (d of d, protons para to the fluoroalkyl group, J_{AB} = 9.3 Hz, J_{BC} = 2.0 Hz), 7.745 (d, broad s in absence of decoupling, total area for δ 7.750 and 7.745 = 4, protons ortho to the fluoroalkyl group, J_{BC} = 2.0 Hz), 8.610 (d, 2, protons ortho to sulfur, J_{AB} = 9.3 Hz); ^{19}F nmr shows two quartets at 74.5 and 75.2 ppm upfield from $CFCl_3$ ($J_{FF} \cong$ 8 Hz); ir ($CHCl_3$) 3620 (w), 2970 (m), 1592 (w), 1300 (m), 1266 (s), 1194 (m), 1141 (m, S=O stretch), 1041 (m), 991 (m), 966 (m), 860 (w); mass spectrum (70 eV) *m/e* (rel intensity) 644 (0.47, $M\cdot^+$), 629 (1.97, $M\cdot^+ - CH_3$), 625 (2.47, $M\cdot^+ - F$), 575 (100.00, $M\cdot^+ - CF_3$), 565 (1.55, $M\cdot^+ - CH_3SO_2$), 559 (3.83, $M\cdot^+ - CF_3O$), 315 (11.58), 179 (23.78); high resolution peak matching techniques show the molecular ion at *m/e* 644.1244 (calcd for **9**, 644.1255) and support the assignments for the fragments listed; uv (ether) λ_{max} 249 nm (log ϵ 4.49).

Anal. Calcd for $C_{26}H_{24}F_{12}O_3S$: C, 48.45; H, 3.75; S, 4.97. Found: C, 48.72; H, 3.70; S, 5.02.

When 0.30 g (1.67 mmol) of water containing 51.3% ^{18}O, 2.34% ^{17}O, and 54.8% ^{2}H was added to a solution of **9** (0.058 g, 9.24 × 10^{-5} mol) and RuO_4 (*ca.* 0.0314 g, 1.91 × 10^{-4} mol) and the solution was stirred overnight, there was no ^{18}O incorporation into the sulfurane oxide molecule as demonstrated by a high resolution isotope ratio mass spectrum of the large fragment ion at *m/e* 575 ($M\cdot^+ - CF_3$).

Cyclic Hexafluorocumyloxysulfurane 14 and Bromosulfurane 15. To a solution of 3.13 g (6.74 mmol) of hydroxy sulfide **11** in 5 ml of dry ether was added 0.3 g (7.5 mmol) of potassium hydride. Addition of 1.90 g (6.74 mmol) of hexafluoro-2-phenyl-2-propoxide to the mixture produced a solid mass. Ether (35 ml) and dry tetrahydrofuran (3 ml) were added with stirring. Additional potassium hydride was added until hydrogen evolution ceased and the mixture was stirred for 2 hr. The excess potassium hydride was removed by filtration and bromine (1.08 g, 6.74 mmol) was added to the filtrate. After 1 hr the mixture was filtered to remove the KBr, which was washed with ether. The solvent was evaporated and the crude product taken up in ether. Addition of petroleum ether to the ether solution gave 0.490 g (13.4%) of crystalline crude bromosulfurane **15**. Recrystallization from ether–petroleum gave yellow needles, mp 190.5–194.5°. Several recrystallization attempts were made but it was not possible to remove small amounts of impurities present: ^{1}H nmr ($CDCl_3$) (only partial spectrum available, concentration too low to see all of aromatic region) δ 1.32 and 1.46 (2 singlets, *tert*-butyl protons), 7.18 and 7.35 (2 singlets, aromatic protons of disubstituted phenyl ring?); ^{19}F nmr ($CDCl_3$) shows two quartets, equal in area, 74.8 and 76.5 ppm upfield from $CFCl_3$; ir ($CHCl_3$) 2970 (s), 1295 (m), 1265 (s), 1225 (broad, s), 1194 (m), 1090 (m), 988 (m), 965 (m); mass spectrum (70 eV) *m/e* (rel intensity) 542 (0.76, $M\cdot^+$ for ^{79}Br), 544 (0.66, $M\cdot^+$ for ^{81}Br), 527 (0.89, $M\cdot^+ - CH_3$), 529 (0.81), 480 (1.02), 464 (65.85), 463 (2.60, $M\cdot^+ - Br$), 449 (100.00, $M\cdot^+ - CH_2Br$), 346 (12.15, $(CH_3)_3CC_6H_3SOC(CF_3)_2 + H$), 331 (71.31, $(CH_3)_2CC_6H_3SOC(CF_3)_2 + H$), 303 (13.58), 217 (17.04), 203 (11.06), 199 (22.99), 197 (23.74), 189 (27.97), 118 (16.50), 117 (13.88), 91 (12.58), 57 (28.24, $^+C(CH_3)_3$).

Anal. Calcd for $C_{23}H_{25}BrF_6OS$: C, 50.84; H, 4.64; Br, 14.70; S, 5.90. Found: C, 51.62; H, 5.06; Br, 14.03; S, 5.75.

The other product of the reaction, cyclic hexafluorocumyloxysulfurane **14**, remained in solution after the bromosulfurane crystallized. The solvent was removed to give 2.187 g (46%) of the crude cyclic sulfurane. Recrystallization in an inert atmosphere box using petroleum ether gave white crystals: mp 140–143.5°; ^{1}H nmr ($CDCl_3$) δ 1.23 (s, 9, *tert*-butyl protons on disubstituted phenyl ring), 1.34 (s, 9, *tert*-butyl protons on trisubstituted phenyl ring), 7.14 (broad s, 4, protons on disubstituted phenyl ring, AB pattern in 220 MHz nmr in CCl_4 at δ 7.26 and 7.19, J_{AB} = 7.0 Hz), 7.24 (m, 5, protons on monosubstituted phenyl ring, 220 MHz (CCl_4) shows two distorted doublets at δ 7.34 and 7.43), 7.54 (broad s, 1, collapses into doublet with irradiation of ^{19}F nuclei at 100 MHz (CCl_4), proton ortho to the fluoroalkyl group), 7.70 (d of d, 1, proton para to the fluoroalkyl group), 8.62 (d, 1, proton on the spiro phenyl ring ortho to sulfur); ^{19}F ($CDCl_3$) shows four quartets 70.6, 71.4, 76.1, and 77.3 ppm upfield from $CFCl_3$; mass spectrum (70 eV) *m/e* (rel intensity) 706 (0.02, $M\cdot^+$), 691 (0.01, $M\cdot^+ - CH_3$), 687 (0.02, $M\cdot^+ - F$), 637 (0.02, $M\cdot^+ - CF_3$), 480 (0.24, $M\cdot^+ + H - (CF_3)_2CC_6H_5$, possible hydrolysis product), 463 (2.10, $M\cdot^+ - O(CF_3)_2CC_6H_5$), 449 (3.21), 244 (52.86, $HOC(CF_3)_2C_6H_5\cdot^+$), 175 (78.25, $HOC(CF_3)_2C_6H_5\cdot^+ - CF_3$), 127 (14.94), 105 (100.00, possibly $C_6H_5CHCH_3^+$), 77 (32.38, $C_6H_5^+$), 69 (25.25, CF_3^+), 51 (15.61, CHF_2^+).

Anal. Calcd for $C_{32}H_{30}F_{12}O_2S$: C, 54.39; H, 4.28; S, 4.54. Found: C, 54.76; H, 4.36; S, 4.57.

From the ^{19}F nmr spectrum of the crude reaction mixture, the yields of cyclic sulfurane **14** and bromosulfurane **15** obtained are 75.5 and 14.6%, respectively. Also found was about 5% each of hydroxy sulfoxide **16** and R_FOH, attributed to hydrolysis. In another run larger amounts of the latter two products were formed.

2-(1,1,1,3,3,3-Hexafluoro-2-hydroxy-2-propyl)-4,4′-di-*tert*-butyldiphenyl Sulfoxide (16). Crude hydroxy sulfide **11** (23.7 g, 0.0504 mol) prepared as above was dissolved in *ca.* 50 ml of benzene and sodium hydride added with stirring until all hydrogen evolution ceased. Bromine (4.03 g, 0.0504 mol) was added to the crude mixture to give a precipitate. Chromatography on alumina with pentane elution removed 4,4′-di-*tert*-butyldiphenyl sulfide. Further elution with ether gave 3.349 g (14.0%) of sulfoxide **16**. Recrystal-

(25) H. Nakata, *Tetrahedron*, **19**, 1959 (1963).

lization from ether–petroleum ether, followed by sublimation (158° at 0.10 mm) gave white crystals, mp 194–195°, which resolidify and remelt at 205–210°. Both forms exhibit identical properties in solution: ^{1}H nmr ($CDCl_3$) δ 1.20 (s, 9, *tert*-butyl on disubstituted phenyl), 1.33 (s, 9, *tert*-butyl on trisubstituted phenyl), 7.36 and 7.43 (m, 4, aromatic protons on disubstituted phenyl ring), 7.66 (partially hidden d of d, 1, proton para to the fluoroalkyl group), 7.75 (broad s, 1, proton ortho to the fluoroalkyl group), 8.27 (d, 1, proton ortho to sulfur on the trisubstituted phenyl ring), 8.80 (broad s, 1, O*H*); ^{19}F nmr ($CDCl_3$) shows two distorted quartets ($J_{FF} \cong 7$ Hz) at 74.8 and 75.4 ppm upfield from $CFCl_3$; ir ($CHCl_3$) 2968 (m), 1396 (w), 1365 (w), 1262 (m), 1218 (m, broad), 1185 (m), 1149 (m), 1076 (w), 998 (w), 964 (m); mass spectrum (70 eV) *m/e* (rel intensity) 480 (64.52, $M\cdot^+$), 465 (14.05, $M\cdot^+ - CH_3$), 464 (11.54, $M\cdot^+ - O$), 463 (3.86, $M\cdot^+ - OH$), 449 (22.58, $M\cdot^+ - CH_3O$), 424 (15.29, $M\cdot^+ - C_4H_8$), 409 (10.03), 343 (14.70), 330 (48.37, $M\cdot^+ - OH - (CH_3)_3CC_6H_4$), 315 (25.06, $M\cdot^+ - (CH_3)_3CC_6H_4 - CH_3OH$), 261 (23.43), 225 (13.41), 181 (37.18), 165 (18.43), 166 (38.54, $CF_3COCF_3\cdot^+$), 167 (13.95, $[CF_3COHCF_3]\cdot^+$), 149 (84.09), 138 (12.67), 135 (76.61), 131 (10.78), 121 (40.30), 117 (17.45), 109 (47.63), 91 (25.30), 74 (29.84), 59 (44.98), 57 (73.67, $^+C(CH_3)_3$); uv (ether) λ_{max} 233 (log ϵ 4.20), shoulder at λ 272 (log ϵ 3.62).

Anal. Calcd for $C_{23}H_{26}F_6O_2S$: C, 57.49; H, 5.45; S, 6.67. Found: C, 57.39; H, 5.41; S, 6.72.

Cyclic *tert*-Butoxysulfurane 18. To 0.6572 g (0.930 mmol) of cyclic hexafluorocumyloxysulfurane **14** in 2 ml of $CDCl_3$ was added 68.7 mg (0.93 mmol) of *tert*-butyl alcohol with shaking. Triethylamine (94.0 mg, 0.93 mmol) was added, the solvent was removed *in vacuo*, and petroleum ether was used to triturate the solid to remove the triethylamine–R_FOH complex, leaving 0.2749 g (55.7%) of crude sulfurane **18**. Recrystallization from ether–petroleum ether gave white crystals: mp 162–163°; ^{1}H nmr ($CDCl_3$, 220 MHz) δ 1.29 (s, 9, ArC(C*H*$_3$)$_3$) 1.41 (s, 9, ArC(C*H*$_3$)$_3$), 1.42 (s, 9, OC(C*H*$_3$)$_3$), 7.39 (m, 4, Ar*H*, disubstituted ring), 7.75 (distorted doublet, 1, proton para to fluoroalkyl group), 7.80 (broad s, 1, proton ortho to fluoroalkyl group), 8.34 (d, 1, Ar*H* ortho to sulfur on trisubstituted ring); ^{19}F nmr ($CDCl_3$) shows two quartets at 76.6 and 77.5 ppm upfield from $CFCl_3$; mass spectrum (70 eV) *m/e* (rel intensity) 536 (0.08, $M\cdot^+$), 521 (0.08, $M\cdot^+ - CH_3$), 494 (0.09), 491 (0.08), 480 (10.34, $M\cdot^+ - C_4H_8$, possible hydrolysis product), 463 (100.00, $M\cdot^+ - OC(CH_3)_3$), 57 (20.34, $[C(CH_3)_3]^+$).

