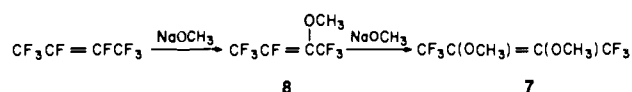
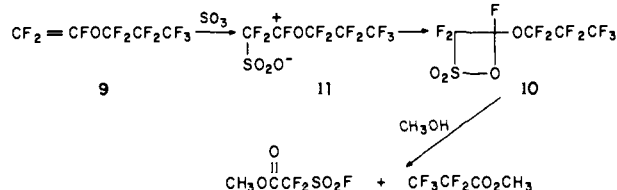


open chain perfluoro-1-alkene has been treated with alkoxide.¹⁰ An olefin such as perfluoro-1-heptene might be expected to yield products of both type **5** and **6** in a stepwise addition-elimination reaction, since both contain the same number of destabilizing vinylic fluorine atoms. Such was found to be the case. The action of sodium methoxide on perfluoro-1-heptene gave both vinyl ether **5** (R = C₄F₉) and allylic ether **6** (R = C₄F₉) 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.



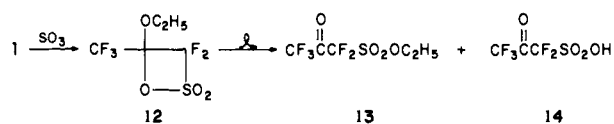
Reaction with Sulfur Trioxide. As was mentioned above, terminal perfluoroalkenes add sulfur trioxide in a direction such that positive charge in the intermediate resides on the carbon bearing the larger number of fluorine atoms. The directive influence of ether oxygen is clearly stronger than that of 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 ¹⁹F 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.

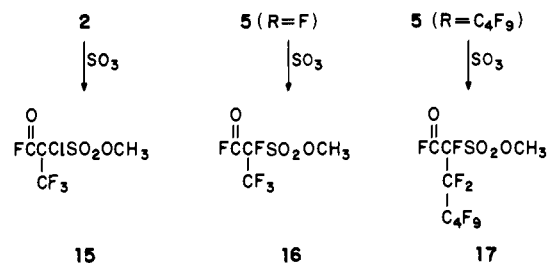
Sultone **10** is stable somewhat above room temperature, unlike the sultones derived from alkyl polyfluorovinyl ethers. The latter types suffer alkyl-oxygen cleavage with rearrangement to β -ketosulfonate esters under mild conditions. For example, vinyl ether **1** reacted exothermically with sulfur 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 ¹⁹F NMR as the major reaction product, but at temperatures near 25 °C gave a mildly

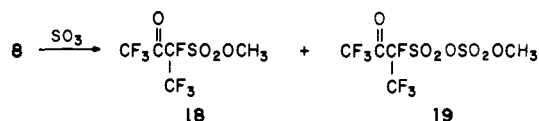
exothermic rearrangement to ketosulfonate ester **13**. Ketosulfonic acid **14** was also obtained as a by-product.¹³

Similarly, fluorovinyl ethers **2**, **5** (R = F), and **5** (R = -C₄F₉) reacted readily with sulfur trioxide to give, after isolation, fluorocarbonylsulfonate esters **15**, **16**, and **17**. A remarkable

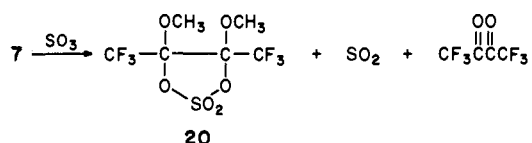


aspect of these rearrangements which any mechanism must accommodate is the preferential migration of methyl (or methoxy) rather than fluoride, as is generally encountered in base-catalyzed isomerizations of fluorinated sultones.²

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**.

