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Oxidation of a γ-Sultene to a Cyclic Orthosulfinate.[1] Reactions of a Trialkoxysulfurane with Bifunctional Substrates as a Reflection of the Polarity Rules in Trigonal Bipyramidal Species

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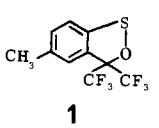
Abstract: Trialkoxysulfurane **2,** the first reported orthosulfinate, is prepared by treatment of sultene **1** with bromine and KOR_F ($R_F = C_6H_5C(CF_3)_2$). Although the reactions of this sulfurane with water, tertiary alcohols, amines, and secondary amides give, respectively, a sultine, sulfinimidates, and amide cleavage products in reactions analogous to those reported previously for dialkoxysulfuranes, **2** differs from them in its reactions with methanol, 1,2-diols, and 1,3-diols to give new trialkoxysulfuranes. The products from methanol, 2,2-dimethyl-1,3-propanediol, and ethylene glycol (**25, 12,** and **13**) undergo intramolecular ligand exchange, shown by variable temperature ^{19}F and ^{1}H NMR studies to have free energies of activation of ca. 11 kcal/mol (−68 °C), 10 or 11 kcal/mol (−74 or −55 °C) and 23 kcal/mol (163 °C), respectively. A permutational isomerization mechanism of a type different from the pairwise exchange of the more usual Berry pseudorotation, a process involving a transition state with "tetrahedral" geometry at sulfur, is proposed to explain these results. In contrast to spirosulfuranes **10, 11, 12,** and **13** and dimethoxysulfurane **25,** sulfurane **2** is shown to exist in solution in a novel conformation having a diequatorial five-membered ring, on the basis of ^{1}H and ^{19}F NMR chemical shift comparisons, the lack of any evidence for ligand exchange processes in the −90 °C ^{19}F NMR spectrum of **2,** and other arguments. The greater apicophilicity of the fluorinated alkoxy ligands of **2** over the methoxy ligands of **25** is suggested to be responsible for the difference in structure. The pyrolyses of spirosulfuranes **10, 11,** and **13** are reported.

Cyclic sulfenates (sultenes) have never been prepared although acyclic analogues have been known for over 60 years.[2] Sultenes, however, have been proposed as reactive intermediates[3] and suggested to explain mass spectral fragmentation.[4] Molecular orbital calculations[5] have predicted the orbital energies and interactions in small ring sultenes as well as similar acyclic sulfenates.[5b] One example of a cyclic sulfenyl carboxylate is known although it polymerizes rapidly at room temperature.[6] Here we report details[7] of the synthesis of sultene **1** and its conversion to aryltrialkoxysulfurane **2,** a compound whose reactions show important contrasts to those of the well-studied diaryldialkoxysulfuranes.[8] This is the first reported aryltrialkoxysulfurane (or orthosulfinate) although thermally unstable trichlorosulfuranes[9] and highly reactive trifluorosulfuranes[10] are well known. One fluorotrialkoxysulfurane has also been reported.[11]



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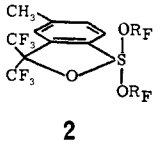
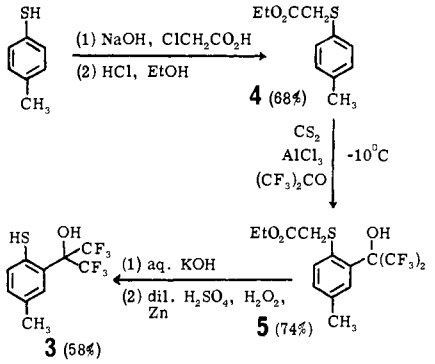


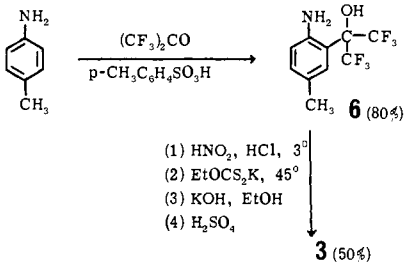
2

Synthesis and Reactions of Sultene 1. Thiol alcohol **3,** a key intermediate in the synthesis of sultene **1,** was prepared by two different methods. In method A (Scheme I), adapted from a procedure by Walker and Leib[12] for halogenating thiophenols, 4-methylthiophenol was protected by reaction with chloroacetic acid in the presence of aqueous NaOH before treatment with hexafluoroacetone in carbon disulfide solution at −10 °C in the presence of aluminum chloride to yield ester alcohol **5.** At 40 °C **5** was contaminated with small amounts of the product resulting from hexafluoroacetone substitution meta to the thioalkyl group. Since the spectra of these two isomers are very similar, the best proof of these assignments is the cyclization to sultene **1** of the thiol (**3**) made from **5.** However, more evidence comes from the lower frequency OH stretch in **5** (3320 vs. 3660 cm^{-1}) and the downfield NMR shift of the OH proton in **5** (δ 8.16 vs. 3.80) which support the idea of internal hydrogen bonding in **5** which is impossible in a 1,3-disubstituted structure. Ester **5** was saponified with aqueous KOH and the resulting carboxylic acid was cleaved to thiol **3**

Scheme I



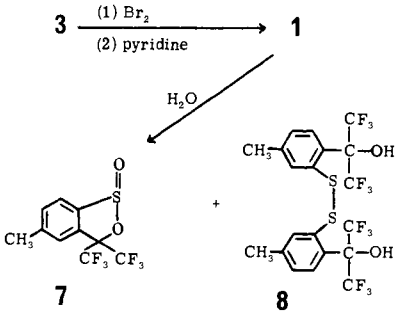
Scheme II



in 58% yield with hydrogen peroxide and dilute sulfuric acid in the presence of zinc dust to reduce any disulfide which might be formed.[12]

Thiol alcohol **3** was more conveniently prepared by the method of Scheme II using the known[13] reaction between hexafluoroacetone and *p*-toluidine in the presence of *p*-toluenesulfonic acid to introduce the fluoroalkyl group.

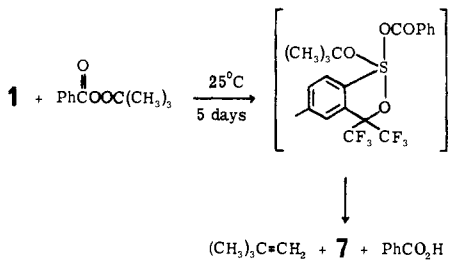
Treatment of **3** with 2 equiv of pyridine and 1 equiv of bromine in CCl_4 produced yellow, crystalline sultene **1**. This



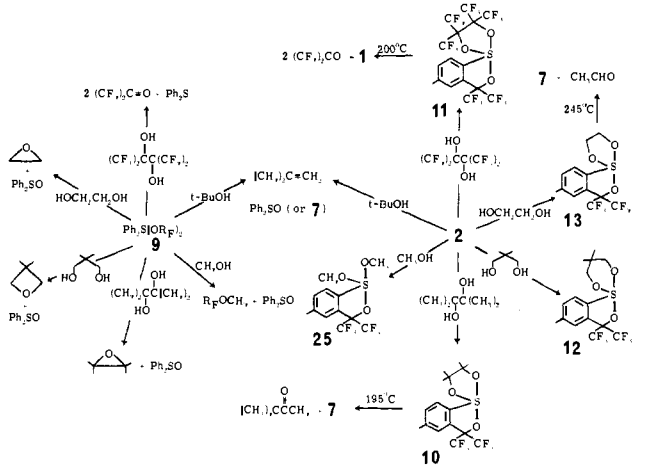
material, unlike an analogous sulfenyl carboxylate,[6] is indefinitely stable at room temperature in the absence of moisture. Exposure to moist air or to wet solvents converts the sultene to a mixture of sultine **7** (identical with authentic material produced by the *tert*-butyl hypochlorite oxidation of **3**) and disulfide **8**.[15]

The yellow color of **1** is associated with a 383-nm maximum (ϵ 70) in its electronic spectrum. This peak (and the yellow color) disappears upon hydrolysis, while other stronger absorptions at 255 and 300 nm are almost unaffected. The 383-nm peak represents a large bathochromic shift over the 262–277 nm bands seen in acyclic alkyl and haloalkyl sulfenates.[16] Similar effects, noted in cyclic disulfides,[17] have been attributed to lone pair repulsions between nonbonding electrons on adjacent atoms in a nearly planar five-membered ring. This explanation is supported by molecular orbital calculations for disulfides but not for sulfenates.[5b] A possible explanation for the bathochromic shift in **1** is enhanced conjugation with the phenyl ring which must be nearly coplanar with the S–O bond. However, this does not account for relatively low extinction

Scheme III



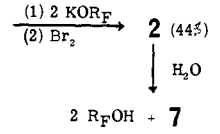
Scheme IV



coefficient of **1** when compared to acyclic sulfenates.[16]

Sultene **1** was found to react slowly with *tert*-butyl perbenzoate at room temperature in CCl_4 solution. After 5 days, NMR integration showed that 79% of the sultene had been oxidized to sultine **7**. Isobutylene was also seen in the ^1H NMR spectrum in 48% of the yield predicted by Scheme III even without taking special precautions to retain this volatile product in the NMR tube. The pictured sulfur insertion into the peroxide bond would give a sulfurane intermediate which would be expected to give the observed products. A related reaction has been reported[18] between sulfoxylates and dioxetanes and analogous biphilic insertions are well known in phosphorus chemistry.[19]

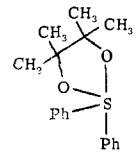
Synthesis and Reactions of Sulfurane 2. Sultene **1** was converted by reaction with bromine and the potassium salt of hexafluoro-2-phenyl-2-propanol (KOR_F) to white, crystalline sulfurane **2**. This compound, although stable indefinitely at room temperature, reacts very rapidly with atmospheric moisture or wet solvents to give sultine **7** and R_FOH. This



behavior is very similar to that of diaryldialkoxysulfurane **9**,[8] an analogy that can be extended to reactions with many alcohols (Scheme IV). Both sulfuranes dehydrate *tert*-butyl alcohol to isobutylene rapidly at room temperature giving diphenyl sulfoxide or sultine **7** as by-products. Similarly *tert*-amyl alcohol gives 2-methyl-2-butene and 2-methyl-1-butene in a 41:59 ratio upon reaction with **9**[8b] and in a 27:73 ratio upon reaction with **2**. However, with diols, **2** has reaction pathways open to it that are not available for **9**. For example, pinacol reacts with **9** to give an epoxide[8c] but with **2** at room temperature the product is spirosulfurane **10**. This compound, the only product observed by NMR, was isolated in 63% yield as a

white, crystalline solid. In contrast to **2**, spirosulfurane **10** is only slowly hydrolyzed (to **7** and diol), a property it shares with several other spirosulfuranes.[8d,20,21] Good evidence for the assigned structure of **10** is seen in its NMR spectrum, which in addition to the nonequivalent trifluoromethyl groups shows five different methyl groups (in C_6D_6). The ^1H NMR spectrum also shows a low-field doublet at δ 8.24 which is highly characteristic for the proton ortho to sulfur in an apical-equatorial bridged arylsulfurane such as **10, 11, 12,** or **13** (vide infra). Many dialkoxy analogues of **10, 11,** and **13** have been studied[21] and x-ray structures have established for three of these[22] the trigonal bipyramidal geometry which we have assumed in this paper.

