References and Notes

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Sulfonation of Acyclic Fluorovinyl Ethers

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Abstract: Contrary to implications in the literature, polyfluorovinyl ethers have been shown to form unstable sultones with sulfur trioxide. Near 25 °C these sultones isomerize easily to β-carbonylsulfonate esters. A fluorovinyl diether was found to lead preferentially to cyclic sulfate, a convenient precursor to a perfluoro α-diketone. Mechanisms for these transformations are proposed. These reactions offer superior routes to the two classes of difunctional fluoroorganics, β-carbonylsulfonates and α-diketones.

Electrophilic attack on fluoroolefins by sulfur trioxide to form fluorinated sultones is a well-documented reaction.[1,2] Terminal olefins are particularly susceptible to the reaction, which appears to proceed through a dipolar intermediate.[2] Stabilization of positive charge by α-fluorine atoms in the intermediate and destabilization by β-fluorine atoms[3] account for the observed orientation and for the fact that internal fluoroolefins are rarely reported to undergo the cycloaddition. In view of the special effectiveness of α-alkoxy groups in stabilization of cations, the known[4] facile addition of sulfur trioxide with fluorovinyl ethers is also compatible with formation of a dipolar intermediate. For the limited number of such reactions already in the literature, sultone and cyclic sulfonate–sulfate anhydride are the reported products.[2,4] As described below, we find the reaction of sulfur trioxide with a series of acyclic fluorovinyl ethers is at variance with these reports.[5]

Syntheses of Representative Fluorovinyl Ethers. A selection of vinyl ethers with varied substituents on the vinyl group was required for this study. Those with a trifluoromethyl group in the 1 position are best obtained by the action of a trialkyl phosphite on hexafluoroacetone;[6] yields of **1** by this route were generally 60% for preparations on a molar scale.

$CH_3CH_2OC(CF_3)=CF_2$ (**1**) $CH_3OCF=CClCF_3$ (**2**)

Vinyl ether **2** was obtained by an unusually facile rearrangement of the allyl ether **3**, which was itself prepared by an S_N2' displacement on **4**.[7]

$$CF_2=CClCF_2Cl \xrightarrow{NaOCH_3} CH_3OCF_2CCl=CF_2 \xrightarrow{\delta} \mathbf{2}$$

4 **3**

Methyl perfluoro-1-alkenyl ethers (**5**) were prepared by treatment of terminal perfluoroalkenes with 1 mol of sodium methoxide. Hexafluoropropene in this reaction gives the vinyl ether in good yield; none of the allylic ether potentially available from S_N2' displacement of fluoride is observed.[8] The intermediate carbanion apparently undergoes loss of the fluoride ion which leads to the more thermodynamically stable product, difluorovinyl ether **5** (R = F) rather than the trifluorovinyl product **6** (R = F).

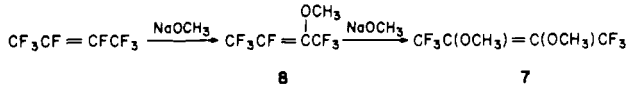
$$CH_3O^- + F_2C=CFCF_2R \longrightarrow CH_3OCF_2-\bar{C}FCF_2R$$

$$CH_3OCF=CFCF_2R \quad (\mathbf{5}) \qquad CH_3OCF_2CF=CFR \quad (\mathbf{6})$$

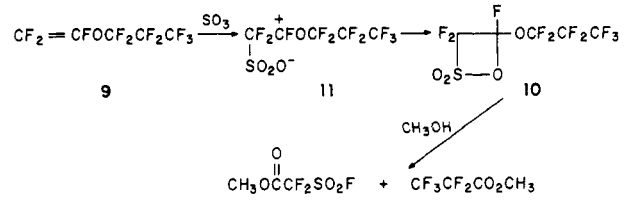
Although such displacements of vinylic halogen are well known,[9] there seems to be no report of a case in which a longer