Anal. Calcd for $C_{27}H_{34}F_6O_2S$: C, 60.43; H, 6.39; S, 5.98. Found: C, 60.40; H, 6.52; S, 6.11.

Cyclic Oxysulfonium Trifluoromethanesulfonate 17. Cyclic hexafluorocumyloxysulfurane **14** (0.7233 g, 1.024 mmol) was dissolved in *ca.* 5 ml of dry ether. One equivalent of trifluoromethanesulfonic acid (triflic acid) was added at −40°, producing an immediate precipitation of white product. The mixture was kept cool for 1 hr and filtered. The precipitate was washed three times with ether and then with pentane at room temperature to give 0.3448 g (55.0% of pure triflate): mp 226–228°; ^{1}H nmr ($CDCl_3$) δ 1.33 (s, 9, *tert*-butyl protons of disubstituted ring), 1.48 (s, 9, ArC(C*H*$_3$)$_3$ of the trisubstituted ring), 7.39 and 7.53 (2 singlets, 4, Ar*H* of the disubstituted ring), 7.72 (s, broad, 1, Ar*H* ortho to the fluoroalkyl group), 7.91 (d of d, 1, Ar*H* para to the fluoroalkyl group), 8.46 (d, 1, Ar*H* ortho to sulfur on the trisubstituted ring); ir ($CHCl_3$) 2985 (m), 1595 (w), 1301 (s), 1272 (s), 1230 (broad, s), 1050 (m), 1031 (s), 1001 (m), 979 (m), 635 (w); ^{19}F nmr ($CDCl_3$) shows two quartets at 74.2 and 76.2 ppm and a singlet at 78.9 ppm upfield from $CFCl_3$.

Anal. Calcd for $C_{24}H_{25}F_9O_4S_2$: C, 47.06; H, 4.11; S, 10.47. Found: C, 47.07; H, 4.36; S, 10.65.

Diphenyl Sulfoxide-^{18}O. Acyclic sulfurane **4** (6.58 g, 9.80 mmol) was dissolved in 20 ml of dry carbon tetrachloride in an inert atmosphere box and the flask was capped with a serum stopple. To this was added 196 μl (9.80 mmol) of labeled water containing 51.3% ^{18}O, 2.34% ^{17}O, and 54.8% ^{2}H excess atom % label. After a minute of shaking, the water disappeared. The solution was then extracted twice with 35-ml portions of 10% sodium hydroxide solution and once with 35 ml of H_2O. The CCl_4 layer was dried over potassium carbonate overnight. Evaporation of the solution yielded an oil which crystallized on addition of petroleum ether to give 0.8582 g of crude product. Recrystallization from ether–petroleum ether gave 0.8194 g (41.3%) of diphenyl sulfoxide-^{18}O; mp 69.5–72.5° (lit.[26] mp 70–71°); mass spectrum (70 eV) shows *m/e* 202 and 204 peaks in the ratio of 1.00:0.918. This corresponds to 48% excess ^{18}O labeling, indicating loss of about 3.3% of the ^{18}O label in the reaction.

Attempted Hydrolysis of Spirosulfurane 3 and Spirosulfurane Oxide 9. Spirosulfurane **3** (44 mg, 7.0×10^{-5} mol) was dissolved in 3 ml of a 9:1 v/v mixture of tetrahydrofuran–water. No change was observed in the ^{19}F spectrum after 2 hr at reflux. Addition of 50 μl of concentrated HCl followed by reflux for 1.5 hr gave no observable change in the ^{19}F nmr spectrum. Addition of 2 ml of 10% sodium hydroxide solution rendered the above solution basic but heterogeneous. Reflux for 2 hr resulted in no change in the ^{19}F nmr spectrum. Evaporating the solvent and using ethanol–water (*ca.* 4:1 ratio) as solvent with 10% aqueous sodium hydroxide gave a more nearly homogeneous mixture. Reflux for several hours resulted in no change in the ^{19}F nmr spectrum. Spirosulfurane oxide **9** (0.0143 g, 2.22×10^{-5} mol) was partially dissolved in 0.90 ml of tetrahydrofuran and 0.10 ml of H_2O and to this was added 50 μl of concentrated HCl. The mixture was refluxed for 0.5 hr. The ^{19}F nmr spectrum showed no reaction had occurred. The mixture was made basic with 50% aqueous sodium hydroxide and reflux was continued for 0.5 hr with no change in the ^{19}F nmr spectrum.

Attempted Oxidation of Sulfide Diol 10 to Give Sulfoxide Diol 13. Method A. Metaperiodate oxidation[27] at 0° in methanol–water gave no reaction after 12 hr.

Method B.[28] Sulfide diol **10** (0.3152 g, 0.500 mmol) was dissolved in *ca.* 10 ml of CCl_4 and excess (*ca.* 1.5 equiv) dinitrogen tetroxide was bubbled into the solution at 0°. After 12 hr at room temperature ^{1}H and ^{19}F nmr spectra indicated formation of spirosulfurane **3** (95%) and *ca.* 5% of spirosulfurane oxide **9**.

Method C.[29] To sulfide diol **10** (0.5359 g, 0.852 mmol) in 5 ml of CCl_4 was added *ca.* 1.92 mmol of ruthenium tetroxide in 6 ml of carbon tetrachloride to give a mixture of spirosulfurane **3** (45%) and spirosulfurane **9** together with unreacted starting material (55% for the two latter compounds by ^{19}F nmr analysis). Addition of 5 ml of the RuO_4 solution converted sulfurane **3** to the sulfurane oxide but there was still alcohol **10** present. This was separated from spirosulfurane oxide **9** by passing the mixture through a 6-in. acid-washed alumina column to give 50 mg of recovered starting material and 128 mg of spirosulfurane oxide **9** (36.7%).

Exchange of Cyclic Hexafluorocumyloxysulfurane 14 and R_FOH. Sulfurane **14** (77.5 mg, 0.110 mmol) was dissolved in 0.44 ml of $CDCl_3$. To this was added at 41°, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, and finally 6.0 equiv of R_FOH. After each quantity of R_FOH was added, the ^{19}F nmr spectrum was obtained and the downfield quartets at 70.6 and 71.4 ppm upfield from $CFCl_3$ were examined for broadening. The final addition of 6 equiv of R_FOH (bringing the volume to 0.55 ml to give a concentration of 1.20 *M* in R_FOH) resulted in exchange coalescence of the downfield quartets.

Reactions of Cyclic Hexafluorocumyloxysulfurane 14. (a) Benzyl Alcohol. To 0.5 ml of a $CDCl_3$ solution of sulfurane **14** (0.119 mmol) was added 1 equiv of freshly distilled benzyl alcohol. The ^{19}F nmr spectrum indicated formation of equal amounts (each 47.5% of the total ^{19}F integral) of R_FOH and benzyloxy cyclosulfurane (chemical shifts of the sulfurane CF_3 quartets are 76.2 and 77.0 ppm upfield from $CFCl_3$) and a small amount (4.8%) of an unknown fluorine-containing compound showing a singlet at 75.4 ppm. The ^{1}H nmr spectrum shows the *tert*-butyl singlets at δ 1.23 and 1.36, the C*H*$_2$Ph protons at δ 4.71, a doublet at δ 8.15 (proton ortho to sulfur on the trisubstituted phenyl ring), and R_FOH at δ 3.81 as well as unassigned aromatic peaks.

(b) Cyclohexyl Alcohol. To 0.5 ml of a $CDCl_3$ solution of sulfurane **14** (0.123 mmol) was added 1 equiv of cyclohexyl alcohol. Results comparable to those obtained with benzyl alcohol were seen in the ^{19}F spectra [46.9% each of the cyclic cyclohexyloxysulfurane (76.0 and 77.0 ppm) and R_FOH with 6.3% of the ^{19}F unknown at 75.4 ppm]. The ^{1}H nmr spectrum shows the *tert*-butyl singlets at δ 1.24 and 1.35, R_FOH at 4.22, and a doublet at 8.21 (proton ortho to sulfur on the trisubstituted phenyl ring) as well as unassigned aromatic and cyclohexyl proton peaks.

(c) Methanol. To 1.0 ml of a $CDCl_3$ solution of sulfurane **14** (0.0894 mmol) was added 1 equiv of methanol which had been previously dried over 4X molecular sieves. Equivalent amounts (46.5%) of cyclic methoxysulfurane and R_FOH were shown by ^{19}F nmr (chemical shifts for the sulfurane are 76.2 and 77.3 ppm)

(26) O. Hinsberg, *Ber. Deut. Chem. Ges.*, **43**, 289 (1910).

(27) N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).

(28) C. C. Addison and J. C. Sheldon, *J. Chem. Soc.*, 2705 (1956).

(29) C. Djerassi and R. R. Engle, *J. Amer. Chem. Soc.*, **75**, 3838 (1953).

with *ca.* 7% of an unknown compound. The ^1H nmr spectrum shows the *tert*-butyl singlets at δ 1.28 and 1.41, OCH_3 at δ 3.49, R_FOH at δ 4.32, and a doublet at δ 8.20, corresponding to a proton ortho to sulfur on the trisubstituted phenyl ring. Addition of a second equivalent of methanol gave a second methyl peak at δ 3.41 in addition to the peak at δ 3.49. Both peaks were considerably broadened but the presence of both peaks suggests slow exchange at 41°.

(d) Hydroquinone. To a solution of 0.0984 mmol of cyclic hexafluorocumyloxysulfurane **14** in 0.5 ml of $CDCl_3$ was added 1 equiv of hydroquinone. During *ca.* 15 min a yellow color developed. The ^{19}F nmr spectrum showed peaks corresponding to hydroxy sulfide **11** and R_FOH (by comparison of ^{19}F and ^1H spectra with those of authentic materials).

Sublimation of Bromosulfurane 15. Bromosulfurane **15** (0.46 g, 0.85 mmol) was placed in a sublimation apparatus and partially sublimed at 136° (0.4 mm) to give an oily yellow material having two sharp singlets in the ^{19}F nmr spectrum at 75.2 and 75.6 ppm in the ratio of 4.1:1 which were not identified although the larger singlet chemical shift corresponds to an impurity common to bromosulfurane **15**. Continuing sublimation at 158° (0.06 mm) gave a solid yellow material. The ^{19}F nmr spectrum of the sublimate indicated that 35.0% of the material was the unchanged bromosulfurane **15**, while 38.5% corresponded to the compound having a sharp singlet (hypobromite?) at 75.2 ppm and 37.5% corresponded to another compound showing a multiplet at 75.7 ppm.

Reaction of Bromosulfurane 15 and Cyclic Oxysulfonium Triflate 17 with Potassium Hexafluoro-2-(*p*-*tert*-butylphenyl)-2-propoxide. A solution containing 0.1340 g (0.247 mmol) of bromosulfurane **15** in 0.7 ml of $CDCl_3$ and a second solution containing 0.0584 g (0.0955 mmol) of the cyclic sulfonium triflate in 0.5 ml of $CDCl_3$ were prepared. To each was added 1 equiv of the *p*-*tert*-butyl derivative of R_FOK. In each case the compounds reacted too rapidly to be followed by ^{19}F nmr and potassium salt precipitated from solution. Monocyclic sulfurane **19** was a major product (34.5% from the reaction with **15** and 45.5% from the reaction with triflate **17**) in each reaction. The ^{19}F nmr spectrum of sulfurane **19** in $CDCl_3$ has four quartets with chemical shifts 71.7, 71.3, 76.5, and 77.6 ppm.

