Pseudorotation and Fragmentation of Perfluoropinacol Orthosulfite.[1a] A Tetraoxysulfurane

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Abstract: Evidence for an intramolecular ligand exchange process having a $\Delta G^{\ddagger}$ of ca. 7.5 kcal/mol at −100 °C has been found in a variable-temperature ^{19}F NMR study of perfluoropinacol orthosulfite (**1**). This is interpreted in terms of pseudorotation. Sulfurane (**1**) also undergoes a novel fragmentation at temperatures above 200 °C to give perfluorotetramethylethylene (**3**), hexafluoroacetone, and sulfur dioxide. Possible mechanisms for this fragmentation and its relationship to other sulfur and phosphorus chemistry are discussed.

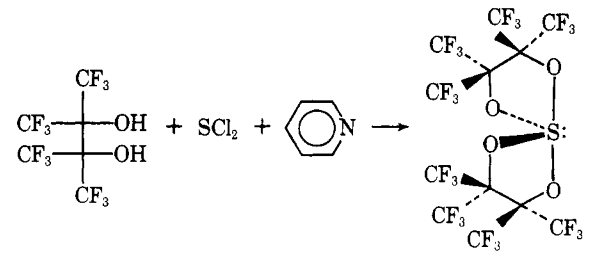
Introduction

Although Berry[2] suggested in 1960 that his pseudorotation mechanism, which involves pair-wise positional interchange of two apical with two equatorial substituents, might apply to sulfur compounds as well as to those of phosphorus, experimental progress in this area has been slow. Phosphorane pseudorotation has been well established[3] and extensively reviewed,[4] while early experimenters with SF_4 encountered problems with impurities,[5,6] bimolecular reactions,[6,7] and conflicting interpretations of data.[6-8] Recent infrared[9] and NMR[10] studies support the Berry mechanism[2] for intramolecular ligand exchange in SF_4. Sheppard[11] has postulated fast pseudorotation in tetra(pentafluorophenyl)sulfurane, and Trost[12a] and Jacobus and Mislow[12b] have postulated pseudorotation to explain reaction products from possible tetraarylsulfurane intermediates. Others have found evidence against certain kinds of pseudorotation in isolated sulfuranes[13] and in postulated sulfurane intermediates.[14] Here we report a study of a spirosulfurane, **1**, without fluorine ligands, whose temperature-dependent NMR spectra we interpret in terms of pseudorotation.

Results and Discussion

Sulfurane (**1**) was synthesized by the method of Allen, Janzen, and Willis[15] in 18% yield from hexafluoroacetone (HFA). This method prepares the disodium salt of perfluoropinacol by reduction of HFA with metallic sodium, followed by treatment with sulfur dichloride. Because of the low yield and the difficulty in scaling up the vacuum line and sealed tube techniques, an alternate synthesis was devised. Perfluoropinacol prepared by the reaction of HFA with triethyl phosphite, a method similar to that of Knunyants et al.,[16] was treated with excess sulfur dichloride and pyridine in ether (Scheme I) to give sulfurane **1** in a two-step process with an overall yield of 42% (based on HFA) or 48% (based on triethyl phosphite). The products prepared by these methods showed identical ^{19}F NMR (multiplets at 67.2 and 69.0 ppm upfield from $CFCl_3$) although the melting points sometimes differed by as much as 15 °C. The product (mp 65.5–67 °C) prepared by Scheme I gave infrared (KBr) and mass spectra identical with those of the lower melting compound (mp 51–53 °C) reported in the literature.[15] Evidence that sulfurane **1** was probably crystallizing in two different forms came from the observation that one sample of **1** melted near the range reported by Allan, Janzen, and Willis,[15] resolidified, and remelted sharply 15 °C higher in temperature. Sulfurane **1** was further characterized by its ^{13}C NMR and negative ion mass spectrum.

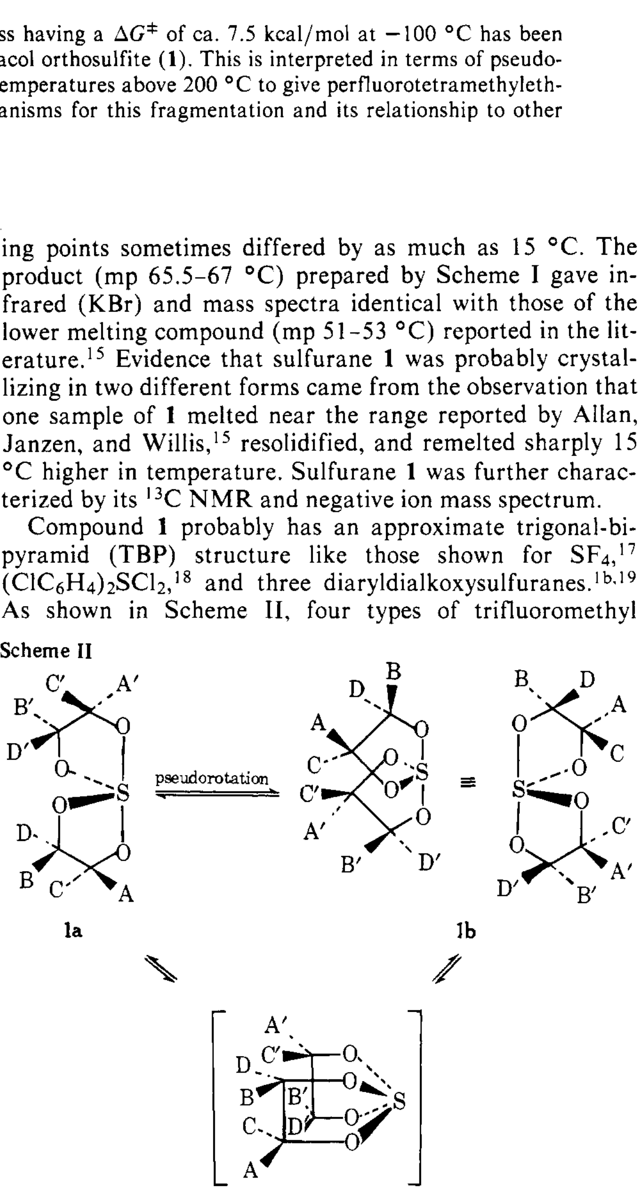
Scheme I



1 (58%)