open chain perfluoro-1-alkene has been treated with alkoxide.[10] An olefin such as perfluoro-1-heptene might be expected to yield products of both type **5** and **6** in a stepwise addition-elimination reaction, since both contain the same number of destabilizing vinylic fluorine atoms. Such was found to be the case. The action of sodium methoxide on perfluoro-1-heptene gave both vinyl ether **5** ($R = C_4F_9$) and allylic ether **6** ($R = C_4F_9$) in substantial amount. Nucleophilic substitution into perfluorocyclohexene was earlier observed to provide an analogous dual pathway to vinyl and allyl ethers as products. Since thermodynamic control would lead in this case to the vinyl ether, stereochemistry of the intermediate carbanion was proposed to be a determining factor.[11] However, we know of no reason to assume kinetic control is exerted in the present acyclic case.

Studies with fluorinated cycloalkenes, especially cyclobutenes, imply a generalization based on stability of carbanionic intermediates that a 1,2-dialkoxypolyfluorocycloalkene is best prepared from a precursor containing two fluorine atoms as vinylic halogen substituents.[12] Adaptation of this reaction to perfluoro-2-butene made 2,3-dimethoxyhexafluoro-2-butene (**7**) available. Controlled reaction of perfluoro-2-butene with 1 equiv of sodium methoxide gave the intermediate monoether **8** in good yield.



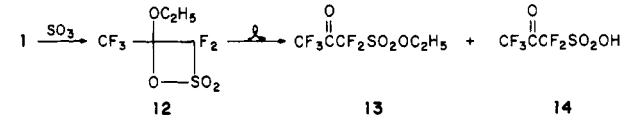
Reaction with Sulfur Trioxide. As was mentioned above, terminal perfluoroalkenes add sulfur trioxide in a direction such that positive charge in the intermediate resides on the carbon bearing the larger number of fluorine atoms. The directive influence of ether oxygen is clearly stronger than that of vinylic fluorine in the cycloaddition reaction with sulfur trioxide. Even perfluoro(propyl vinyl ether) (**9**), in which oxygen has reduced basicity and lowered capacity for stabilization of adjacent positive charge, gives a sultone (**10**). Dipolar intermediate **11** is presumably formed despite the increased



destabilizing influence of additional fluorine β to the cationic center.

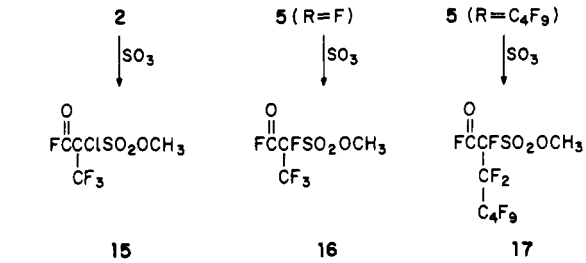
The structure of **10** was determined by the unusually large downfield ^{19}F NMR shift observed for the ring CF resonance and by the formation of methyl fluorosulfonyldifluoroacetate on methanolysis. Pyrolysis of **10** resulted in fragmentation to sulfur dioxide, acid fluorides, and difluoromethylene, the latter leading to perfluorocyclopropane as the isolated product.

Sultone **10** is stable somewhat above room temperature, unlike the sultones derived from alkyl polyfluorovinyl ethers. The latter types suffer alkyl-oxygen cleavage with rearrangement to β-ketosulfonate esters under mild conditions. For example, vinyl ether **1** reacted exothermically with sulfur trioxide at −20 to 0 °C to give the sultone (**12**) with regio-



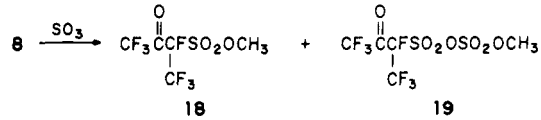
specificity opposite to that observed with hexafluoropropene. Cycloadduct **12** could be identified by ^{19}F NMR as the major reaction product, but at temperatures near 25 °C gave a mildly exothermic rearrangement to ketosulfonate ester **13.** Ketosulfonic acid **14** was also obtained as a by-product.[13]