Reactions of Hydroxy Sulfoxide 16. (a) With Triflic Acid. To 0.0872 mmol of hydroxy sulfoxide **16** in 0.5 ml of $CDCl_3$ was added 0.90 equiv of triflic acid and the ^1H and ^{19}F nmr spectra were recorded (chemical shifts reported in Results section). Addition of an additional 1.10 equiv of triflic acid resulted in the formation of cyclic sulfonium triflate **17**, as determined by comparison of the nmr data with those of authentic material.

(b) With Acyclic Sulfurane 4. A solution of 0.106 mmol of hydroxy sulfoxide **16** in 0.5 ml of $CDCl_3$ was poured into a vial containing 1 equiv of acyclic sulfurane **4** under nitrogen. The ^{19}F nmr spectrum of the resulting mixture showed that 1 equiv each of cyclic hexafluorocumyloxysulfurane **14** and R_FOH were produced (comparison with authentic compounds).

Reactions of Cyclic *tert*-Butoxysulfurane 18. (a) With Aqueous Base. To a solution of *ca.* 0.15 mmol of cyclic *tert*-butoxysulfurane **18** in 0.5 ml of $CDCl_3$ was added several drops of 10% aqueous sodium hydroxide. No change was apparent in the ^{19}F spectrum immediately after addition. After 24 hr at room temperature, there was *ca.* 29% conversion to hydroxy sulfoxide **16** (by ^{19}F nmr).

(b) With Methanolic KOH. Cyclic *tert*-butoxysulfurane **18** (0.387 mmol) was partially dissolved in 0.4 ml of a solution made by dissolving 5 g of potassium hydroxide in 25 ml of methanol. The ^1H nmr spectrum of the *tert*-butyl region showed that no exchange with methoxide had occurred since the three *tert*-butyl of **18** were still present. After 48 hr there was *ca.* 21% conversion to hydroxy sulfoxide **16** as determined by ^{19}F nmr. Other products were detected but were not isolated. Addition of 2 drops of 20% aqueous HCl to the solution gave rapid and complete hydrolysis to hydroxy sulfoxide **16** and *tert*-butyl alcohol.

Spirosulfurane 3 Interactions. (a) With Optically Active Solvent.[30] To a solution of *ca.* 50 mg of spirosulfurane **3** in 0.5 ml of carbon tetrachloride (*ca.* 0.157 *M*) was added *ca.* 20 mg of the optically active solvent (*S*)-(+)-2,2,2-trifluorophenylethanol. No change was observed in the 56-MHz ^{19}F nmr spectrum from that in achiral solvent over the temperature range 41 to −95° nor in the 220-MHz ^1H nmr spectrum at probe temperature.

(b) With Europium Shift Reagent. To a solution of spirosulfurane **3** (0.0849 mmol) in 0.3 ml of $CDCl_3$ was added a solution of 23.8 mg of $Eu(fod)_3$ in 0.4 ml of $CDCl_3$ giving concentrations of 0.12 *M* for **3** and 0.03 *M* for the shift reagent. No change was observed in the ^{19}F nmr spectrum.

Attempts to Reduce Spirosulfurane Oxide 9. (a) Stannous Chloride and Acetyl Chloride.[31] Spirosulfurane oxide **9** (0.0126 mmol) was dissolved in 0.14 ml of dimethylformamide and 0.36 ml of acetonitrile and 1.8 equiv of stannous chloride and 1 equiv of acetyl chloride were added at 0°. The ^{19}F nmr spectrum showed no reaction. Addition of 8.9 equiv of $SnCl_2$ and 9.1 equiv of acetyl chloride, followed by heating of the solution at 100° for 12.5 hr gave no change in the ^{19}F nmr spectrum from that of starting material.

(b) Triphenylphosphine.[32] **Method A.** Spirosulfurane oxide **9** (0.064 mmol) and triphenylphosphine (1 equiv) were suspended in 2 ml of glacial acetic acid with 0.34 mmol of boron trifluoride etherate. The solution was heated to reflux for 1.5 hr, an additional 0.27 mmol of BF_3-etherate was added, and reflux was continued for 4.5 hr. Addition of water caused precipitation of unreacted starting material, **9**.

(c) Triphenylphosphine. Method B. Spirosulfurane oxide **9** (0.0769 mmol) and triphenylphosphine (0.0675 mmol) were melted at 190° and this temperature was maintained for 80 min. On cooling and dissolving the material in $CDCl_3$, the ^{19}F nmr spectrum showed that no reaction had taken place.

(d) Phosphorus Trichloride. Spirosulfurane oxide **9** (0.0127 mmol) was dissolved in 0.5 ml of methylene dichloride. To this was added 5 equiv of phosphorus trichloride and the solution was heated to reflux for 2.5 hr. Addition of 0.30 ml of PCl_3 followed by reflux for 19 hr gave no reaction as evidenced by the ^{19}F nmr spectrum.

Attempts to Alkylate Spirosulfurane 3 and Spirosulfurane Oxide 9. To separate solutions of spirosulfurane **3** and spirosulfurane oxide **9** in $CDCl_3$ was added 1 equiv of methyl fluorosulfonate. There were no changes in the ^{19}F or ^1H nmr spectra from those of starting material and reagent.

Bromination with Bromosulfurane 15. To bromosulfurane **15** (0.6669 g, 1.23 mmol), partially dissolved in 25 ml of dry ether, was added 1.42 equiv of bromine, The ^{19}F and ^1H nmr spectra indicated formation of hydroxy sulfide **11**. This was confirmed by addition of authentic material. No other products were isolated from this reaction.

Reaction of Diphenyl Sulfoxide and R_FOH with Chlorine. Ether 23 and Ether 24. To diphenyl sulfoxide (15.0 g, 0.0743 mol) was added 41.9 g (0.1486 mol) of R_FOK in 300 ml of dry carbon tetrachloride containing 1,4-endoxocyclohexane[22b] (6.7 ml, 7.27 g, 0.135 mol). The mixture was stirred for 1 hr to dissolve 95–98% of the material. The flask was covered with aluminum foil and 1.7 ml (2.63 g, 0.0371 mol) of chlorine gas was bubbled into the stirred solution. An aliquot withdrawn for ^{19}F nmr analysis revealed peaks for several compounds to be described later, plus an unassigned broad peak at 70.5 ppm corresponding to 3.25% of the total ^{19}F integral. After about 15 min an additional 1.7 ml (0.0371 mol) of chlorine gas was bubbled into the stirred reaction medium and a second aliquot was withdrawn for ^{19}F nmr. The peak at 70.5 ppm had nearly disappeared at this time. Stirring was continued for 75 min. The KCl was filtered and the CCl_4 was evaporated to leave an oil and a solid residue. Suspension of this petroleum ether, followed by filtration, gave 10.5 g (84%) of diphenyl sulfone. The oily product which remained (22.8 g) was distilled (81–90.5° (0.02 mm)). Three portions of approximately 300 mg were injected into a Waters liquid chromatograph using a Porasil preparative column with isooctane as the eluent to give two peaks corresponding to the two products, which were further purified by bulb to bulb distillation. The product with longer retention time was 1-(1,1,1,3,3,3-hexafluoro-2-phenyl-2-propoxy)-4-(1,1,1,3,3,3-hexafluoro-2-propyl)benzene (**23**): ^1H nmr (100 MHz, $CDCl_3$) δ 3.99 (septet, 1, J_{HF} = 9 Hz, $(CF_3)_2CH$, collapses to singlet at δ 3.99 upon ^{19}F irradiation), 6.91 and 7.26 (AB pattern, 4, J_{AB} = 9 Hz, Ar*H* on disubstituted ring), 7.62 (m, 5, Ar*H* on monosubstituted ring); ^{19}F nmr ($CDCl_3$) 65.8 (d, 6, $(CF_3)_2CH$, J_{HF} = 9 Hz) and 71.2 ppm (s, 6, $OC(CF_3)_2C_6H_5$); ir (neat) 1613 (m), 1513 (s), 1358 (m), 1222 (broad, s), 1143 (s), 1066 (m), 983 (m), 942 (m), 715 (s), 675 (m); mass spectrum (70 eV) *m/e* (rel intensity) 470

(30) W. H. Pirkle, R. L. Muntz, and I. C. Paul, *J. Amer. Chem. Soc.*, 93, 2817 (1971). We thank Dr. Pirkle for supplying a sample of the optically pure reagent and for carrying out this experiment.

(31) G. V. Kaiser, R. D. G. Cooper, R. E. Koehler, C. F. Murphy, J. A. Webber, I. G. Wright, and E. M. Van Heyningen, *J. Org. Chem.*, 35, 2430 (1970).

(32) H. H. Szmant and O. Cox, *J. Org. Chem.*, 31, 1595 (1966).

(10.93, $M\cdot^+$), 450 (3.36, $M\cdot^+ - HF$), 431 (1.39, $M\cdot^+ - HF_2$), 373 (1.93, $M\cdot^+ - HF - C_6H_5$), 227 (100.00, $C_6H_5C(CF_3)_2^+$), 207 (14.22), 177 (17.18), 127 (20.63).

Anal. Calcd for $C_{18}H_{10}F_{12}O$: C, 45.97; H, 2.14. Found: C, 45.77; H, 2.19.

The product with shorter retention time was 1-(1,1,1,3,3,3-hexafluoro-2-phenyl-2-propoxy)-4-(1,1,3,3,3-pentafluoro-2-propenyl)-benzene (**24**): ^1H nmr (100 MHz, $CDCl_3$) δ 6.81 and 7.10 (AB pattern, 4, Ar*H* of disubstituted ring, J_{AB} = 4 Hz), 7.46 (m, 3, meta and para Ar*H* of monosubstituted ring); ^{19}F nmr ($CDCl_3$) 60.2 and 60.7 (d of d, 3, $CF_3C{=}CF_2$, J_{FF} = ~11 Hz), 71.2 (s, 6, $OC(CF_3)_2C_6H_5$), 76.1 and 78.3 ppm (m, 2 total, $CF_3C{=}CF_2$); ir (neat) 3031 (w), 1734 (s, fluorinated alkene), 1608 (w), 1508 (s), 1354 (s), 1224 (s, broad), 1133 (s), 1094 (m), 1067 (s), 1012 (s), 983 (s), 955 (s), 942 (m), 833 (m), 715 (s), 691 (m); mass spectrum (70 eV) *m/e* (rel intensity) 450 (29.81, $M\cdot^+$), 431 (4.16, $M\cdot^+ - F$), 353 (2.82, $M\cdot^+ - HF - C_6H_5$), 227 (100.00, $C_6H_5C(CF_3)_2^+$), 223 (15.43), 207 (12.40), 195 (8.65), 187 (5.89), 177 (16.42), 145 (13.16), 127 (17.52).

Anal. Calcd for $C_{18}H_9F_{11}O$: C, 48.02; H, 2.01. Found: C, 48.05; H, 2.11.

The yields of the ethers by ^{19}F nmr integration were 77% for ether **23** and 15% for ether **24**. There was about 8.0% of unidentified ^{19}F products. The presence of unreacted R_FOK, broadened by exchange with some R_FOH, was detected in the ^{19}F nmr. The overall conversion to products was about 78%.

