De LaHiguera and Mr. L. L. Huckstep. We thank Dr. L. L. Hatfield for the sample of IV and Mr. W. Conover, of Indiana University, Bloomington, Ind., for recording the spectra of IV and V.

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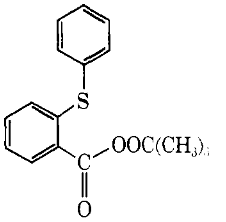
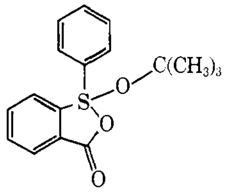
## Sulfuranes. I. A Stable Tetracoordinate Tetracovalent Sulfur Compound in Solution

*Sir:*

For several years interest in our laboratory[1] in compounds of sulfur involving an expansion of the valence octet has centered about studies of neighboring group participation in the decomposition of peresters related to **1**. Compound **2** was postulated as a possible intermediate leading to some of the products observed in the decomposition of **1**. Numerous literature citations might be advanced in support of the postulated intermediacy of tetracovalent sulfur compound **2**. Indirect evidence for similar intermediates has been seen in kinetic,[2] spectroscopic,[3] and product[4] studies in several laboratories. In the special case of halide ligands both liquid[5] and crystalline[6,7] tetracoordinate sulfur compounds have been characterized. The geometry of sulfur tetrafluoride and its analogs[5] seems well established. The crystal structure of the unstable adduct of chlorine to 4,4′-dichlorodiphenyl sulfide was found[7] to involve approximately trigonal-bipyramid 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. In contrast, the 1:1 adduct of thiophane with bromine has quite a different type structure with a tricoordinate sulfur atom.[8]

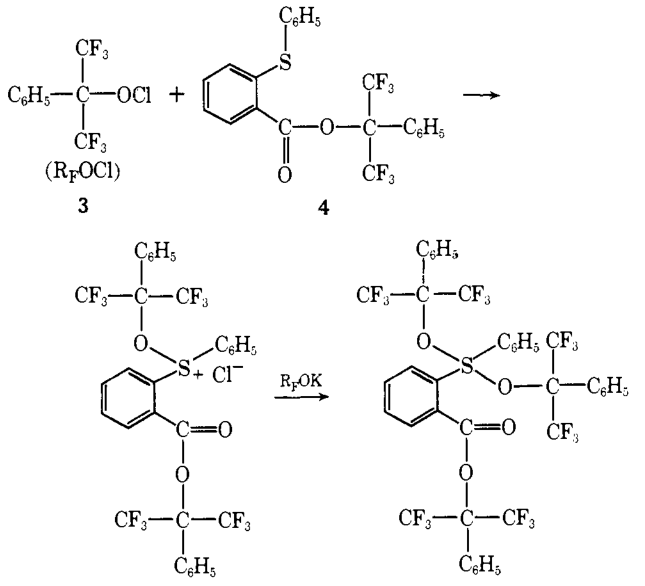


**1**



**2**

Dialkoxydialkyl- and hydroxyalkoxydialkylsulfuranes[9–12] have been suggested as intermediates in displacement reactions of alkoxysulfonium salts. On the other hand, stereochemical results of the base-catalyzed hydrolyses of *cis*- and *trans*-1-ethoxy-3-methylthietanium hexachloroantimonates have led to the suggestion[11] that in this case, in contrast to the situation for the analogous phosphetanium salt, intermediates with two alkoxy groups attached to sulfur have a very short lifetime relative to the half-life for pseudorotation, or perhaps represent transition states for a direct S$_N$2 displacement on sulfur.



**3** **4** **5** **6**

Hexafluoro-2-phenyl-2-propanol ($R_FOH$) is converted to hypochlorite **3** ($R_FOCl$) by chlorination of the alkoxide ($R_FOK$) in anhydrous $CFCl_3$ at −78°.[13] Reaction of **3** with sulfide **4** in $CH_2Cl_2$ at −78° results in formation of alkoxysulfonium chloride **5**. Sulfurane **6** is formed upon addition of the alkoxide, $R_FOK$, in ether to **5** at −78°. A more convenient synthesis of **6** involves treatment of a mixture of **4** and $R_FOK$, in ether at −78°, with chlorine.

