tracted with sodium hydroxide solution (10%, 50 mL). Acidification of alkaline layer afforded hydroxamic acids **20–25** in 55–60% yield.

Preparation of Thioxanthenones 15–17.[11] 2-(Arylthio)benzoic acid (0.01 mol) was treated with concentrated sulfuric acid (10 mL) for 1 h at room temperature. Decomposition of reaction mixture in crushed ice gave a sticky residue. It was extracted with benzene. The organic layer after washing with sodium hydroxide solution (10%, 2 × 50 mL) and on evaporation afforded thioxanthenones in 60–65% yield.

Preparation of Dibenzo[*b*,*e*]thiepin-11(6*H*)-ones 29–31.[9-13] 2-[(Arylthio)methyl]benzoic acid (0.01 mol) was treated with concentrated sulfuric acid (10 mL). After the workup as described earlier, **29–31** were obtained in 60–65% yield.

Preparation of 2-[(Arylmethyl)sulfinyl]benzamides 26–28.[9] 2-[(Arylmethyl)thio]benzoic acid[9] (0.01 mol) was refluxed with phosphorus pentachloride (3.5 g) in dry benzene (30 mL) for 2 h. After the removal of volatile material, the residue was cooled and treated with aqueous ammonia (30%, 15 mL). 2-[(Arylmethyl)thio]benzamide, which precipitated, was filtered off and dissolved in acetone (10 mL). Hydrogen peroxide (10%, 1 mL) was added to it, and the mixture was kept overnight at room temperature. It was then decomposed in cold water to give **26–28** in 55–60% yield.

General Method of Reactions of Hydroxamic Acids in PPA. Hydroxamic acid (1.0 g) was treated with PPA [P_2O_5 (20 g), H_3PO_4 (12 mL)]. The reaction mixture was heated in an oil bath at 120–125 °C for 2 h. After cooling, the reaction mixture was treated with crushed ice and extracted with chloroform (2 × 30 mL). The organic layer was washed successively with saturated sodium bicarbonate solution (2 × 25 mL), sodium hydroxide solution (10%, 2 × 25 mL), and water. The organic layer, on evaporation gave products. In each case the structure of the product was established on basis of spectral data and comparison with authentic sample prepared by standard methods described above.

Preparation of 2-(Phenylthio)benzamide (19).[12] *O*-Phenyl-2-(phenylthio)benzohydroxamic acid **18** (0.5 g, 0.0015 mol) was treated with PPA (10 g of P_2O_5 + 6 g of H_3PO_4) at 125 °C for 2.5 h. After the usual workup as given in the method described above, it afforded a neutral residue. The neutral residue was fractionally crystallized from methanol to give a compound, mp 207 °C, yield 55%. The mother liquors from the above furnished a compound with mp 178 °C.

The compound with mp 207 °C was identified as thioxanthenone (**15**). The compound with mp 178 °C was identical with 2-(phenylthio)benzamide (**19**).

Registry No. **12**, 89114-60-3; **12** (acid chloride), 53732-61-9; **13**, 104351-53-3; **13** (acid chloride), 61485-96-9; **14**, 89114-61-4; **14** (acid chloride), 43183-12-6; **15**, 492-22-8; **16**, 15774-82-0; **17**, 40478-82-8; **18**, 104351-54-4; **19**, 31913-94-7; **20**, 104351-55-5; **20** (acid), 1531-80-2; **21**, 104351-56-6; **21** (acid), 104351-51-1; **22**, 104351-57-7; **22** (acid), 104351-52-2; **23**, 104373-43-5; **23** (acid), 1699-03-2; **24**, 104351-58-8; **24** (acid), 5202-10-8; **25**, 104351-59-9; **25** (acid), 82387-28-8; **26**, 54705-25-8; **26** (thioether), 54705-18-9; **27**, 104351-60-2; **27** (thioether), 104351-62-4; **28**, 104351-61-3; **28** (thioether), 104351-63-5; **29**, 1531-77-7; **30**, 5202-11-9; **31**, 82387-29-9; CH_3OHN_2·HCl, 593-56-6; $C_6H_5ONH_2$·HCl, 6092-80-4.

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(11) Szmant, H. H. *J. Org. Chem.* **1953**, *18*, 745.

(12) Dhareshwar, G. P.; Hosangadi, B. D. *Indian J. Chem., Sect. B* **1978**, *16B*, 143.

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Fluorosulfonation. Insertion of Sulfur Trioxide into Allylic C–F Bonds[1,2]

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Insertion of sulfur trioxide into allylic C–F bonds of both terminal and internal fluoro olefins is shown to form the most stable olefinic products. A mechanism involving fluoroallyl cations as intermediates is proposed. State-of-the-art ab initio calculations of the ground-state energies for two isomeric unsaturated fluoro ethers establish the slightly greater stability (5.7 kcal/mol) of a vinyl ether over the corresponding fluoro olefin. A description of the optimized geometries of these molecules is also presented.

The early literature on reactions of fluoro olefins with sulfur trioxide shows that terminal fluoro olefins normally undergo cycloaddition to form sultones.[3,4] These sultones are readily isolated unless nonfluorinated substituents are present to facilitate further reaction.[5] On the other hand, few instances of detectable cycloadducts with internal fluoro olefins have been reported.[6,7] As is illustrated below, cycloaddition of SO_3 to an internal fluoro olefin bearing no electron-donating substituents is generally so sluggish that insertion into allylic C–F bonds is the pre-

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(1) Contribution no. 4133 from E. I. du Pont de Nemours & Company, Central Research & Development Department, Experimental Station, Wilmington, DE 19898.

(2) (a) For a preliminary communication on part of this work, see: Krespan, C. G.; England, D. C. *J. Am. Chem. Soc.* **1981**, *103*, 5598. (b) For details on the early syntheses and reactions of *F*-allyl fluorosulfate, see also: U.S. Pat. 4 206 138, 1980; U.S. Pat. 4 235 804, 1980; U.S. Pat. 4 292 449, 1981.

(3) England, D. C.; Dietrich, M. A.; Lindsey, R. V. *J. Am. Chem. Soc.* **1960**, *82*, 6181.

(4) Knunyants and Sokolski (Knunyants, I. L.; Sokolski, G. A. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 583) review the literature on synthesis and reactions of fluorinated β-sultones.

(5) (a) Krespan, C. G.; Smart, B. E.; Howard, E. G. *J. Am. Chem. Soc.* **1977**, *99*, 1214. (b) Smart, B. E.; Krespan, C. G. *J. Am. Chem. Soc.* **1977**, *99*, 1218.

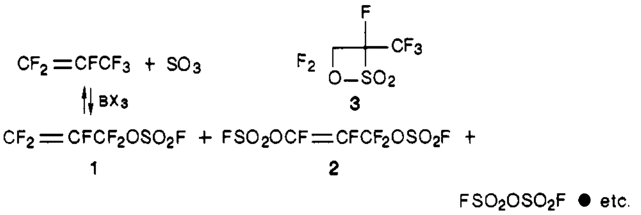
(6) (a) Several cycloadditions which are tabulated in ref 4 may be in error. As documented here, $CF_3CCl{=}CClCF_3$ was found to undergo allylic insertion only, rather than the cycloaddition ascribed to ref 6b. Studies (ref 8) with SO_3 and $CF_3CCl{=}CCl_2$ also found that C–F insertion is the only reaction to occur with or without catalyst. Furthermore, the several stable sultones obtained from alkyl fluorovinyl ethers as cited in ref 4 are at variance with more recent work (see ref 5a). (b) *Chem. Abstr.* **1958**, *52*, 15493.

(7) Smart (Smart, B. E. *J. Org. Chem.* **1976**, *41*, 2353) reports perhaps the earliest examples of insertion in the special case of SO_3 and polyfluorocyclobutenes. No cycloadducts were detected.

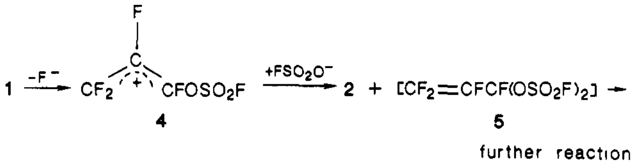
0022-3263/86/1951-4460$01.50/0

ferred reaction. For simple terminal fluoro olefins, the reactions catalyzed by trivalent boron are known to provide major amounts of C–F insertion products[2] in competition with cycloadduct formation.