Compound **1** probably has an approximate trigonal-bipyramid (TBP) structure like those shown for SF_4,[17] $(ClC_6H_4)_2SCl_2$,[18] and three diaryldialkoxysulfuranes.[1b,19] As shown in Scheme II, four types of trifluoromethyl groups are predicted for this structure. The ^{19}F NMR shows only two multiplets at 67.2 and 69.0 ppm upfield from $CFCl_3$ at 28 °C, but the presence of a ligand exchange process involving four magnetically nonequivalent CF_3 groups is shown by the broadening of the lower field peak below −40 °C, reaching a maximum around −100 °C (see Figure 1). This peak splits into two broad absorptions, which sharpen upon cooling to −150 °C although the remaining peak only broadens down to −150 °C. This clear evidence for four nonequivalent CF_3 groups in the −150 °C spectrum, evidence adduced in studies of solutions of **1** in two solvents and over a fourfold range of concentrations, rules out a square-pyramidal structure (**1c**) for **1** but is consistent with interconversion of **1a** and **1b** by pseudorotation via **1c**.

Scheme II



1a **1b**

1c

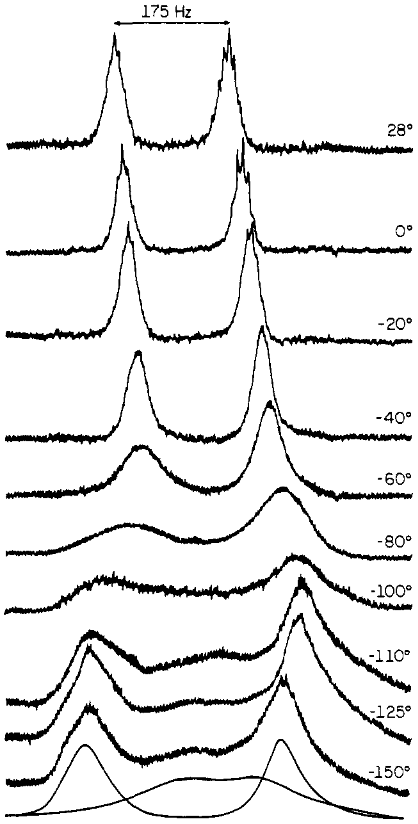
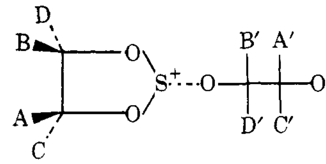


Figure 1. Observed 94.1 MHz ^{19}F NMR spectra of sulfurane **1** in $CFCl_3$ at temperatures from 28 to −100 °C and in CF_2Cl_2 from −100 to −150 °C. The bottom trace shows how the −150 °C spectrum can be resolved into one broad peak (relative area, 2) and two sharper overlapping peaks (relative area, 1 for each peak).

The temperature-dependent ^{19}F NMR line shapes seen for sulfurane (**1**) can be explained by postulating a pseudorotation mechanism which interchanges exo trifluoromethyl groups A and B and also interchanges endo groups C and D (see Scheme II). Such a mechanism, avoiding pseudorotation pathways involving structures with apical electron pairs,[1a] does not interconvert endo and exo groups. In accordance with this we find separate signals for the exo and endo CF_3 groups in the ^{19}F and ^{13}C NMR spectra at room temperature.

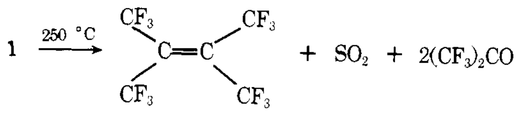
The assignments of CF_3 peaks in the −150 °C spectrum cannot be made unequivocally.[20] However the two resolved peaks in the −150 °C spectrum at 66.7 and 70.0 ppm are, in the room-temperature spectrum, coalesced in the downfield multiplet at 67.2 ppm. At the estimated coalescence temperature (−100 °C) for this two-site exchange the $\Delta G^{\ddagger}$ is 7.5 kcal/mol, as calculated from the coalescence temperature using the Gutowsky–Holm equation,[21] estimating the chemical shift difference between the two resolved multiplets to be 315 Hz (at 94.1 MHz) from the −150 °C spectrum. This calculated $\Delta G^{\ddagger}$, ca 7.5 kcal/mol at −100 °C, can be compared with the pseudorotation barrier for SF_4 estimated to be 10.0 ± 0.5 kcal/mol from infrared studies[9] and >4.5 kcal/mol from NMR studies complicated by intermolecular processes.[5,6] Mechanisms involving bimolecular processes with intermediates similar to the dimers suggested by Muetterties and Phillips[7] for SF_4 can be ruled out since at −80 °C, a temperature where line shape is sensitive to rate, no difference was seen between the ^{19}F NMR spectrum of a saturated solution of **1** in $CFCl_3$ and the spectrum of a solution one-fourth as concentrated. This also rules out catalysis of pseudorotation by nucleophiles through square-pyramidal structures analogous to SF_5^-,[22,23] as suggested by Sheppard for SF_4[11] and for $C_6F_5SF_3$.[13a] Those mechanisms involving the intermediacy of sulfonium ion **2** can be eliminated since they would render exo and endo CF_3 groups equivalent (CF_3 groups A′ and C′ and groups B′ and D′ in **2**), while simultaneously equilibrating apical and equatorial CF_3 groups A and B and also C and D. Since the exo and endo CF_3 groups show no exchange in the ^{19}F NMR at 200 °C, processes involving formation of zwitterion **2**, inversion of the sulfurane through a planar transition state, or pseudorotation mechanisms for the interchange of exo and endo groups,[24] must have a $\Delta G^{\ddagger}$ exceeding 24.5 kcal/mol. This can be compared with inversion barriers of 25 to 29 kcal/mol observed in sulfonium ions by others[25] and inversion barriers greater than 25.3 and 27 kcal/mol in a sulfurane[1b] and a selenurane,[26] respectively. NMR experiments at temperatures above 200 °C were discouraged by observations of the decomposition of **1**.