We have obtained nmr evidence for the covalent nature of the S–O bonds in **5** and **6** by using the hexafluorocumyloxy ligands as $^{19}$F nmr probes. The six fluorines of compound **4** give a single nmr peak, which broadens markedly at low temperatures (−70°). Figure 1 shows low-temperature spectra for **5** and **6**. The

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(11) R. Tang and K. Mislow, *ibid.*, **91**, 5644 (1969); K. Mislow, *Accounts Chem. Res.*, **3**, 321 (1970).

(12) This nomenclature, based on the name "sulfurane" for the hypothetical $SH_4$ molecule, is loosely analogous to that used for the phosphorus analogs, the oxyphosphoranes. See F. Ramirez, *ibid.*, **1**, 168 (1968). The term "sulfoxal" has also been suggested[10] to describe compounds of structure $R_2S(OR)_2$, such as **6**.

(13) 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).

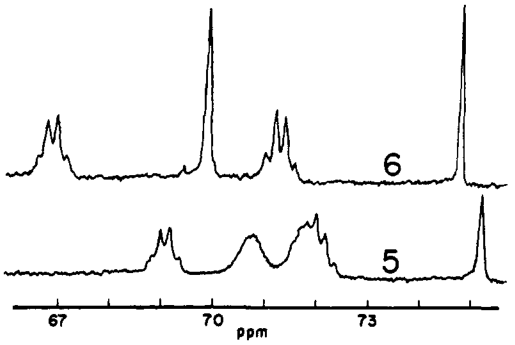
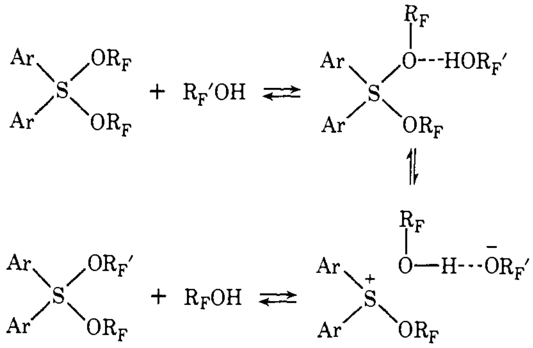


Figure 1. $^{19}F$ nmr spectra of **5** in $CFCl_3$-$CH_2Cl_2$ (1.5:1.0) at −45° and of **6** in ether at −44°. Chemical shifts are in parts per million upfield from $CFCl_3$. The small peak at 69.4 ppm in the spectrum of **6** is from a small amount of unreacted **4**.

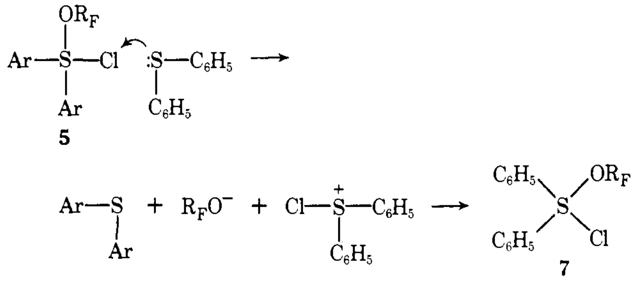
four three-fluorine multiplets seen in the spectrum of **5** (the two overlapping high-field multiplets are seen more clearly resolved at other temperatures) provide evidence for the presence of the chiral center[14] at sulfur. We tentatively assign the two quartets at 69.1 and 72.1 ppm (upfield from $CFCl_3$) 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. (The tentative assignment of the more nearly resolved quartets resulting from four-bond spin–spin coupling, $J_{FF}$ = 10.7 Hz, to the *S*-alkoxy peaks 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**.) 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.