Terminal Double Bonds. The first case of catalyzed C–F insertion of SO$_3$ produced *F*-allyl fluorosulfate (1) from *F*-propene.[2] Catalysts for this reversible transformation were trivalent boron compounds BX$_3$, without which sultone 3 was formed exclusively. The boron-catalyzed reaction has since been shown to yield lesser amounts of *E*/*Z* bis(fluorosulfate) 2, as well as carbonyl-containing byproducts and the anhydrides (FSO$_2$)$_2$O and (FSO$_2$O)$_2$SO$_2$.



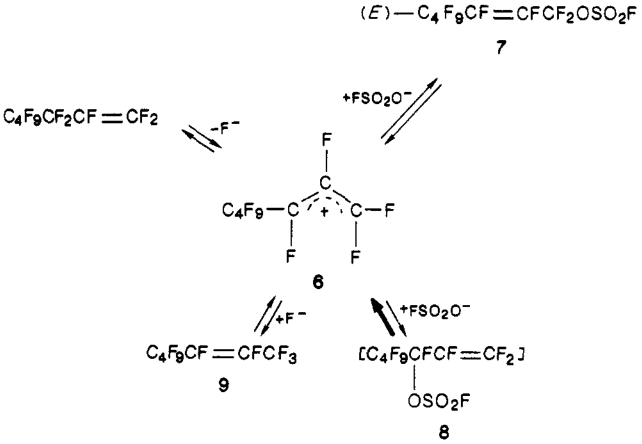
This finding has some bearing on the reaction mechanism, since 1, as the presumed precursor to 2, must undergo double-bond migration if allylic fluorine is the activated position in the molecule, i.e., intermediate 4 is implicated.



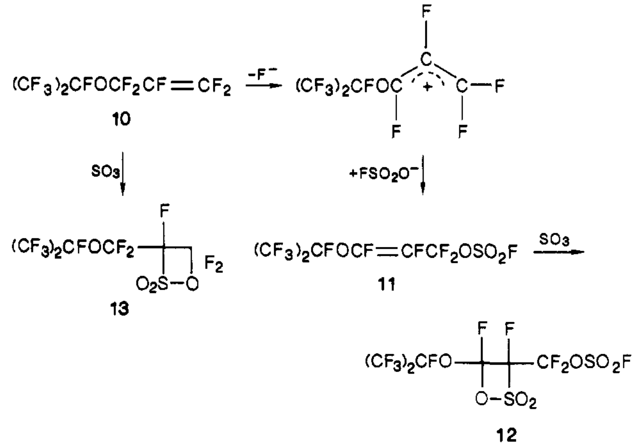
Such interchangeability of fluoride ion and fluorosulfate ion is the same as that observed in interconversions of 1 and *F*-propene, except that unsymmetrical cation 4 would also be expected to produce a 1,1-bis(fluorosulfate) (5). *gem*-Fluorosulfates such as 5, however, appear to be unstable under the reaction conditions and lead irreversibly to carbonyl compounds and pyrosulfuryl derivatives. Although carbonyl products derived from *F*-propene were only detected by IR, such products have been isolated from other olefins as described below.

Low regioselectivity in the conversion of 1 to bis(fluorosulfates) via 4 in a reversible reaction can be accounted for by an electronic similarity between F and FSO$_2$O groups. For *F*-alk-1-enes such as *F*-hept-1-ene, however, the postulated unsymmetrical cationic intermediate (6) provides terminal fluorosulfate 7 selectively,[9] as befits a reversible process in which the more thermodynamically stable product 7 with double bond migrated to an internal position is favored over 8. Rearranged olefin 9 was also formed, as expected for a reversible process of fluorine transfer, along with 2,1-sultone.

Whether or not 7 is the kinetically favored product is unknown. In any case, indirect evidence was obtained that conversion of whatever amount of 8 is formed to product 7 must go through cation 6 rather than by a concerted 1,3-shift. The ^{19}F NMR spectrum of related fluorosulfate 1 showed no appreciable signal averaging at 150 °C, indicating a barrier of at least 18 kcal/mol for rearrangement of 1 via a degenerate 1,3-fluorosulfate shift.



F-Allyl ethers[2] are another class of compound capable of producing an unsymmetrical allylic cation. In the case of ether 10, the predominant reaction is again sulfonation at the terminal position with migration of the double bond to give 11 and then 12; minor amounts of sultone 13 are also formed.[10]



Regioselective formation of 11 (and 12) in the reversible fluorosulfonation reaction suggests that an *F*-alkoxy substituent destabilizes a double bond less than a fluorine atom. Indeed, it has recently been reported[10] that *F*-(allyl isopropyl ether), 10, can be isomerized to *F*-(propenyl isopropyl ether) 14 by using SbF$_5$ as the catalyst. We are

$$\underset{\mathbf{14}}{CF_3CF{=}CFOCF(CF_3)_2}$$

generally interested in calculating the properties of fluoro-substituted olefins[11] and have calculated the energy difference between the model compounds *F*-(allyl methyl ether) (15) and *F*-(propenyl methyl ether) (16) in order to verify the experimental prediction.

The calculations were done by using ab initio molecular orbital theory with a double-ζ basis set augmented by polarization functions on carbon and oxygen. Such a basis set provides a good description of the energies and structures of a wide range of fluorocarbons.[11-14] The ge-

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(8) Sterlin, S. R.; Cherstkov, V. F.; German, L. S.; Knunyants, I. L. *J. Fluorine Chem.* **1985**, *29*, 178.

(9) Experiments related to *F*-hept-1-ene were carried out by Dr. David Baillargeon of these laboratories. Somewhat similar results have been obtained with *F*-hex-7-ene: Cherstkov, V. F.; Sterlin, S. R.; German, L. S.; Knunyants, I. L. *Izv. Akad. Nauk SSSR, Ser. Khim* **1982**, 2791; *Chem. Abstr.* **1983**, *98*, 143032w.

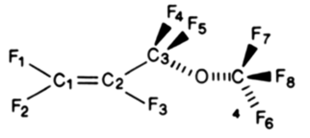
(10) This system has also been examined by Cherstkov et al. (Cherstkov, V. F.; Sterlin, S. R.; German, L. S.; Knunyants, I. L. *Izv. Akad. Nauk SSSR, Ser. Khim* **1982**, 2796; *Chem. Abstr.* **1983**, *98*, 142902t) with similar results, except that no 2:1 SO$_3$/ether adduct was reported.

(11) Dixon, D. A.; Fukunaga, T.; Smart, B. E. *J. Am. Chem. Soc.* **1986**, *108*, 1585.

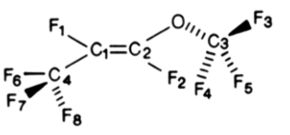
(12) Dixon, D. A.; Smart, B. E.; Fukunaga, T. *J. Am. Chem. Soc.* **1986**, *108*, 1585.

(13) Dixon, D. A. *J. Phys. Chem.* **1986**, *90*, 54.