It is not surprising that **9** does not form a cyclic product with 2,3-dimethyl-2,3-butanediol, as **2** does, since the product (compound **14**) would violate electronegativity rules[23,24] by



14

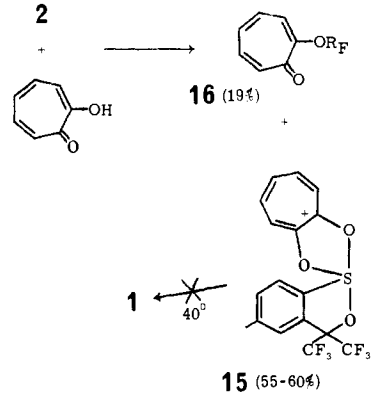
requiring a phenyl to occupy an apical position. Spirosulfurane **10** decomposes when heated in solution to 195 °C for 10 min, yielding pinacolone and sultine **7**. Extending the parallel between **9** and **2**, it is interesting to speculate that the epoxide might be the initial fragmentation product from **10** and might be rearranging to the observed pinacolone. Also noteworthy is the field desorption mass spectrum of **10** where the major fragmentation pathway is to **7** and epoxide (or pinacolone) but where decomposition to sultene **1** and acetone is also important.

A similar difference in reaction pathways is seen in the reaction of **2** and **9** with perfluoropinacol. Sulfurane **9** oxidizes perfluoropinacol to hexafluoroacetone, becoming reduced to diphenyl sulfide in the process,[8g] but like pinacol, perfluoropinacol forms a stable spirosulfurane upon reaction with **2**. This sulfurane, **11,** shows a low-field doublet at δ 8.38 in the ^1H NMR for the proton ortho to sulfur characteristic of the apical-equatorial rings it must have because of its spiro nature. The ^{19}F NMR shows two very broad signals at ϕ 66 and 67.5 consistent with the presence of four strongly coupled trifluoromethyl groups of slightly different chemical shift. The spectrum resembles the low temperature NMR spectrum reported earlier for a fluxional tetrakisalkoxysulfurane containing perfluoropinacol rings.[8g] At 200 °C spirosulfurane **11** fragments to sultene **1** and hexafluoroacetone, the only products seen by ^{19}F NMR. Thus, the parallel with the reaction of dialkoxysulfurane **9** holds, the only difference being the inability of **9** to form cyclic intermediates without encountering the same destabilizing influences that would be present in **14**. It should be noted that a similar fragmentation of a spirosulfurane to hexafluoroacetone and a cyclic sulfoxylate has been postulated.[8g]

The reactions of **2** and **9** with ethylene glycol also illustrate the advantage of having two electronegative apical ligands in order for sulfuranes to be isolable. Dialkoxysulfurane **9** rapidly gives ethylene oxide[8e] and diphenyl sulfoxide even at −50 °C while at room temperature trialkoxysulfurane **2** rapidly forms spirosulfurane **13,** readily isolated in 74% yield as white crystals. The sulfurane ortho-to-sulfur proton doublet is seen at δ 7.90 and the four nonequivalent methylene protons show a complex second-order pattern at δ 3.8–4.1 for three of the protons, even at 220 MHz, and a triplet of doublets at δ 4.31 for the other proton. At 26 °C **13** gives a pair of quartets in its ^{19}F NMR spectrum at ϕ 73.7 and 75.0 consistent with the assigned spirosulfurane structure. However, the 9 Hz fluorine-fluorine coupling coalesces at about 163 °C showing that an exchange process is occurring with a $\Delta G^{\ddagger}$ estimated from the Gutowsky-Holm equations[25] to be ca. 23 kcal/mol at 163 °C. Evidence for broadening is also seen in the complex methylene region of the 60-MHz ^1H NMR spectrum of **13** at this temperature. At higher temperatures decomposition of the sulfurane prevents usable spectra from being obtained. Spirosulfurane **13** was more resistant to pyrolysis than **10** or **11**. Heating to 245 °C for 20 min gave complete conversion to sultine **7** and sultene **1** in a 7:3 ratio, showing that the parallel to the reactions of **9** does not always hold. The only other product identified was 6% of acetaldehyde.

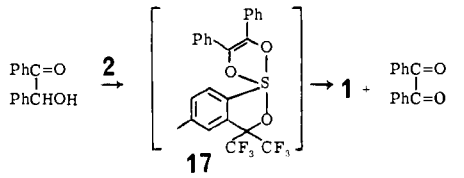
As expected, **9** reacts with 2,2-dimethyl-1,3-propanediol to give the oxetane[8e] while **2** gives a spirosulfurane (**12**), in 45% isolated yield, containing a novel six-membered ring. The ^1H NMR spectrum of **12** contained the expected low-field doublet, from the proton ortho to sulfur, at δ 8.43 as well as two different aliphatic methyl resonances. However, only two doublets were seen in the ^1H NMR for the four methylene protons instead of the expected four doublets and only one CF_3 resonance was seen in the ^{19}F NMR. Upon cooling, the downfield ^1H NMR doublet went through coalescence at around −55 °C (at 100 MHz) splitting into two doublets separated by 21.5 Hz at −95 °C, corresponding to a $\Delta G^{\ddagger}$ of ca. 11 kcal/mol[25] at −55 °C for the process equilibrating the methylene protons, by a mechanism to be discussed later in this paper. The higher field doublet was split into two overlapping doublets at −95 °C. Similarly, the ^{19}F NMR peak of **12** went through coalescence at −74 °C (56.26 MHz) changing into a pair of quartets (highly distorted toward an A_3B_3 pattern) separated by about 21 Hz at −95 °C. This corresponds[25] to an exchange process with a $\Delta G^{\ddagger}$ of ca. 10 kcal/mol at −74 °C. These low temperature NMR spectra are compatible with the assigned trigonal bipyramidal structure of **12.**

To test the generality of the spirosulfurane-forming reaction, other 1,2-dihydroxy compounds and α-hydroxy ketones were treated with sulfurane **2.** Oxalic acid reacted to give a solution whose ^1H NMR did not show the low-field doublet seen in all arylsulfuranes with apical-equatorial rings.[21,22] The ^{19}F NMR spectrum showed a singlet at ϕ 71.0 due to the bishexafluorocumyl ester of oxalic acid (a chemical shift similar to that of other hexafluorocumyl esters[27]), and other peaks due to sulfinate **7** and hexafluorocumyl alcohol (R_FOH). Tropolone reacted with **2** to give a solution whose ^1H NMR did contain a low-field proton doublet at δ 8.46 strongly indicative of formation of spirosulfurane **15** (60% yield by integration). The



15 (55-60%)

^{19}F NMR spectrum was consistent with the presence of **15** in 55% yield along with a 19% yield of another product giving a singlet at ϕ 70.0 (similar to that of hexafluorocumyl ethers[8b]). In contrast another α-hydroxy ketone, benzoin, reacted rapidly with sulfurane **2** to give a yellow solution giving NMR spectra identical with those of authentic samples of sultene **1,** benzil, and R_FOH. Catechol reacted with **2** to form sultene **1,** *o*-qui-



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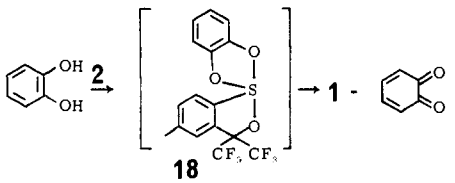
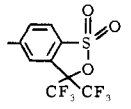


18

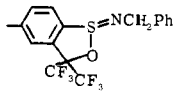
none, and R_FOH. If spirosulfuranes **17** and **18** are intermediates in these oxidations, they are so unstable that no spectroscopic evidence for their presence was seen.

The synthetically attractive fragmentation of these spirosulfuranes in which both C–O bonds are broken to form sultone **19** does not appear to occur in any case examined. Spirosulfuranes **10, 11,** and **13** also showed no evidence for this type of fragmentation. This is in accord with the failure to form a cyclic sulfate in the earlier reported pyrolysis of a spiro tetrakisalkoxysulfurane.[8g]



19

Like dialkoxysulfurane **9**,[8f] **2** appears to react with primary amines to form sulfur–nitrogen double bonds. Benzylamine and isopropylamine give solutions probably containing, respectively, sulfinimidates **20** and **21,** recognized by the diastereotopic methylene protons in the NMR of **20** and the diastereotopic methyl groups of **21.** A pair of trifluoromethyl quartets were also present in the ^{19}F NMR of both compounds. Further work is underway in these laboratories to isolate and characterize these compounds. These *N*-alkyl sulfinimidates are novel in that all previously prepared sulfinimidates have had *N*-arenesulfonyl substitution.[26]



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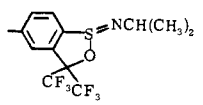
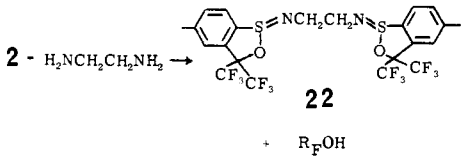


21

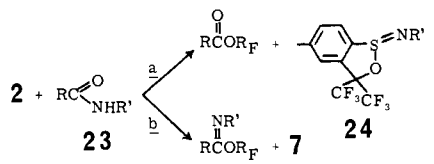
Ethylenediamine has the possibility of reacting with **2** to form a spirosulfurane analogous to **10, 11,** or **13** or to form bissulfinimidate **22.** From the NMR integration of the reaction



22

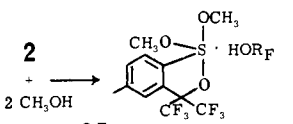
mixture, which showed that 1 mol of amine reacted with 2 mol of **2,** and from the lack of a low-field aromatic doublet in the ^1H NMR as in **10, 11,** and **13,** it is likely that bissulfinimidate **22** forms and not a spirosulfurane.

