Sulfuranes. V.[1] The Chemistry of Sulfur(IV) Compounds. Dialkoxydiarylsulfuranes[2]

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Abstract: Dialkoxydiarylsulfuranes **1** and **2**, the first two reported members of a new class of sulfur compounds having the structure $Ar_2S(OR)_2$, are synthesized by two routes. Treatment of the corresponding sulfide with 1 molar equiv of hexafluoro-2-phenyl-2-propyl hypochlorite (R_FOCl) is followed by addition of 1 mol of the alkoxide R_FOK to the intermediate alkoxysulfonium chloride. Or, an ether solution of the diaryl sulfide and 2 mol of R_FOK is treated with 1 mol of chlorine at −78°. Symmetrical sulfurane **1** is conveniently prepared in high yield by the latter procedure. This crystalline sulfurane was isolated, characterized, and found to be stable indefinitely at room temperature. The ^{19}F nmr spectra of sulfurane **2** and its precursor sulfonium chloride, **5**, provide evidence for the prochiral (**2**) or chiral (**5**) geometry about sulfur and for the covalent nature of the bonding between sulfur and the alkoxy ligands in solution. The spectroscopic data for **2** are compatible with its having, in solution, trigonal-bipyramidal geometry about sulfur with the two electronegative alkoxy ligands occupying apical positions, as has been established by X-ray studies for crystalline sulfurane **1**. Exchange of sulfurane alkoxy ligands with R_FOH (variable temperature ^{19}F nmr) is faster than exchange with R_FOK, suggesting a dissociative mechanism for exchange. Alcohols lacking β protons, such as perfluoro-*tert*-butyl alcohol or neopentyl alcohol, show rapid exchange with **1** in an equilibrium mixture of dialkoxydiarylsulfuranes. Exchange of added diphenyl sulfide with alkoxysulfonium chloride **5** is much faster than exchange with sulfurane **2**, suggesting that nucleophilic displacements on the chlorine of alkoxysulfonium chlorides are fast relative to displacements on the alkoxy oxygens of sulfuranes. Upon heating an ether solution of **1** at 77° for 55 hr or heating molten **1** up to 175° for a short period, 1 equiv of R_FOH and 1 equiv of a mixture of nuclear alkoxylation products **10** are generated. The ortho:meta:para ratios in the product mixture **10** (49:18:33 in the melt up to 175°, 61:14:25 at 77° in ether in a sealed tube) favor ortho substitution in a manner suggestive of an intramolecular rearrangement of the alkoxysulfonium ion. However, when **1** is boiled for several days in ether in the presence of an aryl sulfide, acetal **11** is formed in yields up to 60%. The mechanism of this reaction is shown to involve a radical chain process with chain carrying solvent radicals, probably analogous to the mechanism for the induced decomposition of benzoyl peroxide seen in the same solvent.

Numerous literature citations might be advanced in support of the idea that tetracoordinate tetracovalent sulfur compounds of structure $R_2S(OR)_2$, such as **1** and **2**, are commonly encountered reaction intermediates of considerable stability. Indirect evidence for such intermediates, or closely related structures, has been seen in kinetic, spectroscopic, and product studies in several laboratories.[4]

The reaction of *tert*-butyl hypochlorite with thioanisole, which was studied by Johnson and Rigau,[5] gave an intermediate phenylmethyl-*tert*-butoxysulfonium chloride for which a covalent structure was postulated to explain certain chemical shift phenomena. Chemical studies of alkoxy ligand exchange processes in related systems also point[5,6] to the intermediacy of alkoxysulfuranes. The nucleophilic addition of chloride ion to an episulfonium sulfur was shown[7] to result in the probable intermediacy of a covalent chlorosulfurane. Evidence for a tetracovalent structure in solution for the 1:1 metastable complex between bis(*p*-fluorophenyl) sulfide and chlorine has been adduced[8] from ^{19}F nmr chemical shift studies. The data do not rule out a linear charge-transfer[9] type complex, however. From a preliminary X-ray investigation Kapovits and Kálmán[10] have postulated a tetracovalent spirodiaryldiacyloxysulfurane, at least in the crystal, as the structure for a compound recently isolated in their laboratories.

Several tetracoordinate sulfur compounds containing halogen ligands have been isolated and characterized, for example, sulfur tetrafluoride[11] and several of its derivatives.[12] They show covalent bonding about the central sulfur atom of a structure having trigonal-

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[1] For paper IV in this series see I. C. Paul, J. C. Martin, and E. F. Perozzi, *J. Amer. Chem. Soc.*, **93**, 6674 (1971).

[2] Preliminary communications: (a) J. C. Martin and R. J. Arhart, *ibid.*, **93**, 2339 (1971); (b) *ibid.*, **93**, 2341 (1971); (c) *ibid.*, **93**, 4327 (1971).

[3] Abstracted from the Ph.D. Thesis of R. J. Arhart, University of Illinois, 1971. Fellow, National Institutes of Health, 1967–1971.

[4] Reference 2a, footnotes 2, 3, and 4. Other cases in which such structures were postulated might have been cited. For example, see B. M. Trost and S. D. Ziman, *J. Amer. Chem. Soc.*, **93**, 3825 (1971); W. A. Pryor and K. Smith, *ibid.*, **92**, 2731 (1970); D. J. Cram, J. Day, D. R. Rayner, D. M. von Schriltz, D. J. Duchamp, and D. C. Garwood, *ibid.*, **92**, 7369 (1970); M. G. Burden and J. G. Moffatt, *ibid.*, **89**, 4725 (1967); E. J. Corey and T. Durst, *ibid.*, **90**, 5553 (1968); E. Ciuffarin and G. Guaraldi, *ibid.*, **91**, 1745 (1969); T. J. Barton and R. G. Zika, *J. Org. Chem.*, **35**, 1729 (1970); V. Caló, G. Scorrano, and G. Modena, *ibid.*, **34**, 2020 (1969); K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, **86**, 1452 (1964); and D. Landini, F. Montanari, H. Hogeveen, and G. Maccagnani, *Tetrahedron Lett.*, 2691 (1964). On the other hand, for evidence against intermediate formation in nucleophilic substitutions at dicoordinate sulfur or in the racemization of optically active sulfoxides with methyllithium see L. Senatore, E. Ciuffarin, and A. Fava, *J. Amer. Chem. Soc.*, **92**, 3035 (1970); J. L. Kice and J. M. Anderson, *J. Org. Chem.*, **33**, 3331 (1968); and J. Jacobus and K. Mislow, *J. Amer. Chem. Soc.*, **89**, 5228 (1967). For a review on nucleophilic substitution at di-, tri-, and tetracoordinate sulfur see E. Ciuffarin and A. Fava, *Progr. Phys. Org. Chem.*, **6**, 81 (1968).

[5] C. R. Johnson and J. J. Rigau, *J. Amer. Chem. Soc.*, **91**, 5398 (1969).