2

Complete pyrolysis of **1** was accomplished by heating it in a sealed tube partially or totally immersed in a 250 °C oil bath. The crude mixture showed two singlets of equal intensity in the ^{19}F NMR at 61.9 and 78.2 ppm upfield from $CFCl_3$ and a strong infrared absorption at 1800 cm^{-1}. Authentic samples of hexafluoroacetone had the same infrared peak and augmented the higher field NMR peak. The other fluorine-containing product was isolated by bulb-to-bulb distillation and identified as perfluorotetramethylethylene (**3**) by the observation of its molecular ion in its 9-eV mass spectrum, by a 1670-cm^{-1} carbon–carbon double bond stretching frequency in its Raman spectrum, and by its ^{13}C NMR. The remaining product was identified as SO_2 by absorbing it in aqueous NaOH solution, oxidizing it with H_2O_2, and precipitating $BaSO_4$ (94%) by adding $BaCl_2$.[27]

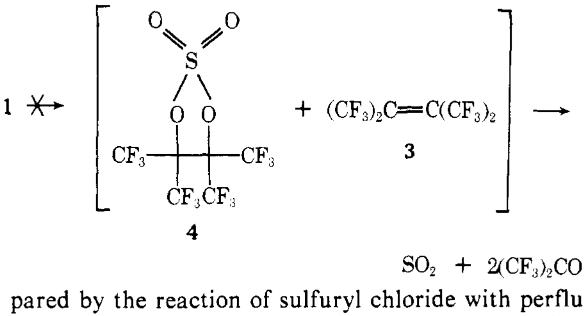
Scheme III



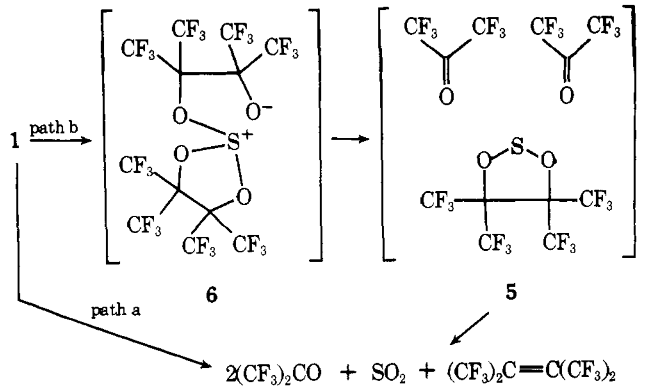
3

To rule out the possibility that the thermal decomposition of **1** was going through a mechanism involving sulfate **4** as an intermediate (Scheme IV), a mixture of **1** with **4**, prepared by the reaction of sulfuryl chloride with perfluoropinacol in the presence of pyridine, was pyrolyzed. Since the sulfate survives the pyrolysis conditions, the highly concerted path a and stepwise path b of Scheme V are left as alternatives. Dittmer[28] has proposed a mechanism for episulfone decomposition involving an intermediate similar to **5**. Attempts to make five-membered ring sulfoxylates similar to

Scheme IV



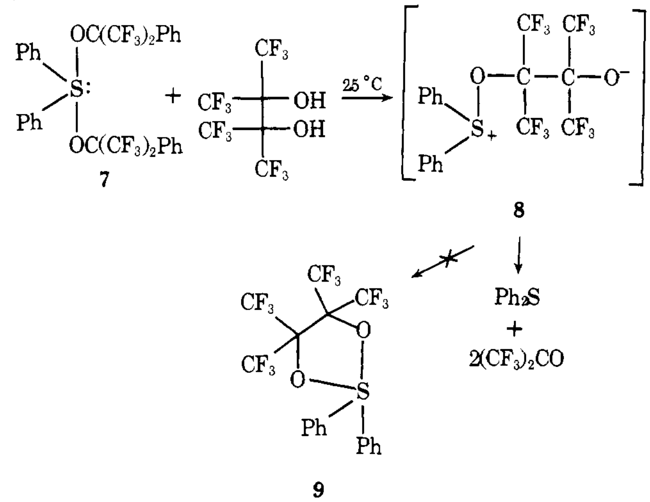
Scheme V



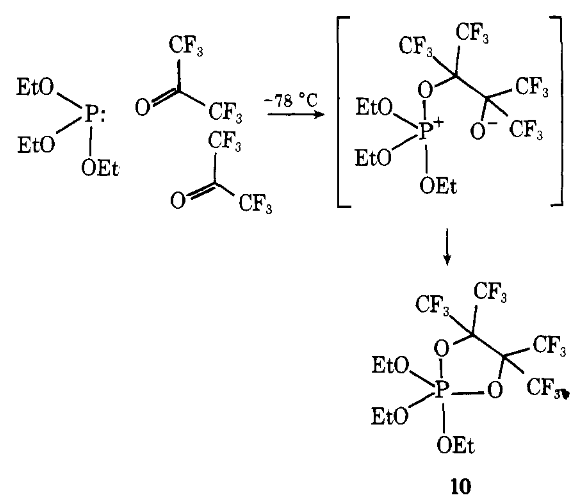
5 have failed.[29,30] Only recently has a five-membered ring cyclic sulfenate been reported.[32] A cyclic sulfoxylate, constrained to the near planarity of a five-membered ring, might be expected to show the same destabilizing lone-pair interactions for which evidence is seen in the analogous cyclic sulfenate.[32]

