Reaction of Sulfur Trioxide with Cyclic Fluorovinyl Ethers

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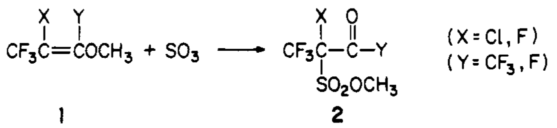
Abstract: A series of four- and five-membered ring polyfluorocyclic vinyl ethers was reacted with 2 equiv of sulfur trioxide to give α,β-unsaturated ketone products. In the five-membered ring series **3**, the enone product **4** and methoxypyrosulfuryl fluoride (**5**) were isolated at relatively low reaction temperatures (<70 °C). For the four-membered ring series **7**, higher reaction temperatures (>80 °C) were required to generate the enone product **8**. Under these conditions, anhydride **5** decomposed to sulfur trioxide and methyl fluorosulfate, and the liberated sulfur trioxide further reacted with enone **8** to give appreciable fluorosulfatocyclobutenyl side products **9**. Sulfur trioxide reacted with 1-methoxytrifluorocyclopropene to give only 2-carboxydifluoroethylenesulfonic acid γ-sultone (**12**). A mechanism which involves sulfur trioxide attack on an allylic fluorine to generate an initial polyfluorocycloalkenyl fluorosulfate ion pair is proposed. These results are compared with acyclic polyfluorovinyl ether reactions.

In the preceding paper we demonstrated that acyclic polyfluorovinyl ethers **1** react with 1 equiv of sulfur trioxide to give β-carbonylsulfonate esters **2**.[1] A mechanism was proposed which involved normal electrophilic attack by sulfur trioxide on the double bond to give a zwitterionic intermediate which bimolecularly collapsed to product. It was of interest to extend this reaction to cyclic fluorovinyl ethers in order to prepare functionalized polyfluorocycloalkanone derivatives. In this paper, we report a study of five-, four-, and three-membered ring polyfluorovinyl ether reactions. Unexpectedly, the cyclic fluorovinyl ethers reacted with sulfur trioxide in a manner quite different from their acyclic analogues. Such reactions proved to be useful routes to polyfluorinated cyclopent-2-en-1-ones and cyclobutenones, including perfluorocyclobutenone.

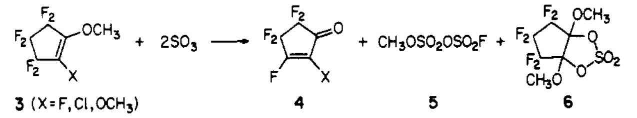


$$CF_3\overset{X}{C}=\overset{Y}{C}OCH_3 + SO_3 \longrightarrow CF_3\underset{SO_2OCH_3}{\overset{X}{C}}-\overset{O}{\overset{\|}{C}}-Y \quad (X = Cl, F)\ (Y = CF_3, F)$$

1 **2**

Results

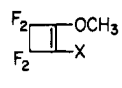
The vinyl ethers **3** (X = F, Cl, OCH_3) readily reacted with 2 equiv of sulfur trioxide at 0–5 °C. After standing at room temperature, the enone products **4** (X = F, Cl) were directly distilled from the reaction mixture in 78–84% yield. If the reaction mixture was kept below 70 °C during distillation, methoxypyrosulfuryl fluoride (**5**) was the major by-product isolated (72–83% yield). In addition to a 66% yield of **4** (X = OCH_3) and a 56% yield of **5**, **6** was isolated in 10% yield when **3** (X = OCH_3) was reacted with 2 equiv of sulfur trioxide.



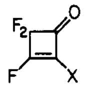
3 (X = F, Cl, OCH_3) **4** **5** **6**

If the reaction mixture was heated to higher temperature (120 °C) during distillation, product **4**, sulfur trioxide, and methyl fluorosulfate (CH_3OSO_2F) were isolated. Under these conditions, **3** (X = Cl) gave a mixture of product **4** (X = Cl) and methyl fluorosulfate which could not be separated by distillation. However, when the mixture was treated with dimethyl sulfide, a solid complex of **4** (X = Cl) along with trimethylsulfonium fluorosulfate was precipitated. Pyrolysis of this solid gave pure **4** (X = Cl).

The cyclobutenyl ethers **7** behaved somewhat differently from their five-membered ring analogues. Although sulfur trioxide (2 equiv) readily reacted with **7** (X = F, Cl) at room temperature, higher temperatures (80–120 °C) were required to generate the ketone products **8**. The major isolated products were the fluorosulfatocyclobutenes (**9**) and methyl fluorosulfate. For example, when **7** (X = F) was treated with 2 equiv of sulfur trioxide and the reaction mixture subsequently was heated to 110–120 °C during distillation, a 22–27% yield of **8** (X = F) and a 30% yield of **9** (X = F) resulted. Methyl fluorosulfate was isolated in ca. 97% yield. If, however, the reaction mixture was kept below 80 °C after the sulfur trioxide was added, no appreciable volatiles were collected in vacuo (120 mm).