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[7] D. C. Owsley, G. K. Helmkamp, and M. F. Rettig, *J. Amer. Chem. Soc.*, **91**, 5239 (1969).

[8] G. E. Wilson, Jr., and M. M. Yang Chang, *Tetrahedron Lett.*, 875 (1971).

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[10] I. Kapovits and A. Kálmán, *Chem. Commun.*, 649 (1971).

[11] E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, **81**, 1084 (1959); F. A. Cotton, J. W. George, and J. S. Waugh, *J. Chem. Phys.*, **28**, 994 (1958); R. E. Dodd, L. A. Woodward, and H. L. Roberts, *Trans. Faraday Soc.*, **52**, 1052 (1956).

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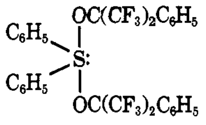
bipyramidal geometry. The crystal structure of the unstable adduct of chlorine to bis(*p*-chlorophenyl) sulfide also shows[13] trigonal-bipyramidal geometry and covalent bonding about sulfur. The analogous adduct of thiophane and bromine, in contrast, shows[14] the linear S–Br–Br characteristic of a charge-transfer complex. Crystalline alkyl- and arylsulfur trichlorides[15] have been isolated but the question of covalent or ionic bonding was not answered.

Dialkoxydialkyl-[16,17] and hydroxyalkoxydialkylsulfuranes[18] have been suggested as intermediates in displacement reactions of alkoxysulfonium salts. Stereochemical results[18] of the base-catalyzed hydrolyses of *cis*- and *trans*-1-ethoxy-3-methylthietanium ions show that the lifetime of any sulfurane intermediate in this system is short relative to the time required for an intramolecular exchange of positions of alkoxy substituents *via* a pseudorotation pathway. This contrasts with the situation for the analogous phosphetanium ions.

In this paper dialkoxydiarylsulfuranes **1** and **2**, the first two members of a new class of sulfur compounds to be characterized, are synthesized and their chemical properties studied. Direct evidence is presented for the covalent nature of the bonding in these sulfuranes in solution. The mechanism for exchange of sulfurane alkoxy ligands is discussed.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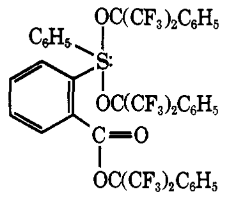
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Experimental Section

Proton and fluorine magnetic resonance spectra were recorded on Varian Associates A-60A, A-56/60A, HA-100, and HR-220 spectrometers. Proton chemical shifts are reported on the δ scale, parts per million downfield from tetramethylsilane internal standard; fluorine chemical shifts are in parts per million upfield from fluorotrichloromethane internal standard. Temperatures were regulated with Varian Associates V-6040 temperature controllers and read with a copper–constantan thermocouple.

Solvents. Chloroform-*d* and fluorotrichloromethane were dried by passage through a column of Woelm neutral alumina. Ether was dried by distillation from $LiAlH_4$ and storage over sodium wire. Methylene chloride and carbon tetrachloride were washed with concentrated sulfuric acid, 10% sodium bicarbonate, and water, dried, and distilled.

Hexafluoro-2-phenyl-2-propyl Hypochlorite (3). A solution of hexafluoro-2-phenyl-2-propanol (R_FOH; 2.74 g, 11.2 mmol; supplied by Peninsular Chemresearch, Inc.) in 20 ml of anhydrous ether was added dropwise with stirring to potassium hydride (0.59 g, 14.7 mmol) suspended in 10 ml of ether surrounded by a Dry Ice bath. After warming to room temperature the reaction mixture was filtered in a dry nitrogen atmosphere to remove excess potassium hydride. Ether was removed from the filtrate *in vacuo* and replaced by anhydrous $CFCl_3$ (15 ml). Chlorine gas, dried over P_2O_5, was condensed into a calibrated trap and measured volumetrically (0.75 ml, 16.2 mmol) at its boiling point. It was distilled into the $CFCl_3$ suspension of R_FOK *in vacuo* at −78°. The light yellow reaction mixture was shaken vigorously and allowed to warm slightly above −78° to assure complete reaction. Suspended KCl was removed by rapid filtration in a −23° cold room. The light yellow filtrate shows ^{19}F nmr ($CFCl_3$, −66°) 69.5 ppm (s); purity 90%, the remainder being R_FOK or R_FOH (75.6 ppm, s).

Hexafluoro-2-phenyl-2-propyl *o*-Phenylthiobenzoate (4). A mixture of *o*-bromobenzoic acid (6.75 g, 33.6 mmol) and cuprous thiophenolate (6.08 g, 35.3 mmol, *ca.* 95% pure) in 30 ml of pyridine was heated at 100° for 1.5 days, with the exclusion of moisture, using the general procedure of Adams, Reifschneider, and Nair.[19] The reaction mixture was cooled, acidified, and extracted with ether. Removal of solvent and recrystallization (benzene) of the crude product gave 5.31 g (68.7%) of acid, mp 169–171° (lit.[20] 166–167°). Treatment of the acid with excess thionyl chloride gave *o*-phenylthiobenzoyl chloride in 87% yield.

A solution of *o*-phenylthiobenzoyl chloride (4.23 g, 17.0 mmol) in 20 ml of anhydrous ether was added dropwise with stirring to R_FOK [from R_FOH (4.01 g, 16.4 mmol) and KH (0.84 g, 21.0 mmol)] in 10 ml of ether at 0°. Recrystallization of the crude product from CH_2Cl_2–pentane gave 5.36 g (71.7% yield) of **4**, mp 114.5–116.5°: ir ($CHCl_3$) 1746 (s), 1587 (w), 1458 (w), 1252 (s, broad, includes four absorptions), 1142 (m), 1907 (s), 1063 (s), 1036 (m), 990 (s), and 946 cm^{-1} (m); ^1H nmr ($CDCl_3$) δ 6.74–7.68 (m, 13 H, broad SC_6H_5 singlet at δ 7.43) and 8.06–8.27 (m, 1 H, proton ortho to carbonyl), ^{19}F nmr ($CDCl_3$) 70.5 ppm (s).

Anal. Calcd for $C_{22}H_{14}F_6O_2S$: C, 57.89; H, 3.09; S, 7.03. Found: C, 57.66; H, 3.14; S, 7.37.

Alkoxysulfonium Chloride 5. A solution of sulfide **4** (61.5 mg, 0.135 mmol) in 0.25 ml of anhydrous CH_2Cl_2 was syringed into an nmr tube at −78° containing a 0.40-ml stock solution of hypochlorite **3** (0.129 mmol by comparison of the ^{19}F nmr integral of **3** with that of weighed internal standard benzotrifluoride) in $CFCl_3$ to give a solution of **5**, ^{19}F nmr ($CFCl_3$:CH_2Cl_2, 1.5:1.0, −45°) 69.1 [q, J_{FF} = 10.7 Hz, 3 F, $SOCCF_3$], 70.7 [m, 3 F, $COCCF_3$], 71.8 [m, 3 F, $COCCF_3$], and 72.1 ppm [q, J_{FF} = 10.7 Hz, 3 F, $SOCCF_3$].