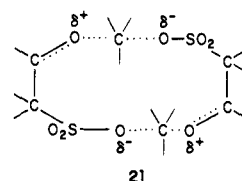


Lastly, vinyl diether **7** was found to undergo facile reaction with sulfur trioxide to give sulfur dioxide and cyclic sulfate **20**,



along with hexafluorobiacyl. Evidence that hexafluorobiacyl 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.



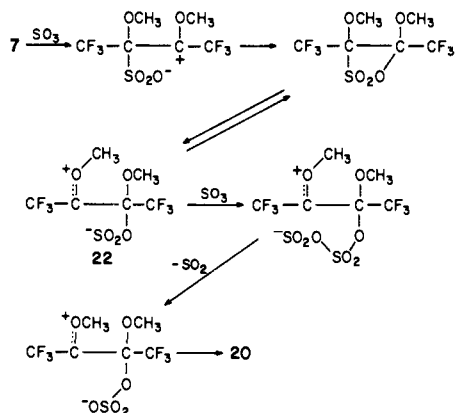
Further evidence for intermolecular alkylation by alkoxy cation is provided by the thermal behavior of sultone **10**. The heavily fluorinated alkyl group is not readily transferred by S_N2 attack of sulfonate as exemplified by transition state **21**, in accord with the well-known resistance of saturated 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 sulfone 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 (SO₂O), 1300–1175 cm⁻¹ (CF, SO₂); NMR ¹H 4.59 (q, *J*_{H11} = 7.2 Hz, 2), 1.51 (t, *J*_{H11} = 7.2 Hz, 3), ¹⁹F –75.0 (t, *J*_{FF} = 8.3 Hz, 3), –107.4 (q, *J*_{FF} = 8.3 Hz, 2). Anal. (C₅H₅F₅SO₄) 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 (CaF₂ plates neat) 3030 (broad) and 2381 (SOH), 1792 (C=O), 1403 (SO₂O), 1300–1110 (CF, SO₂); NMR (neat) ¹H 10.2 (s), ¹⁹F –76.2 (t, *J*_{FF} = 7.5 Hz, 3), –108 (q, *J*_{FF} = 7.5 Hz, 2). Anal. (C₃HF₅O₄S) C, H, F, S.

The addition of sulfur trioxide to ethyl pentafluoroisopropenyl ether was also carried out at –10 to –5 °C and the ¹⁹F 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 sulfone **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 ¹⁹F 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), ¹⁹F –74.5 (AA', *J*_{AX+AX'} = 32 Hz, 2), –80 (m, 2). Anal. (C₄H₃ClF₄O) 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 ¹⁹F –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), ¹⁹F +34.2 (q, *J*_{FF} = 10.2 Hz, 1), –70.3 (d, *J*_{FF} = 10.2 Hz, 3). Anal. (C₄H₃ClF₄SO₄) 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 SO₃ (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 (SO₂O), 1300–1100 (CF, SO₂); NMR ¹H 4.26 (s), ¹⁹F 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. (C₄H₃F₅O₄S) C, H, F, S.

1-Methoxyperfluoro-1-heptene (5, R = C₄F₉) and 1-Methoxyperfluoro-2-heptene (6, R = C₄F₉). 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 = C₄F₉), 10.6 g (21%). A sample, bp 49–50 °C (50 mm), indicated 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 = C₄F₉), with weak resonances for the cis isomer also present. For *trans*-**6** (R = C₄F₉), ¹H 3.80 (s), ¹⁹F –66.0 (d, *J*_{FF} = 23 Hz, 2, CF₂O), –81.9 (t into t, *J*_{FF} = 10, 2 Hz, 3, CF₃), –118.0 (t into d, *J*_{FF} = ~12, ~12 Hz, 2, CF₂CF₂C=), –124.8 (m, 2, CF₂), –127.2 (m, 2, CF₂), and –145.5 (m, 2, =CF). Anal. (C₈H₃F₁₃O) 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 = C₄F₉): IR 3030, 2985, and 2882 (satd CH), 1757 (CF=CFO–), 1330–1100 (CF, COC); NMR ¹H 3.98 (m, 7, trans CF=CFOCH₃) and 3.88 (m, 3, cis CF=CFOCH₃), ¹⁹F –81.7 (t into t, *J*_{FF} = 10, 2 Hz, 3, CF₃), –92.1 (d into t, *J*_{FF} = 18, 7 Hz, 0.3, cis CF=CFOCH₃), –111.4 (d into t into m, *J*_{FF} = 119, 28 Hz, 0.7, trans CF=CFOCH₃), –117.5 (m, 2, CF₂), –123.8 (broad, 2, CF₂), –124.8 (broad, 2, CF₂), –127.1 (m, 2, CF₂), –183.5 (broad, 0.3, cis CF=CFOCH₃), and –191.7 (d, *J*_{FF} = 119 Hz, 0.7, trans CF=CFOCH₃).