Table I. Optimized Geometric Parameters for 15 and 16[a]



15

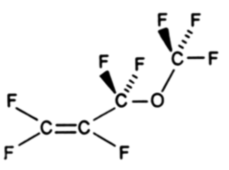


16

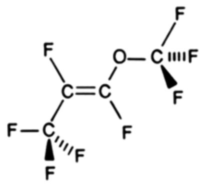
15		16	
Bond Lengths			
$r(C_1{=}C_2)$	1.308	$r(C_1{=}C_2)$	1.309
$r(C_2{-}C_3)$	1.510	$r(C_1{-}C_4)$	1.519
$r(C_3{-}O)$	1.372	$r(C_2{-}O)$	1.340
$r(C_4{-}O)$	1.357	$r(C_3{-}O)$	1.357
$r(C_1{-}F_1)$	1.299	$r(C_4{-}F_1)$	1.320
$r(C_1{-}F_2)$	1.296	$r(C_2{-}F_2)$	1.311
$r(C_2{-}F_3)$	1.327	$r(C_3{-}F_3)$	1.303
$r(C_3{-}F_4)$	1.328	$r(C_3{-}F_4)$	1.315
$r(C_3{-}F_5)$	1.325	$r(C_3{-}F_5)$	1.315
$r(C_4{-}F_6)$	1.308	$r(C_4{-}F_6)$	1.314
$r(C_4{-}F_7)$	1.314	$r(C_4{-}F_7)$	1.322
$r(C_4{-}F_8)$	1.313	$r(C_4{-}F_8)$	1.323
Bond Angles			
$\theta(C_2C_1F_1)$	124.1	$\theta(C_2C_1C_4)$	122.5
$\theta(C_2C_1F_2)$	124.4	$\theta(C_2C_1F_1)$	121.5
$\theta(F_1C_1F_2)$	111.5	$\theta(C_4C_1F_1)$	116.0
$\theta(C_1C_2C_3)$	124.4	$\theta(C_1C_2O)$	125.1
$\theta(C_1C_2F_3)$	120.9	$\theta(C_1C_2F_2)$	120.7
$\theta(C_3C_2F_3)$	114.7	$\theta(OC_2F_2)$	114.1
$\theta(C_2C_3O)$	108.5	$\theta(C_2OC_3)$	119.7
$\theta(C_2C_3F_4)$	110.4	$\theta(OC_3F_3)$	107.2
$\theta(C_2C_3F_5)$	109.7	$\theta(OC_3F_4)$	116.6
$\theta(OC_3F_4)$	110.4	$\theta(OC_3F_5)$	111.7
$\theta(OC_3F_5)$	110.6	$\theta(F_3C_3F_4)$	109.1
$\theta(F_4C_3F_5)$	107.2	$\theta(F_3C_3F_5)$	109.3
$\theta(C_3OC_4)$	123.2	$\theta(F_4C_3F_5)$	107.9
$\theta(OC_4F_6)$	106.6	$\theta(C_1C_4F_6)$	110.3
$\theta(OC_4F_7)$	112.3	$\theta(C_1C_4F_7)$	111.3
$\theta(OC_4F_8)$	112.3	$\theta(C_1C_4F_8)$	111.0
$\theta(F_6C_4F_7)$	108.6	$\theta(F_6C_4F_7)$	108.4
$\theta(F_6C_4F_8)$	108.8	$\theta(F_6C_4F_8)$	108.3
$\theta(F_7C_4F_8)$	108.1	$\theta(F_7C_4F_8)$	107.4

[a] Bond lengths in Å. Bond angles in degrees.

ometries were initially optimized in C_s symmetry in the following conformations:



15



16

Previous experience has shown that twisting about the C–O bond in perfluorovinyl ethers leads to a more stable conformation.[14,15] After partial convergence of the above C_s structures, rotation by 90° about the C_2–C_3 bond in **15** and about the C_2–O bond in **16** was carried out. (See Table I for numbering scheme). The rotated structures were of lower energy. Geometry optimization was completed on the rotated structures.

The optimized geometries are given in Table I and molecular graphics views of the molecules are given in Figure 1. The structures exhibit the expected trends. The most striking feature is the nonplanarity of these systems. The optimum dihedral angle about the C_2–C_3 bond in **15** is 89.2° while the optimum dihedral angle about the C_2–O bond in **16** is 91.8°. The C=C bond distances in both **15** and **16** are short and are comparable to the calculated[11] C=C bond distances (with this basis set) in C_2F_4 ($r(C{=}C) = 1.307$ Å) and C_2F_3H ($r(C{=}C) = 1.307$ Å). The SCF bond distances are too short as compared to experiment as are the C–F values. Correction factors from calculations on the fluoroethylenes[11] are +0.016 Å for $r(C{=}C)$ and +0.011 Å for $r(C{-}F)$.

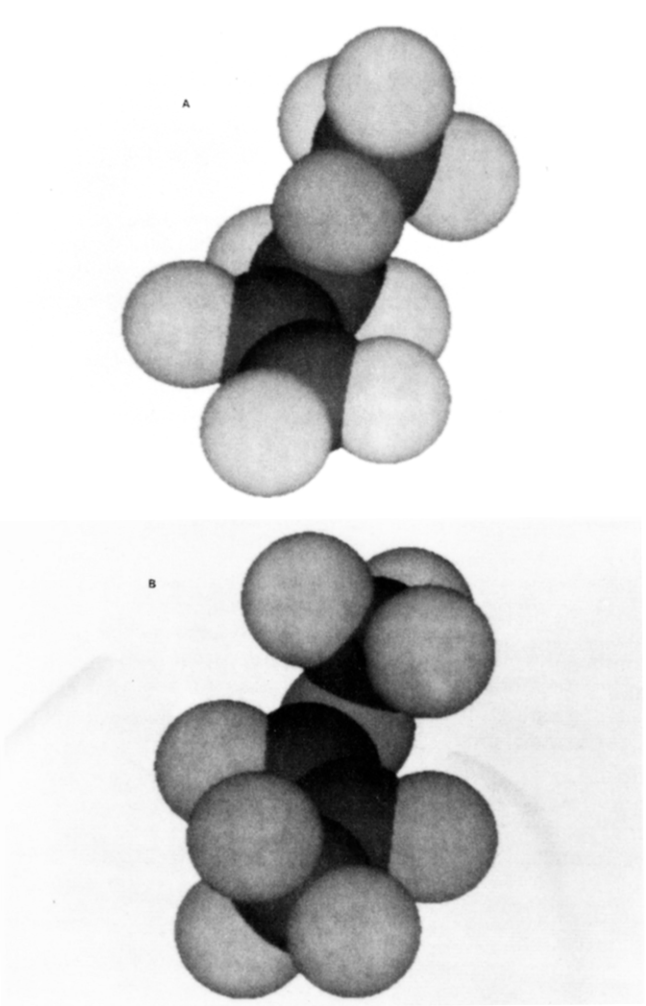


Figure 1. Molecular graphics view of (a) **15** and (b) **16**. The dark atoms are C, the light atom is O, and the intermediate shaded atoms are the fluorines.

The C_2–C_3 bond in **15** is a normal C–C bond between an sp^2 and an sp^3 center.[16] The C–O bond distances are shorter than a normal C–O ether or alcohol bond if no fluorines are present.[17] However, substitution of fluorines leads to a shorter C–O bond.[15,17] This shortening is due in large part to an increase in the ionic character of the bond because of an increased positive charge at carbon due to the substituted fluorines. The C_4–O bond is shorter and more ionic than the C_3–O bond which is consistent with this argument. Carbon C_4 has three fluorines bonded to it and is thus more positive than C_3 which has only two bonded fluorines. The C_1–F bonds are quite short and are 0.007 to 0.01 Å shorter than the C–F bonds in C_2F_4.[11] The

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(14) Dixon, D. A., unpublished work.

(15) Pacansky, J.; Liu, B. *J. Phys. Chem.* **1985**, *89*, 1883.

(16) The calculated value for $r(C{-}C)$ in propene is 1.507 Å and in hexafluoropropene is 1.514 Å. Reference 14.

(17) (a) An average experimental value for $r(C{-}O)$ is 1.426 ± 0.005 Å. *Tables of Interatomic Distances and Configurations in Molecules and Ions*; Sutton, L. E., Ed.; Special Publication No. 18 (The Chemical Society, London, 1985). (b) The experimental bond distance $r(C{-}O)$ in $(CF_3)_2O$ is 1.369 ± 0.004 Å. Lowrey, A. H.; George, C.; D'Antonio, P.; Karle, J. *J. Mol. Struct.* **1980**, *63*, 243.