Dialkoxydiarylsulfurane 2. The potassium alkoxide prepared from R_FOH (32.4 mg, 0.133 mmol) and excess KH (7.0 mg, 0.175 mmol) in 0.25 ml of anhydrous ether was syringed into a 0.13 mmol sample of **5** in $CFCl_3$–CH_2Cl_2. Filtration of the colorless reaction mixture at −23° (cold room) gave a solution of **2** whose purity appeared (by ^{19}F nmr) not to be as good as that of samples prepared by treatment of a mixture of **4** and R_FOK, in ether at −78°, with chlorine. Exclusion of water is more difficult in the stepwise procedure. A detailed description of this more successful *in situ* synthesis is given below for the preparation of diphenylsulfurane **1**.

Sulfurane **2** prepared in this manner shows ^{19}F nmr (ether, −44°) 66.9 [q, J = 10.5 Hz, 6 F, $SOCCF_3$], 69.9 [s, 6 F, $COC(CF_3)_2$], and 71.4 ppm [q, J = 10.5 Hz, 6 F, $SOCCF_3$].

Dialkoxydiphenylsulfurane 1. A solution of previously distilled R_FOH (18.88 g, 77.4 mmol) in 80 ml of anhydrous ether was added dropwise with mechanical stirring to potassium metal (3.05 g, 77.9 mg-atoms) in 200 ml of ether in a specially designed 1-l. flask containing a sintered-glass filter at the bottom. A positive stream of dry nitrogen was directed through the filter up through the reaction mixture. After reaction of the potassium a solution of previously distilled diphenyl sulfide (7.22 g, 38.7 mmol) in 80 ml of ether was added to the soluble alkoxide. The reaction flask was then surrounded by powdered Dry Ice. Chlorine was passed through a P_2O_5 drying tower and condensed (1.8 ml, 38.8 mmol) into a calibrated trap. It is important to avoid an excess of chlorine. Since our preliminary description[2] of this synthesis it has been reported to us from other laboratories that the use of excess chlorine can lead to a somewhat violent reaction, presumably between chlorine and ether during the work-up of the reaction mixture. The desired volume of liquid chlorine was obtained by sweeping away a slight excess in a stream of dry nitrogen. When the proper volume of liquid chlorine was reached in the calibrated trap the gas stream was diverted to carry the evaporating chlorine into the reaction mixture *via* the sintered-glass bubbler. The mixture was then allowed to warm to *ca.* 0° while stirring. A receiver was attached to the bottom of the vessel and positive nitrogen pressure from the top was used to filter

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[19] R. Adams, W. Reifschneider, and M. N. Nair, *Croat. Chem. Acta*, **29**, 277 (1957).

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the ether solution from the precipitated potassium chloride. Removal of the ether from the filtrate *in vacuo* left white, crystalline **1**. Purification of the product by grinding the crystals and removing volatile impurities (excess diphenyl sulfide or R$_F$OH) at high vacuum ($<10^{-4}$ Torr) at room temperature gave 21.5 g (82.7%) of **1**, mp 107–109° (sealed tube): ir (CCl$_4$) 1258 (s), 1208 (s), 1168 (s), 1060 (s), 962 (m), 945 (m), 710 (m), and 675 cm^{-1} (m); uv (isooctane) λ_{max} 226 nm (ϵ, 10^4, only approximate because of overlap with diphenyl sulfoxide impurity); 220 MHz ^{1}H nmr (CDCl$_3$) δ 8.0 (m, 4 H, ortho protons of SC$_6$H$_5$), 7.4 (m, 10 H, meta and para protons of SC$_6$H$_5$ and ortho protons of the alkoxy phenyl), and 7.2 (m, 6 H, meta and para protons of the alkoxy phenyl), ^{19}F nmr (ether, −43°) 69.3 [s, SOC(C*F*$_3$)$_2$] and 74.6 ppm (s, small R$_F$OH impurity peak resulting from hydrolysis of **1**); mass spectrum, molecular ion at *m/e* 672 (1.8% of the base peak, 28 eV ionizing voltage), prominent fragmentation peak at *m/e* 429 corresponding to loss of one alkoxy ligand to give an alkoxysulfonium ion, other prominent fragments at *m/e* 227, 201, 109, 77, and 69, high-resolution peak matching *m/e* 672.0987 (calcd for **1**, 672.0992).

Anal. Calcd for $C_{30}H_{20}O_2F_{12}S$: C, 53.57; H, 3.00; S, 4.77. Found: C, 54.11; H, 3.20; S, 4.65.

Purification of **1** can be effected also by crystallization from pentane–ether.

Pyrolysis of 1. A sample of sulfurane **1** (1.26 g) was heated in an evacuated short-path distillation apparatus in an oil bath at a temperature raised gradually to 175° over a period of 45 min. The sulfurane melted at 107–109°. Over the period of reaction 1 equiv of R$_F$OH was collected at high vacuum in a receiver cooled by liquid nitrogen. The nonvolatile light yellow oil was composed of 1 equiv of a mixture of alkoxylation products **10a, b,** and **c**. The nmr and ir spectra of the recovered R$_F$OH were identical with those of an authentic sample.

Alkoxylation products **10** were distilled in high vacuum (bp 115° at *ca.* 3×10^{-3} Torr) through a short column: ir (CCl$_4$) 1486 (w), 1468 (m), 1221 (s), 1192 (s), 1110 (s), 980 (m), and 941 cm^{-1} (m); ^{1}H nmr (CCl$_4$) δ 6.3–7.7 (m, SC$_6$H$_5$ singlets of both meta and para isomers at δ 7.33), ^{19}F nmr (CCl$_4$) 69.6 (s, 49%, ortho isomer) and 69.8 ppm (s, 51%, meta and para); mass spectrum, molecular ion at *m/e* 428.

Anal. Calcd for $C_{21}H_{14}F_6OS$: C, 58.85; H, 3.30; S, 7.49. Found: C, 58.32; H, 3.05; S, 7.38.

Pyrolysis of 1 in Ether. A sample of **1** (110 mg) in 0.5 ml of anhydrous ether in an nmr tube was degassed by three freeze–thaw cycles and sealed under vacuum. After heating at 77° for 55 hr the sample of the decomposition mixture showed 1 equiv of R$_F$OH and 1 equiv of alkoxylation products **10** (61% ortho isomer, 39% meta and para), by ^{19}F nmr.

Isolation and Characterization of Isomeric 10a, b, c. Preparative glpc of the isomeric mixture of alkoxylation products on 5% SE-30 on Chromosorb W (AW/DMCS) separates the para isomer (**10c**) [220 MHz ^{1}H nmr (CCl$_4$) δ 6.81 and 7.12 (two d, 4 H, AB quartet), 7.21 (s, 5 H, SC$_6$H$_5$), 7.50 (m, 3 H, meta and para protons of the alkoxy phenyl), and 7.62 (m, 2 H, ortho protons of the alkoxy phenyl), ^{19}F nmr (CCl$_4$) 69.8 ppm (s)], from the ortho (**10a**) and meta (**10b**) isomers. A mixture of **10a** and **b** showed ^{19}F nmr (CCl$_4$) 69.6 (s, **10a**) and 69.8 ppm (s, **10b**).