7 (X = F, Cl, OCH_3)



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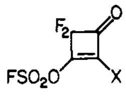

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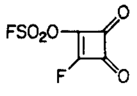

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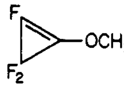
Methoxypyrosulfuryl fluoride (**5**) does not appreciably decompose to sulfur trioxide and methyl fluorosulfate until at ca. 100 °C. Sulfur trioxide and methyl fluorosulfate do not react at 25–70 °C. This evidence suggests that **5** is a primary reaction intermediate which decomposes under the reaction conditions involving elevated temperatures. Sulfur trioxide adds to perfluorocyclobutenone **8** (X = F) to give **9** at room temperature.

When treated with 2 equiv of sulfur trioxide, vinyl ether **7** (X = OCH_3) gave a complex mixture of products which were not identified. With 4 equiv of sulfur trioxide, a modest yield (29%) of material tentatively identified as **10** was isolated along with a 79% yield of methyl fluorosulfate. Product **10** rapidly hydrolyzed to squaric acid when exposed to the atmosphere. 1-Methoxytrifluorocyclopropene (**11**) exploded on contact with sulfur trioxide at room temperature. When a slurry of **11** in dry 1,2,2-trichlorotrifluoroethane at −50 °C was cautiously treated with 2 equiv of sulfur trioxide and the reaction mixture was slowly warmed to room temperature, **12** was isolated in 66% yield.



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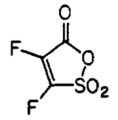

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It must be emphasized that 2 equiv of sulfur trioxide for each equivalent of cyclic vinyl ether is necessary in these reactions. If only 1 equiv of sulfur trioxide is employed, approximately half of the starting material is recovered. The results contrast with the acyclic vinyl ether reactions where only 1 equiv of sulfur trioxide is required for complete reaction.[1]

The product structures were readily confirmed by IR (Table I), NMR, and mass spectral data. The only structural as-

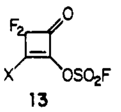
Table I. Cycloalkenone Carbon-Oxygen and Carbon-Carbon Double Bond Vibrational Stretching Frequencies[a]

Cycloalkenone	νC=O, cm^{-1}	νC=C, cm^{-1}
4, X = F[a]	1792	1724
4, X = Cl[a]	1786	1667
4, X = OCH_3[b]	1782	1686
8, X = F[c]	1845	1725
8, X = Cl[b]	1822	1668
9, X = F[b]	1838	1702
9, X = Cl[b]	1823	1630

[a] CCl_4 solution. [b] Neat liquid. [c] Gas phase.

signments which were not straightforward were those for the enone adducts **9** (X = F, Cl). Structure **13** was a possible alternative.

In fluorinated cyclobutenes, vinyl fluorine and allyl fluorine cross ring couplings are typically 16-19 Hz, whereas vinyl fluorine and adjacent allyl couplings are 4 to 8 Hz.[2] This also appears to be the case in fluorinated cyclobutenones; for example, the ring fluorine coupling in **14** is 19.0 Hz while the coupling in **8** (X = Cl) is 5.2 Hz.[3] The observed 17.8 Hz coupling in the enone **4** (X = F) adduct therefore is consistent only with structure **9** (X = F).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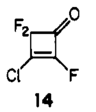
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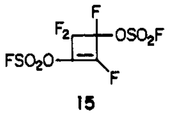
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Similarly, from model fluorosulfatocyclobutenes, e.g., **15**, the fluorine of the vinyl fluorosulfato group couples with the β-geminal ring fluorines by ca. 1.5 Hz, but does not couple (<0.1 Hz) with the γ-allyl fluorine.[4] In **9** (X = F), the fluorosulfato fluorine couples with the geminal ring fluorines by 1.7 Hz. The observed 2.5 Hz coupling in the enone **8** (X = Cl) adduct is consistent only with structure **9** (X = Cl).