The importance of covalent bonding in the S–Cl bond of **5** is not determined in this experiment. Chemcial-shift changes in the proton spectra of the similar compound, diphenyl-*tert*-butoxysulfonium chloride, which result from its treatment with $BCl_3$, parallel those seen by Johnson and Rigau[3] for another alkoxysulfonium chloride. The size of the chemical-shift differences, and certain observations of chemical behavior, led to the suggestion[3] that a covalent chloride had been converted to an ionic tetrachloroborate in this related reaction. The fact that some signals move to higher field upon treatment of the sulfonium chloride with $BCl_3$, rather than to lower field as one might predict on the basis of consideration of charge alone, is not really inconsistent with this interpretation. We are, however, reluctant to conclude that the shifts seen are the result of the change from covalent to ionic structures until data are available to rule out the alternative explanation of the chemical shifts based on possible ion aggregation phenomena[15] which might occur as the gegenion is changed from chloride to tetrachloroborate.

The conversion of **5** to **6** 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 for the six fluorines of the ester alkoxy group. The sulfurane alkoxy fluorines give the two six-fluorine quartets expected for the prochiral geometry about sulfur.[14] Exchange of alkoxy ligands on the sulfur of **5** or **6** with small amounts of alcohol in the solutions ($R_FOH$, seen as the singlet at highest field in the spectra of Figure 1) is slow on the nmr time scale at −60°, but faster, giving line broadening and eventually complete coalescence of peaks, at higher temperatures. Exchange of the alkoxy groups of **6** with added potassium alkoxide ($R_FOK$) is much slower than that seen with $R_FOH$. This is consistent with the operation of some variant of the dissociative mechanism for exchange pictured below. Further work directed toward a determination of the stereochemistry of the exchange process should provide more definitive evidence as to this mechanism.



Reaction of **5** with diphenyl sulfide to give **7** by exchange of the sulfide moiety is quite facile. Exchange of diphenyl sulfide with **6**, on the other hand, occurs very slowly, if at all. This suggests that nucleophilic displacements on chlorine by sulfide sulfur proceed much more readily than similar displacements on the oxygen of our alkoxy ligand.



Our spectroscopic data for sulfurane **6** are compatible with its having the expected[5,7,16,17] trigonal-bipyramid geometry about sulfur with the two electronegative alkoxy ligands occupying apical positions. Other more nearly tetrahedral geometries are not ruled out, however. We can rule out pseudorotation pathways for the interchange of alkoxy ligand positions about sulfur which are of sufficiently low energy to be rapid on the nmr time scale.

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(14) For a discussion of nmr chemical shifts of diastereotopic nuclei see K. Mislow and M. Raban, *Top. Stereochem.*, **1**, 1 (1967).

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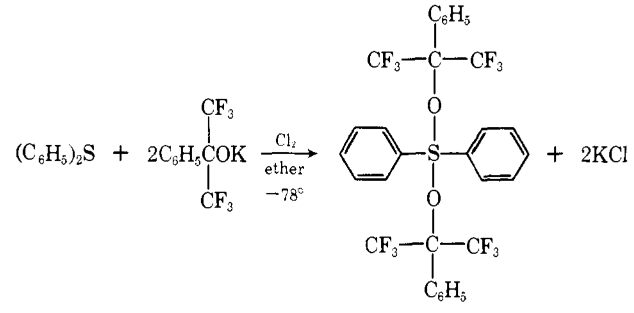
## Sulfuranes. II. The Isolation and Characterization of a Crystalline Dialkoxydiarylsulfurane

*Sir:*

In the preceding paper[1] spectroscopic evidence was advanced for the covalent nature of the S–O bonds of an unsymmetrical dialkoxydiarylsulfurane in solution. We now describe the isolation and characterization of a crystalline symmetrical dialkoxydiarylsulfurane (**1**) of surprising stability.