The yields of **10a, b,** and **c** were determined for both of the above pyrolyses from ^{19}F nmr integrals and glpc area ratios of the original isomeric mixtures. These yields were corroborated by nearly complete resolution of the ^{19}F nmr singlets of the meta and para isomers on a 220 MHz nmr spectrometer. By maximization of the field strength it was possible to observe ^{19}F spectra with the 220-MHz proton probe of a Varian HR-220 spectrometer. A DuPont No. 310 curve resolver was used to further resolve the peaks for the meta and para isomers.

Reaction of 1 in Ether in the Presence of Aryl Sulfides 6, 7, 9, and Thioanisole. Sulfurane **1** was heated at 35° in ether for several days in the presence of phenyl trifluoromethyl sulfide (**6**), 1,2-dichlorobenzo[*b*]thiophene[21] (**7**), β-naphthyl phenyl sulfide[22] (**9**), or thioanisole. As a particular example, 1 equiv of **6** in 0.3 ml of anhydrous ether was added to an nmr tube containing 124 mg of **1** in 0.4 ml of ether. The sample was heated at 35° for several days and the reaction followed by ^{19}F nmr spectroscopy. The minimum yield of acetal **11** (some was destroyed under the reaction conditions) was determined by comparison of ^{19}F nmr integrals of both the acetal and R$_F$OH and the acetal and sulfide **6**. A small ^{19}F nmr peak at 69.5 ppm (present to about the same extent in samples containing **7** and **9**) is attributed to a trace of nuclear alkoxylation product **10a**.

Evaporation of solvent gave acetal **11**, ^{19}F nmr (CDCl$_3$) 69.1 (q, J_{FF} = 10.7 Hz, 3 F, C*F*$_3$) and 71.7 ppm (q, J_{FF} = 10.7 Hz, 3 F, C*F*$_3$) as expected for an R$_F$O group bonded to a chiral carbon center, ^{1}H nmr (CDCl$_3$) δ 1.13 (t, J_{HH} = 7 Hz, 3 H, C*H*$_3$), 1.43 (d, J_{HH} = 5.3 Hz, 3 H, C*H*$_3$), 3.57 (m, J_{HF} broadening, 2 H, C*H*$_2$), and 5.11 (broad q, J_{HH} = 5.5 Hz, J_{HF} broadening, 1 H, C*H*). These spectra of **11** are identical with those of a sample prepared by α chlorination of ether with *tert*-butyl hypochlorite and displacement of chloride by R$_F$OK. Acetal **11** is hydrolyzed, by shaking with H$_2$O, to give acetaldehyde, ethanol, and R$_F$OH (by nmr).

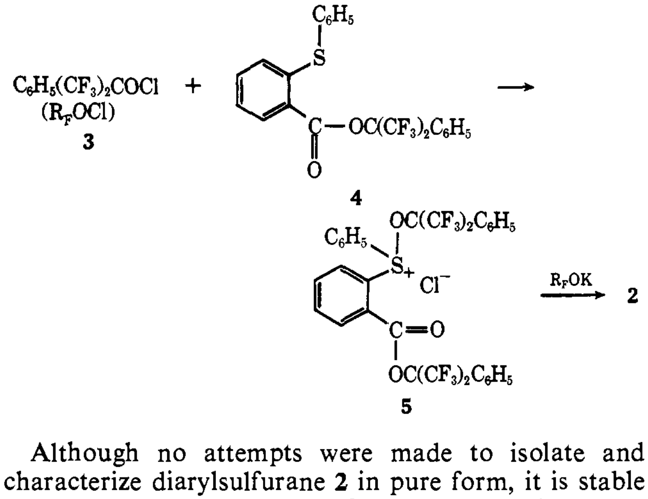
Diphenyl sulfide was isolated from the product mixture by preparative glpc on 5% SE-30 on Chromosorb W (AW/DMCS) and characterized by comparison with an authentic sample.

Thioanisole (1 equiv) in 0.3 ml of anhydrous ether was added to an nmr tube containing 143 mg of sulfurane **1** in 0.4 ml of ether. The sample was heated at 35° for several days and the reaction followed by ^{19}F nmr spectroscopy. No acetal was seen. The nmr showed C$_6$H$_5$SCH$_2$OR$_F$ (**12**) in 70% yield (by comparison of its ^{19}F nmr integral with that of R$_F$OH).

Evaporation of solvent gave **12**, ^{19}F nmr (CDCl$_3$) 70.2 ppm (s); 100 MHz ^{1}H nmr (CDCl$_3$) δ 4.95 (septet, J_{HF} = 0.6 Hz, C*H*$_2$, width at half-peak height, 2.1 Hz, upon irradiation at 94.0862 MHz, 0.6 Hz). These spectra are identical with those of a sample of **12** prepared by heating a mixture of sulfurane **1** and excess thioanisole in chloroform-*d* at 60° for several days.

Results and Discussion

Synthesis. Hexafluoro-2-phenyl-2-propanol (R$_F$OH) is converted to hypochlorite **3** (R$_F$OCl) by chlorination of a suspension of the alkoxide (R$_F$OK) in anhydrous CFCl$_3$ at −78°.[23] Hypochlorite **3** is quite susceptible to hydrolysis as has been noted for several similar fluoroalkyl hypochlorites.[23] The alkoxide is generated by reaction of the alcohol in anhydrous ether with potassium hydride. Reaction of hypochlorite **3** in CFCl$_3$ with sulfide **4** in CH$_2$Cl$_2$ at −78° results in formation of alkoxysulfonium chloride **5**. No attempts were made to isolate **5** since it was seen to be unstable at room temperature in the CFCl$_3$–CH$_2$Cl$_2$ solvent system. Unsymmetrical sulfurane **2** is formed upon addition of an ether solution of R$_F$OK to **5** at −78°. Moisture must be avoided at all stages since the hypochlorite, alkoxysulfonium chloride, and sulfurane are all rapidly hydrolyzed, the sulfurane to give R$_F$OH and the sulfoxide corresponding to **4**.



Although no attempts were made to isolate and characterize diarylsulfurane **2** in pure form, it is stable at room temperature, at least for periods of a day or so.

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[21] A sample was kindly supplied by Professor D. Neckers, Hope College, Holland, Mich.

[22] Prepared by the method of ref 19.

[23] For related syntheses of fluoroalkyl hypochlorites see D. E. Young, L. R. Anderson, D. E. Gould, and W. B. Fox, *J. Amer. Chem. Soc.*, **92**, 2313 (1970).