Similarly, fluorovinyl ethers **2, 5** (R = F), and **5** ($R = -C_4F_9$) reacted readily with sulfur trioxide to give, after isolation, fluorocarbonylsulfonate esters **15, 16,** and **17.** A remarkable

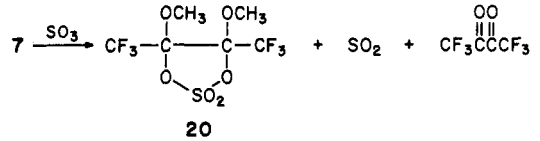


aspect of these rearrangements which any mechanism must accommodate is the preferential migration of methyl (or methoxy) rather than fluoride, as is generally encountered in base-catalyzed isomerizations of fluorinated sultones.[2]

Electrophilic attack on **8** by sulfur trioxide was slow even at 25 °C, so reaction was carried out at reflux with excess sulfur trioxide present. The expected β-ketosulfonate ester **18** was isolated, along with the mixed anhydride **19.**

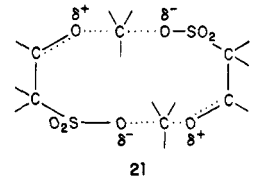


Lastly, vinyl diether **7** was found to undergo facile reaction with sulfur trioxide to give sulfur dioxide and cyclic sulfate **20,**



along with hexafluorobiacetyl. Evidence that hexafluorobiacetyl is a secondary product was obtained by its formation in high yield on treatment of **20** with sulfuric acid.

Mechanistic Considerations. Primary products of attack of sulfur trioxide on fluorovinyl ethers are the sultones expected from a two-step process in accord with the mechanism proposed for fluoroolefins in general.[2] In the vinyl ether case, the dipolar intermediate appears to be sufficiently well stabilized to be accessible from the sultone at moderate temperatures; reversible formation of this species accounts best for the observed final products. The oxonium moiety of this intermediate, as a powerful alkylating agent, is capable of intermolecular alkylation of sulfonate anion to form the carbonylsulfonate ester. Intramolecular transfer of the alkyl group is unlikely, since the geometry of the requisite six-membered ring in the transition state would mandate an angle between leaving and entering groups of much less than 180°. Therefore an intermolecular mechanism such as that involving the large-ring bimolecular transition state **21** is postulated.



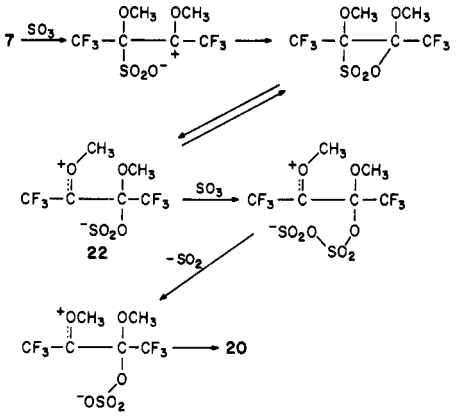
Further evidence for intermolecular alkylation by alkoxy cation is provided by the thermal behavior of sultone **10.** The heavily fluorinated alkyl group is not readily transferred by S_N2 attack of sulfonate as exemplified by transition state **21,** in accord with the well-known resistance of saturated fluorocarbon derivatives to such displacements. Indeed, under forcing

conditions **10** forms products expected from homolytic decomposition.

In the one case (with vinyl ether **8**) where sultone formation was slow and was carried out in the presence of excess sulfur trioxide, sulfur trioxide competed successfully with intermolecular alkylation for sulfonate ion to form a new dipolar species.[14] Alkylation of this intermediate led to the mixed anhydride **19.**

The presence of the second methoxy group in **7** resulted in an abrupt change in reaction path. Even when **7** was reacted at very low temperature with only 1 equiv of sulfur trioxide, the 1:2 stoichiometry of the reaction was maintained and starting vinyl ether **7** (predominantly trans) was recovered. Thus it appears that in this case a new and well-stabilized dipolar species, **22,** could be formed which reacted preferentially with sulfur trioxide as indicated in the redox reaction shown in Scheme I.