Reaction of Diphenyl Sulfoxide with Potassium Perfluoro-*tert*-butoxide: Bis(perfluoro-*tert*-butoxy)diphenylsulfurane (26). A suspension of 2.6000 g (9.92 mmol) of potassium perfluoro-*tert*-butoxide and 1.0000 g (4.96 mmol) of diphenyl sulfoxide in 20 ml of carbon tetrachloride was cooled to 0° and stirred magnetically. Chlorine (0.25 ml, 5.50 mmol) was condensed into a trap and added over a 30-min period. The mixture was warmed to room temperature and stirred for 15 hr. Filtration in an inert atmosphere box (removing *ca.* 1.8 g of unreacted potassium perfluoro-*tert*-butoxide plus KCl) followed by evaporation of the solvent yielded 1.67 g of crude material. Recrystallization of this from carbon tetrachloride–pentane yielded 0.2607 g (48%) of diphenyl sulfone, mp 119.5–122° (lit.[33] mp 125°). Concentration of the mother liquors yielded 0.28 g of bis(perfluoro-*tert*-butoxy)diphenylsulfurane (**26**); mp 113–116°; ^1H nmr (220 MHz) δ 7.51 (m, 6, meta and para protons), 7.84 (d of d, 4, ortho protons); ^{19}F nmr 71.3 ppm (s); mass spectrum (70 eV) *m/e* (rel intensity) 656 (0.03, $M\cdot^+$), 579 (0.06), 455 (0.08), 421 (80.85, $M\cdot^+ - C_4F_9O$), 344 (1.56, $M\cdot^+ - C_4F_9O - C_6H_5$), 218 (1.91), 202 (12.06, $M\cdot^+ - C_4F_9O - C_4F_9$), 186 (100, $M\cdot^+ - 2C_4F_9O$), 125 (19.15), 119 (17.73) [DADI metastable mass spectrum showed only one peak at *m/e* 437 resulting from the molecular ion; this possibly corresponds to $(C_6H_5)_2[(CF_3)_3CO]S{=}O\cdot^+$]; ir ($CHCl_3$) 1478 (w), 1445 (w), 1261 (s, broad), 1168 (m), 1143 (s), 1111 (s), 979 (s), 965 (s), 658 (w).

Anal. Calcd for $C_{20}H_{10}F_{18}O_2S$: C, 36.60; H, 1.54; S, 4.89. Found: C, 36.74; H, 1.85; S, 4.92.

Concentration of the mother liquors gave an additional 0.448 g, mp 106.5–113.5°, and 0.131 g (by ^{19}F nmr analysis of an oil weighing 0.237 g) of the sulfurane to give a total yield of 52% of the sulfurane. Based on the recovery of the ^{19}F products, the conversion was about 60%.

Reaction of Bis(perfluoro-*tert*-butoxy)diphenylsulfurane (26) and *tert*-Butyl Alcohol. Sulfurane **26** (0.0769 mmol) was dissolved in 0.5 ml of $CDCl_3$. To this was added 1 equiv of *tert*-butyl alcohol. The ^1H nmr showed that 1 equiv of isobutylene was formed and the ^{19}F nmr showed $(CF_3)_3COH$.

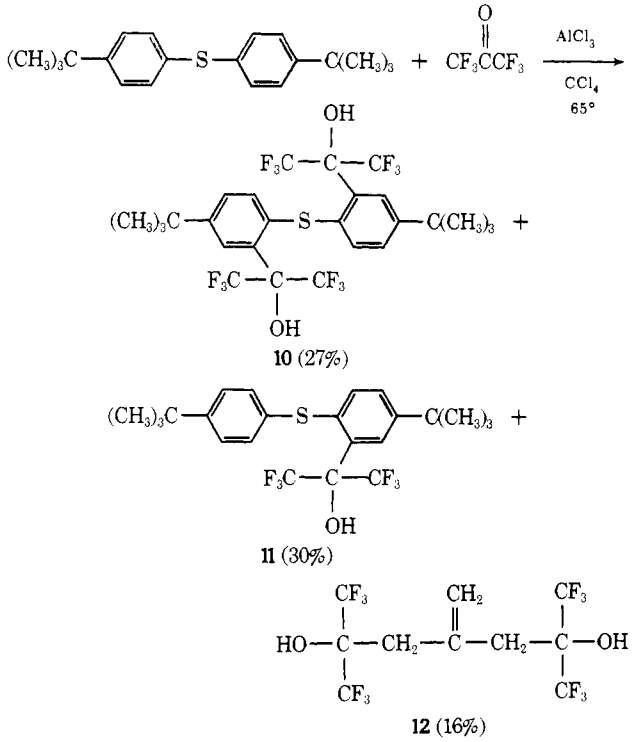
Reaction of Diphenyl Sulfoxide-^{18}O with Potassium Perfluoro-*tert*-butoxide and Chlorine. Diphenyl sulfoxide-^{18}O (0.7690 g, 3.69 mmol, 48 atom % excess ^{18}O), 0.9939 g (3.69 mmol) of perfluoro-*tert*-butoxide, and 0.33 ml (0.361 g, 3.69 mmol) of 1,4-endoxocyclohexane were dissolved in 20 ml of dry carbon tetrachloride and excess chlorine gas (0.18 ml, 3.96 mmol) was bubbled into the reaction vessel. The precipitated KCl was removed by filtration. Partial evaporation and repeated addition of aliquots of petroleum ether gave 0.2483 g of diphenyl sulfone and 0.4085 g of crude sulfurane **26**. Diphenyl sulfoxide (0.0157 g) was recovered at the end of the reaction giving an overall conversion to sulfone and sulfurane of 81.5%. Isotope ratio mass spectra of the sulfone and sulfurane showed that the diphenyl sulfone contains nearly all of the ^{18}O label. The relative proportions of $M\cdot^+$:$(M\cdot^+ + 2)$:$(M\cdot^+ + 4)$ (correcting for natural abundance ^{18}O) is 100.00:145.00:54.00 for the labeled diphenyl sulfone. The sulfurane shows the following mass spectrum: $(M\cdot^+ - 1)$, 13.5; $(M\cdot^+)$, 121.7; $(M\cdot^+ + 1)$, 34.7; $(M\cdot^+ + 2)$, 10.5. This is slightly above the observed value for $(M\cdot^+ + 2)$ of 9.55 at natural abundance but the ion at *m/e* 421 indicates no excess labeling, suggesting <1% ^{18}O incorporation into **26**.

Reaction of Diphenyl Sulfoxide and Chlorine. Approximately 1.5 equiv of chlorine was bubbled into a solution of diphenyl sulfoxide (1.000 g, 4.95 mmol) in 20 ml of carbon tetrachloride. After 52 hr at room temperature a 3.0-ml aliquot of this solution was passed through a neutral alumina liquid chromatography (lc) column using $CHCl_3$/MeOH gradient elution. The first fraction (0.0380 g, 28.9%) (yields are quoted as mole percentages) was diphenyl sulfide as identified by glpc and lc retention times, and by ^1H nmr and ir (comparison with authentic material). The second fraction (0.0107 g, 8.2%) was diphenyl sulfone, mp 125–126° (lit.[33] mp 125°, lc retention time and the ^1H nmr agreed with authentic material). The final fraction (0.0763 g, <63%) was seen to consist of several compounds but separation was not achieved. The predominant compound is diphenyl sulfoxide (^1H nmr).

Results

Synthesis. Spirosulfurane **3** was prepared by treating sulfide diol **10** with potassium hydride in ether, then with bromine in carbon tetrachloride. Sulfide diol **10** was prepared (Scheme I) by the aluminum chlo-

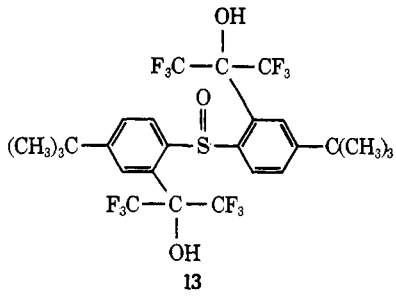
Scheme I



ride catalyzed alkylation of bis(*p*-*tert*-butylphenyl)-sulfide[23] with hexafluoroacetone in carbon tetrachloride in a sealed tube at 65°. The *p*-*tert*-butyl groups of the sulfide, intended to block para attack of hexafluoroacetone, undergo some electrophilic displacement. Subsequent reaction of the resulting isobutylene gives olefin **12** in 16% yield.[24] Diol **10** and alcohol **11** were obtained in 27 and 30% crude yields, respectively, by chromatography on alumina.

Evidence for the thermodynamic stability of spirosulfurane **3** was provided in unsuccessful attempts to oxidize sulfide diol **10** to the corresponding sulfoxide diol **13**. While treatment of the sulfide with sodium metaperiodate in basic methanol gave no reaction under the usual[27] reaction conditions, oxidations with N_2O_4[28]

(33) F. Mauthner, *Ber. Deut. Chem. Ges.*, **39**, 3594 (1906).



13

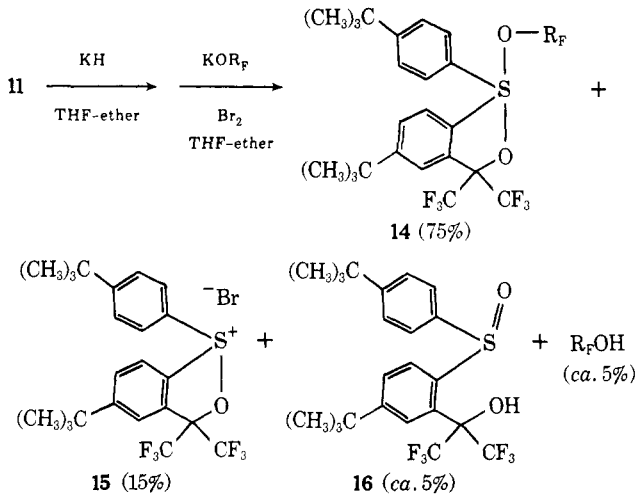
and RuO_4[29] provided spirosulfurane **3** and spirosulfurane oxide **9** under mild conditions, but no sulfoxide diol **13**.

The synthesis of spirosulfurane oxide **9** was first effected by the oxidation of spirosulfurane **3** in carbon tetrachloride with excess ruthenium tetroxide in the presence of a small amount of water. The requirement of water in this oxidation was demonstrated by treatment of **9** with a carbon tetrachloride solution of ruthenium tetroxide which had been dried over phosphorus pentoxide. The reaction converted a part of the sulfurane to sulfurane oxide, then stopped. Addition of a drop of water with shaking resulted in immediate complete reaction (90% isolated yield).

When the oxidation was carried out in the presence of water-^{18}O (51.3 atom % excess), no oxygen-18 was found in the product sulfurane oxide. If an unstable hydrate of ruthenium tetroxide is the reactive species in this oxidation, the isotopic tracer results require that the hydrate involve no equilibration of the oxygen atoms from RuO_4 with the oxygen of the hydrating water. A more likely rationale for the requirement of water in this reaction would invoke hydrolysis of some ruthenate ester intermediate to form hydrated ruthenium dioxide, which precipitates removing water from the solution.

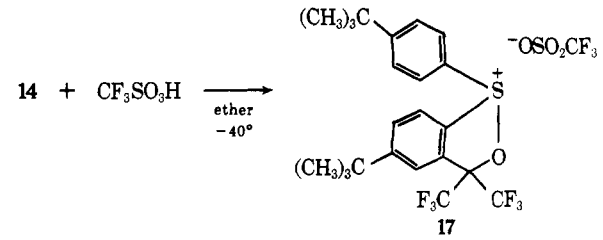
The reaction of an equimolar mixture of the potassium salt of **11** and potassium hexafluoro-2-phenyl-2-propoxide (KOR_F) with bromine in tetrahydrofuran–ether as solvent gives cyclic hexafluorocumyloxysulfurane **14** in 75% yield (by ^{19}F nmr, 46% isolated), Scheme II, and bromosulfurane **15** (15% by ^{19}F nmr)

Scheme II



in addition to small amounts of hydrolysis products R_FOH and sulfoxide alcohol **16** (*ca.* 5% of each by ^{19}F nmr). The mass spectra show small molecular ions for both **14** and **15** (0.02 and 0.76% of base peaks, respectively, at an ionization potential of 70 eV).