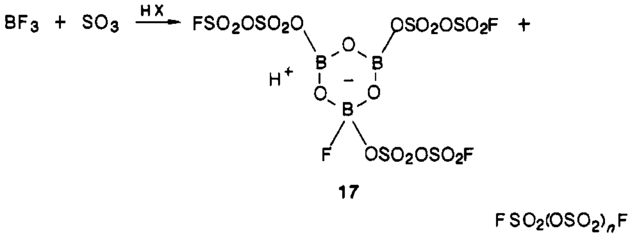
C_2–F bond is longer than the C_1–F bonds but is shorter than the C(H)–F bond in C_2F_3H.[11] The C_3–F bonds are longer than the C_4–F bonds consistent with the bond-length differences in CF_2H_2 and CF_3H.[18]

The bond angles for **15** are typical of those observed in other fluorocarbons. The $F_1C_1F_2$ bond angle is quite small as compared to a nominal sp^2 value of 120° and is similar to the value found in C_2F_4 (θ(FCF) = 112.6°).[11] The $C_3C_2F_3$ bond angle is larger (114.7° as compared to $\theta(F_1C_1F_2)$ = 111.5°) and is comparable to θ(HCF) = 115.7° in C_2F_3H.[11] The bond angles at C_3 show small deviations from the ideal tetrahedral values and the FCF bond angle of 107.2° is similar to the FCF bond angle of 109° found in CF_2H_2.[14] The bond angle at oxygen ($\theta(C_3OC_4)$) opens up from the tetrahedral value to 123.2°. This follows the trend observed in perfluorodimethyl ether where θ(COC) = 119.1 ± 0.8°.[17b] The FC_4F bond angles average to 108.5° in good agreement with the FCF bond angle of 108.4° found for CF_3H.[14]

The structure of **16** also follows expected trends. The C_1–C_4 bond is ~0.01 Å longer than the C_2–C_3 bond found in **15**. The C_1–F_1 bond distance is 0.01 Å longer than $r(C_2–F_2)$, consistent with the result that the oxygen bonded at C_2 is more electronegative than the carbon bonded at C_1. The CF_3 groups are similar with the C_3–F bond distances being shorter than the C_4–F bond distances. This is again consistent with electronegativity effects since the O bonded to C_3 is more electronegative than the C bonded to C_4. There are two essentially equivalent bonds in each CF_3 group and these are longer than the other C–F bond. (These approximately "equivalent" C–F bonds were exactly equivalent by symmetry in the C_s structures.) Both $\theta(OC_2F_2)$ and $\theta(C_4C_1F_1)$ are quite similar to θ(HCF) in C_2F_3H and consistent with electronegativity effects, $\theta(OC_2F_2)$ is smaller than $\theta(C_4C_1F_1)$. The value for $\theta(C_2OC_3)$ is essentially identical with θ(COC) in CF_3OCF_3[17b] and 4° smaller than $\theta(C_3OC_4)$ in **15**. The CF_3 groups in **16** have normal bond angles.

The calculated energy difference is 5.7 kcal/mol with **16** more stable than **15**. The applied basis set usually gives good values for fluorocarbon energetics especially for a simple isomerization reaction, and we expect an accuracy of ±1 kcal/mol.[11-14] The substantial value for ΔE shows that **15** should be essentially completely converted to **16** at thermodynamic equilibrium. We also note that this calculation is quite large, 147 contracted basis functions. However, with new advances in hardware and software, ab initio molecular orbital calculations of this kind can be done and can provide useful structural and energetic data about reasonably sized organic molecules.

Catalyst is required with all these terminal olefins to promote allylic fluorosulfate formation at the expense of thermal 2 + 2 cycloaddition, which leads irreversibly to sultone. Attempts to prepare $B(OSO_2F)_3$ from BCl_3 and FSO_2OH proceeded part way with ready evolution of HCl to give an involatile fluorosulfate containing appreciable acidic hydrogen, probably a mixture of "ate" complexes. Part of the material volatilized with cracking at 70 °C (0.01 mm).[19] An aprotic route starting from $BrOSO_2F$[20] was similarly unsuccessful. Even gaseous BF_3, a reactive allylic fluorosulfonation catalyst, did not form $B(OSO_2F)_3$ with liquid SO_3. Instead, there was obtained a well-defined white solid whose properties and analyses correlate best with structure **17** and/or isomers. The small amount of protic acid necessary to form **17** could arise from adventitious moisture in the SO_3.



Solid **17** is itself a strong catalyst for insertion of SO_3 into a C–F bond to form **1**. Thus, even though effective catalyst combinations are obtained from sulfur trioxide to which has been added a few percent of a trivalent boron compound,[2] a spectrum of potential catalysts are evidently available which may include tetracoordinated as well as tricoordinated boron. Protic acids of the type HBR_4 can be exceptionally strong in compositions where R = OSO_2X[20,21] and may be capable of initiating reaction by protonation of allylic fluorine. Since sulfonated B(III) compounds should be strong Lewis acids, they may also attack at an allylic fluorine atom.[22]

The formation of sulfonic anhydrides, $FSO_2(OSO_2)_nF$, as coproducts with **17** in the BF_3/SO_3 reaction has a counterpart in the instability of many (acyloxy)boranes at 20 °C. The following dismutation to anhydride and oxyborane is common.[24]

$$B(OCOR)_3 \rightarrow (RCO_2)_2BOB(O_2CR)_2 + (RCO)_2O$$

As a result of these studies of catalyst and conditions, convenient synthesis conditions for *F*-allyl fluorosulfate have been defined as described in the Experimental Section.

Internal Carbon–Carbon Multiple Bonds. The postulate that catalysts for SO_3 insertion generate an ion pair containing a stabilized fluorocarbonium ion or a related intermediate bearing a large δ^+ charge requires that an internal olefin such as *F*-but-2-ene would form allylic fluorosulfate *without* migration of the double bond. Formation of allyl cation **18** as the reactive intermediate should lead to terminal fluorosulfate **19**, just as the closely related **6** gives **7**. Absence of double-bond migration would tend to rule out a concerted fluoro-ene type of reaction.

The actual reaction gave the predicted result. *F*-but-2-ene reacted with SO_3 (Sulfan B containing approximately 0.05 wt % of trimethylborate as stabilizer) at 100–150 °C to give products derived from attack at the terminal positions. In addition to formation of **19**, replacement of *gem*-fluorine atoms resulted in formation of acyl fluoride

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(18) The calculated value for r(C–F) in CF_2H_2 is 1.346 Å and in CF_3H is 1.322 Å. Reference 14.

(19) See also: Engelbrecht, A.; Tschager, E. *Z. Anorg. Allg. Chem.* **1977**, *433*, 19. The system $B(OSO_2F)_3/FSO_3H$ was found to be too unstable for detailed study. The somewhat more stable $B(OSO_2CF_3)_3/CF_3SO_2OH$ system was shown to have an acidity comparable to that of $SbF_5 \cdot 3SO_3/FSO_3H$, the most acidic system known.

(20) D. Des Marteau, private communication. The reaction of BCl_3 with $BrOSO_2F$ was found to be a complicated one giving many products, none of them $B(OSO_2F)_3$. A glassy solid was obtained in addition to volatiles.

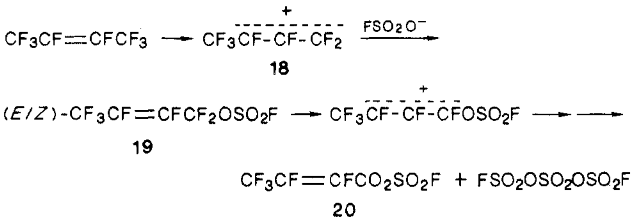
(21) Schmidt, M.; Siebert, W. *Comprehensive Inorganic Chemistry*; Pergamon Press: Oxford, 1973; Vol. 2, p 875. The only really strong acid in the H_3BO_3/oleum system is $HB(HSO_4)_4$, which easily protonates sulfuric acid to give $H_3SO_4^+ + B(HSO_4)_4^-$ in solution.

(22) Attempts during the present work to generate *F*-allyl cation from *F*-propene and BF_3 were unsuccessful. The stronger Lewis acid SbF_5, however, is known to give *F*-allyl cation with *F*-propene,[23] and antimony(V) fluoride was later shown to be an active catalyst for allylic fluorosulfonation.[8]

(23) Chambers, R. D.; Parkin, A.; Matthews, R. S. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2107.