A sample which had been evaporated to dryness under reduced pressure and maintained as a solid material under vacuum for 12 hr at room temperature showed no observable decomposition by ^{19}F nmr spectroscopy.

A more convenient synthesis of **2** involves treatment of a solution of **4** and R_FOK, in ether at −78°, with chlorine. Symmetrical sulfurane **1** was prepared in solution by both of the routes described for **2**. It too is most conveniently prepared by the illustrated route involving treatment of an ether solution of R_FOK, from reaction of the alcohol with potassium metal, and diphenyl sulfide with chlorine at −78°. Filtration of

$$(C_6H_5)_2S + 2R_FOK \xrightarrow[\substack{\text{ether}\\ -78^\circ}]{Cl_2} \mathbf{1} + 2KCl$$

potassium chloride followed by solvent removal from the filtrate *in vacuo* leaves white, crystalline **1** in high yield. Moisture must be avoided as in the preparation of **2** since **1** is rapidly hydrolyzed to diphenyl sulfoxide and R_FOH. The crystalline material is stable indefinitely at room temperature and can be handled quite easily in a dry box.

In the more convenient synthetic route for preparation of **1**, it is not known whether the chlorine reacts initially with diphenyl sulfide to form diphenyl sulfide dichloride[24] or with R_FOK to form hypochlorite **3**. Neither of the unsymmetrical sulfides, phenyl trifluoromethyl sulfide (**6**) nor 1,2-dichlorobenzo[*b*]thiophene (**7**), reacts with **3** to form an alkoxychlorosulfurane below −10°. Upon warming to room temperature the hypochlorite is destroyed by chlorination reactions, as evidenced by the regeneration of R_FOH. The fact that these two sulfides, each containing a fairly electropositive sulfur atom, do not react with hypochlorite **3** suggests that the reaction of both sulfide **4** and diphenyl sulfide with **3** most likely involves some type of nucleophilic displacement by sulfur on the chlorine atom of **3**.

Bonding in Sulfuranes 1, 2, and 5. The hexafluorocumyloxy ligands of **2** and **5** have been used as ^{19}F nmr probes to obtain evidence for the covalent nature of the S–O bonds. The six fluorines of sulfide **4** give a single nmr peak, which broadens markedly at low temperatures (−70°). The four three-fluorine multiplets seen in the spectrum[25] of **5** [$CFCl_3$:CH_2Cl_2, 1.5:1.0, −45°] provide evidence for the chiral[26] center at sulfur. We tentatively assign the two quartets at 69.1 and 72.1 ppm (upfield from $CFCl_3$) to the diastereotopic trifluoromethyl groups of the *S*-alkoxy ligand, and the unresolved multiplets at 70.7 and 71.8 ppm to the trifluoromethyl groups of the ester alkoxy substituent.[27]

The chemical shift differences for the two sets of geminal trifluoromethyl groups increase with decreasing temperature, with the ester alkoxy peaks showing the greater temperature dependence. Both the ester alkoxy and *S*-alkoxy multiplets broaden with decreasing temperature, probably the result of a temperature–viscosity effect. At −70° the fine structure of the *S*-alkoxy quartets is almost completely gone, and the higher field multiplets of an ester alkoxy and an *S*-alkoxy trifluoromethyl group are completely overlapped. The two ester alkoxy multiplets coalesce to a single peak at *ca.* −30°.

The importance of covalent S–Cl bonding in **5**, or any of its analogs studied in this work, remains unclear. The similar compound diphenyl-*tert*-butoxysulfonium chloride, observed upon the treatment of diphenyl sulfide with *tert*-butyl hypochlorite at −78°, shows chemical shift changes upon reaction with BCl_3 which could result from conversion of a covalent chloride to an ionic tetrachloroborate. The singlet for the *tert*-butoxy protons in methylene chloride at −62° shifted from δ 1.69 to 1.72 upon treatment of the alkoxysulfonium chloride with BCl_3 while the chemical shift difference of the aromatic multiplets at δ 7.85 (3 H, meta and para) and 8.30 (2 H, ortho) is decreased as the peaks move to δ 7.90 and 8.15.

These changes parallel closely the nmr changes seen[5] upon treatment of methylphenyl-*tert*-butoxysulfonium chloride with silver tetrafluoroborate, changes which when considered in light of certain observations of chemical behavior led Johnson and Rigau[5] to suggest that they reflect the conversion of a covalent chloride to an ionic tetrafluoroborate. The fact that some signals move to higher field upon formation of the tetrafluoroborate from the sulfonium chloride, rather than to lower field as one might predict on the basis of consideration of charge alone, while unexpected, is not really inconsistent with this interpretation. Data are not available in this case, however, to rule out the alternative explanation of the chemical shifts based on possible ion aggregation phenomena[28] which might occur as the gegenion is changed from chloride to tetrafluoroborate. The chemical shift difference seen by Wilson and Chang[8] for the fluorine multiplets of bis(*p*-fluorophenyl)chlorosulfonium trichloromercurate and of its precursor bis(*p*-fluorophenyl) sulfide dichloride (^{19}F nmr multiplet > 400 Hz upfield from that for the ionic trichloromercurate), formed by treatment of the sulfide with chlorine, is in the correct direction for the postulated conversion of covalent chloride to ionic chlorosulfonium salt and probably too large in magnitude to be the result of ion aggregation differences between chloride and trichloromercurate.

The conversion of **5** to **2** gives a compound which shows in its nmr clear evidence for two covalent S–O bonds. The destruction of the chirality at sulfur by the introduction of the second enantiotopic alkoxy ligand results in a single peak at 69.9 ppm for the six fluorines of the ester alkoxy group of **2** (in ether at −44°). The *S*-alkoxy fluorines give two six-fluorine quartets at 66.9 and 71.4 ppm, as expected for the prochiral geometry about sulfur.[26] Excess R_FOK shows a single upfield peak at *ca.* 75 ppm.

The S–O bonds of sulfurane **1** and of its precursor diphenyl(hexafluoro-2-phenyl-2-propoxy)sulfonium chloride (**8**) are also covalent. The ^{19}F nmr spectrum of **8** (ether, −40°) consists of a singlet 0.3 ppm downfield from the singlet for **1**. Addition of R_FOK converts all of the lower field peak into the higher field

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(24) R. J. Maner, Ph.D. Thesis, University of Iowa, 1968.

(25) The ^{19}F nmr spectra of both **5** and **2** are shown in ref 2a.

(26) For a discussion of nmr chemical shifts of diastereotopic nuclei see K. Mislow and M. Raban, *Top. Stereochem.*, 1, 1 (1967); G. J. D. Peddle and G. Redl, *J. Amer. Chem. Soc.*, **92**, 365 (1970).

(27) The assignment of the more nearly resolved quartets resulting from four-bond spin–spin coupling, J_{FF} = 10.7 Hz, to the *S*-alkoxy fluorines is made on the basis of the similarity of peak shape and temperature dependence to that of the related peaks in the phenyl ester analog of **5** [^{19}F nmr ($CFCl_3$:CH_2Cl_2, 1.0:1.0, −68°) two broad quartets at 68.7 and 70.0 ppm, J = 10 Hz; with decreasing temperature the quartets broaden and their chemical shift difference increases].