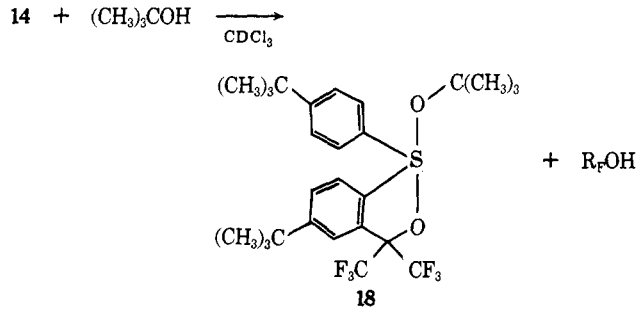
Cyclic oxysulfonium triflate **17** was precipitated upon



17

treatment of an ether solution of cyclic hexafluorocumyloxysulfurane **14** with triflic acid at −40° in ether. This salt-like compound, which bears a full formal positive charge on sulfur, exhibits two ^{19}F quartets at 74.2 and 76.2 ppm.

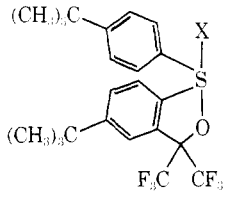
When *tert*-butyl alcohol is added to cyclic sulfurane **14**, cyclic *tert*-butoxysulfurane **18** is formed. This is



18

in marked contrast to the rapid dehydration of *tert*-butyl alcohol which acyclic sulfurane **4** brings about at −60° to yield isobutylene.[5] The crystalline *tert*-butoxy sulfurane was isolated in 56% yield. The methoxy, benzyloxy, and cyclohexyloxy analogs, prepared in a similar manner, were not isolated. The ^{19}F chemical shifts of the two quartets found for these compounds, together with the ^{19}F nmr data on related species, are presented in Table I. The ^{19}F chemical

Table I. ^{19}F Nmr Shifts for Various Cyclosulfuranes in Chloroform-*d* in ppm Upfield from Fluorotrichloromethane



Sulfurane, X =	Downfield quartet, ppm	Upfield quartet, ppm
OCH_3	76.2	77.3
$OCH_2C_6H_5$	76.2	77.0
OC_6H_{11}	76.0	77.0
$OC(CH_3)_3$, **18**	76.5	77.5
$OC(CF_3)_2C_6H_5$,[a] **14**	76.1	77.3
$OC(CF_3)_2C_6H_4C(CH_3)_3$,[b] **19**	76.5	77.6
Br,[c] **15**	74.6	76.5
$^-OSO_2CF_3$,[d] **17**	74.2	76.2
16	74.8	75.4

[a] CF_3 groups on the five-membered ring; those on the alkoxy ligand are 71.4 and 70.6 ppm upfield from $CFCl_3$. [b] CF_3 groups on the five-membered ring; those on the alkoxy ligand are 71.7 and 71.3 ppm upfield from $CFCl_3$. [c] Or the corresponding ion pair. [d] CF_3 group on the anion gives a singlet 78.9 ppm upfield from $CFCl_3$.

shifts of the cyclic sulfuranes having monodentate alkoxy ligands are all quite similar, *ca.* 76 and 77 ppm.

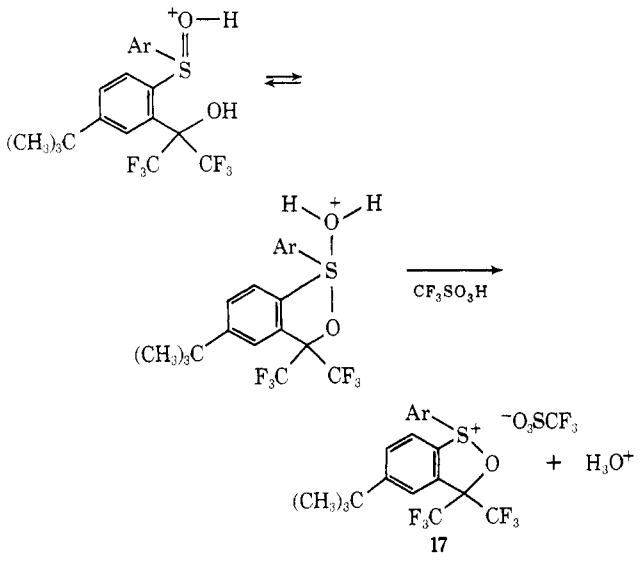
Reactions of Monocyclic Sulfuranes. Treatment of a solution of cyclic hexafluorocumyloxysulfurane **14** in chloroform-*d* with either aqueous base or acid results in very rapid hydrolysis to give sulfoxide alcohol **16**

$$\mathbf{14} \underset{Ph_2S(OR_F)_2}{\overset{H_2O}{\rightleftharpoons}} \mathbf{16}$$

4

and R_FOH. Treatment of **16** with acyclic sulfurane **4**, a powerful dehydration agent, reforms cyclic sulfurane **14**.

The cyclization of sulfoxide alcohol **16** is also accomplished by treatment with acids; for example, treatment with 0.90 equiv of triflic acid in $CDCl_3$ gives a species, presumably protonated, showing a small upfield shift of the trifluoromethyl quartets in the ^{19}F nmr (75.0 and 75.5 ppm relative to the neutral species **16** at 74.8 and 75.4 ppm) and downfield shifts of the *tert*-butyl groups (δ 1.31 and 1.41 relative to the neutral species at δ 1.25 and 1.35). The smaller separation between CF_3 nmr peaks of **16**, at lower field than any of the acyclic alkoxysulfuranes of Table I, is consistent with the predominance of the open chain sulfoxide alcohol rather than the cyclic hydroxysulfurane in the ring-chain tautomerism expected for **16**. Addition of 1.10 equiv of triflic acid to this solution gives the ^{19}F nmr spectrum characteristic of cyclic oxysulfonium triflate **17** and a further downfield shift of the *tert*-butyl



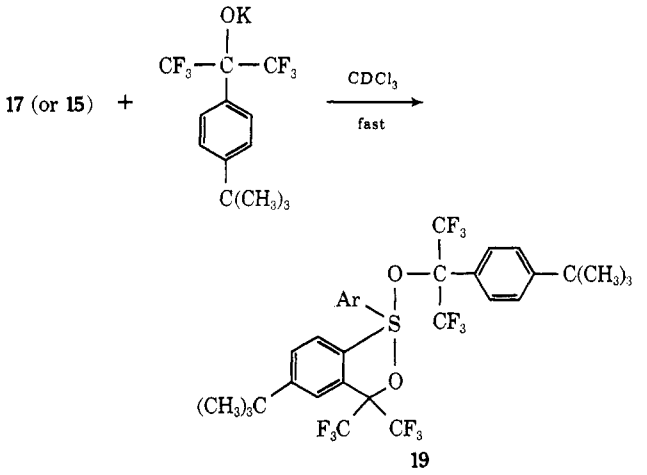
17

groups (δ 1.39 and 1.50). One mole of acid has little apparent effect on the ring chain tautomerism but 2 mol of acid, by protonating the water to give hydronium ion, shift the equilibrium toward the cyclic sulfonium ion.

In a related reaction, addition of triflic acid to a solution of bromosulfurane **15** in ether also results in the formation of **17**. This observation provides evidence for the postulated gross structure of the bromosulfurane.

Addition of hydroquinone to a solution of cyclic sulfurane **14** in chloroform-*d* results in the formation of 1 equiv of sulfide alcohol **11**, 1 equiv of benzoquinone, and 1 equiv of R_FOH. In contrast, when hydroquinone was added to solutions of spirosulfurane **3** or spirosulfurane oxide **9** in chloroform-*d*, there were no changes in the ^{19}F nmr spectra nor was there any development of a yellow color. A mechanism analogous to one previously proposed[34] for the acyclic sulfurane is suggested here.

The approximate rates of reaction of triflate **17** and



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bromosulfurane **15** with the more soluble analog of KOR_F, potassium hexafluoro-2-(*p*-*tert*-butylphenyl)-2-propoxide, in chloroform-*d* were examined in order to provide a possible basis for choice between the covalent and the ionic structures for **15**. The observation of a slower rate of reaction for **15** would suggest that its structure is the covalent one. Both rates were too fast to observe. This suggests that the formation of byproduct bromosulfurane in the original synthesis of **14** (Scheme II) may have resulted from heterogeneity developed during the course of the reaction rather than from a *bona fide* slow reaction of the alkoxide with a covalent bromosulfurane. We cannot therefore choose between covalent and ionic structures upon the basis of this experiment.

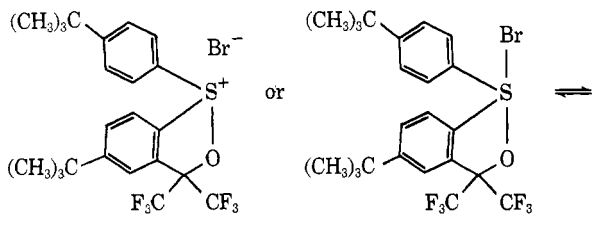
The similarity of the ^{19}F chemical shifts for bromosulfurane **15** and cyclic oxysulfonium triflate **17** favors the ionic structure for **15**. On the other hand, the chemical shifts for the two peaks occurring at lowest field in the carbon-13 nmr spectrum of bromosulfurane **15**, tentatively assigned in a later section of this paper to the carbons bonded to sulfur, are *ca.* 6 ppm smaller than the analogous chemical shifts[35] for **17**, while agreeing closely with those for covalent sulfurane **14**. The carbon-13 spectra clearly favor the covalent formulation for the bromosulfurane. Perhaps the equilibrium between ionic and covalent forms is rapid on the nmr time scale; more work will be required to settle this point.

The observation that bromosulfurane **15** sublimes unchanged, along with some new, undetermined products (as determined by ^{19}F nmr) argues for the covalent nature of this species. The covalent species responsible for the molecular ion in the mass spectrum and for the sublimation may well be formed in an equilibrium between the covalent or ionic form of bromosulfurane **15** and hypobromite **20**.

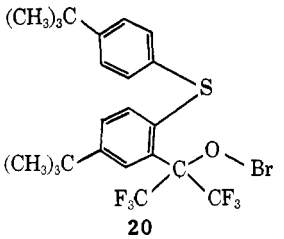
When a solution of bromosulfurane **15** in diethyl ether was treated with 1.4 equiv of bromine, nmr data in-

(34) L. J. Kaplan and J. C. Martin, *J. Amer. Chem. Soc.*, **95**, 793 (1973).

(35) Private communication from Mr. T. M. Balthazor. We thank Mr. Balthazor for allowing us to use his data for the carbon-13 nmr spectrum of **17**.



15



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dicated that **15** was reduced over a 15-min period to sulfide alcohol **11**, identified by comparison with authentic material. In another reaction bromosulfurane **15** was dissolved in ether which had been exposed to air for a period of time. Bromosulfurane **15** was reduced to sulfide **11** over a period of *ca.* 15 min with loss of the characteristic yellow color of the bromosulfurane. Bromosulfurane **15** is considerably more stable in freshly prepared dry ether, suggesting that traces of peroxides initiate this reaction. A radical-chain mechanism similar to that established[36] for bromination with *N*-bromosuccinimide is an attractive possibility for this reaction, involving either hypobromite or covalent bromosulfurane as the positive bromine source. Further work will be done on this problem.

Reactivity of Monocyclic Sulfuranes. The cyclic *tert*-butoxysulfurane **18** is very rapidly hydrolyzed in the presence of acid to give sulfoxide alcohol **16** and *tert*-butyl alcohol. A solution of **18** in chloroform-*d*, however, reacts only slowly with 10% aqueous sodium hydroxide in a heterogeneous mixture, giving only 29% of sulfoxide alcohol after 24 hr at room temperature. It gives no detectable cyclic methoxysulfurane and only a slow conversion to sulfoxide alcohol **16** in a homogeneous solution in methanolic KOH (a 21% conversion to sulfoxide alcohol **16** after 48 hr at room temperature). Acidification of this solution, however, leads to instantaneous hydrolysis. The cyclic methoxysulfurane (not isolated from solution, see Table I) in chloroform-*d* was also found to be relatively unreactive toward 10% aqueous base.