Sulfurane **2** reacts with *N*-methylbenzamide (**23,** R = Ph; R′ = CH_3), 96% by path a and 4% by path b, in a reaction somewhat less selective than the analogous reaction of dialkoxysulfurane **9** with the same substrate in which only products analogous to those derived via path a were detected.[27] The reaction of *N*-phenylpivalamide (**23,** R = *t*-Bu; R′ = Ph) also shows less selectivity when the sulfurane reagent is **2** (10% path a, 90% path b) than when it is **9** (100% of the path analogous to b).[27] Steric factors are probably determining the major products from **2,** as was suggested in amide cleavage by **9.**[27] The lower selectivity of **2** in these reactions may reflect a lower steric requirement for the ligands of **2** compared to those of **9.**

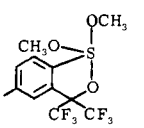


23 24

Unlike dialkoxysulfurane **9,** which reacts with methanol within seconds at −50 °C to form hexafluorocumyl methyl ether and diphenyl sulfoxide,[8b] sulfurane **2** only exchanges its alkoxy ligands with added methanol at −20 °C. Analysis by ^1H or ^{19}F NMR shows no detectable **2** remaining upon addition of 2 equiv of methanol. If the reaction mixture is kept at room temperature overnight or if the reaction is performed at room temperature, considerable further reaction, to give hexafluorocumyl methyl ether and sultine **7,** is seen. Crystallization from an ether–pentane mixture gave a 42% yield of white, air-sensitive crystals giving ^1H and ^{19}F NMR spectra and elemental analysis consistent with their being a 1:1 complex (**25a**) of dimethoxysulfurane **25** and hexafluorocumyl alcohol. Treatment with KH to remove the alcohol allowed crystallization of pure **25.** Since the ^1H and ^{19}F NMR spectra of **25a** are identical with the sum of the spectra of **25** and hexafluorocumyl alcohol, it is likely that crystal packing forces are responsible for the isolation of the complex rather than any specific strong interaction.

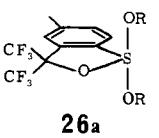


25a (42%)

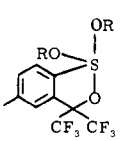


25 (16%)

Conformational Preferences and Fluxional Behavior. Since two covalent structures **26a** and **26b** satisfy both the electronegativity rules[23,24] and the restriction against diapical linkage of five-membered rings, compounds **2** and **25** present a rare opportunity to study the relative importance of steric, electronegativity, and ring-strain[24] effects in determining the conformations of sulfuranes. Table I shows that cyclic arylsulfuranes synthesized in this work and by others can be separated into two distinct classes on the basis of the chemical shift of the aromatic proton ortho to sulfur and of the trifluoromethyl groups present in the five-membered ring. The first three entries in the table show no downfield shift of the aromatic proton ortho to sulfur compared to the other aromatic protons while all the other entries do. The first three compounds also give spectra with fluorine chemical shifts at considerably lower field than those for all the other fluorine-con-



26a



26b

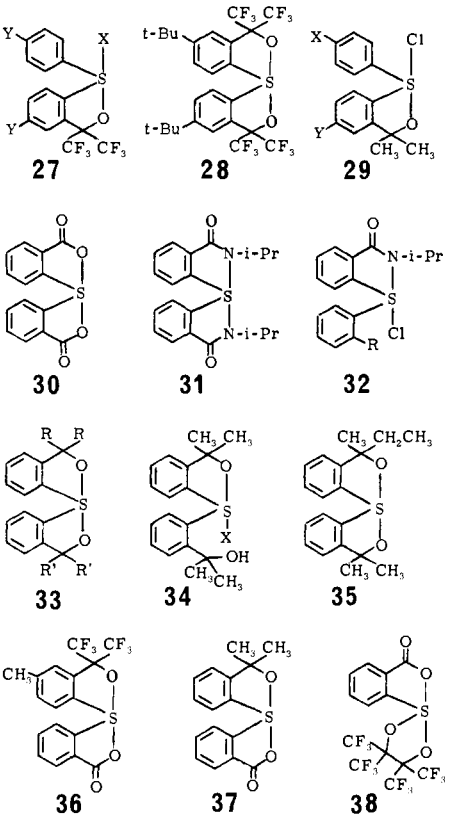
Table I. NMR Chemical Shifts of Cyclic Arylsulfuranes

Sulfurane	δ^a	ϕ^b	Fluorine multiplicity
2	~7.6[c,e]	71.4	s
26, R = $OC(CF_3)_2$-$C_6H_4C(CH_3)_3$	~7.7[d,e]	72.4	s
26, R = $OC(CF_3)_3$	~7.6[d,e]	72.9	s
10	8.24[c]	75.35	q
		76.23	q
11	8.38[c]	74.4	q
		75.5	q
12	8.43[c]	75.4	q
		75.8	q
13	7.90[c]	75.0	q
		76.4	q
25	8.22[c]	76.2	s[f]
15	8.46[c]	74.3	q
		76.7	q
27, X = OR_F; Y = *t*-Bu	8.62[g]	76.1	q
		77.3	q
27, X = OCH_3; Y = *t*-Bu	8.20[g]	76.2	q
		77.3	q
27, X = OC_6H_{11}; Y = *t*-Bu	8.21[g]	76.0	q
		77.0	q
27, X = OCH_2Ph; Y = *t*-Bu	8.15[g]	76.2	q
		77.0	q
27, X = $OC(CH_3)_3$; Y = *t*-Bu	8.34[g]	76.6	q
		77.5	q
28	8.225[g]	73.9	q
		77.0	q
27, X = Cl, Y = CH_3	9.14[h]	74.6	q
		76.4	q
29, X = Y = H	9.33[h]		
29, X = Y = CH_3	9.18[h]		
29, X = Cl; Y = H	9.34[h]		
29, X = H; Y = Cl	9.29[h]		
29, X = NO_2; Y = H	9.31[h]		
29, X = H; Y = NO_2	9.20[h]		
30	8.2[i,j]		
31	8.07[k]		
32, R = (C=O)-$NHCH(CH_3)_2$	9.66[k]		
32, R = H	9.43[k]		
33, R = R′ = CH_3	8.33[k]		
33, R = R′ = H	8.02[k]		
33, R = CH_3; R′ = CF_3	8.30[k]	73.9	q
	8.42[k]	74.8	q
34, X = Cl	8.20[k]		
34, X = Br	8.20[k]		
35	8.36[k]		
36	8.11[i]	73.9	q
	8.13[i]	76.9	q
37	8.15[i]		
38	8.57[i]		

[a] ^1H chemical shift for the doublet or multiplet assigned to the proton ortho to sulfur. [b] ^{19}F chemical shift for the $-C(CF_3)_2-$ group attached to the aromatic ring if it is present. [c] This work. [d] Reference 38. [e] The exact chemical shift and multiplicity of the aromatic proton ortho to sulfur are unknown because the other aromatic protons on the ring have similar chemical shifts. [f] Variable temperature ^1H NMR shows fast ligand exchange is occurring at room temperature. [g] Reference 8d. [h] J. C. Martin and T. M. Balthazor, *J. Am. Chem. Soc.*, in press. [i] P. Livant and J. C. Martin, *J. Am. Chem. Soc.*, in press. [j] I. Kapovits and A. Kálmán, *Chem. Commun.*, 649 (1971), report that in Me_2SO they see all the aromatic protons around δ 7.71. In $CDCl_3$ we see a four-proton multiplet from δ 7.79 to 7.83 and a four-proton multiplet from δ 8.16 to 8.22 assigned to the two protons ortho to sulfur and the two protons ortho to the carbonyl groups. [k] L. Adzima and J. C. Martin, private communication.

taining compounds. Except for **25** the other compounds are all forced to have apical-equatorial linked rings by their spiro nature or by the electronegativity rules.[23,24] It should be noted that x-ray structure determinations[22] have confirmed this for **28, 30,** and **31.**

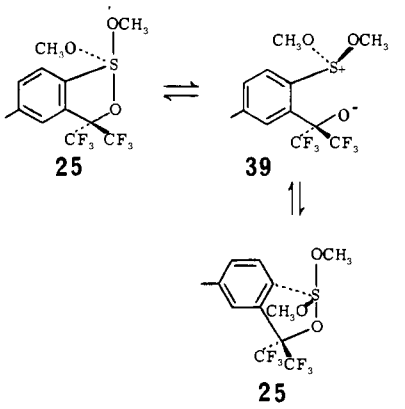
While these criteria suggest that **25** should have structure **26b,** its ^1H and ^{19}F NMR show only one sharp resonance each at room temperature for the methoxy and trifluoromethyl groups as predicted for structure **26a.** However, low temperature NMR shows that a ligand exchange process is occurring since the methoxy singlet splits into two peaks below its −68 °C coalescence temperature (at 100 MHz). From this coalescence temperature and the 7-Hz separation of the two peaks at −90 °C, a $\Delta G^{\ddagger}$ of ca. 11 kcal/mol at −68 °C can be calculated using the Gutowsky-Holm equation.[25] Scheme V shows one possible mechanism for this process involving an intermediate or transition state with "tetrahedral" geometry at sulfur (with or without the zwitterionic character shown in **39**) giving the desired equivalence of the two methoxy and trifluoromethyl groups.



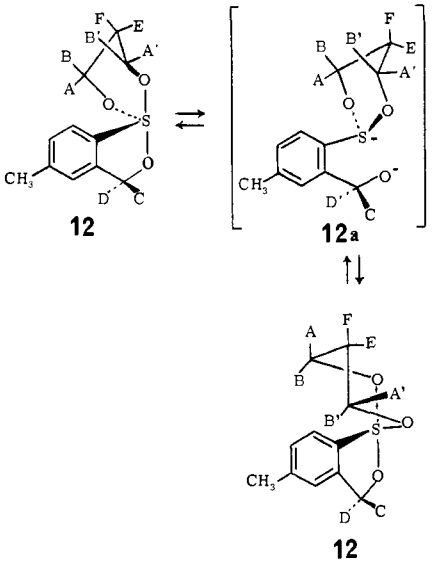
Support for the mechanism in Scheme V comes from the study of spirotrialkoxysulfuranes. The variable temperature ^1H and ^{19}F NMR spectra of **12** are compatible with the exchange mechanism shown in Scheme VI. In structure **12a** with approximately tetrahedral geometry at sulfur, trifluoromethyl groups C and D are equivalent as are protons A and A′ and also B and B′ while methyl groups E and F and protons A and B and also A′ and B′ remain distinct. Thus rapid processes involving a transition state similar to **12a** would result in the observed coalescence of four methylene doublets into two doublets and of two trifluoromethyl resonances into one singlet while not affecting methyl groups E and F.