Zwitterion 6, ruled out earlier as an intermediate in ^{19}F NMR exchange reactions observable by NMR at temperatures below 200 °C, might be an intermediate leading to 5. An analogous intermediate 8 can explain the reaction of sulfurane 7[13c,d] with perfluoropinacol to give hexafluoroacetone and diphenyl sulfide (see Scheme VI). Structure 8 is similar to postulated intermediates leading to epoxides from the reaction of 7 with other 1,2-glycols.[33] The formation of phosphorane 10 from hexafluoroacetone and triethyl phosphite is, as shown in Scheme VII, similar to the reverse of the decomposition of 8 (Scheme VI) or the decomposition of 1 (Scheme V). Zwitterion 6 is probably an intermediate in the synthesis of 1 from SCl_2 and perfluoropinacol (Scheme VIII), but at room temperature cyclization is favored. At the pyrolysis temperatures, fragmentation to 5 plus two ketone molecules is favored. Cyclization of 6 to 1 is unfavorable at high temperatures due to the large entropy loss involved in ring formation. By extension of ring strain and polarity rules from phosphorane chemistry,[4a,34] a process consistent with the known structures of several sulfuranes,[1b,19] cyclization of 8 would be unfavored even at low temperatures since the sulfurane 9 that would be formed must have an apical phenyl group.

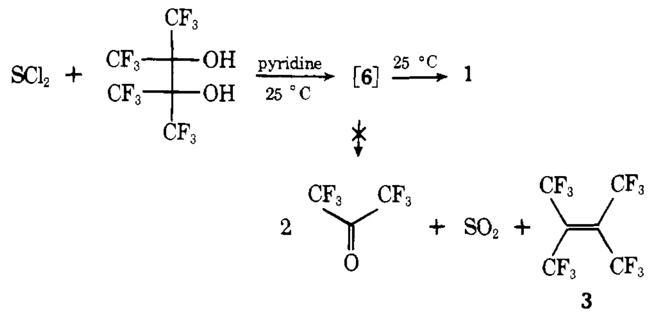
Scheme VI



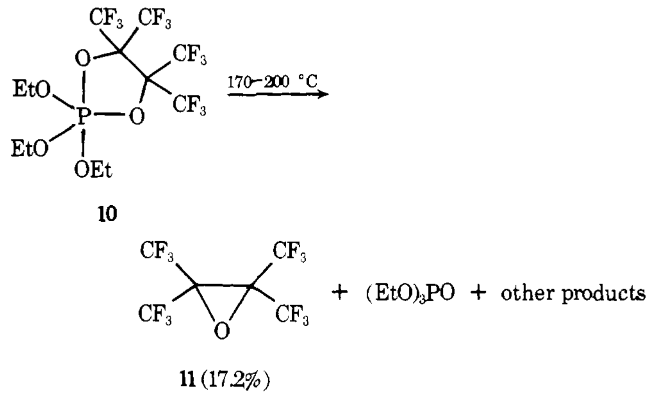
Scheme VII



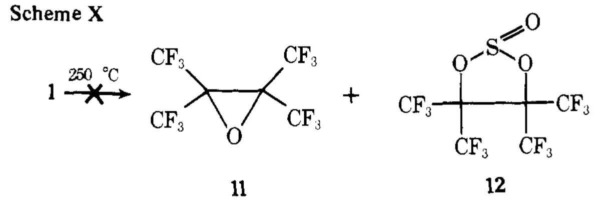
Scheme VIII



Scheme IX

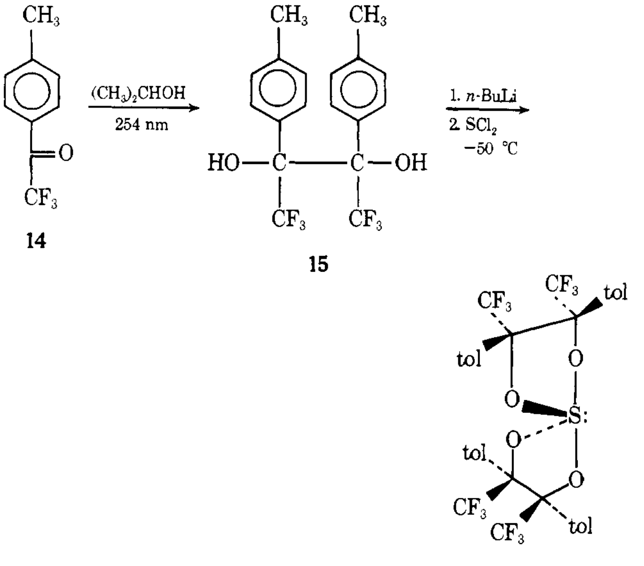


Scheme X



The pyrolysis of sulfurane 1 can be contrasted to that of a similar phosphorane 10, which gives epoxide 11, triethyl phosphate, and other products[16b] (Scheme IX). The failure of 1 to undergo a reaction yielding epoxide 11 and sulfite 12 (Scheme X) can be attributed to the lower sulfur-oxygen double bond strength in 12 compared with that of its phosphorus analogue. (For example, the sulfur-oxygen bond strength in Ph_2SO has been estimated to be 89 kcal/mol[35] and the phosphorus-oxygen bond in Ph_3PO 128.4 kcal/mol.[36]) This difference in bond strengths explains many of the contrasts between sulfur and phosphorus chemistry: such as the fact that the reaction of phosphorus ylides with ketones gives olefins and phosphine oxides,[37] while sulfur ylides give epoxides plus sulfides;[38] or the observation that pentaethoxyphosphorane reacts with hydroquinone to give *p*-ethoxyphenetole and triethyl phosphate,[39] while sulfurane 7 gives quinone plus diphenyl sulfide.[40]

Attempts were made to synthesize sulfurane 13 with the expectation that its variable-temperature ^{19}F NMR spectra would be simple enough to allow the use of quantitative line shape analysis as a probe for pseudorotation processes. Diol **15** was prepared by the ultraviolet irradiation of a 2-propanol solution of ketone **14**,[41] a method similar to that previously used to make the phenyl analogue,[42] in a reaction yielding 24% of one isomer of diol **15** and 6% of a more soluble isomer. The diastereomers were identified by converting them to the cyclic sulfites with pyridine and thionyl chloride and analyzing by gas chromatography. The major product gave two GC peaks showing it was meso, while the minor product gave one sulfite peak as expected for racemic diol. In the ^{19}F NMR the racemic sulfite showed two peaks of equal intensity while the meso sulfite showed two peaks of slightly different intensity (1.0:0.84) consistent with the presence of two meso sulfite isomers in unequal amounts.