(24) (a) Brown, H. C.; Stocky, T. P. *J. Am. Chem. Soc.* **1977**, *99*, 8218. (b) A referee has pointed out the related formation of sulfonic anhydride $CH_3(OSO_2)_nOCH_3$ from $(CH_3O)_2SO_2 + SO_3$ as reported by Wazer, J. R.; Grant, D.; Dungan, C. J. *J. Am. Chem. Soc.* **1965**, *87*, 3333.

and fluorosulfonic anhydrides. The acyl fluoride was isolated as the acyl fluorosulfate **20** after further reaction with SO_3.[25] Product from attack at the double bond was not detected.



$$CF_3CF{=}CFCF_3 \longrightarrow \underset{\mathbf{18}}{CF_3\overset{+}{\overline{CF-CF-CF_2}}} \xrightarrow{FSO_2O^-}$$

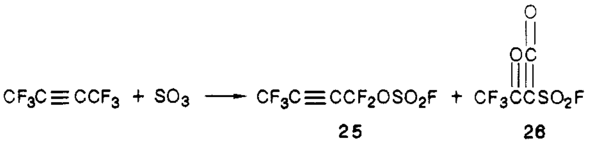
$$\underset{\mathbf{19}}{(E/Z)\text{-}CF_3CF{=}CFCF_2OSO_2F} \longrightarrow CF_3\overset{+}{\overline{CF-CF-CFOSO_2F}} \longrightarrow\longrightarrow$$

$$\underset{\mathbf{20}}{CF_3CF{=}CFCO_2SO_2F} + FSO_2OSO_2OSO_2F$$

2,3-Dichlorohexafluoro-2-butene gave similar results under milder conditions. Fluorosulfate **21** could be isolated in moderate yield, and strong evidence was obtained for the formation of **22–24**.

$$CF_3CCl{=}CClCF_3 \rightarrow \underset{\mathbf{21}}{CF_3CCl{=}CClCF_2OSO_2F} + FSO_2OSO_2F + \underset{\mathbf{22}}{CF_3CCl{=}CClCO_2SO_2F} + \underset{\mathbf{23}}{FSO_2OCF_2CCl{=}CClCF_2OSO_2F} + \underset{\mathbf{24}}{FSO_2OCF_2CCl{=}CClCO_2SO_2F}$$

Extension to an acetylene, *F*-but-2-yne, demonstrated that an internal triple bond, in contrast to a double bond, is susceptible to attack by SO_3. The mixture of products included unusual acylketene **26**, believed to arise from initial cycloaddition of SO_3 to the triple bond, in addition to fluorosulfate **25**.



$$CF_3C{\equiv}CCF_3 + SO_3 \longrightarrow \underset{\mathbf{25}}{CF_3C{\equiv}CCF_2OSO_2F} + \underset{\mathbf{26}}{CF_3\overset{\overset{\overset{O}{\|}}{OC}}{\underset{}{C}}CSO_2F}$$

Experimental Section[26]

Synthesis Conditions for *F*-Allyl Fluorosulfate (1). A study of the variables associated with the preparation of *F*-allyl fluorosulfate indicated little difference in which source of sulfur trioxide is used or in whether distilled or undistilled sulfur trioxide is used, provided it contains 1–1.5 wt % of added trimethylborate. A shortened reaction time at 35 °C has made the synthesis even more convenient. As an example, a 1.4-L Monel tube charged with 300 g (3.75 mol) of undistilled sulfur trioxide, 3.0 g (0.03 mol) of trimethylborate, and 788 g (5.25 mol) of *F*-propene was agitated for 6 h at 35 °C. Rapid distillation of liquid products gave 586 g of liquid, bp 25–65 °C. Fractionation through a spinning band column gave 450 g (52%) of 95% pure product **1**, bp 60–65 °C. Pure material, 343 g (40%), bp 62–64 °C, was obtained by redistillation (ref 2a reports bp 63–64 °C for **1**).

Tetrafluoropropenediyl 1,3-Bis(fluorosulfate) (2). A mixture of 240 g (3.0 mol) of SO_3, 3 g of BF_3, and 525 g (3.5 mol) of *F*-propene charged into a 1200-mL metal tube was reacted at 25 °C for 3 days and then at 100 °C for 8 h. Fractionation afforded 61.3 g (9%) of crude sultone **3**, bp 46–60 °C, and 146.9 g (21%) of **1**, bp 60 °C (1 atm), 44 °C (350 mm). Further distillation gave 155.4 g of a mixture, bp 49–56 °C (50 mm), containing **2** along with byproducts such as $FSO_2OSO_2OSO_2F$, identified by ^{19}F NMR. The center cut, 64.6 g, bp 53–56 °C (50 mm), was dissolved in 150 mL of diethyl ether at 5 °C and then stirred overnight at 25 °C. Distillation gave, after a foreshot of byproducts, 36.0 g of bis(fluorosulfate) **2**, bp 54–55 °C (50 mm). The *Z*/*E* ratio was 1:1.3 by ^{19}F NMR. For (*E*)-**2**: ϕ 49.1 (t of d, J_{FF} = 8.0, 1.5 Hz, 1 F, FSO_2OCF_2), 47.6 (d of d, J_{FF} = 8.6, 5.1 Hz, 1 F, $FSO_2OCF{=}$), –72.6 (ddd, J_{FF} = 27.0, 11.9, 8.0 Hz, 2 F, CF_2), –111.7 (dtd, J_{FF} = 122.9, 27.0, 5.1 Hz, 1 F, $FSO_2OCF{=}$), –170.7 (dtdd, J_{FF} = 122.9, 11.9, 8.6, 1.5 Hz, 1 F, $—CF_2CF{=}$). For (*Z*)-2: ϕ 49.3 (t of m, J_{FF} = 8.1 Hz, 1 F, FSO_2OCF_2), 47.4 (m, 1 F, $FSO_2CF{=}$), –72.2 (m, 2 F, CF_2), –91.7 (dtd, J_{FF} = 35.9, 7.7, 6.1 Hz, 1 F, $FSO_2OCF{=}$), –166.2 (dtdd, J_{FF} = 35.9, 11.8, 1.4, 1.4 Hz, 1 F, $—CF_2CF{=}$). IR: 1765 (C=C), 1490 cm^{-1} and sh (OSO_2F). Redistillation with the pot temperature kept below 80 °C gave an analytical sample, bp 44–46 °C (25 mm).

Anal. Calcd for $C_3F_6O_6S_2$: F, 36.76. Found: F, 36.74.

***F*-2-Heptenyl 1-Fluorosulfate (7).** *F*-Hept-1-ene (10.5 g, 0.030 mol), sulfur trioxide (2.4 g, 0.030 mol), and trimethylborate (0.05 g, 0.5 mmol) were kept at 25 °C for 2 days and then at 100 °C for 4 days. Fractionation gave 1.7 g of an approximately 1:1 mixture of *F*-hept-1-ene and *F*-hept-2-ene bp 23–30 °C (90 mm), identified by ^{19}F NMR. Further distillation gave 2.9 g, mainly sultone, bp 26–60 °C (50 mm), followed by 3.7 g (29%) of *E* isomer of fluorosulfate **7**, bp 62–66 °C (50 mm). IR: 1480 cm^{-1} (SO_2F). NMR: ^{19}F ϕ 49.2 (t, J_{FF} = 8 Hz, 1 F, OSO_2F), –72.8 (dddm, J_{FF} = 24, 8, 8, Hz, 2 F, $OCF_2C{=}$), –81.8 (tt, J_{FF} = 10, 2.5 Hz, 3 F, CF_3), –119.2 (m, 2 F, CF_2), –125.1 (m, 2 F, CF_2), –127.1 (m, 2 F, CF_2), –152.8 (dtm, J_{FF} = 141, 26 Hz, 1 F, $CF{=}$), –156.5 (dttm, J_{FF} = 141, 25, 8 Hz, 1 F, $CF{=}$). No indication of the presence of either (*Z*)-**6** or isomeric fluorosulfate **7** was found. A similar reaction conducted at 25 °C for 6 weeks gave sultone only.

***F*-(Allyl Isopropyl Ether) (10).** A mixture of 75.6 g (1.3 mol) of KF, 800-mL of diglyme, and 216 g (1.3 mol, 130 mL at –80 °C) of *F*-acetone was stirred at 5 °C until the KF dissolved. Then 299 g (1.30 mol) of *F*-allyl fluorosulfate was added with cooling to maintain 0–5 °C, and the mixture was stirred there for 3 h and then at 25 °C overnight. It was diluted with 2 L of water, and the lower layer was washed with 500 mL of water, dried, filtered, and distilled to afford 305.9 g (74%) of ether **10**, bp 58–60 °C. IR: 1800 ($CF{=}CF_2$), 1300–1100 cm^{-1} (CF, CO). NMR: ^{19}F ϕ –69.8 (m, 2 F, $OCF_2C{=}$), –81.4 (td, J_{FF} = 5.6, 2.2 Hz, 6 F, CF_3), –92.9 (ddt, J_{FF} = 54.1, 39.8, 7.5 Hz, 1 F, *cis*-$CF_2CF{=}CF$), –105.9 (ddt, J_{FF} = 117.5, 54.1, 24.3 Hz, 1 F, *trans*-$CF_2CF{=}CF$), –146.3 (tm, J_{FF} = 22.2 Hz, 1 F, CF), –190.7 (ddt, J_{FF} = 117.5, 39.8, 13.7 Hz, 1 F, $CF_2CF{=}CF$).