A prediction of the mechanism shown in Schemes V and VI is that analogous spirosulfuranes with two five-membered rings (**10, 11, 13**) should render this ligand exchange much slower than **12** or **25** because of the five-membered ring effect. This destabilization of "tetrahedral" sulfur or phosphorous derivatives containing five-membered rings relative to trigonal bi-

Scheme V



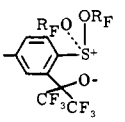
Scheme VI



pyramidal (TBP) species derived from them has been seen in phosphate esters,[24a,28] sulfates,[29] sulfites,[30] and sulfuranes.[8d] In hydrolysis of phosphate esters[24a] a five-membered ring was found to lower the activation energy for hydrolysis by 8.5 kcal/mol over the acyclic analogue while six-membered rings had little effect. Ionization reactions of alkoxysulfuranes with five-membered rings linking apical and equatorial positions have been shown[8d] to be slowed by several orders of magnitude by the action of this structural feature. As predicted, sulfuranes **10, 11,** and **13** show, by NMR spectroscopy, four different substituents on their aliphatic rings and two distinct trifluoromethyl groups on the other ring. In the case of **13,** high temperature ^{19}F NMR gave a $\Delta G^{\ddagger}$ for the process analogous to that of Scheme VI of ca. 23 kcal/mol at 163 °C, roughly 12 kcal/mol higher than $\Delta G^{\ddagger}$ for acyclic analogue **25** or six-membered ring analogue **12.** This is postulated to be yet another manifestation of the "five-membered ring effect" on sulfurane reactivity.[21]

Several formal analyses of the possible rearrangements of TBP molecules[31a] or more specifically sulfuranes[31b,32] have been published. In the notation of Musher[31] the mechanism of Scheme V or Scheme VI would be described as an M_4 mode while Dungundji, Marquarding, and Ugi[32] would call these changes of skeletal symmetry type $\bar{C}$, D, $\bar{E}$, or F. From the NMR data (equivalence of the trifluoromethyl groups of **25** and **12** at room temperature and nonequivalence of the methyl groups (E and F) of **12** at the high temperature limit) one can exclude processes that differ from Scheme VI only in not inverting the chirality of the molecule, i.e., processes exchanging the positions of attachment of the two oxygens of the six-membered ring of **12** or the two methoxy groups of **25.** These would either be called M_2 processes[31] or skeletal symmetry changes of type C, $\bar{D}$, E, or $\bar{F}$.[32] Musher notes that for systems with simple monodentate ligands the M_2 and the M_4 modes fall into the same observable process (OP_1).[33] In this system they are distinguishable. Many trifluorophosphoranes have also been seen to rearrange by this same observable process.[31b,34] The single step Berry pseudorotation[24a] or turnstyle rotation[24b] ligand exchange mechanisms favored for permutational isomerization of many phosphoranes[24] and sulfuranes,[8g,35] fall into the category of observable process OP_2.[33,34] Such "non-Berry" isomerizations have also been observed for certain pentacoordinate metal hydrides.[36]

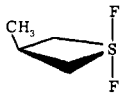
Sulfurane **2,** like **25,** shows only one type of alkoxy group and one type of ring trifluoromethyl group in its room temperature NMR spectrum. However, unlike **25,** it shows no peak broadening or splitting in the 94.1-MHz ^{19}F NMR spectrum, even at −90 °C. There is also no characteristic downfield doublet for the aromatic proton ortho to sulfur, and the ring trifluoromethyl groups occur at unusually low field in the ^{19}F NMR spectrum (see Table I). Whether **25** is at temperatures where ligand exchange is slow or fast on the NMR time scale, it shows those chemical shifts characteristic of sulfuranes containing apical-equatorial bridged aromatic rings. Thus rigid structure **26b** and similar structures equilibrating by the mechanism of Scheme V and Scheme VI can be ruled out for **2.** It should be noted that the higher electron-withdrawing ability of the fluorinated alkoxy groups of **2** relative to the methoxy groups of **25** might be expected to slow down this equilibration mechanism via a zwitterionic transition state with positive charge on sulfur, making it easier to detect by dynamic NMR methods than the exchange in **25.** Zwitterionic structure **40** is rejected, for the ground state, on the basis of the solubility



of **2** in nonpolar solvents such as CCl_4, on the basis of analogies with other sulfuranes for which x-ray structures are available,[22,37] and on the slow rate of reaction of **2** with trifluoromethanesulfonic acid.[38] It would be expected that alkoxide **40** would be very rapidly protonated by the acid, causing immediate changes in the ^{19}F NMR spectrum, but this does not happen. Thus **26a** is left as the structure best fitting the experimental data. (An x-ray structure of **2,** underway in this laboratory, should help to resolve this question.) Two sulfurane analogues of **2** having other monodentate fluoroalkoxy ligands show NMR spectra similar to that of **2**[38] (see Table I) and are also assigned structure **26a.**

The apparent preference for the diequatorial five-membered ring fusion in **2** and two other similar compounds with fluoroalkoxy ligands is at first glance surprising, in view of contrasting experience in phosphorane chemistry.[39] Although a few structures are known in which four-, five-, and six-membered rings link equatorial positions of phosphoranes,[24b,40] these are all cases in which the great difference in a icophilicities[39] pushes two fluoro or alkoxy ligands into the apical position with two less electronegative carbon ligands of the ring being forced into the diequatorial geometry. A similar difference in apicophilicity would tend to favor the observed[41] diequatorial disposition of the four-membered ring in sulfurane **41.**

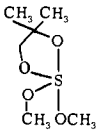
Since all three alkoxy ligands of **2** are derived from aryltrifluoromethylcarbinols, effects on the conformational equilibria from electronegativity differences must be small. The prefer-



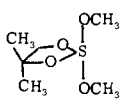
41

ence for the diequatorial linkage in sulfurane **2** can be rationalized by reference to the smaller bond angles in the equatorial plane which have been reported for sulfuranes[22,37,42] (104.4–108.1°) relative to the near 120° of the three bond angles in the equatorial plane of phosphorane analogues.[43] As expected, sulfuranes similar to **2** with apical ligands of similar electronegativity (*p-tert*-butylhexafluorocumyloxy[38]) or of greater electronegativity (perfluoro-*tert*-butoxy[38]) show the same conformation by NMR. On the other hand, less electronegative ligands such as methoxy (compound **25**) show the low-field ^{1}H NMR doublet and the nonequivalent alkoxy ligands and ring trifluoromethyl groups characteristic of structure **26b**. Thus the electronegativity rules appear to be the major factor in determining the conformations of these compounds. It can be argued that steric factors could be important since the bulk of the methoxy group is much less than that of the other three ligands that have been used. Evidence against this argument comes from a preliminary study with a bulkier aliphatic alcohol, menthol, which when treated with sulfurane **2** in CCl_4 gives a solution with a ^{1}H NMR doublet at δ 8.18 (J = 8.5 Hz) compared to the methoxy compound (**25**) doublet at δ 8.22 (J = 8.3 Hz). The similarity of these spectra supports the idea that steric bulk of the alkoxy group has little effect on the sulfurane conformation and that both sulfuranes have the apical-equatorial bridged ring (**26b**).

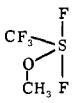
Of the methoxy sulfuranes (**27** (X = OMe; Y = C(CH_3)$_3$),[8d] **42**,[18] and **43**[44]) previously reported, the latter two



42a



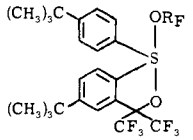
42b



43

show interesting conformational preferences. Sulfurane **43** shows two signals in its ^{19}F NMR spectrum for the apical fluorine ligands due to its methoxy substituent which appears locked (on the NMR time scale at −40 °C) in a conformation with the oxygen–carbon bond in the plane of the apical sulfur–fluorine bonds.[44,45] Sulfurane **42** shows two methyl, methoxy, and methylene signals in its ^{1}H NMR spectrum[18] showing that it adopts conformation **42a**, in which both equatorial alkoxy groups can adopt the orientation apparently favored by sulfurane **43**. Conformer **42b** would force both equatorial alkoxy groups into an orientation perpendicular to this, possibly explaining the failure of the molecule to adopt this conformation. For sulfuranes **2** and **25** the choice is between conformer **26a**, with one unfavorable equatorial alkoxy ligand orientation, and **26b** with no equatorial alkoxy group forced into the wrong geometry. Since only one unfavorable interaction is involved instead of two, other factors such as electronegativity and possibly the angle strain in the five-membered ring take precedence. A recent review[39] has analyzed these often conflicting effects of apicophilicity, ring strain, π-donor substituent orientation, and steric factors in phosphoranes.

Ligand Exchange Rates. The addition of R_FOH to an ether solution of sulfurane **2** broadens the pair of quartets seen in the 56.4-MHz ^{19}F NMR spectrum without affecting the singlet from the ring trifluoromethyl groups. At 41 °C a 3.3 M or greater concentration of R_FOH in the solution is needed to coalesce the 10-Hz coupling of the quartets. This corresponds[25] to a second-order rate constant for exchange of 7 M^{-1} s^{-1} at 41 °C which is roughly nine times slower than that of dialkoxysulfurane **44** and five orders of magnitude slower than that



44

of sulfurane **9**. This exchange probably involves a dissociative mechanism like that proposed for **9**[8a,8c] or **44**.[8d] In support of this a more acidic alcohol, perfluoro-*tert*-butyl alcohol, causes coalescence of the 10-Hz ^{19}F NMR coupling in **2** even when added in concentrations as low as 0.06 M. Most of the difference in the rate of ligand exchange between **2** and **9** is probably due to the five-membered ring effect seen in studies with sulfurane **44**.[8d] We attribute the slower exchange rate of R_FOH with **2** than with **44** to the added influence on the transition state for ionization of a destabilizing inductive effect from the equatorial alkoxy substituent.

Additional work exploring these interesting differences between sulfuranes containing two and three alkoxy groups is underway in this laboratory.

Experimental Section

Fluorine chemical shifts are reported on the ϕ scale in parts per million upfield from fluorotrichloromethane and proton and carbon chemical shifts on the δ scale in parts per million downfield from Me_4Si. Elemental analyses of new compounds are within 0.4% of theoretical values unless otherwise noted. All reactions involving sultene **1** or sulfurane **2** were done in an inert atmosphere box under nitrogen. Unless otherwise indicated the reactions were done at room temperature.