(28) R. L. Buckson and S. G. Smith, *J. Phys. Chem.*, **68**, 1875 (1964).

peak of **1** and excess $\mathrm{R_FOK}$ gives an additional sharp peak at *ca.* 6 ppm higher field than that for **1**.

Structure of 1 and 2. The trigonal-bipyramidal geometry[29] of sulfur tetrafluoride[11] and its organic derivatives[12] and analogous cyclic alkoxyphosphoranes[30] is well established. For the trigonal-bipyramidal geometry the more electronegative ligands preferentially occupy the apical positions (less s character in the bonds from the central atom) whereas the less electronegative ligands preferentially occupy equatorial positions (more s character).[31]

The crystal structure of the unstable 1:1 adduct of bis(*p*-chlorophenyl) sulfide with chlorine was found[13] to involve trigonal-bipyramidal geometry about sulfur, with the *p*-chlorophenyl groups and an unshared pair of electrons occupying the equatorial plane and the chlorine atoms occupying apical positions. A preliminary X-ray investigation[10] of a compound postulated to have the structure of a spirodiaryldiacyloxysulfurane showed that the molecule did have symmetry properties in the crystal appropriate for a sulfurane. The final structure awaits completion of the X-ray determination.

Sulfurane **1** has been shown[1] to have a trigonal-bipyramidal geometry about sulfur in the crystal. The spectroscopic data for both **1** and **2** are compatible with their also having this expected[10-13] geometry in solution with the two electronegative alkoxy ligands occupying apical positions.[31] Other more nearly tetrahedral geometries are not ruled out, however, by the nmr studies. Pseudorotation[30] pathways for the interchange of alkoxy ligand positions about sulfur which are of sufficiently low energy to be rapid on the nmr time scale ($\Delta\delta$ *ca.* 250 Hz) can be ruled out, as can rapid inversions of geometry about sulfur *via* a planar configuration. One solution of *ca.* 0.09 *M* **2** in ether containing *ca.* 0.05 *M* $\mathrm{R_FOH}$ showed no appreciable coalescence of the trifluoromethyl quartets even at 15°, only a slight broadening. The simultaneous broadening seen for the $\mathrm{R_FOH}$ singlet is suggestive of an intermolecular exchange of alkoxy ligands with the alcohol rather than an intramolecular pseudorotation pathway for the exchange process responsible for this observed broadening of the quartet peaks at 15°.

Exchange. The exchange of the alkoxy ligands of either **1** or **2** with added $\mathrm{R_FOK}$ is much slower than that seen with $\mathrm{R_FOH}$. The ^{19}F nmr spectra of a sample of **1** (containing *ca.* 28% $\mathrm{R_FOH}$) in $\mathrm{CCl_4}$ at −15 and +37° are shown in Figure 1.

The effect of temperature on the rate of alkoxy exchange is strikingly illustrated by the marked broadening of sulfurane and $\mathrm{R_FOH}$ ^{19}F nmr peaks at +37°. Enough potassium hydride was added to this sample to convert the alcohol to $\mathrm{R_FOK}$. The resulting solution at +37° showed sharp peaks for sulfurane (69.6 ppm) and alkoxide (76.6 ppm) in a dramatic demonstration that ligand exchange is indeed more rapid with $\mathrm{R_FOH}$ than with $\mathrm{R_FOK}$. Addition of $\mathrm{R_FOH}$ to the sample containing $\mathrm{R_FOK}$ results in exchange broadening as expected. These results are consistent with the operation of some variant of the dissociative mechanism for exchange pictured in Scheme I.

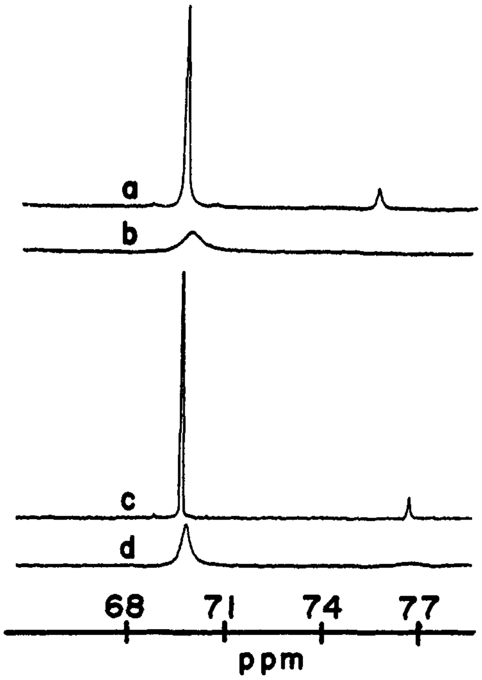
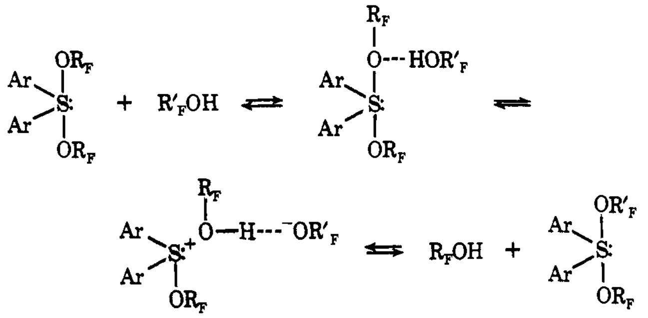


Figure 1. ^{19}F nmr spectra of **1** in $\mathrm{CCl_4}$. Chemical shifts are in parts per million upfield from $\mathrm{CFCl_3}$: (a) *ca.* 0.21 *M* **1** and *ca.* 0.06 *M* $\mathrm{R_FOH}$ at −15°; (b) *ca.* 0.21 *M* **1** and *ca.* 0.06 *M* $\mathrm{R_FOH}$ at +37°; (c) *ca.* 0.21 *M* **1** and *ca.* 0.04 *M* $\mathrm{R_FOK}$ at +37°; (d) *ca.* 0.21 *M* **1**, *ca.* 0.11 *M* $\mathrm{R_FOH}$, and $\mathrm{R_FOK}$ at +37°.

Scheme I



The exchange of alkoxy ligands with $\mathrm{R_FOH}$ is much faster in solvents $\mathrm{CDCl_3}$ and $\mathrm{CCl_4}$ than in ether. The latter is more able to serve as a hydrogen bond acceptor toward $\mathrm{R_FOH}$, reducing its effectiveness as a general acid catalyst for the exchange. Ligand exchange of **1** with other alcohols is also rapid. Alcohols lacking β protons, such as perfluoro-*tert*-butyl alcohol[32] or neopentyl alcohol, show rapid exchange in an equilibrium mixture of relatively stable dialkoxydiarylsulfuranes. Exchange with other alcohols, acids, and other active hydrogen compounds appears also to be rapid, with

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[29] For reviews of pentacoordinate compounds having trigonal-bipyramidal geometry see E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, 20, 245 (1966); E. L. Muetterties, *Accounts Chem. Res.*, 3, 266 (1970).