Scheme I



Experimental Section

Ethyl 2-Ketopentafluoropropanesulfonate (13) and 2-Ketopentafluoropropanesulfonic Acid (14). Dropwise addition of 88 g (1.1 mol) of sulfur trioxide to 176 g (1.0 mol) of ethyl pentafluoroisopropenyl ether maintained at 0–5 °C resulted in a nearly colorless reaction mixture. A dark reaction mixture resulted after standing overnight. Fractionation afforded 145.1 g (57% conversion) of **13,** bp 48–52 °C (12 mm). The center cut from a similar reaction had bp 71 °C (42 mm): IR (neat) 2994 and 2933 (satd CH), 1786 (C=O), 1410 (SO_2O), 1300–1175 cm^{-1} (CF, SO_2); NMR ^1H 4.59 (q, J_{HH} = 7.2 Hz, 2), 1.51 (t, J_{HH} = 7.2 Hz, 3), ^{19}F −75.0 (t, J_{FF} = 8.3 Hz, 3), −107.4 (q, J_{FF} = 8.3 Hz, 2). Anal. ($C_5H_5F_5SO_4$) C, H, F.

A higher boiling fraction, bp 52 °C (12 mm), −71 °C (5 mm), was redistilled to give 35.6 g (16% conversion) of **14:** bp 81–82 °C (6.2 mm); IR (CaF_2 plates neat) 3030 (broad) and 2381 (SOH), 1792 (C=O), 1403 (SO_2O), 1300–1110 (CF, SO_2); NMR (neat) ^1H 10.2 (s), ^{19}F −76.2 (t, J_{FF} = 7.5 Hz, 3), −108 (q, J_{FF} = 7.5 Hz, 2). Anal. ($C_3HF_5O_4S$) C, H, F, S.

The addition of sulfur trioxide to ethyl pentafluoroisopropenyl ether was also carried out at −10 to −5 °C and the ^{19}F NMR spectrum taken on crude product at −20 °C to show −77.6 (d, J_{FF} = 15 Hz, 3), −94.6 (A branch d, J_{FF} = 173 Hz, 1), and −100.5 (B branch d into q, J_{FF} = 172, 15 Hz, 1) for sultone **12** along with resonances for 15% of open-chain isomer **13** and small impurity peaks. When the product mixture was allowed to warm, a mildly exothermic reaction set in with concomitant darkening. Determination of the ^{19}F NMR spectrum next day established that **12** had disappeared and **13** had increased dramatically.

1-Methoxy-2-chlorotetrafluoropropene (2). A solution of 16.2 g (0.30 mol) of sodium methoxide in 200 ml of dry methanol was added dropwise over 2 h to 55.0 g (0.30 mol) of 2,3-dichlorotetrafluoropropene (**4**)[16] in 50 ml of methanol at 0 °C. After stirring 30 min at 0 °C and an additional 2 h at room temperature, the reaction mixture was quenched in 500 ml of cold water. The organic layer was washed with 100 ml of water and saturated aqueous sodium chloride. The mixture was distilled to give 3.0 g of crude recovered **4,** bp 40–50 °C, and 23.8 g of 3-methoxy-2-chlorotetrafluoropropene (**3**), bp 71–73 °C: NMR ^1H 3.92 (t, J_{HF} = 1.3 Hz), ^{19}F −74.5 (AA'm, $J_{AX+A'X}$ = 32 Hz, 2), −80 (m, 2). Anal. ($C_4H_3ClF_4O$) C, H, Cl, F.

After **3** had stood overnight, VPC analysis indicated a mixture of **3** and two other compounds. The mixture was redistilled to give only **2** (cis + trans), bp 89–92 °C. Product from a similar preparation was a mixture of 55% trans **2:** NMR ^{19}F −62.5 (d, J_{FF} = 25.5 Hz, 3), −84.2 (q into q, J_{FF} = 25.5, ~1 Hz, 1), and 45% cis **2:** −62.8 (d, J_{FF} = 11 Hz, 3), −77.2 (q into q, J_{FF} = 11, ~1 Hz, 1).