Ethyl [2-(1-Trifluoromethyl-1-hydroxy-2,2,2-trifluoroethyl)-4-methylphenylthio]acetate (5). Ethyl (4-methylphenylthio)acetate was prepared by the reaction of 4-methylthiophenol with chloroacetic acid in the presence of aqueous NaOH followed by esterification with a solution of HCl in ethanol. This ester (115.1 g, 0.547 mol) was dissolved in 1.2 L of carbon disulfide containing 30 g of aluminum chloride. Hexafluoroacetone (70 mL, 0.67 mol) was added to the solution over a 2-h period with mechanical stirring at −10 °C. An additional 1 L of carbon disulfide was added as necessary for efficient stirring. The reaction was quenched with ice and 500 mL of water and the organic layer was combined with the methylene chloride extracts of the aqueous layer (1.2 L). Upon concentration and cooling 153.1 g (74.3%) of white crystals of **5** (mp 96–98.5 °C) were obtained: ^{1}H NMR ($CDCl_3$) δ 1.21 (t, 3.0, J = 7 Hz, CH_2CH_3), 2.39 (s, 3.0, $ArCH_3$), 3.68 (s, 2.02, $-SCH_2-$), 4.16 (q, 1.9, J = 7 Hz, CH_2CH_3), 7.25 (d, 1.0, J = 8 Hz), 7.54 (d, 1, J = 8 Hz), 7.59 (s, 1, H ortho to the fluoroalkyl group), 8.16 (s, 1.1, OH); ^{19}F NMR (CH_2Cl_2) ϕ 74.4 (s); mass spectrum (70 eV) m/e (rel intensity) 376 (100, $M^{+}\cdot$), 303 (87.0), 288 (13.4), 285 (37.9), 273 (39.3), 219 (48.4); IR (CCl_4) 3320 (s), 3025 (m), 1740 cm^{-1} (s). Anal. ($C_{12}H_{10}F_6O_3S$) C, H.

When the reaction was done at 40 °C, small amounts of the product resulting from hexafluoroacetone substitution meta to the thioalkyl group could be isolated by mechanically separating the larger orange crystals (mp 75–78 °C). ^{1}H NMR ($CDCl_3$) δ 1.21 (t, 3, J = 7 Hz), 2.41 (s, 3.0, $ArCH_3$), 3.69 (s, 2.1, $-SCH_2-$), 3.80 (s, 1.0, OH), 4.20 (q, 2.1, J = 7 Hz), 7.36 and 7.50 (AB pattern, 1.8, J_{AB} = 9 Hz), 7.51 (s, 1, proton ortho to fluoroalkyl group); ^{19}F NMR (CCl_4) ϕ 75.8 (s); mass spectrum (70 eV) m/e (rel intensity) 376 (100, $M^{+}\cdot$), 330 (23.7), 303 (71.1), 289 (17.9), 285 (40.4), 233 (85.1); IR (CCl_4) 3660 (s), 3050 (s), 1740 cm^{-1} (s).

[2-(1-Trifluoromethyl-1-hydroxy-2,2,2-trifluoroethyl)-4-methylphenylthio]acetic Acid (45). Ester **5** (136.95 g, 0.364 mol) was boiled for 2 h with 1 L of water containing 54 g (0.8 mol) of KOH. The addition of 85 mL of concentrated HCl precipitated acid **45** as a white powder which after air drying overnight weighed 133.0 g (105% apparent yield): mp 128–132 °C; ^{1}H NMR ($CDCl_3$) δ 7.86 (s, 1.9, OH), 7.62 (s, 1.0, H ortho to the fluoroalkyl group), 7.56 and 7.23 (AB pattern, 2.0, J_{AB} = 9 Hz), 3.65 (s, 1.9, CH_2), 2.38 (s, 3.0, CH_3).

2-(1-Trifluoromethyl-1-hydroxy-2,2,2-trifluoroethyl)-4-methylphenylthiol (3). Method A. We used a method similar to that of Walker

and Leib.[12] H_2O_2 (30%, 80 mL) was added over a 2-h period to a solution of acid **45** (131.0 g, 0.376 mol) in 1300 mL of H_2O and 150 mL of concentrated H_2SO_4 while continuously passing steam through the reaction mixture. Zinc dust was added in small portions (100 g total) toward the end of the steam distillation to reduce any disulfide. The distillate was filtered to give 76.1 g of light yellow solids. Recrystallization from ether–pentane gave 60.67 g (55.6%) of white crystals of **3** (mp 91–94.5 °C): ^{1}H NMR (CCl_4) δ 7.45 (s, 1.1, ortho to fluoroalkyl group), 7.11 and 7.37 (AB pattern, 1.9, J_{AB} = 8 Hz), 6.33 (s, 0.9, OH), 3.68 (s, 0.9, SH), 2.38 (s, 3.1, CH_3); ^{19}F NMR (CCl_4) ϕ 74.8 (s); mass spectrum (70 eV) *m/e* (rel intensity) 290 (100, $M^{+\cdot}$), 272 (32.6), 221 (80.3, M − CF_3), 151 (99.9, $ArCO^+$), 124 (86.3); IR (CCl_4) 3580 (w), 3320 (m), 3040 (w), 2930 (w), 2564 (w), 1604 (w), 1567 (w), 1404 (m), 1130–1260 (s), 968 (s), 953 cm^{-1} (s). Anal. ($C_{10}H_8F_6OS$) C, H.

Method B. *p*-Toluidine (500.1 g, 4.67 mol) and *p*-toluenesulfonic acid (11.5 g) were dissolved in 450 mL of chlorobenzene and heated to 145 °C in a three-neck flask equipped with a dry ice cooled condenser.[13] Hexafluoroacetone (727 g, 4.38 mol) was distilled into the stirring reaction mixture over a 5-h period. Solvent was removed under vacuum (100 °C, 20 Torr) and the resulting tan solid was recrystallized from ether to yield 958.8 g (80.1%) of fine white crystals of **6**, mp 111–112 °C (lit.[13] 109–110 °C).

The next step is based on a literature procedure for converting aromatic amines to thiols.[14] In a typical preparation 200 g (0.733 mol) of amine **6** was boiled for 1 h with 350 mL of H_2O and 155 mL of concentrated HCl. The mixture was cooled to 3 °C and a cold solution of 60.4 g (0.875 mol) of $NaNO_2$ in 125 mL of H_2O was added over a 1-h period with stirring. After 30 min at 3 °C, this solution was added over a 1.5-h period to a stirred solution of 143 g (0.892 mol) of potassium ethyl xanthate in 180 mL of H_2O at 45 °C. After 30 min at 45 °C, the mixture was extracted with ca. 300 mL of ether to give a deep red solution from which the ether was removed under vacuum. To the residue, dissolved in 473 mL of boiling ethanol, was added 175 g (3.1 mol) of KOH in small portions. After 1 h, the ethanol was removed under vacuum and replaced by 500 mL of H_2O and 100 mL of concentrated H_2SO_4. Zinc dust (5 g) was added and the mixture was steam distilled. Ether extraction of the distillate followed by recrystallization from ether–pentane yielded 92.9–117.6 g (42–55%) of **3** (mp 93–97 °C).

5-Methyl-3,3-bis(trifluoromethyl)-3*H*-2,1-benzoxathiole (1), Sultene 1. To thiol alcohol **3** (21.03 g, 72.5 mmol) suspended in 150 mL of CCl_4 at 0 °C was added bromine (3.71 mL, 72.4 mmol), then pyridine (11.7 mL, 145 mmol), with stirring over a 5-min period. Since the ^{1}H NMR spectrum of the reaction mixture contained two benzylic methyl peaks around δ 2.4, an additional 0.58 mL (11.3 mmol) of Br_2 was added to bring about the disappearance of the minor upfield peak. The mixture was filtered under nitrogen to give a clear yellow solution from which 19.8 g (95%) of yellow crystals (mp 46–49 °C) was obtained by removal of the solvent under vacuum. Recrystallization from pentane gave analytically pure sultene **1** (mp 49–50.5 °C): ^{1}H NMR (CCl_4) δ 2.41 (s, 3, CH_3), 6.98 and 7.31 (AB pattern, 2, J_{AB} = 8 Hz), 7.25 (broad s, 1, H ortho to fluoroalkyl group); ^{19}F NMR (CCl_4) ϕ 76.6 (d, J_{HF} = 1 Hz); mass spectrum (70 eV) *m/e* (rel intensity) 288 (51.9, $M^{+\cdot}$), 219 (100, M − CF_3), 150 (52.8), 121 (30.4); ultraviolet (hexane) 255 nm (ϵ 11 000), 300 (1500), 383 (70). The 383-nm peak gave a four-point Beer's law plot with concentrations from zero to 0.0156 M and a correlation coefficient of 0.9997. Anal. ($C_{10}H_6F_6OS$) C, H.

5-Methyl-3,3-bis(trifluoromethyl)-3*H*-2,1-benzoxathiole 1-Oxide (7). To thiol alcohol **3** (1.007 g, 3.47 mmol) suspended in 25 mL of CCl_4 was added *tert*-butyl hypochlorite (1.00 mL, 8.82 mmol) with stirring at room temperature. Solvent was removed under vacuum from the warm solution giving a colorless oil which crystallized upon addition of cold pentane to give sultine **7** as white crystals (0.647 g, 61%): mp 64–65 °C; ^{1}H NMR ($CDCl_3$) δ 2.56 (s, 3, CH_3), 7.58 (broad s, 1, H ortho to fluoroalkyl group), 7.62 and 7.80 (AB pattern, 2, J_{AB} = 8 Hz); ^{19}F NMR ($CDCl_3$) 2 quartets ϕ 75.2 and 76.05, J = 9 Hz; mass spectrum (70 eV) *m/e* (rel intensity) 304 (100, $M^{+\cdot}$), 288 (1.36, M − O), 256 (2.67, M − SO), 240 (13.0, M − SO_2), 237 (58.3), 235 (31.8, M − CF_3), 166 (74.1); IR ($CHCl_3$) 3042 (w), 2938 (w), 1600 (m), 1311 (s), 1279 (s), 1242 (s), 1177 (s), 1063 (s), 979 cm^{-1} (s). Anal. ($C_{10}H_6F_6O_2S$) C, H.

Reaction of Sultene 1 with H_2O. It was noticed that crystals of **1** upon a few minutes exposure to air decomposed to an oil which gave ^{1}H and ^{19}F NMR spectra containing new peaks. To show that this was due to the reaction of **1** with water vapor, some water was added to a CCl_4 solution of the sultene in an NMR tube. After a few hours the solution had lost its yellow color and its ^{1}H NMR spectrum no longer contained the sultene singlet at δ 2.41 but instead had singlets at 2.37 (area 2) and 2.57 (area 1). The ^{19}F NMR spectrum showed quartets at ϕ 75.3 and 76.1 (area 1 each) and a singlet at ϕ 74.2 (area 4). The ^{19}F quartet and the low-field ^{1}H singlet are identical with those of authentic sulfinate **7**. The other product has been identified as disulfide **8**.[15]

Reaction of Sultene 1 with *tert*-Butyl Perbenzoate. Sultene **1** (60 mg, 0.21 mmol) and *tert*-butyl perbenzoate (50 mg, 0.26 mmol) were dissolved in CCl_4 in an NMR tube. No evidence of any rapid reaction was seen in the ^{1}H or ^{19}F NMR. After 5 days at room temperature, the ^{1}H NMR showed that 79% of the sultene had been oxidized to sultine **7**, with 48% of isobutylene and other products.