$(C_6H_5)_2S + 2C_6H_5C(CF_3)_2OK \xrightarrow[\text{ether}\ -78^\circ]{Cl_2} (C_6H_5)_2S[OC(CF_3)_2C_6H_5]_2 + 2KCl$

**1**

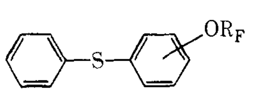
Sulfurane **1** was prepared in solution by both of the routes described in the preceding communication.[1] It is most conveniently prepared by the illustrated route involving treatment of an ether solution of the potassium salt of hexafluoro-2-phenyl-2-propanol ($R_FOH$), prepared by reaction of the alcohol with potassium metal, and diphenyl sulfide with chlorine at −78°. Filtration removes the potassium chloride and removal of the ether from the filtrate *in vacuo* leaves white, crystalline **1** in nearly quantitative yield. Moisture must be avoided at all stages since the sulfurane is hydrolyzed very rapidly to give diphenyl sulfoxide and $R_FOH$. The synthesis can easily be carried out on a large scale. The product is purified by grinding the crystals and removing volatile impurities (excess diphenyl sulfide or $R_FOH$) at high vacuum ($<10^{-4}$ Torr) at room temperature or by recrystallization from pentane; mp 107–109°. *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. The crystalline material is stable indefinitely at room temperature.

The mass spectrum shows a sizable (1.8% of the base peak at low ionizing voltage) molecular ion peak at *m/e* 672 and a prominent fragmentation peak at *m/e* 429 corresponding to loss of one alkoxy ligand to give an alkoxysulfonium ion. High-resolution peak matching techniques show the molecular ion at *m/e* 672.0987 (calcd for **1**, 672.0992): ir ($CCl_4$) 1258 (s), 1208 (s), 1168 (s), 1060 (s), 962 (m), 945 (m), 710 (m), and 675 cm$^{-1}$ (m). The 220-MHz proton nmr ($CCl_4$) shows peaks at $\delta$ 8.1 (m, 4, ortho protons of $SC_6H_5$), 7.5 (m, 10, meta and para protons of $SC_6H_5$ and ortho protons of the alkoxy phenyl), and 7.3 ppm (m, 6, meta and para protons of the alkoxy phenyl). The $^{19}F$ spectrum (ether, −43°) shows a single peak at 69.3 ppm (upfield from $CFCl_3$) together with an ubiquitous $R_FOH$ impurity peak at 74.6 ppm resulting from hydrolysis of **1**. At high temperature both peaks begin to show exchange broadening.

The exchange of alkoxy ligands with $R_FOH$ is much faster in solvents $CDCl_3$ and $CCl_4$, which are less able than is ether to serve as hydrogen bond acceptors toward $R_FOH$. To one sample in $CCl_4$, showing marked broadening of sulfurane and $R_FOH$ $^{19}F$ nmr peaks at room temperature, was added enough potassium hydride to convert the alcohol to $R_FOK$. The resulting solution showed sharp peaks for sulfurane and alkoxide in a dramatic demonstration that ligand exchange is more rapid with $R_FOH$ than with $R_FOK$. A mechanistic interpretation has been given.[1]

Ligand exchange of **1** with other alcohols is also rapid. Alcohols lacking $\beta$ protons, such as perfluoro-*tert*-butyl alcohol[2] 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 subsequent reaction of the sulfurane providing a basis for several synthetic applications, some of which are described in another paper.[3]

Compounds analogous to **1**, but bearing halogen ligands, are very unstable,[4] decomposing in the range −40 to 10°. 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, decomposes only slowly in solution at room temperature. Upon boiling an ether solution of **1** for several days, or heating molten **1** at 120° a few hours, 1 equiv of $R_FOH$ and 1 equiv of a mixture of nuclear alkoxylation products, **2a**, **b**, and **c**, are generated.



2a (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 at 120°, 61:14:25 at 77° in ether in a sealed tube) favor ortho substitution in a pattern similar to that seen for several intramolecular aromatic rear-

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[1] I: J. C. Martin and R. J. Arhart, *J. Amer. Chem. Soc.*, **93**, 2339 (1971).

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

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[4] R. J. Maner, Ph.D. Thesis, University of Iowa, 1968; N. C. Baenziger, R. E. Buckles, R. J. Maner, and T. D. Simpson. *J. Amer. Chem. Soc.*, **91**, 5749 (1969); I. B. Douglass, K. R. Brower, and F. T. Martin, *ibid.*, **74**, 5770 (1952); D. C. Owsley, G. K. Helmkamp, and M. F. Rettig, *ibid.*, **91**, 5239 (1969); see also C. Walling and M. J. Mintz, *J. Org. Chem.*, **32**, 1286 (1967).