Anal. (C₈H₃F₁₃O) 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 = C₄F₉) 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 = C₄F₉) 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 (SO₂O), and 1330–1100 (CF, SO₂); NMR ¹H 4.27 (s), ¹⁹F 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. (C₈H₃F₁₃O₄S) 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 ¹H 3.82 (m), ¹⁹F –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. (C₅H₃F₇O) 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 CF₃CHFCOFCF₃, then a mixture of SO₃ 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 SO₃ 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 (SO₂O), 1330–1100 (CF, SO₂); NMR ¹H 4.25 (s), ¹⁹F –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. (C₅H₃F₇O₄S) C, H, F, S.

For **19**, IR (CaF₂ plates) 2967 (satd CH), 1786 (C=O), 1433 (SO₂O), 1330–1100 (CF, SO₂); NMR ¹H 4.30 (s), ¹⁹F –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. (C₅H₃F₇O₇S₂) 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); ¹⁹F 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. (C₅F₁₀SO₄) C, F, S.

Although **10** was stable at 70 °C, pyrolysis at 200 °C for 4 h in a sealed tube gave SO₂ 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 ¹H 3.52 (s), ¹⁹F (56.4 MHz) –85.8 (t, *J*_{FF} = 1.5 Hz, 3), –123.9 (q, *J*_{FF} = 1.5 Hz, 2). Anal. (C₃H₃F₃SO₄) 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 ¹H 3.83 (s, cis OCH₃), 3.73 (s, trans OCH₃), ¹⁹F –65.4 (s, cis CF₃), –65.7 (s, trans CF₃).

Anal. Calcd for C₆H₆F₆O₂: 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 Hexafluorobiacyetyl. 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 SO₃ 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 SO₂ (identified by IR) and 9.3 g (24%) of yellow hexafluorobiacyetyl, bp 19–20 °C (lit. bp 20 °C).

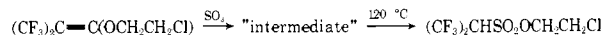
Distillation of higher boilers gave 43.2 g (68%) of cis-trans isomers of **20**: bp 77–89 °C (40 mm); IR (CaF₂ plates) 3030, 2985, and 2882 (satd CH), 1433 (SO₂O), 1320–1150 (CF, SO₂); NMR ¹H 3.89 (s, OCH₃), 3.78 ppm (m, OCH₃), ¹⁹F –74.5 (m, CF₃), –769 (s, CF₃).

Anal. Calcd for C₆H₆F₆O₆S: 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.

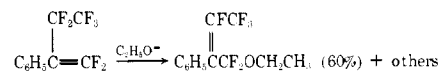
The analysis and an extraneous CH₃O band in the ¹H NMR spectrum indicate the presence of a small amount of dimethyl sulfate as an impurity. The identity of **20** was confirmed by converting it to hexafluorobiacyetyl in high yield with sulfuric acid. A mixture of 38.8 g (0.12 mol) of crude **20** and 100 ml of concentrated H₂SO₄ (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 hexafluorobiacyetyl by comparison of the IR spectrum with that of an authentic sample.

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