Anal. Calcd for $C_6F_{12}O$: C, 22.80; F, 72.14. Found: C, 22.64; F, 71.88.

***cis*- and *trans*-*F*-(3-(Fluorosulfato)allyl Isopropyl Ether) (11) and Sultones 12 and 13 from Reaction of 10 with SO_3.** A 100-mL Carius tube was charged with 63.0 g (0.20 mol) of ether **10** and 16.0 g (0.20 mol) of commercial SO_3 (Sulfan B)[27] sealed and stored at 5 °C for 8 weeks. The reaction mixture was distilled to give 16.8 g of fuming liquid, bp 45–53 °C, and then 5.8 g of a mixture of sultone **13** and **11**, bp 40–45 °C (40 mm), followed by 12.8 g (16%) of **11**, bp 45–48 °C (40 mm). For **11**: IR 1760 (C=C), 1490 cm^{-1} (OSO_2F). ^{19}F NMR indicated a 1.7:1 *E*/*Z* mixture. For (*E*)-**11**: ϕ 48.6 (t, J_{FF} = 7.9 Hz, 1 F, SO_2F), –72.4 (ddd, J_{FF} = 27.9, 12.0, 7.9 Hz, 2 F, CF_2), –80.9 (ddd, J_{FF} = 4.0, 2.7, 2.7 Hz, 6 F, CF_3), –102.0 (dtd of septets, J_{FF} = 122.3, 27.9, 11.5, 4.0 Hz, 1 F, $—OCF{=}$), –140.4 (dd of septets, J_{FF} = 11.5, 8.2, 2.7 Hz, 1 F, $(CF_3)_2CF$), –174.1 (dm, J_{FF} = 122.3 Hz, 1 F, $—CF_2CF{=}$). For (*Z*)-**11**: 48.4 (t, J_{FF} = 8.4 Hz, 1 F, SO_2F), –72.2 (m, 2 F, CF_2), –80.1 (ddt, J_{FF} = 5.5, 2.7, 2.7 Hz, 6 F, CF_3), –88.6 (ddm, J_{FF} = 31.3, 15.2 Hz, 1 F, $—OCF{=}$), –139.1 (dm, J_{FF} = 15.2 Hz, 1 F, $(CF_3)_2CF$), –169.5 (dtm, J_{FF} = 31.3, 11.9 Hz, 1 F, $—CF_2CF{=}$).

Anal. Calcd for $C_6F_{12}O_4S$: C, 18.19; S, 8.10. Found: C, 18.15; S, 8.18.

The foreshot showed bands for **11** along with additional bands attributable to **13**, notably 1445 cm^{-1} (sultone). ^{19}F NMR showed the presence of 1.9:1:3.3 of (*E*/*Z*)-**11**/**13** with bands for **13** at ϕ –74.6 (m, 2 F, CF_2), –81.3 (m, 6 F, CF_3), –145.7 (t of septets, J_{FF} = 22.0, 2.3 Hz, F, $(CF_3)_2CF$), –151.8 (td, J_{FF} = 8.1, 7.1 Hz, 1 F, ring CF) with AB branches for ring CF_2 at –82.4 (ddt, J_{FF} = 108,

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[25] Krespan, C. G.; England, D. C. *J. Org. Chem.* **1975**, *40*, 2937. The general reaction is reported to proceed readily but to be reversible at elevated temperatures.

[26] NMR spectra were taken at 94.1 MHz on 20% solutions in CCl_4 with $CFCl_3$ as internal reference, and IR spectra were obtained on 10% solutions in CCl_4 unless otherwise specified.

[27] Allied Chemical Corp. specifications for Sulfan B are 99.4% SO_3, 0.05–0.075% $B(OCH_3)_3$, and 0.10–0.14% G. E. Silicone SF96, with maxima of 0.20% H_2SO_4 and 0.02% SO_2 as impurities. The trimethylborate is present as a stabilizer which retards polymer formation.

7.1, 2.5 Hz, 1 F) and −89.5 (dt, J_{FF} = 108, 12.5 Hz, 1 F).

A higher fraction, bp 51 °C (5 mm), 17.3 g (36%) was compound **12**. IR: 1490 (OSO_2F), 1445 (sultone), 1300–1100 cm^{-1} (CF, CO, SO_2). ^{19}F NMR indicated a 1.4:1 mixture of isomers (cis and trans identity unknown). For the major isomer: ϕ 51.2 (m, 1 F, SO_2F), −77.1 (AB center, 2 F, CF_2O), −77.6 (m, 1 F, ring OCF), −80.9 (m, 6 F, CF_3), −145.2 (d of septets, J_{FF} = 18.7, 2.5 Hz, 1 F, $(CF_3)_2C\mathit{F}$), −149.0 (td, J_{FF} = 6.7, 4.2 Hz, 1 F, ring $C\mathit{F}CF_2$). For the minor isomer of **12**: ϕ 51.2 (m, 1 F, SO_2F), −77.1 (AB center, 2 F, CF_2O), −80.9 (m, 6 F, CF_3), −84.5 (br m, 1 F, ring OCF), −144.7 (d of septets, J_{FF} = 20.2, 2.1 Hz, 1 F, $(CF_3)_2C\mathit{F}$), −149.6 (m, 1 F, ring $C\mathit{F}CF_2$).

Anal. Calcd for $C_6F_{12}O_7S_2$: C, 15.13. Found: C, 15.15.

BF_3/SO_3 Adduct 17. Liquid SO_3 (48.0 g, 0.60 mol) was stirred at 25 °C while BF_3 gas was passed in. A mild exotherm and absorption of BF_3 were noted until 11.0 g (0.16 mol) of BF_3 had been added, when solid plugged the inlet tube. Evacuation at 25 °C (0.025 mm) gave 23 g of white, dry, slightly fuming solid residue **17**. IR (CaF_2 plates) (Fluorolube and Nujol mulls): 1500 (rel weak, SO_2F), 1290 cm^{-1} (strong, unassigned).

Anal. Calcd for $B_3HF_4O_{21}S_6$: B, 5.09; F, 11.91; S, 30.16. Found: B, 4.97; F, 11.39; S, 30.02.

The elemental analysis corresponds most nearly to a structure such as **17**. The presence of $B(OSO_2)_n\mathit{F}$ groups may be related to the strong IR absorption at 1290 cm^{-1}. The presence of -$(OSO_2)_{n>1}F$ groups in **17** was supported by treatment of the solid at 25 °C with a small proportion of concentrated H_2SO_4; a mobile liquid phase was formed which showed ^{19}F NMR peaks compatible with $FSO_2(OSO_2)_n\mathit{F}$ (neat sample: ϕ 4 singlets near 50 with 2 major components at 50.9 and 50.4). The insolubility of solid **17** in various organic media also suggests boron ate complexes such as **17** to be the main or only components.