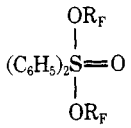
Addition of R_FOH to a solution of cyclic sulfurane **14** in chloroform-*d* at 41° produces coalescence of the downfield pair of quartets in the 56.4 MHz ^{19}F nmr spectrum, but only at concentrations greater than 1.2 *M* in R_FOH. The exchange rate constant is probably most accurately estimated from the concentration of R_FOH at which the ^{19}F peaks for the alkoxy ligand are broadened into the base line, 1.20 *M*. This corresponds[37] to a second-order rate constant for exchange of 60 M^{-1} sec^{-1}. It is clear that the rate of degenerate ligand exchange of **14** with R_FOH at 41° is only *ca.* 10^{-4} as fast as the rate estimated from similar data reported earlier[34] for acyclic sulfurane **4**.

Reactivity of Spirosulfurane 3 and Spirosulfurane Oxide 9. The most notable feature of the chemistry of spirosulfurane **3** and spirosulfurane oxide **9** is their unreactivity toward hydrolysis. Sulfurane **3** does not react with *tert*-butyl alcohol at room temperature and is stable to treatment with 9:1 tetrahydrofuran–water heated to reflux, and to hydrochloric acid or sodium hydroxide in the same solvent system when heated to reflux for 2 hr. Similar treatment of sulfurane oxide **9** with hydrochloric acid or sodium hydroxide gives no reaction.

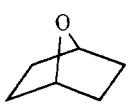
The nmr spectrum of chiral spirosulfurane **3** shows no evidence for nonequivalence of enantiomers in a 0.17 *M* solution in the chiral medium (*S*)-(+)-2,2,2-trifluorophenylethanol (0.23 *M* in carbon tetrachloride). Pirkle and his coworkers[30] have found such nonequivalence in a wide variety of chiral solutes when basic groups in the molecule provide a site for hydrogen bonded association with the optically active acidic fluoroalcohol. This suggests that the basicity of the sulfur or oxygen lone pairs in **3** is very low. A related observation, that **3** shows no detectable chemical shift change upon making the solution 0.033 *M* in 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione, reflects a lack of basicity of the sulfurane toward this lanthanide shift reagent[38] as well. Neither sulfurane **3** nor sulfurane oxide **9** gave evidence in their nmr spectra for methylation when treated with methyl fluorosulfonate in chloroform.

Attempts to reduce the sulfurane oxide to the sulfurane, using reagents which reduce sulfoxides to sulfides, were unsuccessful. The methods tried were: (1) treatment of **9** with stannous chloride and acetyl chloride in dimethylformamide–acetonitrile at 0°;[31] (2) reflux of a solution of **9** and triphenylphosphine in acetic acid in the presence of boron trifluoride for 4.5 hr;[32] (3) treatment of **9** in a melt at 190° with triphenylphosphine for 80 min; and (4) reflux of a solution of **9** in a 5:3 v/v mixture of CH_2Cl_2/PCl_3 for 19 hr.

Oxidations of Diphenyl Sulfoxide. Direct oxidation of acyclic sulfurane **4** by ruthenium tetroxide failed to yield the corresponding acyclic sulfurane oxide **21**.



21



22

The only detected products were diphenyl sulfone, diphenyl sulfoxide, and R_FOH. The products are postulated to arise from traces of moisture leading to hydrolysis of sulfurane **4** to give sulfoxide which is oxidized by RuO_4 to give the sulfone. An analog of the reaction by which acyclic sulfurane **4** was synthesized was utilized in an attempt to form acyclic sulfurane oxide **21**. This entailed treatment of 1 equiv of diphenyl sulfoxide in the presence of 2 equiv of R_FOK with 1 equiv of chlorine in carbon tetrachloride. The potassium alkoxide, which is quite insoluble in carbon

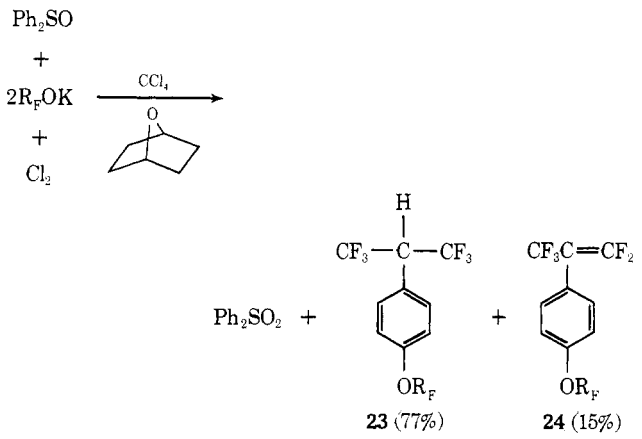
(36) J. Adam, P. A. Gosselain, and P. Goldfinger, *Bull. Soc. Chim. Belg.*, **65**, 523 (1956); J. C. Martin and R. E. Pearson, *J. Amer. Chem. Soc.*, **85**, 354, 3142 (1963); G. A. Russell, C. DeBoer, and K. M. Desmond, *ibid.*, **85**, 365 (1963); C. Walling, A. L. Rieger, and D. D. Tanner, *ibid.*, **85**, 3129 (1963).

(37) (a) R. S. Drago, "Physical Methods in Inorganic Chemistry," Van Nostrand-Reinhold, New York, N. Y., 1965, pp 281–285; (b) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 223.

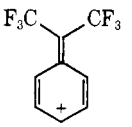
(38) B. Feibush, M. F. Richardson, R. E. Sievers, and C. S. Springer, Jr., *J. Amer. Chem. Soc.*, **94**, 6717 (1972).

tetrachloride, was rendered soluble by the addition of 1,4-endoxocyclohexane (**22**) as cosolvent. The cosolvent was chosen since (1) it was known to be relatively inert toward chlorine;[39] and (2) it was expected to show good complexing ability with the exposed lone pair of electrons. It dissolves *ca.* 2 mol of potassium alkoxide for each mole of 1,4-endoxocyclohexane. The reaction was followed by ^{19}F nmr spectroscopy. The presence of a small amount (*ca.* 3.3% of ^{19}F products) of a possible intermediate was noted at 70.5 ppm upfield from $CFCl_3$ after addition of one-half of the chlorine. The solution was stirred for 1.25 hr after addition of all of the chlorine and the potassium chloride was removed by filtration. Diphenyl sulfone (84%) was obtained in addition to two ethers, **23** and **24**, which were separated by liquid chromatography (Scheme III). The ethers

Scheme III



accounted for 60 and 12%, respectively, of the ^{19}F peak areas, with 22% of the ^{19}F products being R_FOK (broadened by exchange with R_FOH) and 6% unidentified products. Since the conversion of R_FOK was only *ca.* 78%, this corresponds to yields of 77% of ether **23**, 15% of ether **24**, and 8% unidentified ^{19}F products. Mass spectra for the ethers **23** and **24** show large (10.93 and 29.81%, respectively) molecular ions. The base peak, at *m/e* 227 for both ethers, is likely cation **25**.



25

An attempt was made to block the para position, to prevent the ether-forming attack by the OR_F group, by using the *p-tert*-butyl analog of R_FOK in this reaction, but there were numerous products of this reaction (six major peaks and four minor ones by gas chromatography) and work-up was not attempted.

An analogous reaction of diphenyl sulfoxide (1 equiv) with potassium perfluoro-*tert*-butoxide (2 equiv) suspended in carbon tetrachloride with chlorine (1.1 equiv) gave a 60% conversion to diphenyl sulfone (48%) and bis(perfluoro-*tert*-butoxy)diphenylsulfurane (**26**) (52%) (Scheme IV). Sulfurane **26** was identified by ^{19}F and ^{1}H nmr, mass spectrum (including a small molecular ion of 0.03% of base peak), and elemental analysis. In addition, the DADI metastable mass

(39) J. C. Martin and P. D. Bartlett, *J. Amer. Chem. Soc.*, **79**, 2533 (1957).

Scheme IV

$$2Ph_2SO + Cl_2 + 2(CF_3)_3COK \xrightarrow[CCl_4]{} (C_6H_5)_2S[OC(CF_3)_3]_2 + Ph_2SO_2 + 2KCl$$

26

spectrum of the molecular ion showed one ion at *m/e* 437, possibly $(CF_3)_3COSO(C_6H_5)_2^+$.

A solution of **26** in chloroform-*d* was found to dehydrate *tert*-butyl alcohol rapidly to give isobutylene, as does sulfurane **4**.

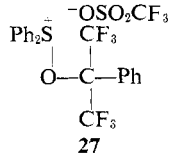
In order to gain insight into the mechanism of the reaction producing acyclic sulfurane **26** and diphenyl sulfone, we prepared oxygen-18 labeled diphenyl sulfoxide by treating acyclic sulfurane **4** with water-^{18}O. The resulting ^{18}O-labeled diphenyl sulfoxide (48.0% excess ^{18}O) with potassium perfluoro-*tert*-butoxide (1 equiv) in carbon tetrachloride–1,4-endoxocyclohexane was treated with 1.07 equiv of chlorine. Diphenyl sulfone (38%) and bis(perfluoro-*tert*-butoxy)diphenylsulfurane (**26**) (21%) were isolated from the reaction mixture. (Some of the sulfurane was hydrolyzed during work-up.) Nearly all (*ca.* 77%) of the ^{18}O label was incorporated into the diphenyl sulfone and only a small amount (<1%) was found in sulfurane **26**. A simple disproportionation reaction of 48.0% excess ^{18}O-labeled diphenyl sulfoxide to yield diphenyl sulfide and diphenyl sulfone would lead to relative proportions of 1:1.84:0.85 for the three peaks of the mass spectrum of the diphenyl sulfone instead of the observed 1:1.45:0.54. The higher than expected $(M\cdot^+)$ and $(M\cdot^+ + 2)$ peaks (indicating a larger than statistical ^{16}O contribution) suggests that about 23% of the reaction pathway involves a C–O bond scission of the unlabeled $(CF_3)_3COK$ and transfer of this unlabeled oxygen to diphenyl sulfoxide. The alternative disproportionation pathway, which would give dilabeled sulfone, was demonstrated by the reaction of diphenyl sulfoxide in carbon tetrachloride with *ca.* 1.5 equiv of chlorine gas. After the solution was stirred for 52 hr, the products isolated by liquid chromatography were diphenyl sulfide (29 mol %), diphenyl sulfone (8%), and recovered diphenyl sulfoxide (less than 63%). Although the yield of diphenyl sulfide is greater than that of diphenyl sulfone, indicating the presence of other oxidized products (the presence of other products in the diphenyl sulfoxide fraction was detected but separation was not achieved), the fact that both are present suggests the operation of a disproportionation pathway, at least to some degree.

Carbon-13 Nuclear Magnetic Resonance Spectra. Carbon-13 nmr spectra were obtained for several of the sulfuranes described in this paper. In order to provide relatively crude models for the sulfuranes, the compounds diphenyl sulfide, diphenyl sulfoxide, and diphenyl sulfone as well as R_FOH were studied (Table II; see paragraph at end of paper regarding supplementary material). It is interesting to note that for the sulfur compounds, the chemical shift of the carbon adjacent to sulfur increases (downfield) for the series diphenyl sulfide (135.589 ppm) < diphenyl sulfone (141.321 ppm) < diphenyl sulfoxide (145.411 ppm).

Carbon-13 nmr data for several sulfuranes and related compounds are also presented in Table II in the microfilm edition. Assignments of the carbon chemical shifts are not complete due to the complexity of the

aromatic regions and in most cases there are other possible interpretations for the assignments. The trifluoromethyl carbons are not assigned in many cases since they cannot be seen due to the low intensity of the quaternary carbon peak which is split into a quartet by $^{13}C-^{19}F$ coupling. In one case (for spirosulfurane **3**) a fluorine-decoupled spectrum was obtained. In this case the CF_3 groups were visible and greatly enhanced in area. The carbon atom to which the CF_3 groups are bonded, however, was not visible in the ^1H decoupled spectrum. Upon irradiation of the fluorine atoms, this peak was easily found. To assign the carbon atoms adjacent to the sulfur atom, the assumption was made that the furthest downfield chemical shift corresponds to this carbon. This assumption was made in consideration of the observed shifts for diphenyl sulfide, diphenyl sulfoxide, and diphenyl sulfone where the α-carbon chemical shifts are furthest downfield. In all but one case (sulfide diol **10**) off-resonance decoupled spectra were obtained to confirm that the downfield peak(s) did indeed correspond to a quaternary carbon. A trend was observed for the chemical shifts of the α carbon for the following acyclic and bicyclic compounds: sulfide diol **10** (152.027 ppm) < hydroxy sulfoxide **16** (154.156 ppm) < spirosulfurane **3** (157.116 ppm) < spirosulfurane oxide **9** (160.786 ppm). The sulfurane compounds having one five-membered ring, cyclic hexafluorocumyloxysulfurane **14**, bromosulfurane **15**, and cyclic oxysulfonium triflate **17**,[35] had α-carbon chemical shifts of 156.982 and 153.619 ppm for **14**, 158.883 and 155.527 ppm for **15**, and 163.729 and 161.389 for the salt-like triflate **17**.[35] The chemical shifts seen for **14** and **15** correspond approximately to that obtained for spirosulfurane **3** (157.116 ppm).