[30] F. Ramirez, S. L. Glaser, A. J. Bigler, and J. F. Pilot, *J. Amer. Chem. Soc.*, **91**, 496 (1969); F. Ramirez, J. Bauer, and C. D. Telefus, *ibid.*, **92**, 6935 (1970); D. Z. Denney, D. W. White, and D. B. Denny, *ibid.*, **93**, 2066 (1971). For the literature prior to 1968 see F. Ramirez, *Accounts Chem. Res.*, 1, 168 (1968); F. H. Westheimer, *ibid.*, 1, 70 (1968). For other possible examples of cyclic phosphoranes see J. H. Finley and D. B. Denney, *J. Amer. Chem. Soc.*, **92**, 362 (1970); L. D. Quin and T. P. Barket, *ibid.*, **92**, 4303 (1970).

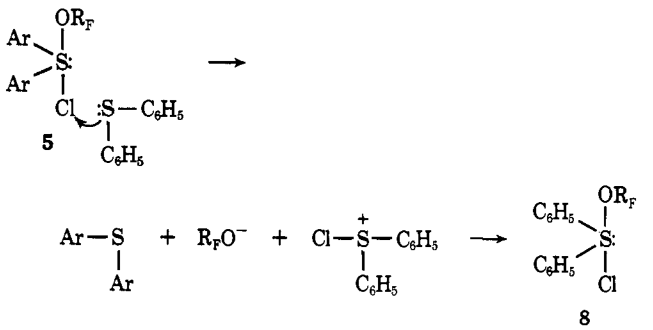
[31] E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, 3, 1298 (1964); E. L. Muetterties, W. Mahler, and R. Schmutzler, *ibid.*, 2, 613 (1963).

[32] D. E. Young, L. R. Anderson, D. E. Gould, and W. B. Fox, *J. Amer. Chem. Soc.*, **92**, 2313 (1970). We are grateful to Dr. Anderson for the gift of a sample of this compound.

subsequent reaction of the sulfurane providing a basis for several synthetic applications.[2c,33]

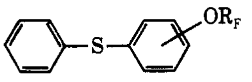
The more facile exchange of our sulfurane ligands with R_FOH than with R_FOK is in contrast to other results reported[6] for such exchange in analogous alkoxysulfonium salts. For example, ethoxysulfonium fluoroborates show only slow alkoxy ligand exchange in isotopically labeled ethanol, but in the presence of ethoxide the exchange is considerably more rapid.[6] Alkoxy exchange of 1-ethoxythioniacyclohexane trichloromercurate in ethanol is quite slow also except when trace amounts of hydrogen chloride are added.[5] Catalysis was shown to be a function of the chloride ion rather than the acidity of the catalyst. At present we have no data bearing on possible explanations of the differences in behavior seen for our sulfuranes and those discussed by Johnson. Several differences in electronic and steric features of the structures could be invoked.

Reaction of chlorosulfurane **5** with diphenyl sulfide to give **8** by exchange of the sulfide moiety is quite facile. Exchange of diphenyl sulfide with **2**, on the other hand, occurs very slowly, if at all. No evidence is seen for new sulfuranes by exchange of **1** in ether with aryl sulfides, such as **6**, **7**, β-naphthyl phenyl sulfide (**9**), or thioanisole. These results suggest that the exchange reaction seen for **5** proceeds by nucleophilic displacement on chlorine by sulfide sulfur, a process which occurs much less readily on the oxygen of our alkoxy ligand. This difference is responsible for the opening of new synthetic applications[33] for our dialkoxysulfuranes which were not available for the halosulfuranes. If the postulated displacement on chlorine is the mechanism for the exchange reaction seen for **5** this provides suggestive evidence for the presence of at least a trace of the covalent chlorosulfurane form in solution. Other mechanisms are, of course, not ruled out.


5

8

Pyrolysis of 1. Compounds analogous to **1**, but bearing chlorine ligands, are relatively unstable, decomposing in the range −40° to 25°. For example, the complex between diphenyl sulfide and chlorine decomposes[24] in CCl_4 at −15°. Solid phenylsulfur trichloride[15b] decomposes below 10°. Alkoxysulfonium chloride **8** decomposes at room temperature as does 9-chloro-9-methyl-9-thiabicyclo[6.1.0]nonane.[7] Diphenyl-*tert*-butoxysulfonium chloride decomposes in CH_2Cl_2 at −40° with a half-life of approximately 30 min.[34] These compounds decompose by a route involving chloride as a nucleophile or by routes involving the generation of a chlorinating agent. In contrast to this, **1**, lacking halogen ligands, is stable in inert solvents for extended periods at room temperature. Upon heating an ether solution of **1** at 77° for 55 hr in a sealed tube, or heating a neat sample gradually to 175° over a 45-min period, 1 equiv of R_FOH and 1 equiv of a mixture of nuclear alkoxylation products **10a**, **b**, and **c** are generated.


10a (ortho)
b (meta)
c (para)

These compounds were identified by elemental analyses, mass spectrometry, and nmr. The ortho: meta:para ratios in the product mixture (49:18:33 in the melt up to 175° over a 45-min period, 61:14:25 in ether at 77° for 55 hr in a sealed tube) favor ortho substitution in a pattern similar to that seen for several intramolecular aromatic rearrangements.[35] The course of the reaction is not affected by the addition of the radical scavenger galvinoxyl or the radical initiator azoisobutyronitrile (AIBN). For example, the same product ratio of **10** (61:14:25) was obtained upon pyrolysis of **1** for 55 hr at 77° in ether containing either galvinoxyl or AIBN. The decomposition shows no chemically induced dynamic nuclear polarization[36] in either dodecane or chlorobenzene solvents. In both of these solvents the ortho isomer was formed in preference to the meta and para. From these data free-radical or radical-pair intermediates seem unlikely. An intramolecular rearrangement of the alkoxysulfonium ion is suggested.

In contrast, when **1** is boiled for several days in ether in the presence of an aryl sulfide, reaction products reminiscent of the radical chain induced decompositions seen for peroxides in diethyl ether are observed.[37]

$$\mathbf{1} + (C_2H_5)_2O \longrightarrow CH_3\overset{OR_F}{\overset{|}{C}}HOCH_2CH_3 + R_FOH + (C_6H_5)_2S$$

11

The acetal product, **11**, is formed in 58% yield when the pyrolysis is carried out in the presence of 1 equiv of aryl sulfide **6**, 33% in the presence of **9**, and 60% in the presence of **7**. The acetal is not stable under the reaction conditions, so observed yields represent minimum yields. From the ^{19}F nmr spectra no more than a trace of nuclear alkoxylation product **10a** is formed. Acetal **11** gives characteristic ^1H and ^{19}F nmr spectra and is rapidly hydrolyzed to acetaldehyde, ethanol, and R_FOH. No **11** is formed in the presence of galvinoxyl nor in the absence of the added aryl sulfide. For example, heating a 0.127 mmol sample of **1** in 0.5 ml of ether at 77° for 55 hr in a sealed nmr tube containing 4.8 mg of galvinoxyl and 0.103 mmol of sulfide **9** results only in the formation of alkoxylation products **10** in the same product ratio (61:14:25) observed pre-

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

(34) Unpublished results from these laboratories; see also C. Walling and M. J. Mintz, *J. Org. Chem.*, **32**, 1286 (1967).