Reaction of *F*-But-2-ene with SO_3. A Carius tube containing 41.5 g (0.21 mol) of *F*-but-2-ene and 16.0 g (0.20 mol) of SO_3 was heated at 100 °C for 6 days. Although two phases were no longer present at 100 °C, they did appear at 25 °C. After 5 days at 150 °C, the mixture remained homogeneous at 25 °C. After another 4 days at 150 °C, the mixture was fractionated. The fraction collected in the −80 °C trap was 18 mL (ca. 28.8 g, 69%) of recovered *F*-but-2-ene, identified by IR and apparently containing a small amount of FSO_2OSO_2F. *F*-2-Butene-1-fluorosulfate (**19**) was obtained as 3.0 g (5% convn, 16% yield) of liquid, bp 46 °C (250 mm). IR: 1720 (C=C), 1485 (OSO_2F), 1300–1100 cm^{-1} (CF, CO, SO_2). MS: *m/e* 280 (M^+), 261 ($M^+ - F$), 211 ($M^+ - CF_3$), 181 ($M^+ - OSO_2F$), 131 ($M^+ - CF_2OSO_2F$), 83 (SO_2F^+), 69 (CF_3^+); M^+ mass measured 279.9451, calcd. for $C_4F_8O_3S$, 279.9440. NMR showed 80:20 *E*/*Z* isomers. For (*E*)-**15**: ^{19}F ϕ 46.5 (tm, J_{FF} = 7 Hz, 1 F along with peak from cis isomer, SO_2F), −69.8 (ddm, J_{FF} = 18, 6 Hz, 3 F, CF_3), −73.0 (ddd, J_{FF} = 23, 7, ~6 Hz, F, CF_2O), with AB for vinylic F at −156.9 (dtqd, J_{FF} = 139, 23, 7, ~1 Hz, 1 F), and −159.2 (dqtd, J_{FF} = 139, 18, 6, 1.5 Hz, 1 F). For (*Z*)-**15**: ϕ 46.5 (tm, J_{FF} = 18 Hz, 1 F, SO_2F), −67.0 (m, 3 F, CF_3), −70.6 (m, 2 F, CF_2O), −139.1 (m, 1 F, =CF), −141.4 (m, 1 F, =CF).

Anal. Calcd for $C_4F_8O_3S$: C, 17.15; F, 54.26. Found: C, 17.07; F, 54.33.

Acyl fluorosulfate **20** was obtained as 4.4 g of a nearly 1:1 mixture with the anhydride $FSO_2OSO_2OSO_2F_7$, bp 55–61 °C (60 mm). IR (CaF_2): 1830 (C=O), 1740 and 1700 (C=C), 1500 and 1490 (OSO_2), 1300–1100 cm^{-1} (CF, CO, SO_2). ^{19}F NMR: ϕ 50.0 for $FSO_2OSO_2OSO_2F$ along with bands for 70:30 *E*/*Z* isomers of **20**. For (*E*)-**20**: ϕ 47.7 (s, 1 F, SO_2F), −69.4 (dd, J_{FF} = 21.0, 8.2 Hz, 3 F, CF_3), −140.3 (dq, J_{FF} = 137, 8.2 Hz, 1 F, $CF_3C\mathit{F}$), −155.9 (dq, J_{FF} = 137, 21 Hz, 1 F, $CF_3C{=}C\mathit{F}$). For (*Z*)-**20**: ϕ 47.6 (s, 1 F, SO_2F), −66.7 (d of overlapping d, J_{FF} = 8.2, 8.2 Hz, 3 F, CF_3), −122.5 (dq, J_{FF} = 11.6, 8.2 Hz, 1 F, CF_3CF), −139.8 (dq, J_{FF} = 11.6, 8.2 Hz, 1 F, $CF_3C{=}C\mathit{F}$).

Anal. Calcd for $C_4F_8O_{12}S_4$: C, 9.23; F, 29.21; S, 24.65. Found: C, 9.36; F, 29.96; S, 24.82.

SO_3 with 2,3-Dichlorohexafluorobut-2-ene. A Carius tube charged with 23.3 g (0.10 mol) of 2,3-dichlorohexafluorobut-2-ene and 16.0 g (0.20 mol) of SO_3 was heated at 100 °C overnight. The contents were distilled to give 11.6 g (37%) of 2,3-dichloropentafluoro-2-butene-1-fluorosulfate (**21**), bp 60–65 °C (50 mm). IR: 1610 (C=CCl), 1485 (SO_2F), 1250–1100 cm^{-1} (CF, CO, SO_2). ^{19}F NMR showed 70:30 *E*/*Z* isomers to be present. For (*E*)-**21**: ϕ 48.9 (t, J_{FF} = 8.1 Hz, 1 F, SO_2F), −63.9 (t, J_{FF} = 1.4 Hz, 3 F, CF_3), −65.7 (dq, J_{FF} = 8.1, 1.4 Hz, 2 F, CF_2O). For (*Z*)-**21**: ϕ 48.8 (tq, J_{FF} = 8.5, 2.5 Hz, 1 F, SO_2F), −60.0 (td, J_{FF} = 15.5, 2.5 Hz, 3 F, CF_3), −63.2 (qd, J_{FF} = 15.5, 8.5 Hz, 2 F, CF_2O).

Anal. Calcd for $C_4Cl_2F_6O_3S$: C, 15.35; Cl, 22.65; S, 10.24. Found: C, 15.48; Cl, 22.59; S, 10.37.

Some higher boilers were present, but attempted distillation with the pot to 140 °C seemed to give pyrolysis products.

Another reaction of 46.6 g (0.20 mol) of 2,3-dichlorohexafluorobut-2-ene with 32.0 g (0.40 mol) of SO_3 was carried out at 150 °C for 3 days in a Carius tube. Distillation gave a spectrum of products. Pyrosulfuryl fluoride, bp 50–51 °C, identified by IR was obtained in 5.7 g (16% based on SO_3) yield, and starting butene, bp 66–67 °C, was recovered in 3.8 g (8%) yield. Crude **21**, bp 64 °C (50 mm), 60 °C (20 mm), was obtained in 18.0 g (29%) yield, along with 5.2 g (9% based on butene) of crude acyl fluorosulfate **22**, bp 51 °C (6 mm). For **22**: IR 1840 and 1830 (C=O), 1630 (C=CCl), 1480 (OSO_2F), 1300–1100 cm^{-1} (CF, CO, SO_2). ^{19}F NMR indicates a 3:1 ratio of *E*/*Z* isomers. For (*E*)-22: ϕ 46.5 (s, 1 F, SO_2F), −64.0 (s, 3 F, CF_3). For (*Z*)-**22**: ϕ 47.0 (s, 1 F, SO_2F), −63.8 (s, 3 F, CF_3).

Anal. Calcd for $C_4Cl_2F_4O_4S$: C, 16.51; Cl, 24.37; S, 11.02. Found: C, 16.44; Cl, 23.34; S, 10.43.

Fractions with bp ~75–85 °C (4 mm) were shown by elemental analysis to contain two molecules of SO_3 per molecule of butene; IR and NMR spectra are explicable on the basis of (*E*/*Z*)-**23** containing an appreciable amount of **24**.

SO_3 with *F*-But-2-yne. A mixture of 17.2 g (0.11 mol) of *F*-but-2-yne and 16.0 g (0.20 mol) of SO_3 was heated in a sealed tube at 100 °C for 4 days. The homogeneous mixture was distilled to give 2.3 g of 1:1 *F*-2-butyne-1-fluorosulfate (**25**) mixed with pyrosulfuryl fluoride, bp 43–44 °C. ^{19}F NMR: ϕ 48.9 (s, 2 F, $\mathit{F}SO_2OSO_2\mathit{F}$), 48.8 (t, J_{FF} = 8.1 Hz, 1 F, SO_2F), −54.0 (t, J_{FF} = 2.6 Hz, 3 F, CF_3), −55.9 (dq, J_{FF} = 8.1, 2.6 Hz, 2 F, CF_2). A sample from another preparation was analyzed by IR, Raman, and MS. IR: 1490 (OSO_2F), 1300–1200 cm^{-1} (CF, CO, SO_2) along with bands for FSO_2OSO_2F. Raman showed a band at 2300 cm^{-1} (C≡C). MS: *m/e* 223 ($M^+ - F$), mass measured 222.9497, calcd for $C_4F_5SO_3$ 222.9488, 149 ($FSO_2OCF_2^+$), 93 ($C_3F_3^+$), 83 (SO_2F^+) along with *m/e* 182 for $FSO_2OSO_2F^+$.