The chemical shift of the α carbon of acyclic sulfurane **4** (145.438 ppm) is much smaller than that obtained for any of the cyclic sulfuranes. It is very similar to the chemical shift of the α carbon of diphenyl sulfoxide (145.411 ppm). When the carbon-13 nmr spectrum of acyclic triflate **27** was examined, there were no downfield



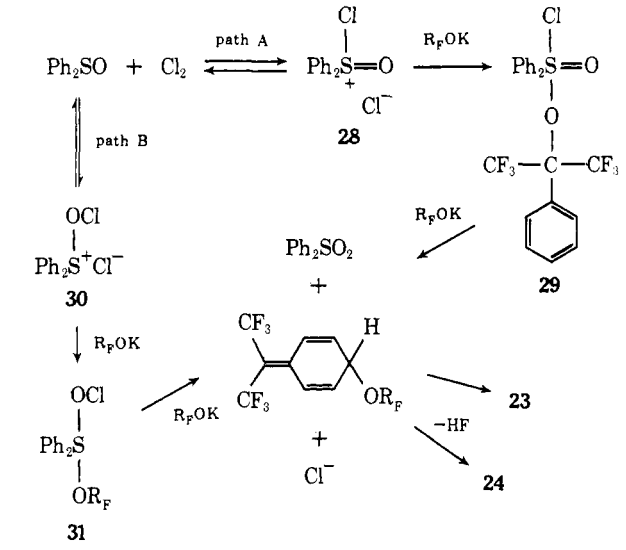
27

peaks observed which correspond to quaternary carbons. Although the α-carbon assignment for **27** was not definite, the chemical shifts of the two quaternary carbons of the benzene rings (128.809 and 123.777 ppm) are at higher field than any of the α-carbon chemical shifts of the compounds examined.

Discussion

Possible Acyclic Sulfurane Oxide Intermediates. The chlorine oxidation of diphenyl sulfoxide in the presence of R_FOK to give sulfone and ethers **23** and **24** is postulated to occur either through a sulfurane oxide intermediate **29** (Scheme V) resulting from initial chlorine attack at the sulfoxide sulfur to form **28** (path A) or through sulfuranyl hypochlorite intermediate **31** resulting from initial chlorine attack at the sulfoxide oxygen to form **30** (path B). In both cases the formation of diphenyl sulfone, a very good, neutral leaving group, tends to drive the reaction to completion.

Scheme V

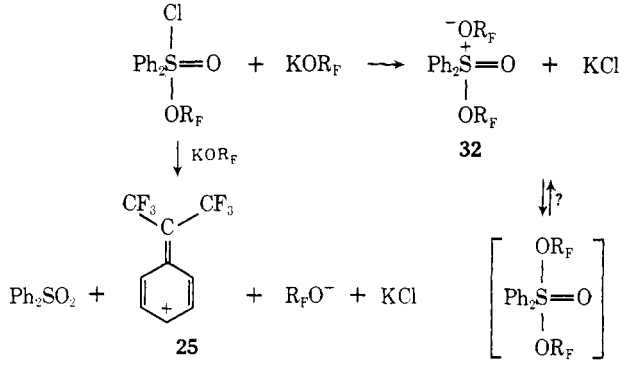


Alkylation of dimethyl sulfoxide is kinetically favored at oxygen but thermodynamically favored at sulfur.[40] Electron pair repulsions would be expected to be more important for Cl^+ attacking on oxygen than for attack at sulfur. Thus path A is *a priori* at least as likely as path B.

In all of the mechanisms advanced in this section for reactions involving sulfoxides, alkoxide ions, and chlorine we suggest initiation of the reaction by attack of chlorine on the sulfoxide. It should be noted that in each case an analogous mechanism could be written involving initial reaction between chlorine and alkoxide to form alkyl hypochlorite, which then acts as the source of positive chlorine in a mechanism closely parallel to that shown. The reaction of R_FOK with chlorine to form R_FOCl has been reported.[5b] We have no evidence which would allow us to choose between these two alternatives.

Scheme VI suggests an ionization pathway which we

Scheme VI



are encouraged to advance by the observation that the base peak of the mass spectrum of **23** at *m/e* 227 corresponds to carbonium ion **25**. An ionization of the chlorine of **29** (or **31**), perhaps with electrophilic assistance from potassium, would lead to formation of diphenyl sulfone and carbonium ion **25** which could then react with a second equivalent of alkoxide to form products.

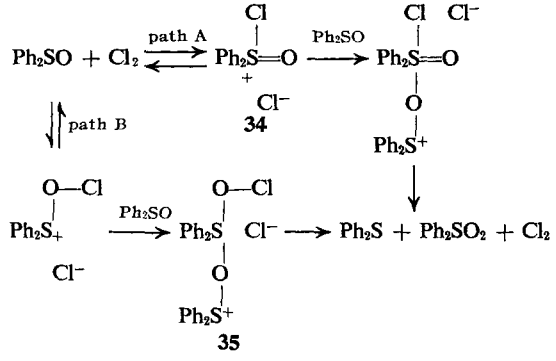
The leaving group ability of diphenyl sulfone in the O-alkylated sulfone cation **32** must rank very high if the

(40) S. G. Smith and S. Winstein, *Tetrahedron*, 3, 317 (1958).

very unstable cation **25**, or its counterpart in the SN2′ step of Scheme VI is to be formed as rapidly at ambient temperature as is observed. In none of the reactions of sulfurane **4**, including its pyrolysis,[5] was evidence seen for the formation of ethers **23** or **24**. The reactions of **4** in which cation **33**, $R_FOSPh_2^+$, is expected to be generated do not, therefore, undergo loss of diphenyl sulfoxide to give **25** or its equivalent. Thus, despite the evidence discussed earlier[41] that diphenyl sulfoxide is a very good leaving group in reactions leading to carbonium ions the leaving group generated in the reaction under discussion here, presumably diphenyl sulfone, is considerably better. Although sulfones are very weakly basic and weakly nucleophilic, protonated sulfones have been observed in "magic acid"[42a] and O-arylated sulfones have been isolated from the reaction of arenediazonium salts with sulfones.[42b]

The observed chlorine-catalyzed disproportionation of diphenyl sulfoxide could well proceed by either of the pathways illustrated in Scheme VII. Intermediates

Scheme VII



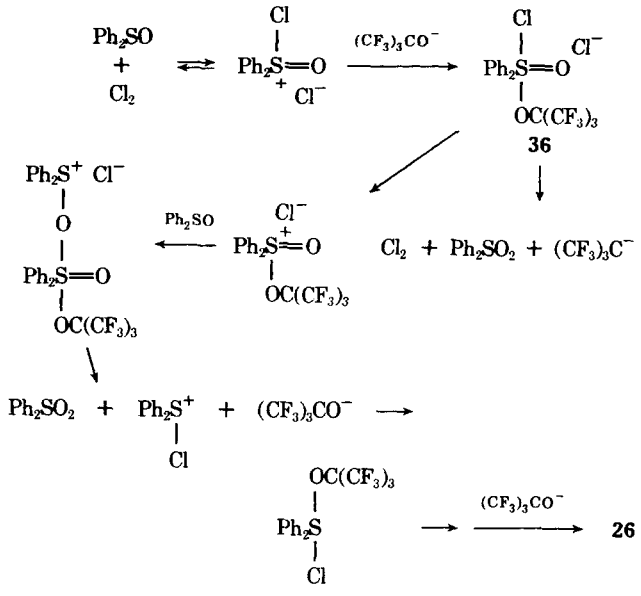
similar to **34** have recently been postulated[43] in discussions of the α chlorination of alkyl sulfoxides.

An alternative which has not been ruled out would involve catalysis of the disproportionation of diphenyl sulfoxide by traces of hydrogen chloride in a mechanism analogous to Scheme VII but involving initial transfer of a proton, rather than a chlorine cation, to the sulfoxide. The reactions between sulfoxides and hydrogen chloride have been the subject of several recent studies.[44]

As expected, the reaction of diphenyl sulfoxide with $(CF_3)_3COK$ and chlorine gives no ether products analogous to **23** or **24** but rapidly forms high yields of diphenyl sulfone and an equimolar amount of bis(perfluoro-*tert*-butoxy)sulfurane **26**. The route to these products involving chlorine-catalyzed disproportionation of the sulfoxide, with sulfurane being formed by the reaction of the resulting diphenyl sulfide with chlorine and alkoxide, would seem not to be fast enough to provide the products in this reaction.

Scheme VIII suggests a route leading to the observed

Scheme VIII



products. An analogous route involving initial attack of Cl^+ on the sulfoxide oxygen as in Scheme VII is, of course, a possibility. In either mechanism it is noted that the diphenyl sulfone would receive labeled oxygen-18 from diphenyl sulfoxide to give the predominant label pattern. The observation that 23% of the reaction pathway involves C–O bond scission could result from alkoxide or chloride ion attack at the chlorine atom of sulfurane oxide **36** to give $^-C(CF_3)_3$, which would continue to give unidentified products, and monolabeled diphenyl sulfone.

The observation that there was a negligible amount of oxygen-18 incorporation into bis(perfluoro-*tert*-butoxy)-diphenylsulfurane (**26**) indicates that there is little contribution by a reaction mechanism involving attack of the anion $^-C(CF_3)_3$ on S-chlorinated diphenyl sulfoxide, **34**, leading eventually to labeled **26**.

The Five-Membered Ring Effect. It is clear from the observations detailed in this paper that the incorporation of the sulfurane function into a five-membered heterocyclic ring has a dramatic effect on its rates of reaction. The reactivity order acyclic > monocyclic > spirobicyclic clearly holds for the hydrolysis of sulfuranes, and very probably the order acyclic ≫ spirobicyclic holds for sulfurane oxide hydrolysis.

An understanding of the relative unreactivity toward base hydrolysis seen for the cyclic sulfuranes, contrasted with the great reactivity of acyclic sulfuranes, may be approached by considering that the hydrolysis of cyclic sulfuranes is the geometric inverse of the hydrolysis of sulfate, sulfite, or phosphate esters. The change of geometry from approximately trigonal bipyramidal to tetrahedral characterizes the reactions of sulfuranes, while the latter reactions go from a tetrahedral ground state to a trigonal bipyramidal transition state. Summing up advances made since the pioneering work in this area by Kumamoto, Cox, and Westheimer,[45] recent reviews[46–48] point out that the hydrol-

(41) R. J. Arhart and J. C. Martin, *J. Amer. Chem. Soc.*, **94**, 5003 (1972).

(42) (a) G. A. Olah, A. T. Ku, and J. A. Olah, *J. Org. Chem.*, **35**, 3904 (1970); (b) G. R. Chalkley, D. J. Snodin, G. Stevens, and M. C. Whiting, *J. Chem. Soc. C*, 682 (1970).

(43) P. Calzavara, M. Cinquini, S. Colonna, R. Fornasier, and F. Montanari, *J. Amer. Chem. Soc.*, **95**, 7431 (1973); J. Klein and H. Stollar, *ibid.*, **95**, 7437 (1973).