1,1-Bis(1-trifluoromethyl - 1 - phenyl-2,2,2-trifluoroethanolato)-5-methyl-3,3-bis(trifluoromethyl)-3*H*-2,1-benzoxathiole (2). To a stirred solution of sultene **1** (26 g, 90 mmol) and the potassium salt of hexafluorocumyl alcohol[46] (R_FOK) (50 g, 177 mmol) in 500 mL of dry CCl_4 was added 4.5 mL of Br_2 (88 mmol) over a 20-min period. Filtration under a dry nitrogen atmosphere followed by solvent removal (50 °C, 0.05 Torr) gave white crystals and some reddish impurities. Recrystallization from ether–pentane gave 29.9 g (44%) of white crystals mp 138.5–140 °C. An analytical sample (mp 140.5–141 °C) showed ^{1}H NMR (CCl_4) δ 2.63 (s, 3, CH_3), 7.28 (broad, s, 10, hexafluorocumyl groups), 7.61 (broad s, 3, trisubstituted ring); ^{19}F NMR (CCl_4) ϕ 70.1 and 72.7 (broad q, 6 each), 71.4 (broad s, 6, ring CF_3); mass spectrum (70 eV) *m/e* (rel intensity) 705 (0.02, M − CF_3), 697 (0.01, M − Ph), 531 (15.5, M − OR_F), 227 (100, $PhC(CF_3)_2^+$); field ionization mass spectrum *m/e* (rel intensity) 774 (0.1, $M^{+\cdot}$), 551 (0.2), 532 (100, M + H − OR_F). Anal. Calcd for $C_{28}F_{18}H_{16}SO_3$: C, 43.42; H, 2.08. Found: C, 42.75; H, 2.26 (the analysis was difficult because of the extreme water sensitivity of **2**).

Low temperature 94.1-MHz ^{19}F NMR studies of sulfurane **2** were carried out in 1:1 ether–THF solution. As the temperature was lowered to −95 °C, no change was seen in the ϕ 71.8 singlet except for a steady drift to lower field and no change was seen in the pair of quartets except for chemical shift changes and a slight broadening of the quartet structure. High temperature 56.4-MHz ^{19}F NMR studies of sulfurane **2** in diphenyl ether at temperatures up to 171 °C showed no significant changes except for a broadening of the two quartets and the R_FOH impurity singlet from ligand exchange.

Exchange of Sulfurane 2 and R_FOH. Sulfurane **2** (10 mg, 0.013 mmol) was added to 400 μL of ether. No appreciable broadening of the sulfurane ^{19}F quartets at ϕ 70.8 and 72.8 was visible until 100 μL of R_FOH was added. The addition of 400 μL of R_FOH (3.3 M R_FOH, 0.016 M **2**) was necessary to coalesce the 10-Hz coupling of the sulfurane quartets in the ^{19}F NMR at 41 °C. An additional 240 μL of R_FOH caused the former quartets to broaden extensively while the large R_FOH singlet broadened slightly to a width at half-height of 5 Hz. The sulfurane singlet at ϕ 71.7 remained unchanged.

Exchange of Sulfurane 2 and Perfluoro-*tert*-butyl Alcohol. Sulfurane **2** (10 mg, 0.013 mmol) was added to 400 μL of CCl_4. The addition of 3.6 μL of perfluoro-*tert*-butyl alcohol was necessary to cause coalescence of the 10-Hz coupling of the sulfurane quartet in the ^{19}F NMR at 41 °C in this solution (0.032 M sulfurane, 0.06 M alcohol). The sulfurane singlet at ϕ 72.4 and the alcohol singlet at 73.3 showed no broadening.

Reactions of Sulfurane 2. A. *tert*-Butyl Alcohol. To a suspension of sulfurane **2** in CCl_4 was added 1 equiv of *tert*-butyl alcohol. The reaction mixture immediately became homogeneous giving ^{1}H NMR peaks due to sulfinate **7** (s, δ 2.54) and isobutylene (m, δ 1.7 and 4.6). Using the integral of the aromatic region as an internal standard, the yields of these products were 97 and 75%, respectively. Hydrolysis of the sulfurane by adventitious water is presumably responsible for the lower yield of isobutylene.

B. Water. The addition of 3 μL of water to a suspension of sulfurane **2** in CCl_4 in an NMR tube produced a rapid reaction giving products whose ^{1}H and ^{19}F NMR spectra were identical with those of an authentic mixture of sulfinate **7** and R_FOH.

C. *tert*-Amyl Alcohol. To 260 mg (0.34 mmol) of sulfurane **2** suspended in CCl_4 was added 30 μL (0.28 mmol) of *tert*-amyl alcohol. Upon shaking the mixture immediately became homogeneous giving a ^{1}H NMR spectrum with peaks due to the following products (yields are figured using the total aromatic integral as an internal standard): sulfinate **7** (97%), 2-methyl-1-butene (61%), and 2-methyl-2-butene

(23%). ^{19}F NMR showed the expected overlapping peaks from **7** and R_FOH.

D. 2,3-Dimethyl-2,3-butanediol. To 1.14 g (1.54 mmol) of sulfurane **2** suspended in CCl_4 was added 0.189 g (1.60 mmol) of 2,3-dimethyl-2,3-butanediol. After a few minutes of stirring, ^1H and ^{19}F NMR showed that the now homogenous solution no longer contained **2.** Solvent and R_FOH were removed by heating the solution to 70 °C under a pressure of 0.1 Torr. The resulting white solid was recrystallized from ether–pentane yielding 0.39 g (63%) of sulfurane **10** as white crystals (mp 108–109.5 °C): ^1H NMR (CCl_4) δ 1.01 (s, 3.0, CH_3), 1.18 (s, 3.1, CH_3), 1.36 (s, 6.3, CH_3), 2.53 (s, 2.7, $ArCH_3$), 7.42 (d, 1.0, proton para to fluoralkyl group, J = 8.5 Hz), 7.51 (br s, 0.9, proton ortho to fluoroalkyl group), 8.24 (d, 1.0, proton ortho to sulfur, J = 8.5 Hz); ^1H NMR (C_6D_6) δ 0.78 (s, 2.8, CH_3), 0.86 (s, 2.8, CH_3), 0.98 (s, 2.8, CH_3), 1.07 (s, 3.1, CH_3), 1.86 (s, 3.3, $ArCH_3$), 6.87 (broad d, 1.0, H para to fluoroalkyl group, J = 8 Hz), 7.6 (broad s, 1.0, H ortho to fluoroalkyl group), 8.13 (d, 1.1, J = 8 Hz, H ortho to S); ^{19}F NMR (CCl_4) ϕ 75.35 (q, J = 9 Hz), 76.23 (q, J = 9 Hz); mass spectrum (70 eV) *m/e* (rel intensity) 405 (0.3, M + H), 389 (2.06, M − CH_3), 335 (1.95, M − CF_3), 305 (35.4), 288 (90.3), 219 (100); field desorption mass spectrum *m/e* (rel intensity) 404 (4.1, $M^{+}\cdot$), 389 (1.7, M − CH_3), 304 (100, M − $C_6H_{12}O$), 288 (16, M − $C_6H_{12}O_2$), 100 (77, $C_6H_{12}O$), 78 (10), 58 (17, C_3H_6O). Anal. ($C_{16}H_{18}F_6O_3S$) C, H.

The addition of water to a CCl_4 solution of **10** converted it to a mixture of 2,3-dimethyl-2,3-butanediol and sultine **7** in about 30 min (by ^1H NMR).

Pyrolysis of Spirosulfurane 10. A solution of crude spirosulfurane **10,** formed by adding 1 equiv of 2,3-dimethyl-2,3-butanediol to a suspension of sulfurane **2** in CCl_4, was sealed in 4-mm glass tubing and refluxed in a 195 °C oil bath for 10 min. Analysis of the solution by ^1H NMR showed that the peaks due to **10** had been replaced by singlets at δ 1.12 (9.0 H) and 2.09 (3.1 H) due to the formation of pinacolone. The presence of sulfinate **7** was shown by a singlet at δ 2.53 (3 H) and by ^{19}F NMR quartets at ϕ 74.8 and 75.6 (J = 9 Hz).

Reaction of Sulfurane 2 with Ethylene Glycol to Give 13. To a suspension of 3.00 g (3.87 mmol) of **2** in 50 mL of CCl_4 was added 0.240 g (3.87 mmol) of ethylene glycol. After stirring for a few minutes the clear solution was evaporated to dryness at 60 °C (0.1 Torr). Recrystallization of the residue from ether–pentane gave 0.99 g (74%) of spirosulfurane **13** as white crystals (mp 95.5–98 °C): ^1H NMR (CCl_4) δ 2.54 (s, 3.0, CH_3), 3.8–4.1 (m, 3.0, 3 of the CH_2 protons), 4.31 (t of d, 1.1, J_{AB} = 1.5, J_{AC} = J_{AD} = 6.5 Hz, 1 CH_2 proton), 7.46 (d, 1.0, J = 8 Hz, H para to the fluoroalkyl group), 7.56 (broad s, 0.9, proton ortho to the fluoroalkyl group), 7.90 (d, 1.0, J = 8 Hz, proton ortho to S); ^{19}F NMR (CCl_4) ϕ 75.0 (q, J = 9 Hz), 76.4 (q, J = 9 Hz); mass spectrum (10 eV) *m/e* (rel intensity) 348 (0.86, $M^{+}\cdot$), 347 (2.5, M − H), 304 (2.3, M − C_2H_4O), 288 (100, M − $C_2H_4O_2$), 279 (37.7, M − CF_3), 219 (14.2). Anal. ($C_{12}H_{10}F_6O_3S$) C, H.

Hydrolysis of Sulfurane 13. To a solution of sulfurane **13** in CCl_4 was added a drop of water. The complex methylene peaks in the ^1H NMR were slowly replaced by a singlet due to ethylene glycol at δ 3.65. The δ 7.90 doublet slowly diminished in intensity as did the δ 2.53 singlet which was replaced by one at δ 2.57 due to sultine **7.** NMR integration showed that about 40% of the sulfurane was gone after 30 min at 40 °C.