14

15

13

The synthesis of sulfurane **13** was attempted by treating meso diol **15** in ether with 2 equiv of *n*-butyllithium, followed by excess SCl_2. Fluorine NMR of the crude reaction mixture showed a large singlet at 68.6 ppm plus many minor products including meso sulfite and variable amounts of meso diol **15**. Large amounts of ketone **14** were also formed unless the reaction mixture was cooled to −50 °C before addition of the SCl_2. The addition of H_2O caused the large 68.6 ppm peak to disappear with a half-life of roughly 8 min, with the diol peak and the two sulfite peaks growing. This strongly suggests that the compound giving the 68.6 ppm singlet is the desired sulfurane **13** or an isomer. Further observations revealed that even when kept dry at room temperature, this sulfurane disappeared overnight yielding sulfite plus a new downfield multiplet. However, the reaction mixture could be kept indefinitely at −20 °C without decomposition. Attempts to purify this reaction mixture by crystallization or liquid chromatography were fruitless due to the complexity of the mixture and its thermal and hydrolytic reactivity. Low-temperature ^{19}F NMR on the crude reaction mixture showed that the sulfurane peak started to broaden below room temperature, becoming very broad by −27 °C, possibly due to a slowing of the expected fast pseudorotation of **13**. Unfortunately, below this temperature the rest of the spectrum started to broaden, perhaps the result of increased viscosity, precipitation of impurities, or other problems. Further studies of this compound were abandoned.

Experimental Section

Fluorine chemical shifts are reported in ppm upfield from fluorotrichloromethane. Carbon-13 spectra are reported using the δ scale, ppm downfield from tetramethylsilane. Elemental analyses of new compounds are within 0.4% of theoretical values.

2,2,2-Triethoxy-2,2-dihydro-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2-dioxaphospholane (10). The procedure of Knunyants[16b] was modified by using a 10% excess of hexafluoroacetone. Triethyl phosphite (78 g, 0.47 mol), purified by distillation through a 15-cm tantalum wire packed column [bp 72–74 °C (35–37 mm)], was added with stirring over a period of an hour to hexafluoroacetone (176 g, 1.06 mol) cooled with dry ice to give 229 g (97.9%) of crude phosphorane **10**: mp −10 to −7 °C (lit.[16a] mp −9 to −8 °C); ^{19}F NMR (CCl_4) 69.7 (s); ^1H NMR δ 1.25 (t, 9 H, J = 7 Hz), 4.04 (quintet, 6 H, J = 7 Hz). Phosphorane **10**, 36 g, was distilled through a 15-cm tantalum wire packed column [bp 67–73 °C (0.4–0.5 mm)] to give 19 g of the purest fraction (mp −6.5 to −4.5 °C) which was used for pyrolysis studies.

1,1,1,4,4,4-Hexafluoro-2,3-bis(trifluoromethyl)-2,3-butanediol (Perfluoropinacol). A procedure similar to that of Knunyants[16] was used. Crude phosphorane **10** (188 g, 0.378 mol) was stirred with 65 ml of concentrated H_2SO_4, cooled, and filtered in a dry bag. The resulting white solid was distilled from 130 ml of 75% H_2SO_4 to yield 148.5 g of crude diol. (The use of 75% rather than concentrated H_2SO_4 was found to reduce the 1,1,1,3,3,3-hexafluoro-2-propanol by product[16b] from 6% to about 1% by ^{19}F NMR.) The product was dried by distillation [bp 60 °C (62 mm)] from 60 ml of concentrated H_2SO_4 to give 106.3 g (84%) of perfluoropinacol: mp near room temperature (lit.[16a] mp 18–20 °C); ^{19}F NMR (neat) 70.2 ppm (s).

Cyclic Bis[tetrakis(trifluoromethyl)ethylene] Orthosulfite (1). Method A. The method of Allen, Janzen, and Willis[15] was used to synthesize **1** from hexafluoroacetone in 18% yield. Melting points of the product varied from 49–50 to 61.5–64 °C (lit.[15] mp 51–53 °C). One sample melted at 50.5–51.5 °C (sealed tube), immediately resolidified, and remelted at 65.5–67 °C. The ^{19}F NMR spectrum of **1** (CCl_4, 41 °C), 67.2 (m, 12 F) and 69.0 (m, 12 F), agrees with that in the literature.[15]