Methyl 1-Fluorocarbonyl-1-chlorotrifluoroethanesulfonate (15). Neat **2** (8.9 g, 0.05 mol) under nitrogen in a 50-ml flask equipped with a water condenser and outlet to a −78 °C trap was treated dropwise over 15 min with 4.0 g (0.05 mol) of sulfur trioxide (exothermic). After the addition had been completed, the reaction mixture was fractionated in vacuo to give 1.6 g of impure **15,** bp 62–65 °C (15 mm), and 7.3 g of pure **15,** bp 64–67 °C (15 mm) (69% total yield): IR (neat) 1850 cm^{-1} (−COF); NMR (neat, ext ref) ^1H 4.22 (s), ^{19}F +34.2 (q, J_{FF} = 10.2 Hz, 1), −70.3 (d, J_{FF} = 10.2 Hz, 3). Anal. ($C_4H_3ClF_4SO_4$) C, H, F, S.

Methyl 1-Fluorocarbonyltetrafluoroethanesulfonate (16). To 48.6 g (0.30 mol) of methyl pentafluoropropenyl ether (86% trans/14% cis) (**5,** R = F) stirred at −20 to −10 °C was added dropwise 28.0 g (0.35 mol) of SO_3 (very vigorous reaction). After the addition had been completed, the mixture was stirred overnight at 25 °C and distilled to give 26.6 g (37%) of sulfonate **16,** bp 64 °C (60 mm), along with considerable tarry residue: IR (neat) 3003 and 2882 (satd CH), 1873 (COF), 1414 (SO_2O), 1300–1100 (CF, SO_2); NMR ^1H 4.26 (s), ^{19}F 32.0 (d into q, J_{FF} = 23.2, 7.6 Hz, 1), −73.5 (d into d, J_{FF} = 7.6, 7.6 Hz, 3), −162.8 (d into q, J_{FF} = 23.2, 7.6 Hz, 1). Anal. ($C_4H_3F_5O_4S$) C, H, F, S.

1-Methoxyperfluoro-1-heptene (5, R = C_4F_9) and 1-Methoxyperfluoro-2-heptene (6, R = C_4F_9). A suspension of 7.60 g (0.14 mol) of sodium methoxide in 100 ml of dry glyme was stirred at −50 °C while 49.4 g (0.14 mol) of perfluoro-1-heptene was added rapidly during 5 min. The resulting mixture was stirred at −40 to −30 °C for 30 min, −20 to −10 °C for 30 min, and then overnight at 25 °C. The reaction mixture was diluted with 500 ml of water, and the lower product layer was washed with 100 ml of water, dried, and distilled. Fractions collected, bp 45–54 °C (50 mm), were shown to be mainly trans isomer of **6** (R = C_4F_9), 10.6 g (21%). A sample, bp 49–50 °C (50 mm), indicated by GLC to have essentially one major and one minor component, was analyzed: IR 3021, 2976, and 2874 (satd CH), 1686 (weak cis CF=CF), 1330–1100 (CF, C-O). Raman spectroscopy showed a strong band at 1701 for the trans CF=CF. NMR indicated mainly *trans*-**6** (R = C_4F_9), with weak resonances for the cis isomer also present. For *trans*-**6** (R = C_4F_9), ^1H 3,80 (s), ^{19}F −66.0 (d, J_{FF} = 23 Hz, 2, CF_2O), −81.9 (t into t, J_{FF} = 10, 2 Hz, 3, CF_3), −118.0 (t into d, J_{FF} = ~12, ~12 Hz, 2, CF_2CF_2C=), −124.8 (m, 2, CF_2), −127.2 (m, 2, CF_2), and −145.5 (m, 2, =CF). Anal. ($C_8H_3F_{13}O$) C, H, F.