The UV spectrum of perfluorocyclobutenone (**8**, X = F) in isooctane shows absorption maxima at 197 nm (ϵ 7910) and 299 nm (ϵ 13). Curiously, hypsochromic shifts occur when cyclobutenone is substituted with fluorines or when a double bond is introduced in perfluorocyclobutanone. Comparable UV maxima for cyclobutenone are 195 and 379 nm[5] and are 195 (ϵ 225) and 379 (ϵ 14) for perfluorocyclobutanone.[6]

The reaction of sulfur trioxide with polyfluorocyclopentenyl ethers represents a convenient, high yield synthesis of polyfluorocyclopent-2-en-1-ones. These procedures complement and in many cases are superior to the previously reported syntheses.[3,7]

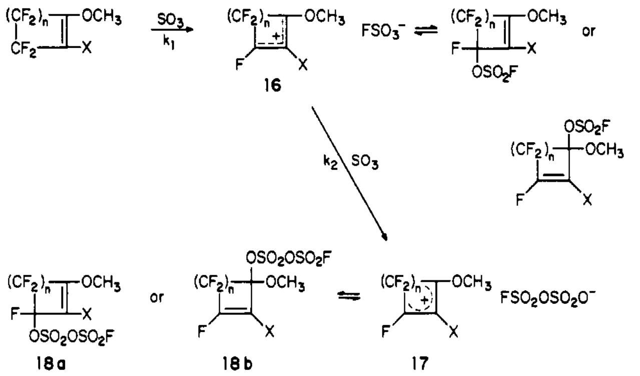
The cyclobutenones (**8**, X = F, Cl) have been synthesized for the first time. Interestingly, perfluorocyclobutenone is a volatile, colorless liquid, bp 45-47 °C, which is indefinitely stable at room temperature. This contrasts with its hydrocarbon analogue which is notoriously unstable and polymerizes at room temperature.[5] Water rapidly hydrolyzes perfluorocyclobutenone to squaric acid.

Discussion

The initial step in the reaction of sulfur trioxide with fluoroolefins is normally an electrophilic attack by sulfur trioxide on the double bond to give a zwitterionic intermediate $^{+}C-C-SO_3^{-}$. Depending upon the fluoroolefin and the reaction conditions, this intermediate usually collapses to a β-sultone or reacts with a second equivalent of sulfur trioxide to give a β-disultone.[8] In the case of acyclic fluorovinyl ethers, the zwitterionic intermediate is stabilized by an alkoxy substituent at the site of positive change and is sufficiently long-lived to decompose bimolecularly to a β-ketosulfonate product.

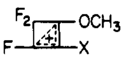
For the acyclic vinyl ethers **3**, **7**, or **11**, normal sulfur trioxide attack on the double bond does not account for the observed products. A competitive pathway which involves sulfur trioxide attack on an allylic fluorine to generate an initial intermediate cycloalkenyl fluorosulfate ion pair (**16**) is proposed (Scheme I).

Scheme I



The intermediate cation **16** is stabilized by conjugative interaction of the oxygen lone pair electrons with adjacent positive charge as well as by normal allylic charge delocalization. In the case of **16** (X = F, n = 0), the intermediate is a particularly stable cyclopropenium cation. Intermediate cyclobutenium cations can be further stabilized by 1,3 π interaction.[9]

In the case of ethers **7** and **11**, there is considerable independent evidence that supports the first step in Scheme I. Antimony pentafluoride reacts with **7**[10] and **11**[17] to give stable, isolable hexafluoroantimonate salts of **19** and **20**, respectively.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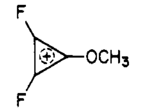
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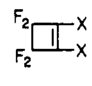
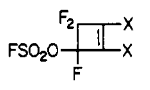

21 (X=F,Cl,H)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The importance of 1,3 interaction to the stability of **19** was demonstrated.[10] Furthermore, the cyclobutenes **21** react with sulfur trioxide to give the products **22** in which sulfur trioxide has initially attacked an allyl fluorine in **21**.[4]

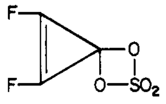
A priori, the first formed 1:1 adduct in Scheme I should directly pyrolyze to the observed product and methyl fluorosulfate. However, it was shown that 2 equiv of sulfur trioxide is required in these reactions, and **5**, not methyl fluorosulfate, is the primary product. Any proposed mechanism naturally must accommodate this observation.

Since it is known that alkali metal (Li, K, Na) fluorosulfates react irreversibly with sulfur trioxide to give pyrofluorosulfates below 50-70 °C,[11] it is reasonable to propose that sulfur trioxide rapidly reacts with **16** to give ion pair **17**. If $k_2 > k_1$ (Scheme I), the need for 2 equiv of sulfur trioxide is explained.

The enone product and **5** are then generated through the pyrolysis of **17**. Since the order of cation **17** stability is expected to be $n = 0 > 1 > 2$, the product from **17** (n = 2) should be formed at the lower pyrolysis temperatures. This is the case.