Cyclic Bis[tetrakis(trifluoromethyl)ethylene] Orthosulfite (1). Method B. To perfluoropinacol (18.38 g, 0.0550 mol) was added a solution of SCl_2 (80 g, 0.78 mol) in 50 ml of dry ether and dry pyridine (100 ml, 1.61 mol) in 100 ml of dry ether. The SCl_2 and pyridine were added simultaneously from two addition funnels over a 30-min period to the stirred reaction mixture at 0 °C. Additional ether (200 ml total) was added in small amounts when the reaction mixture got too thick to be stirred well. An aliquot of the solution showed (^{19}F NMR) a sulfurane **1** to perfluoropinacol ratio of 16:1, so another 15 ml of SCl_2 in 30 ml of ether and 30 ml of pyridine in 60 ml of ether were added as before. The ether layer was decanted and the remaining solids were extracted with three 200-ml portions of ether. Removal of the ether gave 20.3 g of yellow-white solid, which was recrystallized from ether. Sulfur impurity was removed by washing the crystals with CS_2 and then subliming the material (0.1 mm) to yield 11.14 g (58.2%) of product (mp 64.5–65.5 °C): ^{19}F NMR (CCl_4, 41 °C) 67.2 (m, 12 F), 69.0 (m, 12 F); ^{13}C NMR (neat, 100 °C) δ 122.2 (q, J = 293 Hz, 4 CF_3's), 121.8 (q, J = 291 Hz, 4 CF_3's), 87.2 (m, 4 quaternary carbons, sharpens to a singlet upon ^{19}F decoupling); mass spectrum (70 eV, positive ion) all 29 peaks reported by Janzen[15] were seen (70 eV, negative ion), *m/e* (rel intensity) 715 (0.13, $M + F^-$), 696 (0.13, $M\cdot^-$), 677 (0.09, $M - F^-$), 627 (0.12, $M - CF_3^-$), 577 (0.14, $M - C_2F_5^-$), 383 (0.96, $C_6F_{13}O_2S^-$), 364 (1.25, $C_6F_{12}O_2S\cdot^-$), 300 (2.4, $C_6F_{12}\cdot^-$), 247 (98.1, $C_5F_9O^-$), 197 (63.5, $C_4F_7O^-$), 128 (100, $C_3F_4O\cdot^-$); (field ionization, positive ion) 627 ($M - CF_3^+$) is more than 100 times the intensity of any other peak; ir (KBr) 1255 (vs, broad, CF_3), 1228 (vs, broad, CF_3), 1110 (m), 1052 (s), 1002 (m), 969 (s), 885 (m), 795 (m), 750 (m), 721 (m), 688 (m), 562 (m), 555 (m), 473 (m).

Low-temperature 94.1 MHz ^{19}F NMR studies on sulfurane **1** were carried out in $CFCl_3$ solution from 28 to −100 °C and in CF_2Cl_2 solution from −100 to −150 °C, as shown in Figure 1. The −100 °C spectra in the two solvents were identical. At −80 °C in $CFCl_3$ a saturated solution of **1** and a solution 25% as concentrated showed identical line shapes. High-temperature ^{19}F NMR studies at 56.4 MHz of molten sulfurane **1** showed no changes from 51 to 200 °C except for a gradual decrease in the separation of the two multiplets from 111 to 73 Hz with fine structure separated by 10 Hz still visible at 200 °C. A dilute solution of **1** in dibenzyl ether at 200 °C showed a spectrum identical with that of the neat liquid.

At higher temperatures, decomposition of **1** became rapid.

Pyrolysis of Sulfurane 1. In a typical reaction, 0.323 g of sulfurane **1** was sealed inside 260 mm of 4-mm glass tubing and then allowed to reflux in a 250 °C oil bath for 20 min. When the sealed glass tubing was cooled and placed inside an NMR tube, ^{19}F NMR of the clear liquid showed the sulfurane multiplets to be completely gone, replaced by singlets at 78.2 (area 1.00) and 61.9 ppm (area 1.02) upfield from external $CFCl_3$. The addition of HFA increased the area of the peak at 78.2 ppm. If the tube was opened at dry ice temperature and slowly allowed to warm to room temperature, the gaseous products boiled away leaving a volatile clear liquid. Traces of gaseous products were removed by a bulb-to-bulb distillation at 0.05 mm. This liquid, which had only a singlet at 61.9 ppm in its ^{19}F NMR, was identified as 1,1,1,4,4,4-hexafluoro-2,3-bis(trifluoromethyl)-2-butene (**3**) by its spectra: 9 eV mass spectrum, *m/e* (rel intensity) 300 (22, $M\cdot^+$), 231 (100, $M - CF_3^+$), 69 (5, CF_3^+); ^{13}C NMR (neat) δ 118.1 (q, J = 281 Hz, CF_3), 135.2 (s, C=C, ^{19}F decoupled); Raman, freq (rel height) 1670 (13, C=C), 1330 (4.5), 1170 (6), 766 (100, CF_3), 335 (18), 285 (57), 190 (18); ir (neat) 1451 (w), 1130–1350 (vs, broad, CF_3), 1014 (m), 909 (m), 863 (m), 713 (m), 671 (m).

The gaseous products were studied by pyrolyzing 0.4 g of sulfurane **1** in a 15-cm combustion tube with a break-seal attached to it. After the tube had been totally immersed in a 250 °C oil bath for 45 min, the gases were transferred on a vacuum line to a 10-cm gas ir cell. The infrared spectrum showed a strong carbonyl band at 1800 cm^{-1} identical with that seen in authentic samples of HFA under the same conditions. Very strong CF_3 absorptions in the 1100–1400 region made it impossible to detect SO_2, the third suspected product, which has its strongest infrared bands at 1151 and 1361 cm^{-1}.[43]

SO_2 Detection and Quantity.[27] Sulfurane **1** (5.3 g, 7.6 mmol) was heated to 250 °C for 1 h in a sealed 250-mm combustion tube. The tube was then opened at dry ice temperature and allowed to warm up to room temperature. The gases given off were bubbled through an aquous NaOH solution (1.26 g, 31.5 mmol). Five milliliters of 15 M H_2O_2 (75 mmol) was added, and the solution was heated on a steam bath for 2 h until oxygen was no longer evolved. The addition of excess $BaCl_2$ solution precipitated 1.454 g (6.23 mmol) of $BaSO_4$ [94% of theoretical since ^{19}F NMR analysis of the liquid remaining in the combustion tube showed an olefin to sulfurane ratio of 87:13, indicating that only 87% (6.61 mmol) of the sulfurane had decomposed].