(35) For a review see H. J. Shine, "Aromatic Rearrangements," Elsevier, Amsterdam, 1967.

(36) See G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, **92**, 7227 (1970); G. L. Closs and D. R. Paulson, *ibid.*, **92**, 7229 (1970), and references cited therein.

(37) E. S. Huyser, "Free-Radical Chain Reactions," Wiley-Interscience, New York, N. Y., 1970, p 262.

viously in the absence of both galvinoxyl and sulfide **9**. No evidence is seen for an exchange of the added aryl sulfide with **1** to give a new sulfurane.

A mechanism for this radical chain process has been suggested.[2b] Radical initiation involving a reaction between sulfide and sulfurane may involve electron transfer or S–S bond formation, as suggested earlier.[2b] Electron transfer reactions may also be preferred to direct displacements in the chain transfer reaction between solvent α-ethoxyethyl radicals and sulfurane to give **11**.

When the pyrolysis is carried out in the presence of thioanisole, acetal **11** is not observed but rather $C_6H_5SCH_2OR_F$ (**12**) is formed in 70% yield along with a trace of **10a**. Heating a 0.127 mmol sample of **1** in 0.5 ml of ether at 77° for 55 hr in a sealed nmr tube containing 6.1 mg of galvinoxyl and 0.10 mmol of thioanisole results, however, only in the formation of alkoxylation products **10** in the same product ratio (61:14:25) observed previously in the absence of both galvinoxyl and thioanisole. A radical chain sequence similar to that leading to **11** is diverted, in the presence of the more reactive hydrogen atom donor thioanisole, to give **12**.

The great reactivity of sulfurane **1** toward active hydrogen compounds (O–H, N–H, S–H, etc.), an indefinite shelf life in the absence of moisture, and the unique pattern of reactivity which results from the absence in **1** of the halogen ligands present in other sulfuranes[7,15b,24,34] make this compound very attractive as a reagent for dehydrations,[2c,33] etherifications,[2c,33] oxidations, and certain cleavage and coupling reactions. The development of synthetic applications of this reagent, and related compounds, will be the subject of forthcoming publications.

Acknowledgment. This work was supported in part by National Science Foundation Grant No. GP 13331. The National Science Foundation also assisted in the purchase of the 220 MHz nmr spectrometer used in this work. Special thanks are due Mr. Robert Thrift for obtaining ^{19}F spectra at 220 MHz.

Sulfuranes. VI.[1] Reactions Involving the Alkoxy Ligands of Dialkoxydiarylsulfuranes. Formation of Olefins and Ethers

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Contribution from the Department of Chemistry, University of Illinois, Urbana, Illinois 61801. Received September 25, 1971

Abstract: Dehydrations of secondary and tertiary carbinols with **1** $[(C_6H_5)_2S(OR_F)_2$, where $R_F = C_6H_5C(CF_3)_2]$ proceed under unusually mild conditions to give generally excellent yields of olefin. The synthetic utility of the reaction is demonstrated by the formation of the hitherto inaccessible unrearranged olefin from the dehydration of tricyclopropylcarbinol (**5**). Tertiary alcohols are dehydrated essentially instantaneously, even at −50° in ether or chloroform. The kinetic isotope effect ($k_H/k_D = 1.54$) for the intramolecular competition in the dehydration of partially deuterated *tert*-butyl alcohol, when considered with evidence for carbonium ion rearrangements in certain cases, favors a mechanism with considerable E1 character. A strong preference for trans coplanar disposition of leaving groups in the dehydration of appropriately chosen secondary carbinols gives evidence for the E2 character in these reactions. Primary alcohols react with **1** to form unsymmetrical ethers (R_FOCH_2R) in the absence of structural features increasing the acidity of β protons. The rate of this reaction with various alcohols ($CH_3OH > (CH_3)_2CHCH_2OH > (CH_3)_3CCH_2OH$) is that expected for an SN2 displacement by R_FO^- on an intermediate, postulated to be the alkoxysulfonium ion ($ROS(C_6H_5)_2^+$), formed by reaction of the alcohol with **1**. A similar intermediate is implicated in the dehydration reactions of tertiary and secondary alcohols. The exchange of alkoxy ligands of **1** with added alcohols is shown by nmr to be fast. Reactions of chloroform solutions of **1** with alcohols, such as neopentyl alcohol, which do not give rapid elimination or ether-forming reactions, lead by a radical-chain process to R_FOCCl_3. In this reaction **1** acts as an oxidizing agent.

The use of stable, crystalline dialkoxydiphenylsulfurane (**1**) as a dehydrating agent for the conversion of alcohols to alkenes was suggested by our preliminary observation[3] that the alkoxy ligands of **1** rapidly exchange with added alcohols, and by our earlier observation[4] of isobutylene in the product mixture from a perester decomposition postulated to give sulfurane **2** as an intermediate. The methallyl chloride seen by Walling and Mintz in the *tert*-butyl hypochlorite oxidation of diphenyl sulfide[5] is most conveniently rationalized to result from chlorination of isobutylene formed by a similar process. We here report results[6] which suggest that **1** is indeed a dehydrating agent with unique properties, potentially of great synthetic utility.

(1) For paper V of this series see R. J. Arhart and J. C. Martin, *J. Amer. Chem. Soc.*, **94**, 4997 (1972).

(2) Abstracted from the Ph.D. Thesis of R. J. Arhart, University of Illinois, Urbana, 1971. National Institutes of Health Predoctoral Fellow, 1967–1971.

(3) J. C. Martin and R. J. Arhart, *J. Amer. Chem. Soc.*, **93**, 2339, 2341 (1971).

(4) W. G. Bentrude and J. C. Martin, *ibid.*, **84**, 1561 (1962); D. L. Tuleen, W. G. Bentrude, and J. C. Martin, *ibid.*, **85**, 1938 (1963); R. J. Arhart, Ph.D. Thesis, University of Illinois, Urbana, 1971.

(5) C. Walling and M. J. Mintz, *J. Org. Chem.*, **32**, 1286 (1967); see also P. S. Skell and M. F. Epstein, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p 26N.

(6) Part of this work has appeared in preliminary form: J. C. Martin and R. J. Arhart, *J. Amer. Chem. Soc.*, **93**, 4327 (1971).