A fraction, bp 50–52 °C (20 mm), 2.5 g, contained both ketene **26** and $FSO_2OSO_2OSO_2F$. IR (CaF_2 plates): 2200 (C=C=O), 1740 (C=O), 1450 (SO_2F), 1250–1100 cm^{-1} (CF, SO_2) with relatively weak bands at 1510 and 1490 cm^{-1} (OSO_2F). ^{19}F NMR: ϕ 74.1 (br s, 1 F, SO_2F), −76.5 (br s, 3 F, CF_3) with a weak singlet at +50.1 for OSO_2F. The mass spectrum was taken on a sample from another preparation: *m/e* 220 (M^+), mass measured 219.9494, calcd for $C_4F_4O_4S$ 219.9453, 201 ($M^+ - F$), 151 ($M^+ - CF_3$), mass measured 150.9534, calcd for C_3FO_4S 150.9501, 83 (SO_2F^+), 69 (CF_3^+), 68 ($M^+ - CF_3 - SO_2F$).

Computational Details. The calculations were done with molecular orbital theory at the ab initio SCF level with an RHF wavefunction.[28] All calculations were done with the program GRADSCF[29] on a CRAY-1A supercomputer. Geometries were optimized at the SCF level using gradient techniques.[30] The basis set for these calculations is of double-ζ quality in the valence space with exponents and coefficients from Dunning and Hay.[31] The basis set is augmented by a set of d polarization functions[31] on all carbons and on oxygen. The basis set has the form (9s5p1d)/[3s2p1d] on C and O and (9s5p)/[3s2p] on F.

Registry No. 1, 67641-28-5; (*Z*)-2, 77212-24-9; (*E*)-2, 77212-25-0; 3, 773-15-9; 7, 104693-06-3; 9, 1582-32-7; 10, 84424-44-2;

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(*E*)-**11**, 85233-47-2; (*Z*)-**11**, 85233-46-1; *cis*-**12**, 104693-07-4; *trans*-**12**, 104693-08-5; **13**, 85233-48-3; **17**, 104693-22-3; (*E*)-**19**, 104693-09-6; (*Z*)-**19**, 104693-10-9; (*E*)-**20**, 104693-11-0; (*Z*)-**20**, 104693-12-1; (*E*)-**21**, 104693-13-2; (*Z*)-**21**, 104693-14-3; (*E*)-**22**, 104693-15-4; (*Z*)-**22**, 104693-16-5; (*E*)-**23**, 104693-17-6; (*Z*)-**23**, 104693-18-7; **24**, 104693-19-8; **25**, 104693-20-1; **26**, 104693-21-2; SO_3, 7446-11-9; $CF_2{=}CFCF_3$, 116-15-4; BF_3, 7637-07-2; $FSO_2OSO_2OSO_2F$, 13709-33-6; $C_4F_9CF_2CF{=}CF_2$, 355-63-5; $C_4F_9CF_2\overline{CFCF_2OS}(O)_2$, 85211-95-6; $CF_3CF{=}CFCF_3$, 360-89-4; FSO_2OSO_2F, 13036-75-4; $CF_3CCl{=}CClCF_3$, 303-04-8; $CF_3C{\equiv}CCF_3$, 692-50-2; trimethyl borate, 121-43-7.

Cycloaddition and Oxygen-Transfer Reactions of 2-(Trifluoromethyl)-3,3-difluorooxaziridine[1]

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The oxaziridine $CF_3\overline{NCF_2O}$ (**1**) cycloadds to various 1,1-difluoroolefins under mild conditions, forming perhalo-1,3-oxazolidines, and to dialkyl ketones, forming the corresponding 1,3,4-dioxazolidines. Reaction of **1** with trimethylsilyl cyanide results in the formation of $(CH_3)_3SiN{=}C{=}NCF_3$ and COF_2, but **1** is unreactive with other alkyl nitriles and isocyanides. With 2,5-dimethylfuran and 2,3-dimethylbutene, **1** reacts rapidly and under mild conditions (~−50 °C) to yield $CF_3N{=}CF_2$ and organic products derived from the transfer of a single oxygen atom.

Our studies of the unusual oxaziridine pentafluoroazapropene oxide (PFAPO), $CF_3\overline{NCF_2O}$ (**1**), have shown thus far that its reaction chemistry is similar in some ways to that of hexafluoropropene oxide (HFPO), $CF_3\overline{CFCF_2O}$.[2,3] Both compounds readily undergo ring opening by nucleophiles, with attack exclusively at the central nitrogen or carbon, respectively. Hexafluoropropene oxide is, however, generally unreactive toward unsaturated systems; cycloaddition reactions of this epoxide with olefins have not been reported and only a single cycloadduct with acetone has been reported.[4,5] Pentafluoroazapropene oxide in contrast, readily reacts with a number of 1,1-difluoroolefins to form 3-(trifluoromethyl)perhalo-1,3-oxazolidines and reacts readily with certain ketones to form 2,2-disubstituted 5,5-difluoro-4-(trifluoromethyl)-1,3,4-dioxazolidines.

Additional differences in reactivity between HFPO and PFAPO are indicated by the isomerization of HFPO to hexafluoroacetone with SbF_5,[3] whereas PFAPO forms a high percentage of a dimer along with small amounts of higher oligomers.[2b] Finally, in this work we report the facile oxygen atom-transfer reaction of PFAPO with electron-rich alkenes, a reaction not observed with HFPO.

Experimental Section

General Methods. All work was carried out in Pyrex or stainless steel (types 304 and 316) vacuum systems equipped with glass–Teflon or stainless steel valves. Pressures were measured with a Wallace and Tiernan Series 1500 differential pressure gauge. Quantities of reactants and products were measured by direct weighing or by PVT measurements. Temperatures were measured by using a digital-indicating iron–constantan thermocouple.

Infrared spectra were recorded with a Perkin-Elmer 337, 1330, 180, or 1430 spectrometer using a 10-cm glass cell fitted with AgCl or KCl windows. NMR spectra were recorded with a Varian XL-100-15 spectrometer by using ~80 mol % $CFCl_3$ as a solvent and an internal reference or with a JEOL FX-90Q spectrometer by using various deuterated media as both solvent and internal lock and ~1% $CFCl_3$ as the internal reference. Hydrogen chemical shifts are reported relative to internal $(CH_3)_4Si$.

Mass spectra were recorded with either a Finnigan 4021-C or a Hewlett-Packard 5985B instrument at 70 eV for electron-impact (EI) and chemical ionization [CI,CH_4] spectra. Samples were introduced by direct gas injection.

Melting points were determined by a modified Stock procedure. Vapor pressures as a function of temperature were determined by using a small isoteniscope.[6] Equations describing pressure as a function of temperature were obtained by a least-squares fit of the data to both linear and quadratic equations, and the best fit is reported.

For further purification of reaction products, GLC was carried out with a Victoreen Series 4000 gas chromatograph equipped for gas injection, TCD, and low-temperature collection. Columns of 10, 2, or 1 ft × $^3/_8$ in. packed with 35% Halocarbon 11-21 polymer oil on acid-washed Chromosorb P were used.

Reagents. The olefins were commercially available and were used as received. Other organic reactants were purified by distillation under vacuum. Oxaziridine **1** was prepared as described previously.[7]

General Procedure for Reaction of Oxaziridine 1 with Olefins. To a ~100-mL Pyrex vessel fitted with a glass-Teflon valve were added **1** (1–3 mmol) and an equamolar amount of olefin by vacuum transfer. The mixture was then heated at 55–100 °C for ~18 h, unless otherwise noted. The products were separated by vacuum fractionation through a series of cold traps, followed by GLC as needed.

(a) With $CF_2{=}CF_2$. Perfluoro-3-methyloxazolidine (**2a**) was obtained in 60% yield; bp 21 °C; $\log P$ (torr) = 6.969 − (949.14/T) − (74200/T^2); ΔH_{vap} = 6.65 kcal/mol; ΔS_{vap} = 22.6 eu; IR (gas) 1415 (m), 1360 (s), 1325 (vs), 1245 (vs), 1165 (m), 1080 (m), 1010 (m), 960 (vw), 910 (m), 745 (w), 700 (w), 680 (w), 580 (w) cm^{-1}; MS (CI, major), m/z 250 [$(M + 1)^+$], 230 [$(M + 1 - HF)^+$], 200 [$(M + 1 - CF_2)^+$], 183 ($C_3F_7N^+$), 154, 152, 134 ($C_2HF_5N^+$), 114; MS (EI, major), m/z (relative intensity) 249 (M^+), 230 [$(M - F)^+$, 100], 199 [$(M - CF_2)^+$], 183 [$(M - COF_2)^+$], 180, 164 ($C_3F_6N^+$),

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