Fractions, bp mainly 66–68 °C (50 mm), 16.5 g (33%), were a mixture of cis and trans isomers of **5** (R = C_4F_9): IR 3030, 2985, and 2882 (satd CH), 1757 (CF=CFO-), 1330–1100 (CF, COC); NMR ^1H 3.98 (m, 7, trans CF=CFOCH$_3$) and 3.88 (m, 3, cis CF=CFOCH$_3$), ^{19}F −81.7 (t into t, J_{FF} = 10, 2 Hz, 3, CF_3), −92.1 (d into t, J_{FF} = 18, 7 Hz, 0.3, cis CF=C*F*OCH$_3$), −111.4 (d into t into m, J_{FF} = 119, 28 Hz, 0.7, trans CF=C*F*OCH$_3$), −117.5 (m, 2, CF_2), −123.8 (broad, 2, CF_2), −124.8 (broad, 2, CF_2), −127.1 (m, 2, CF_2), −183.5, (broad, 0.3, cis *C*F=CFOCH$_3$), and −191.7 (d, J_{FF} = 119 Hz, 0.7, trans *C*F=CFOCH$_3$).

Anal.($C_8H_3F_{13}O$) C, H, F.

Methyl 1-Fluorocarbonylperfluorohexane-1-sulfonate (17). Sulfur trioxide (3,3 g, 0.041 mol) was added dropwise to 14.7 g (0.041 mol) of *cis*- and *trans*-**5** (R = C_4F_9) cooled at 0–5 °C. The reaction mixture was allowed to come to 25 °C, stirred there for 1 h, and then distilled to give 4.6 g (31%) of recovered olefin **5** (R = C_4F_9) and 2.6 g (15% conv, 22% yield) of sulfonate ester **17:** bp 55–58 °C (2.4 mm); IR 2976 (satd CH), 1862 (COF), 1420 (SO_2O), and 1330–1100 (CF, SO_2); NMR ^1H 4.27 (s), ^{19}F 31.6 (d into t, J_{FF} = 24, 12 Hz, 1), −81.6 (t into t, J_{FF} = 10.2, 2.2 Hz, 3) −116.1 (broad, 2), and −161.3 (d into t into t, J_{FF} = 24, ~12, ~12 Hz, 1). Anal. ($C_8H_3F_{13}O_4S$) C, H.

2-Methoxyheptafluoro-2-butene (8). A suspension of 27.0 g (0.50 mol) of sodium methoxide in 300 ml of dry diglyme was stirred at −40 °C while 100 g (0.50 mol) of perfluoro-2-butene was distilled in. The mixture was then stirred at −40 °C for 15 min, at 5 °C for 45 min, and at 25 °C for 4 h. Distillation afforded 70.9 g (67%) of vinyl ether **8,** bp 50–58 °C. A sample of **8** prepared similarly in tetrahydrofuran

and washed with water to remove solvent had bp 50–52 °C and was analyzed: IR 2967 and 2874 (satd CH), 1689 (C=C), 1330–1100 (CF, COC); NMR ^{1}H 3.82 (m), ^{19}F −66.5 (d, J_{FF} = 1.5 Hz, 3) −148.1 (q into q, J_{FF} = 22.3, 8.1 Hz, 1) for trans isomer with minor amounts cis isomer present. Anal. ($C_5H_3F_7O$) C, H, F.

Methyl 2-Keto-1-trifluoromethyltetrafluoropropanesulfonate (18) and Methoxy 2-Keto-1-trifluoromethyltetrafluoropropyl Pyrosulfate (19). To 36.0 g (0.17 mol) of **8** stirred at 30 °C was added dropwise 16.0 g (0.20 mol) of sulfur trioxide from a freshly opened ampule. The mixture was stirred 30 min and distilled to give a small amount of $CF_3CHFCOCF_3$, then a mixture of SO_3 and starting olefins, bp 50–68 °C, with only 3.6 g of product, bp 52–57 °C (25 mm). The lower distillation cuts were recombined, another 16.0 g (0.20 mol) of SO_3 was added, and the mixture was refluxed 2 h. The pot temperature rose from 50 to 68 °C and leveled during this period. Distillation afforded 9.3 g of **18,** bp 60–61 °C (25 mm), for a total of 12.8 g (26%) with previous distillate, and 21.0 g (33%) of **19,** bp 89–90 °C (10 mm). For **18,** IR (neat) 2976 (satd CH), 1779 (C=O), 1412 (SO_2O), 1330–1100 (CF, SO_2); NMR ^{1}H 4.25 (s), ^{19}F −73.3 (d into q, J_{FF} = 7.6, 1.5 Hz, 3), −75.5 (d into q, J_{FF} = 18.5, 1.5 Hz, 3), −173.7 (q into q, J_{FF} = 18.5, 7.6 Hz, 3). Anal. ($C_5H_3F_7O_4S$) C, H. F, S.