1,1,1,4,4,4-Hexafluoro-2,3-bis(trifluoromethyl)-2,3-butanediol Cyclic Sulfate 4. To perfluoropinacol (1.37 g, 4.10 mmol) in 15 ml of anhydrous ether, sulfuryl chloride (5.0 g, 37 mmol) and pyridine (3.9 g, 49 mmol) were added alternately in small amounts with stirring and cooling in an ice bath until in the ^{19}F NMR the pinacol peak at 72.1 ppm had been completely replaced by the sulfate singlet at 68.4 ppm (lit.[44] 66.5). This mixture was poured into 15 ml of ice-cold concentrated H_2SO_4 with stirring. The ether layer was decanted from the acid layer which was extracted with 10 ml of additional ether. The sulfate in the ether extracts was purified by a simple distillation using a bath temperature of 130 °C (lit. bp 120–122[15] and 131–132 °C[44]). The product consisted of a 96:4 ratio of perfluoropinacol sulfate to perfluoropinacol by ^{19}F NMR integration; mass spectrum (70 eV) *m/e* (rel intensity) 377 (2.05, $M - F^+$), 327 (10.2, $M - CF_3^+$), 147 (14.2, $C_3F_5O^+$), 97 (25.0, CF_3CO^+), 69 (100, CF_3^+), 64 (1.38, $SO_2\cdot^+$), 48 (1.53, SO^+). At 10 eV, the 327 peak was the strongest.

This perfluoropinacol sulfate was unaffected (^{19}F NMR) by the conditions needed for the pyrolysis of sulfurane **1** (250 °C for 30 min).

Pyrolysis of Sulfurane 1 with Sulfate 4. Sulfurane **1** (150 mg, 0.22 mmol) and sulfate **4** (71 mg, 0.18 mmol) were heated in a sealed tube at 248 °C for 21 min. A ^{19}F NMR spectrum of this product showed that the sulfurane peaks at 67.9 and 70.0 ppm had been replaced by the singlets for olefin **3** and HFA at 62.0 and 78.7 ppm, while the sulfate peak at 68.4 ppm was unchanged by the pyrolysis.

Reaction of Sulfurane 7 with Perfluoropinacol. Under a dry nitrogen atmosphere diaryldialkoxysulfurane (**7**)[13c,d] (200 mg, 0.298 mmol) in 0.5 ml of CCl_4 was poured into an NMR tube containing perfluoropinacol (99.1 mg, 0.297 mmol). Immediate evolution of a gas was noted. The ^{19}F NMR spectrum showed singlets at 71.2 ppm (excess perfluoropinacol due to partial hydrolysis of **7**), 76.5 ppm (hexafluorocumyl alcohol), and 83.5 ppm (hexafluoroacetone hydrate). The ^1H NMR spectrum showed multiplets at δ 7.1 due to diphenyl sulfide and 7.5 from diphenyl sulfoxide (formed by hydrolysis of (**7**). The presence of diphenyl sulfide and diphenyl sulfoxide was confirmed by a GLC comparison against authentic samples using a 1-ft 5% SE-30 on Chromosorb W column at 150 °C.

Pyrolysis of Phosphorane 10. Phosphorane **10** (200 μl) was sealed in 4-mm glass tubing and heated to 198 °C for 5 min. The ^{19}F NMR of the resulting colorless liquid showed many absorptions including a singlet at 66.5 ppm (20% of total fluorine) due to perfluorotetramethylethylene oxide (**11**). No trace of olefin **3** was seen in the ^{19}F NMR spectrum. Epoxide **11** was isolated by preparative GLC on a 5-ft 20% SE-30 on Chromosorb W column at 38 °C. Epoxide **11** gave a mass spectrum quite different from that of olefin **3**. The 70 eV mass spectrum of **11** showed *m/e* (rel intensity) 316 (0.13, $M\cdot^+$), 297 (25.4, $M - F^+$), 247 (7.11, $M - CF_3^+$), 159 (10.08), 147 (31.2), 97 (23.6, CF_3CO^+), 69 (100, CF_3^+).

2,2,2-Trifluoromethyl-1-(4-methylphenyl)ethanone (14). The literature procedure[41] was modified by using lithium trifluoroacetate instead of trifluoroacetic acid. The salt was made by adding 55.27 g (0.748 mol) of lithium carbonate to a solution of 170.3 g (1.49 mol) of trifluoroacetic acid in 300 ml of H_2O. After filtration of the solution, the salt, obtained by evaporation of the solution under reduced pressure, was dried further at 110 °C and 0.5 Torr to yield 177.4 g (1.48 mol) of white powder. This salt (202.8 g, 1.69 mol) was ground in a mortar and pestle under a dry nitrogen atmosphere and dissolved in 500 ml of anhydrous ether. This was added over a period of 1 h to an ice-cooled solution of Grignard reagent in 150 ml of ether (prepared from 260.9 g or 1.53 mol of 4-bromotoluene). The reaction was quenched with 250 ml of H_2O and 150 ml of concentrated HCl. The ether layer was separated and combined with 500 ml of ether used to wash the aqueous layer. Removal of ether gave 250 ml of a red liquid which was distilled through a 15-cm tantalum wire column to yield 80.3 g (28% based on 4-bromotoluene compared with 10–16% by literature methods[41]) of a slightly yellowish liquid (bp 113.5–115.5, 93–94 Torr): ^1H NMR (neat) δ 2.34 (s, 3.0, CH_3), 7.89 and 7.21 (AB pattern, 4.0, J_{AB} = 8.5 Hz); ^{19}F NMR (ether) triplet 72.0 ppm upfield from $CFCl_3$ (J = 1.2 Hz); mass spectrum (70 eV) *m/e* (rel intensity) 188 (18.1, $M\cdot^+$), 119 (100, $CF_3C_6H_4CO^+$), 91 (79.4); ir 1720 (s), 1610 (s), 1208 (s), 1178 (s), 1149 (s). Anal. ($C_9H_7F_3O$) C, H.