(44) K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, **86**, 1452 (1964); H. Kwart and H. Omura, *ibid.*, **93**, 7250 (1971); H. Kwart and P. S. Strilko, *Chem. Commun.*, 767 (1967); H. Kwart, R. W. Body, and D. M. Hoffman, *ibid.*, 765 (1967); H. Kwart, E. N. Givens, and C. J. Collins, *J. Amer. Chem. Soc.*, **91**, 5532 (1969); H. Kwart and J. L. Irvine, *ibid.*, **91**, 5541 (1969).

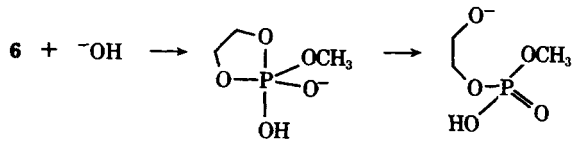
(45) J. Kumamoto, J. R. Cox, Jr., and F. H. Westheimer, *J. Amer. Chem. Soc.*, **78**, 4858 (1956).

(46) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

(47) R. F. Hudson and C. Brown, *Accounts Chem. Res.*, **5**, 204 (1972).

(48) S. J. Benkovic in "Comprehensive Chemical Kinetics," Vol. 10, C. H. Bamford and C. F. H. Tipper, Ed., Elsevier, New York, N. Y., 1972, pp 1–56.

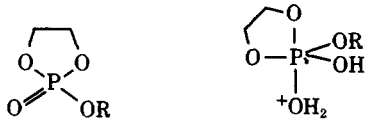
yses in acid or base of five-membered cyclic esters of phosphoric acid proceed more rapidly by many orders of magnitude than their acyclic analogs. For example, the base hydrolysis of methyl ethylene phosphate, which proceeds through a transition state thought to resemble phosphorane **37**, is faster by a factor of more than 10^6 than that of its acyclic analog trimethyl phosphate.[7]



37

The geometry of **37**, a phosphorane bearing an oxide anion ligand, is assumed to be approximately trigonal bipyramidal, as pictured. It should be noted that sulfurane oxide **9**, which is isoelectronic with this proposed intermediate, has recently been shown[1] by an X-ray crystal structure to have this geometry, with the oxide ligand in the equatorial plane of an approximate trigonal bipyramid.

Westheimer's[46,49] calculations of ring strain suggest that much of the acceleration of hydrolysis of **38** and



38 **39**

its analogs results from the relief of strain which accompanies the change of geometry to that illustrated for **39**. The endocyclic O–P–O angle of *ca.* 90° is essentially unstrained in **39** whereas the 99° endocyclic O–P–O angle[49] of **38** is considerably strained. On the other hand, Aksnes and Bergeson[9] have shown that much of the acceleration of hydrolysis rates results from a relatively favorable entropy of activation for the cyclic phosphates. Sulfates[10a] and sulfites[10b] manifest five-membered ring effects similar to those seen for the phosphorus analogs. The major source of acceleration for cyclic sulfites has also been shown to arise in a favorable entropy of activation.[50] This has been discussed in terms of the "entropy strain,"[50a,51] which results from the relatively larger geometric constraints on the ground state, relative to the transition state, for attack of nucleophile on the sulfur of cyclic sulfites than for attack on the sulfur of acyclic sulfites.

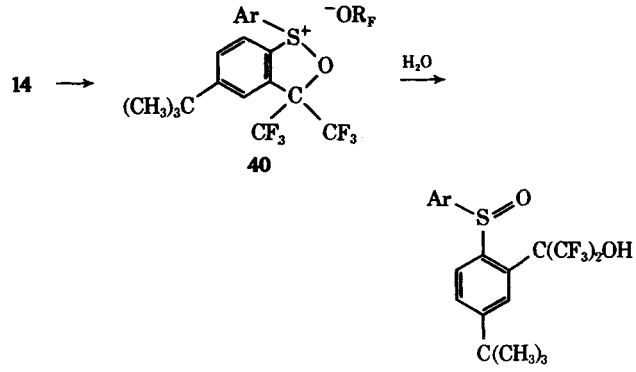
Whatever the proper rationale for the five-membered ring effect, it is likely that its inverse is operating in slowing down the dissociation which converts our trigonal-bipyramidal sulfuranes to tetrahedral alkoxysulfonium ions in the transition state for hydrolysis of our sulfuranes and sulfurane oxides. Trost and Ziman[52] have interpreted reactivity patterns observed for dihydrothiophenium salts in terms of an enhanced stability of 5-membered ring cyclic sulfuranes.

(49) D. A. Usher, E. A. Dennis, and F. M. Westheimer, *J. Amer. Chem. Soc.*, 87, 2320 (1965).

(50) (a) P. A. Bristow, J. G. Tillett, and D. E. Wiggins, *J. Chem. Soc. B*, 1360 (1968); (b) N. Pagdin, A. K. Pine, J. G. Tillett, and H. F. van Woerden, *ibid.*, 3835 (1962); (c) R. E. Davis, *J. Amer. Chem. Soc.*, **84**, 599 (1962).

(51) R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 670.

(52) B. M. Trost and S. D. Ziman, *J. Amer. Chem. Soc.*, **93**, 3825 (1971).



40

Archie and Westheimer[53] have reported kinetic evidence for hydrolysis of pentaaryloxyphosphoranes by an addition–elimination process involving a hexacoordinated phosphorus intermediate or transition state. Both acid and base catalysis were observed. An analogous mechanism for the acid-catalyzed solvolyses of sulfuranes cannot rigorously be ruled out, but a number of observations made in this work and previously[5,34] favor the alternative dissociative mechanism. These include: (a) the accumulation of positive charge on sulfur which is reflected in the ρ (*ca.* -3) for the ligand exchange reactions of **4**; (b) our failure to see a base-catalyzed ligand exchange reaction for cyclic sulfuranes and the observation of a slower reaction of **4** with KOR_F than with HOR_F; (c) our failure to see the slowing of sulfurane solvolysis reactions as the steric bulk of ligands is increased, an effect strongly evident in the phosphorane reaction,[53] presumably the result of the increase in steric repulsions accompanying the change in coordination number of phosphorus on going to the transition state. The monocyclic sulfuranes show a reactivity toward aqueous base (**14** > **18**) which parallels anionic leaving group ability for the apical monodentate ligands (R_FO > *t*-BuO).

The inertness of spirosulfurane **3** and spirosulfurane oxide **9** represents the action of the five-membered ring effect superposed on the entropy advantage usually enjoyed by complexes of bidentate ligands. In the case of **3** the evidence suggests that the dehydration of sulfoxide diol **13**, a compound which we were unable to observe or isolate, to give bicyclic sulfurane is thermodynamically as well as kinetically favored.

An additional possible source of deactivation of the cyclic sulfuranes of this study stems from the substitution of the electron-withdrawing fluoroalkyl substituent into the positions ortho to sulfur on the equatorial aryl rings. A study of substituent effects on the degenerate ligand exchange reactions of analogs of **4** substituted in the equatorial S-aryl rings established[34] a rough value of ρ for the reaction of -3, reflecting the increase in positive charge on sulfur in the transition state for ligand exchange. Using the σ value for the *p*-C(OH)-$(CF_3)_2$ substituent (0.3, determined from ^{19}F chemical shift data[54]) as a reasonable estimate for the *o*-fluoroalkyl substituents of the sulfurane and a ρ value estimated as -3 we see that the rate deceleration expected from this substituent effect would be a factor of 8 for the monocyclic sulfuranes and 64 for the spirosulfuranes.

(53) W. C. Archie, Jr., and F. W. Westheimer, *J. Amer. Chem. Soc.*, **95**, 5955 (1973).

(54) W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969, p 348.

This represents a minor part of the five-membered ring effects seen in this study.

Another factor lowering the energy of the spiro or monocyclic sulfuranes relative to their acyclic analogs is related to possible repulsive interactions between the π electrons of the equatorial aryl rings and the apical substituents. These would be minimized in the geometry of the spiro system, with the planes of the aryl rings perpendicular to the equatorial plane. The complete X-ray structures of **3** and **9**, which will be presented in a later paper, provide a basis for bond length comparisons supporting this interpretation over an alternative explanation for the lack of reactivity of monocyclic and spirobicyclic sulfuranes which might invoke some steric inhibition of resonance interactions between the annelated aromatic rings and the product sulfonium sulfur.[55]

(55) Phosphoranes show parallel reductions in reactivity upon inclusion of the phosphorus in a five-membered ring (or in two such rings in a spirophosphorane). For a recent review with leading references, see P. Gillespie, F. Ramirez, I. Ugi, and D. Marguading, *Angew. Chem., Int. Ed. Engl.*, **12**, 91 (1973). For analogies in selenium chemistry, see H. J. Reich, *J. Amer. Chem. Soc.*, **95**, 964 (1973).

The reduced reactivity of derivatives of the monocyclic sulfurane **14** opens the way to isolation of sulfuranes with new apical ligand functionality. Further work now underway will probe for applications of these derivatives as reagents in organic synthesis.

Acknowledgment. This work was supported in part by a grant from the National Science Foundation (GP-30491X). Departmental instrumentation grants from the National Science Foundation for 220-MHz proton and Fourier transform ^{13}C nmr instrumentation, and from the National Institutes of Health for our mass spectrometry laboratory are acknowledged.

Supplementary Material Available. A complete listing of carbon-13 nmr spectroscopic data is to be found in the table which will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-3155.

Association and Solvation Reactions of Protonated Gaseous Amino Acids

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Received November 19, 1973

Abstract: High-pressure mass spectrometric measurements were made to determine the thermodynamic values of the gas phase solvation of protonated amino acids (valine and proline) by individual molecules of several solvents. The enthalpies of monomolecular solvation by both hydrogen-bonding solvents H_2O and NH_3 and a nonhydrogen-bonding solvent CH_3NO_2 are found to be in the range of 20 ± 2 kcal/mol. The exothermicities of the gaseous association reactions of protonated and neutral entities for valine and proline are found to be of similar magnitude (~20 kcal/mol).

Reversible association reactions of protonated ions with neutral molecules of the type

$$MH^+ + M \rightleftharpoons M_2H^+ \quad (1)$$

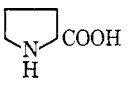
and the association of ions with gaseous solvent molecules of the type

$$X^+ + \text{solvent} \rightleftharpoons X^+ \text{solvent} \quad (2)$$

have been investigated extensively recently using high-pressure mass spectrometric techniques.[1-4] The results are providing a better understanding of the intrinsic properties of ionic reactions, as in the gas phase such reactions are observed in the absence of liquid solvent effects.[5] To date, investigations of gaseous ion–solvent interactions have been limited to the reactions of small ions, mainly of inorganic interest.

(1) F. H. Field, *J. Amer. Chem. Soc.*, **91**, 2827 (1969).
(2) S. L. Bennett and F. H. Field, *J. Amer. Chem. Soc.*, **94**, 5186 (1972).
(3) R. Yamdagni and P. Kebarle, *J. Amer. Chem. Soc.*, **95**, 3504 (1973).
(4) P. A. Leclercq and D. M. Desiderio, *Org. Mass Spectrom.*, **7**, 515 (1973).
(5) P. Kebarle in "Ion-Molecule Reactions," Vol. 2, J. L. Franklin, Ed., Plenum Press, New York, N. Y., 1972, Chapter 7.

In the present study we have investigated the association of protonated ions of the amino acids valine ($(CH_3)_2CHCH(NH_2)COOH$) and proline



with neutral molecules of valine and proline, with the proton-bonding solvents H_2O and NH_3, and with the nonproton-bonding solvent CH_3NO_2. In addition to their intrinsic interest as ion–molecule interactions, the energetics of the solvation reactions of protonated amino acid molecules are of potential interest in the physical chemistry of protein conformation, while the association reactions may be of potential interest in exobiological processes.

Experimental Section

The scope of quantitative mass spectrometric gaseous ionic studies is limited at the present time to compounds of relatively high volatility. Problems of volatility restricted our studies in amino acids to those reported. The low volatility of these compounds also renders the pressure of the vapor of such samples in the ion source inde-