Pyrolysis of Spirosulfurane 13. A solution of crude spirosulfurane **13,** formed by the addition of 1 equiv of ethylene glycol to a suspension of sulfurane **2** in CCl_4, was sealed in 4-mm glass tubing and heated to 245 °C until the methylene peaks of **13** had disappeared from the ^1H NMR spectrum (20 min). Two singlets were present in the aromatic methyl region at δ 2.6 (area 7, sultine **7**) and 2.45 (area 3, sultene **1**). These assignments were confirmed by the ^{19}F NMR which showed sultine quartets of relative area 7 at ϕ 75.2 and 76.1 (J = 9 Hz) and a sultene doublet at 76.4 (area 3, J_{HF} = 1 Hz). No peaks for sultone 19 at ϕ 75.3 were detectable. The only other assignable peaks present in the ^1H NMR spectrum were a doublet at δ 2.12 and a quartet at δ 9.70 (J = 2.9 Hz) due to acetaldehyde. Integration of the methyl doublet showed that it was about 6% as intense as the sum of the two aromatic methyl peaks.

High Temperature ^{19}F NMR Studies of 13. At 26 °C a solution of spirosulfurane **13** in $(CD_3)_2SO$ showed a pair of quartets in its 56.26-MHz ^{19}F NMR spectrum at ϕ 73.7 and 75.0 (J = 9 Hz). At 163 °C the 9 Hz fine structure coalesced and the remaining two peaks began to broaden. Useful spectra could not be obtained at higher temperatures because of extensive sample decomposition.

5-Methyl-3,3-bis(trifluoromethyl)-3*H*-2,1-benzoxathiole 1,1-Dioxide (19). To a solution thiol alcohol **3** (1.443 g, 4.97 mmol) in CCl_4 at 0 °C was added a CCl_4 solution of ruthenium tetroxide[47] until the yellow color remained. Filtration of the mixture to remove RuO_2 and removal of the solvent and excess RuO_4 under vacuum followed by sublimation of the resulting solid at 70 °C and 0.1 Torr gave sultone **19** as a white powder (0.573 g, 36%): mp 67–69.5 °C; ^1H NMR (CCl_4) δ 2.60 (s, 3.0, CH_3), 7.53 (broad s, 0.9, H ortho to the fluoroalkyl group), 7.66 and 7.75 (AB pattern, 2.1, J_{AB} = 8.0 Hz); ^{19}F NMR (CCl_4) ϕ 75.3 (d, J_{HF} = 1.3 Hz); mass spectrum (10 eV) *m/e* (rel intensity) 320 (94.1, $M^{+}\cdot$), 251 (100, M − CF_3), 201 (24.7, M − C_2F_5), 137 (15.1, M − $C_2F_5SO_2$); IR ($CHCl_3$) 3055 (w), 1603 (m), 1386 (s), 1314 (s), 1280 (s), 1247 (s), 1170 (s), 1081 (s), 978 cm^{-1} (s). Anal. ($C_{10}H_6F_6O_3S$) C, H.

Reaction of Sulfurane 2 with Perfluoropinacol. A solution of crude spirosulfurane **11** was formed by the addition of 1 equiv of perfluoropinacol[8g] to a suspension of **2** in CCl_4. The ^1H NMR spectrum of the clear solution showed a doublet at δ 8.38 (H ortho to S in **11**, J = 9 Hz), a singlet at 2.61 ($ArCH_3$ of **11**), a broad singlet at 3.37 (OH of R_FOH by-product), and an unresolved multiplet at 7.1–7.9 (aromatic protons). The ^{19}F NMR spectrum showed very broad peaks due to the perfluoropinacol ring of **11** at ϕ 66 (3 F) and 67.5 (9 F), multiplets from the two CF_3 groups on the other ring at 74.4 and 75.5, and an R_FOH singlet at 75.5. The addition of 2 μL of H_2O to the NMR tube had no immediate effect on the spectrum.

The CCl_4 solution of spirosulfurane **11** was sealed in 4-mm glass tubing and heated to 200 °C for 10 min. The solution turned bright yellow and its ^{19}F NMR spectrum now showed overlapping singlets at ϕ 76.2 (hexafluoroacetone) and 76.3 (R_FOH) and a doublet at 76.6 (J = 1 Hz, sultene **1**). No peaks for $(CF_3)_2C{=}C(CF_3)_2$ (ϕ 61.9[8g]) or its epoxide (66.5[8g]) were seen.

More Reactions of Sulfurane 2. A. 2,2-Dimethyl-1,3-propanediol. To a suspension of sulfurane **2** (2.13 g, 2.75 mmol) in CCl_4 was added 0.30 g (2.9 mmol) of 2,2-dimethyl-1,3-propanediol. After stirring for a few minutes the clear solution was evaporated to dryness at 70 °C (0.1 Torr). Recrystallization of the residue from ether–pentane gave 0.48 g (45%) of spirosulfurane **12** as a fine white powder (mp 107–108.5 °C): ^1H NMR (CD_2Cl_2, 28 °C) δ 0.92 (s, 3.2, CH_3), 1.12 (s, 2.9, CH_3), 2.51 (s, 2.9, $ArCH_3$), 3.86 (d of m, 2.0, CH_2, J = 11.8 Hz), 4.16 (d, 1.9, CH_2, J = 11.4 Hz),[48] 7.50 (d of m, H para to the fluoroalkyl group, J = 8.1 Hz), and 7.59 (m, H ortho to the fluoroalkyl group) corresponding to 2.2 protons total, 8.43 (d, 0.9, H ortho to S, J = 8.1 Hz). At −95 °C the 4.16 doublet had split into two doublets at δ 4.46 (J = 11.5 Hz) and 4.25 (J = 12.2 Hz) while the δ 3.86 doublet became two small peaks at δ 4.08 and 3.88 and a peak roughly twice as large at δ 3.99. The downfield pair of doublets went through coalescence at about −55 °C (100 MHz). ^{19}F NMR ($CDCl_2$, 26 °C) ϕ 76.0 (d, J_{HF} = 1.3 Hz). Upon cooling the spectrum went through coalescence at −74 °C (56.26 MHz) becoming, at −95 °C, a pair of quartets (highly distorted toward an A_3B_3 pattern) at ϕ 75.4 and 75.8. Mass spectrum (70 eV) *m/e* (rel intensity) 391 (0.2, M + H), 390 (0.004, $M^{+}\cdot$), 371 (0.37, M − F), 360 (0.13), 321 (1.41, M − CF_3), 305 (100, M − C_5H_9O), 304 (6.3, M − $C_5H_{10}O$), 288 (4.0, M − $C_5H_{10}O_2$), 219 (21.7, M − $C_5H_{10}O_2CF_3$), 56 (36.9, C_4H_8), 41 (10.2, C_3H_5). Anal. ($C_{12}H_{12}F_6O_3S$) C, H.

A solution of sulfurane **12** in CCl_4 took 8 min to hydrolyze completely (by ^1H NMR) to sultine **7** and 2,2-dimethyl-1,3-propanediol when a drop of water was added.

B. Oxalic Acid. To a suspension of sulfurane **2** in $CDCl_3$ was added dropwise a solution of oxalic acid in $CDCl_3$ until all **2** was gone (by NMR). The ^1H NMR spectrum showed a singlet at δ 2.54 ($ArCH_3$ of sultine **7**), a singlet at 3.3 (R_FOH), and aromatic peaks from 7.2 to 7.8. ^{19}F NMR ϕ 71.0 (s, $(COOR_F)_2$), 75.2 (q, J = 8 Hz, **7**) 76.2 (q, J = 8 Hz, **7**), 76.2 (s, R_FOH).

C. Tropolone. To a suspension of **2** in CCl_4 was added a solution containing 1 equiv of tropolone. The resulting orange solution's ^1H NMR spectrum showed two overlapping singlets at δ 2.48 and 2.50 (3.1, $ArCH_3$ of **7** and spirosulfurane **15**), 5.1 (s, 1.8, R_FOH), 6.3–7.8 (m, 16.5), 8.46 (d, 0.6, J = 8.5 Hz, proton ortho to sulfur of **15**); ^{19}F NMR ϕ 70.0 (s, 1.2, ether **16**), 74.3 (q, 1.4, J = 9 Hz, **15**), 75.3 (q, 1.2, J = 9 Hz, **7**), 75.9 (s, 11.5, R_FOH and R_FO^-), 76.0 (q, 1.2, J = 9 Hz, **7**), 76.7 (q, 1.4, J = 9 Hz, **15**).

D. Benzoin. To a suspension of sulfurane **2** in $CDCl_3$ was added 1 equiv of benzoin in $CDCl_3$. The solution immediately turned yellow and gave a simple ^{19}F NMR spectrum, ϕ 76.0 (s, 12, R_FOH), 76.2 (d, 6, J_{HF} = 1 Hz, sultene **1**). ^1H NMR δ 2.41 (s, 3.0, $ArCH_3$ of **1**),

3.5 (s, 1.7, R_FOH), 6.9–8.1 (m, 22.9). The ^1H NMR spectrum from δ 6.9 to 7.1 and from δ 7.9 to 8.1 was identical with that of an authentic sample of benzil.

E. Catechol. A $CDCl_3$ solution containing 1 equiv of catechol was added to a $CDCl_3$ suspension of **2** resulting in the immediate formation of a dark yellow solution: ^{19}F NMR ϕ 76.0 (s, 12.4, R_FOH), 76.2 (d, 5.6, J_{HF} = 1 Hz, sultene **1**); ^1H NMR δ 2.43 (s, 3.2, $ArCH_3$ of **1**), 3.5 (s, 1.8, R_FOH), 6.4 and 7.0 (m, 3.7, *o*-benzoquinone), 7.2–7.9 (m, 13.5, aromatic protons of **1** and R_FOH). Upon standing the solution deposited large amounts of a dark solid (decomposition products of *o*-benzoquinone).

F. Benzylamine. To a suspension of **2** in CCl_4 was added 1 equiv of benzylamine forming a homogeneous solution containing sulfinimidate **20** and R_FOH: ^1H NMR (CCl_4) δ 2.55 (s, 3.0, $ArCH_3$ of **20**), 3.7 (s, 1.8, R_FOH), 3.9 (m, 1.8, CH_2 of **20**), 7.1–7.8 (m, 18.4, aromatic H of 20 and R_FOH); ^{19}F NMR (CCl_4) ϕ 74.1 and 75.7 (quartets from **20**, J = 9 Hz), 75.5 (s, R_FOH).