For **19,** IR (CaF_2 plates) 2967 (satd CH), 1786 (C=O), 1433 (SO_2O), 1330–1100 (CF, SO_2); NMR ^{1}H 4.30 (s), ^{19}F −72.4 (d into q, J_{FF} = 7.9, 1.5 Hz, 3), −75.2 (d into q, J_{FF} = 18.3, 1.5 Hz, 3), −170.3 (q into q, J_{FF} = 18.3, 7.9 Hz, 1). Anal. ($C_5H_3F_7O_7S_2$) C, H, F, S.

2-Heptafluoropropoxy-2-hydroxytrifluoroethane-1-sulfonic Acid β-Sultone (10), Its Pyrolysis and Methanolysis.[17] A mixture of 32 g (0.12 mol) of heptafluoro-*n*-propyl trifluorovinyl ether and 20 g (0.25 mol) of sulfur trioxide was sealed at −196 °C in a heavy-walled glass tube and allowed to warm. After an exothermic reaction had occurred, the reaction mixture stood overnight at 25 °C and was then distilled to afford 28 g (67%) of sultone **10:** bp 66 °C (180 mm); ^{19}F NMR (56.4 MHz) −83.5 (t, J_{FF} = 7.6 Hz, 3), −84.1 (A branch m, J_{FF} = 151 Hz, 1), −86.5 (B branch m, J_{FF} = 151 Hz, 1), −90.3 (m, 1), −99.8 (A branch m, J_{FF} = 160 Hz, 1), −101.2 (B branch m, J_{FF} = 160 Hz, 1), −131.4 (s, 2). Anal. ($C_5F_{10}SO_4$) C, F, S.

Although **10** was stable at 70 °C, pyrolysis at 200 °C for 4 h in a sealed tube gave SO_2 and perfluorocyclopropane along with acid fluoride.

Addition of 19 g of **10** to 25 ml of cold methanol gave a mixture which was warmed to 25 °C, washed with cold water, dried, and distilled. Methyl pentafluoropropionate, 6.4 g, bp 59–60 °C, was identified by IR, NMR, and elemental analysis. Methyl fluorosulfonyldifluoroacetate, 5.8 g, bp 75 °C (180 mm), was also obtained: IR 1795 (C=O); NMR ^{1}H 3.52 (s), ^{19}F (56.4 MHz) −85.8 (t, J_{FF} = 1.5 Hz, 3), −123.9 (q, J_{FF} = 1.5 Hz, 2). Anal. ($C_3H_3F_3SO_4$) C, H, F, S.

2,3-Dimethoxyhexafluoro-2-butene (7). A mixture of 112.5 g (0.56 mol) of perfluoro-2-butene and 200 ml of methanol was stirred at 0–5 °C while a solution of 64.8 g (1.2 mol) of sodium methoxide in 350 ml of methanol was added over a 1-h period. The mixture was allowed to come to 25 °C, stirred overnight, and refluxed for 2 h. Most of the methanol was distilled off and the distillate shaken with 1.2 l. of water. The lower layer was separated, combined with the higher boiling residue, and the whole washed with 3 × 1.2 l. of water. The product layer was then dried, filtered, and distilled to give a mixture of cis-trans isomers of **7,** bp 68–74 °C (250 mm), 63.6 g (51%): IR 3021, 2967, and 2865 (satd CH), 1656 (C=C), 1330–1100 (CF, COC); NMR ^{1}H 3.83 (s, cis OCH_3), 3.73 (s, trans OCH_3, ^{19}F −65.4 (s, cis CF_3), −65.7 (s, trans CF_3).