1,1,1,4,4,4-Hexafluoro-2,3-bis(4-methylphenyl)-2,3-butanediol (15). The literature procedure[42] for the phenyl analogue was followed with changes in the workup procedure. Ketone **14** (49.9 g, 0.265 mol) was mixed with 220 g of 2-propanol in a quartz flask which was irradiated with low-pressure mercury lamps in a Rayonet reactor for 4 days. The ^{19}F NMR spectrum of the crude reaction mixture, diluted with 2-propanol, showed only two singlets of equal area 70.0 and 70.1 ppm upfield from $CFCl_3$ presumably due to meso and racemic diol.

Removal of solvent under vacuum resulted in 49.5 g of a tan gummy solid which was sublimed at 115 °C and 0.15 Torr to give 29.9 g of a slightly yellow-white powder. Several recrystallizations from pentane–ether mixtures gave 11.84 g (23.6%) of meso diol (mp 171.5–173.5 °C) and 3.23 g (6.4%) of racemic diol (mp 116.8–117.2 °C). The separation could be conveniently followed by ^{19}F NMR which showed in ether a singlet at 69.6 ppm (meso) and a singlet at 69.4 ppm upfield from $CFCl_3$ (racemate) or by gas chromatography on a 5-ft 20% SE-30 on Chromosorb W column at 200 °C (retention times: racemate, 10.7 min; meso, 12.0 min). The assignments of racemic and meso structures were made by conversion of each diol to the cyclic sulfite by addition of excess pyridine and thionyl chloride to an ether solution of the diol. The ^{19}F NMR spectrum of the solution after filtration showed only two peaks, at 69.8 and 68.6 ppm (height 0.84:1), for the meso sulfite and two peaks, at 72.5 and 70.9 ppm (height 1.0:0.97), for the racemic sulfite. GLC using the previously mentioned column at 206 °C showed only one peak for the racemic sulfite (retention time 17.5 min) other than the solvent peak. The meso sulfite showed two peaks of roughly equal area at retention times of 9.7 and 15.4 min, as expected for the two meso isomers.

Meso Diol 15: ^1H NMR ($CDCl_3$) δ 2.34 (s, 5.6, CH_3), 3.48 (broad s, 2.1, OH), 7.11 and 7.40 (AB pattern, 8.3, J_{AB} = 8.5 Hz); ^{19}F NMR ($CDCl_3$) singlet 71.0 ppm upfield from $CFCl_3$; mass spectrum (10 eV) *m/e* (rel intensity) 378 (1.2, $M\cdot^+$), 358 (0.4, M

– HF), 189 [100, $CH_3C_6H_4C(CF_3)OH$], 170 (18.5). Anal. ($C_{18}H_{16}F_6O_2$) C, H.

Racemic Diol 15: ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 6.0, CH_3), 3.48 (broad s, 2.0, OH), 7.05 and 7.27 (AB pattern, 8.1, J_{AB} = 8.5 Hz); ^{19}F NMR ($CDCl_3$) 71.0 (s); mass spectrum (10 eV) *m/e* (rel intensity) 378 (1.3, $M\cdot^+$), 358 (0.4, M – HF), 189 [100, $CH_3C_6H_4C(CF_3)OH$], 170 (16.0). Anal. ($C_{18}H_{16}F_6O_2$) C, H.

Attempted Synthesis and Isolation of Sulfurane 13. In a typical experiment, 2.92 mmol of *n*-butyllithium were syringed into a stirred solution of 0.552 g (1.46 mmol) of meso diol **15** in ether. The mixture was cooled in a –50 °C bath with stirring while 0.20 ml (3.11 mmol) of SCl_2 was added. After filtration under a dry atmosphere, the ^{19}F NMR spectrum showed singlets at 68.0 ppm (relative area 5), 68.2 (7), 68.3 (8), 68.4 (8), and 68.6 (34) as well as several unresolved peaks at 69.2 to 69.6 ppm upfield from $CFCl_3$ (8). When the addition of SCl_2 was done at temperatures higher than –50 °C, a large triplet at 72.0 ppm due to ketone **14** was also present. The large peak at 68.6 ppm disappeared rapidly when the ether solution was saturated with H_2O (25% left after 15 min, 5% after 35 min), forming peaks at 68.3 and 69.4 ppm (cyclic sulfite of meso diol **15**) and at 69.6 ppm (meso diol **15**). The presence of sulfite was confirmed by a GLC comparison with authentic material (5-ft 20% SE-30 on Chromosorb W column at 205 °C). Crude meso diol **15** could be isolated from the hydrolyzed reaction mixture by crystallization (mp 160–168 °C) and authentic diol enriched the 69.6 ppm ^{19}F NMR peak.

Upon standing overnight at room temperature in the absence of water, the reaction mixture decomposed with the 68.6 ppm peak replaced by sulfite peaks at 69.4 and 68.3 ppm and a multiplet around 57.9 ppm upfield from $CFCl_3$ of areas 25.5, 42, and 66.5, respectively. Many other smaller peaks and multiplets were also present. If protected from moisture, the reaction mixture could be kept for months at –20 °C without changes in the ^{19}F NMR. Attempts to purify the mixture by crystallization from cold ether or ether–pentane gave only sulfur (an expected byproduct of the reaction) or meso diol **15** as crystalline products. High pressure liquid chromatography using a 4-ft alumina column or a 1-ft Micro Styragel column with ether or ether–pentane distilled from $LiAlH_4$ as the eluent was also unsuccessful in effecting purification.

The low-temperature ^{19}F NMR of this reaction mixture, studied at 56.4 MHZ, showed that the tentatively identified sulfurane peak at 68.6 ppm broadened much faster than the other peaks: temperature (width at half-height in Hz) 41 (2), 25 (3), 3 (4), –10 (5), –27 (18), –40 °C (peak lost under other nearby peaks). At lower temperatures all peaks in the spectrum were broadened, possibly due to viscosity or precipitation of impurities.

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