G. Isopropylamine. One equivalent of isopropylamine was added to a CCl_4 suspension of sulfurane **2.** The resulting clear solution of sulfinimidate **21** and R_FOH gave a ^1H NMR spectrum: δ 1.04 and 1.08 (two broad doublets, 6.6, J = 6 Hz, $CH(CH_3)_2$ of **21**), 2.55 (s, 2.9, $ArCH_3$ of **21**), 3.0 (broad m, 1.1, $CH(CH_3)_2$ of **21**), 4.2 (broad s, 1.8, R_FOH), 7.2–7.9 (m, 12.6, aromatic H of **21** and R_FOH); ^{19}F NMR (CCl_4) ϕ 74.3 and 75.7 (quartets from **21**, J = 9 Hz), 74.8 (s, R_FOH and R_FO^-).

H. Ethylenediamine. To a CCl_4 suspension of **2** in an NMR tube, ethylenediamine was added dropwise until the solution was homogeneous and no **2** was detectable by NMR. ^1H NMR (CCl_4) δ 2.50 (s, 6.0, $ArCH_3$ of **22**), 2.87 (broad s, 3.5, CH_2 of **22**), 4.38 (s, 4.2, R_FOH), 7.3–7.9 (m, 26.4, aromatic H of **22** and R_FOH); ^{19}F NMR (CCl_4) ϕ 75.3 (q, J = 8.5 Hz, **22**), 76.2 (s, R_FOH), 76.7 (8, J = 8.5 Hz, **22**).

I. *N*-Methylbenzamide. To a suspension of sulfurane **2** in $CDCl_3$ was added a solution containing 2 equiv of *N*-methylbenzamide in $CDCl_3$. Sulfurane **2** took several minutes to disappear from the ^{19}F NMR being replaced by singlets at ϕ 69.7 and 70.5 (4:96 ratio of areas) due to $CH_3N{=}C(OR_F)Ph$ and $PhCO_2R_F$ (lit. ϕ 70.4[27]). Also formed was a singlet at 75.6 (R_FOH) and quartets at 74.7 and 76.2 (J = 9 Hz) from the other product, *N*-methyl sulfinimidate **24** (R' = CH_3). The ^1H NMR showed a singlet at δ 2.52 due to the aromatic methyl group of **24** and a broad singlet at δ 2.58 of roughly equal area due to the NCH_3 of **24.**

J. 2,2-Dimethyl-*N*-phenylpropanamide. To a suspension of **2** in $CDCl_3$ was added a solution of 1 equiv of *N*-phenyl-2,2-dimethylpropionamide in $CDCl_3$. The ^{19}F NMR spectrum of **2** in the resulting solution was reduced by half after 10 min and undetectable after 90 min, being replaced by singlets at ϕ 69.5 and 70.7 (90:10 ratio of areas) due to $PhN{=}C(OR_F)C(CH_3)_3$ and $(CH_3)_3CCO_2R_F$ (lit. ϕ 70.1[27]), respectively. An authentic sample of each of these two substances[27] added to the reaction mixture increased the NMR peak assigned to it. Also present were quartets at ϕ 75.0 and 75.9 (J = 9 Hz) due to sultine **7** and an R_FOH singlet at 75.8.

1,1-Bis(methanolato)-5-methyl-3,3-bis(trifluoromethyl)-3*H*-2,1-benzoxathiole (25). To a stirred suspension of sulfurane **2** (2.40 g, 3.10 mmol) in CCl_4 at −20 °C was added 0.25 mL (6.2 mmol) of CH_3OH. NMR analysis of the crude reaction product showed no traces of the hexafluorocumyl methyl ether by-product formed at higher temperatures, which could easily have been detected by its CH_3 septet at δ 3.48 (lit.[8b] 3.54) and its CF_3 multiplet at ϕ 71.3 (lit.[8b] 70.5). After the homogeneous solution was allowed to stir for 30 min, solvent and some of the hexafluorocumyl alcohol by-product were removed at 0.1 Torr and 25 °C. Recrystallization from ether–pentane gave 0.77 g (42%) of white crystals, mp 68–70 °C, shown by NMR and elemental analysis to be a 1:1 complex of dimethoxysulfurane **25** and hexafluorocumyl alcohol. ^1H NMR ($CDCl_3$) δ 2.52 (s, 3.0, $ArCH_3$), 3.77 (s, 6.0, OMe), 4.1 (broad s, 0.9, OH), 7.45 (m, 3.8, H para to the fluoroalkyl group in **25** and H meta para to the fluoroalkyl group of R_FOH), 7.60 (broad s, 1.1, H ortho to the fluoroalkyl group in the sulfurane), 7.74 (m, 2.1, H ortho to the fluoroalkyl group of the alcohol), 8.20 (d, 1.0, J = 8.2 Hz, H ortho to S in **25**); ^{19}F NMR ($CDCl_3$) ϕ 75.9 (s, 6.0, R_FOH), 76.4 (d, J_{HF} = 1.3 Hz, 6.0, **25**). Anal. ($C_{21}H_{18}F_{12}O_4S$) C, H.

To 0.65 g (1.1 mmol) of the sulfurane–alcohol complex in ether was added 0.10 g (2.5 mmol) of KH slowly with stirring. After 1 h the mixture was filtered, pentane was added to the filtrate, and 60 mg (16%) of white crystals of **25** (mp 74–76 °C) were isolated at −20 °C: ^1H NMR (CD_2Cl_2, 28 °C) δ 2.50 (s, 2.9, $ArCH_3$), 3.74 (s, 6.1, OCH_3), 7.47 (d of m, 1.0, J = 8.3 Hz, H para to the fluoroalkyl group), 7.59 (m, 1.0, H ortho to the fluoroalkyl group), 8.22 (d, 1.0, J = 8.3 Hz, H ortho to S). At −90 °C the methoxy peak was split into two peaks at δ 3.72 and 3.79 (100 MHz) which coalesced at −68 °C. ^{19}F NMR (CD_2Cl_2, 26 °C) ϕ 76.2 (d, J_{HF} = 1.3 Hz), at −88 °C the doublet became a broad peak with a width at half-height of 5 Hz (56.26 MHz); ^{13}C NMR (CD_2Cl_2, 30 °C) δ 21.6 (s, $ArCH_3$), 55.5 (s, OMe), 118.0 (s), 119.0 (s), 127.8 (s), 130.7 (s), 132.2 (s); mass spectrum (70 eV) *m/e* (rel intensity) 350 (0.3, $M^{+\cdot}$), 331 (2.7, M − F), 319 (100, M − OCH_3), 304 (1.0, M − C_2H_6O), 288 (10.4, M − $C_2H_6O_2$), 281 (13.3, M − CF_3), 219 (71.1, M − CF_3 − $C_2H_6O_2$), 150 (11.1).[49] Anal. ($C_{12}H_{12}F_6O_3S$) C, H.

The addition of water to a CCl_4 solution of **25** resulted within a few seconds in the complete hydrolysis of the sulfurane, forming methanol and sultine **7,** recognized by their ^1H NMR spectra.

Acknowledgment. This research was supported in part by a grant from the National Science Foundation (MPS 75-17742) and in part by Fellowships for G.W.A. from Abbott Laboratories, the Phillips Petroleum Co., and the Dow Chemical Co.

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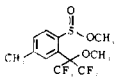
(49) At probe temperatures greater than the 75 °C melting point of **25**, sample decomposition occurred causing the M − OCH_3 to M+· ratio to decrease from 300 to 2.7. This large relative increase in the molecular ion could be due to a new type of sulfurane rearrangement to **46**. Sultine **7** and its



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fragmentation peaks were also very prominent at these high probe temperatures.

Reactions of Trialkoxysulfuranes (Orthosulfinates) with Trifluoromethanesulfonic Acid.[1] The First Isolation of a Dialkoxysulfonium Salt and the Mechanisms of Decomposition of Such Salts

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Abstract: Trialkoxysulfuranes **1a**, **1b**, and **1c** are synthesized. Their reactions with trifluoromethanesulfonic (triflic) acid give, respectively, triflate esters **2a** and **2b** and dialkoxysulfonium triflate **10c**, the first isolated dialkoxysulfonium salt. From oxygen-18 labeling studies and relative rates of reactions, a mechanism involving rate-determining formation of high energy fluorinated carbonium ions, in an ionization reaction involving a sultine leaving group, is proposed for the formation of triflate esters **2a** and **2b**. Comparisons with other sulfurane and alkoxysulfonium chemistry are advanced.

Interesting differences between the reactions of dialkoxy- and trialkoxysulfuranes with bifunctional reagents have recently been reported.[1] Here we describe the reactions of trifluoromethanesulfonic acid (triflic acid) with several trialkoxysulfuranes and constrast this to the alkoxysulfonium ion formation seen in the reactions of triflic acid with acyclic[2] and cyclic[3] dialkoxysulfuranes. While alkoxysulfonium salts can also easily be prepared by alkylation of sulfoxides,[4] dialkoxysulfonium ions have only recently been detected in solution[5] as thermally unstable fluorosulfonates or as triflates stable in the presence of a high concentration of methyl triflate. Here we report the first isolation of a dialkoxysulfonium salt and the mechanism of decomposition of other dialkoxysulfonium ions postulated to be intermediates in reactions of trialkoxysulfuranes with triflic acid.

Experimental Section

Fluorine chemical shifts are reported on the ϕ scale in parts per million upfield from fluorotrichloromethane and proton chemical shifts are reported on the δ scale in parts per million downfield from Me_4Si. Sulfuranes **1a–c**, sultene **9**, and sulfonium triflate **10c** were prepared and transferred in an inert atmosphere box under nitrogen. The reported elemental analyses are within 0.4% of theoretical values unless otherwise noted.

Reaction of 1a with Trifluoromethanesulfonic acid (TfOH). To a solution of sulfurane **1a**[1] in ether or $CDCl_3$ in an NMR tube at 41 °C was added 1 equiv of TfOH. The solution became homogeneous over 5–10 min as the TfOH singlet at ϕ 77.8 ($CDCl_3$) or 79.1 (ether) in the ^{19}F NMR spectrum diminished in intensity. The sulfurane peaks at ϕ 70.1, 71.4, and 72.7 also disappeared over this time interval being replaced by (in $CDCl_3$) a quartet of triplets at ϕ 71.0 (6.1 F) and a septet at 74.4 (2.9 F) of hexafluorocumyl triflate **2a** ($PhC(CF_3)_2OSO_2CF_3$, R_FOTf), quartets at 74.9 (3.4 F) and 75.9 (J = 8 Hz) due to sulfinate **3**, and an overlapping singlet at 75.8 due to hexafluorocumyl alcohol (R_FOH) (10.9 F total).

The reaction was repeated on a larger scale to isolate the R_FOTf. To a suspension of 0.98 g (1.27 mmol) of sulfurane **1a** in CCl_4 was added 0.198 mL (2.23 mmol) of TfOH. After being stirred for 15 min, the homogeneous solution was extracted with aqueous KOH to remove excess acid and sulfinate **3**. Solvent was removed at 0.05 Torr leaving