Anal. Calcd for $C_6H_6F_6O_2$: C, 32.16; H, 2.70; F, 50.87. Found: C, 32.40; H, 3.06; F, 50.82.

The use of glyme (59%) or tetrahydrofuran (66%) as reaction medium at low temperature gave improved yields, even for a reaction carried out at −40 °C with inverse addition, but thorough water washing is essential to remove solvent. Otherwise the ether solvent tends to codistill with product, bp 94–100 °C when pure.

2,3-Dimethoxyhexafluorobutane-2,3-diol Cyclic Sulfate (20) and Hexafluorobiacetyl. A mildly exothermic reaction of 44.8 g (0.20 mol) of **7** and 36.0 g (0.45 mol) of sulfur trioxide was kept below 45 °C by external cooling during the SO_3 addition. The mixture was then heated at 100–110 °C at 1 atm while volatiles were collected in a cold trap. Distillation of the volatiles gave considerable SO_2 (identified by IR) and 9.3 g (24%) of yellow hexafluorobiacetyl, bp 19–20 °C (lit. bp 20 °C).

Distillation of higher boilers gave 43.2 g (68%) of cis-trans isomers of **20:** bp 77–89 °C (40 mm); IR (CaF_2 plates) 3030, 2985, and 2882 (satd CH), 1433 (SO_2O), 1320–1150 (CF, SO_2); NMR ^{1}H 3.89 (s, OCH_3), 3.78 ppm (m, OCH_3), ^{19}F −74.5 (m, CF_3), −769 (s, CF_3).

Anal. Calcd for $C_6H_6F_6O_6S$: C, 22.51; H, 1.89; F, 35.60; S, 10.01. Found: C, 22.41; H, 2.14; F, 33.30; S, 10.96.

The analysis and an extraneous CH_3O band in the ^{1}H NMR spectrum indicate the presence of a small amount of dimethyl sulfate as an impurity. The identity of **20** was confirmed by converting it to hexafluorobiacetyl in high yield with sulfuric acid. A mixture of 38.8 g (0.12 mol) of crude **20** and 100 ml of concentrated H_2SO_4 (two layers) was stirred and heated to 80 °C, where gas evolution commenced. The mixture was slowly heated to 120 °C while yellow solid was collected in a −80 °C cold trap, 18.4 g (79%), identified as pure hexafluorobiacetyl by comparison of the IR spectrum with that of an authentic sample.

References and Notes

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$$(CF_3)_2C{=}C(OCH_2CH_2Cl) \xrightarrow{SO_3} \text{"intermediate"} \xrightarrow{120\ ^\circ C} (CF_3)_2CHSO_2OCH_2CH_2Cl$$

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$$C_6H_5C(CF_2CF_3){=}CF_2 \xrightarrow{C_2H_5O^-} C_6H_5CCF_2OCH_2CH_3\ (60\%) + \text{others}$$

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(15) Boiling points are uncorrected. IR spectra were recorded on a Perkin-Elmer 21 spectrophotometer and unless otherwise indicated are for 20% solutions in CCl_4. ^{1}H NMR spectra were taken on a Varian A60 spectrometer with 20% solutions in CCl_4; chemical shifts are reported in parts per million downfield from tetramethylsilane as internal standard. ^{19}F NMR spectra were recorded at 94.1 MHz on a Varian XL 100 spectrometer with CCl_4 solutions; chemical shifts are reported in parts per million downfield from trichlorofluoromethane as internal standard. Stabilized sulfur trioxide, Sulfan B, was used as obtained. The composition was presumed to be largely monomer with varying amounts of higher oligomers present, depending on the particular sample.[1a]

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(17) The synthesis and reactions of sultone **10** were carried out by Dr. D. C. England of these laboratories.