At higher pyrolysis temperatures, **5** decomposes to methyl fluorosulfate and sulfur trioxide (vide supra). Under the reaction conditions, sulfur trioxide further reacts with **8** to give **9**; but the less reactive enones **4** do not further react with sulfur trioxide under these conditions. Although difluorocyclopropenone is not detected in the reaction of **11**, the observed product **12** could conceivably arise from thermolysis of the cycloadduct **23**, or from direct ring opening attack of sulfur trioxide on the enone.

It is curious that sulfur trioxide appears to preferentially abstract allylic fluorines from cyclic fluorovinyl ethers but



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preferentially adds to the double bond of acyclic fluorovinyl ethers. In the three- and four-membered ring ethers, it is reasonable to suggest that these systems can give unusually stable cycloalkenyl cations, but this is not the case for the five-membered ring ethers. There is no evidence to support 1,3 π participation in cyclopentenyl or acyclic alkenyl cations.[9] It is not obvious why sulfur trioxide reacts with **3** (X = F) to give cation **16** (X = F, *n* = 2) while, e.g., **1** (X, Y = F) does not give the cation **24**. In fact, cation **24** is expected to be more stable

$$CF_2 \overset{---}{=} \underset{+}{C}F \overset{---}{=} CFOCH_3\ {}^{-}OSO_2F$$

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than **16** (X = F, *n* = 2) since the latter contains four inductively deactivating β-fluorines.

A possibility is that sulfur trioxide indeed may initially add to the double bond in the cyclic ethers, but unfavorably strained β-sultones would result. Also, the torsional angle between the methoxy and sulfite groups in the zwitterionic adduct from the cyclic ethers would lead to unfavorable geometries for bimolecular reaction. The zwitterionic intermediates in the acyclic cases are conformationally mobile and can achieve the optimum geometry necessary for bimolecular reaction.[1] Sulfur trioxide therefore adds reversibly to the cyclic fluorovinyl ether double bonds, but the initial product determining attack on an allylic fluorine is irreversible.[12]

Experimental Section

The ^{1}H NMR and ^{19}F NMR spectra were obtained on a Varian Associates XL-100 spectrometer. The ^{1}H NMR spectra are referenced to internal tetramethylsilane, and the ^{19}F NMR spectra are referenced to internal trichlorofluoromethane. Infrared spectra were recorded on a Perkin-Elmer 467 spectrophotomer. Baker and Adams stabilized sulfur trioxide (Sulfan) was employed. All boiling points are uncorrected.

1-Chloro-2-methoxyhexafluorocyclopentene (**3**, X = Cl) was prepared by the procedure of Anello, Price, and Sweeney:[13] yield, 55%; bp 89–90 °C (200 mm) [lit. bp 130–132 °C].

1-Methoxypentafluorocyclobutene (**7**, X = F) was prepared from hexafluorocyclobutene and sodium methoxide:[4] yield, 70%; bp 87–88 °C [lit.[14] bp 87 °C (747 mm)].

1-Chloro-2-methoxytetrafluorocyclobutene (**7**, X = Cl) was prepared from 1,2-dichlorotetrafluorocyclobutene and sodium methoxide:[4] yield, 81%; bp 62–63 °C (100 mm) [lit.[15] bp 117 °C].

1,2-Dimethoxytetrafluorocyclobutene (**7**, X = OCH_3) was prepared from hexafluorocyclobutene and sodium methoxide:[4] yield, 74%; bp 68–71 °C (60 mm) [lit.[16] bp 36 °C (11 mm)].

1,2-Dimethoxyhexafluorocyclopentene (**3**, X = OCH_3). A stirred solution of 95 g (0.45 mol) of octafluorocyclopentene in 200 ml of methanol was chilled to 0 °C and treated dropwise over 1 h with 51.3 g (0.95 mol) of sodium methoxide in 300 ml of ether. After standing overnight at room temperature, the reaction mixture was heated for 1 h at 60 °C. The majority of the methanol solvent was distilled off (1 atm), and the residual material was diluted with 100 ml of methylene dichloride and was quenched in 1 l. of water. Concentrated hydrochloric acid (35 ml) was added to break the emulsion, and the organic layer was withdrawn. The aqueous phase was extracted with methylene chloride (50 ml), and the combined organic phases were washed with 100 ml of water, dried (Na_2SO_4), and distilled to give 66.9 g (63%) of **3** (X = OCH_3): bp 77–77.5 °C (45 mm) [lit.[7a] bp 148–149 °C]; NMR (CCl_4) ^{1}H δ 4.00 (s), ^{19}F φ −112.5 (t, 4, *J* = 4.5 Hz), −130 (p, 2, *J* = 4.5 Hz).

1-Methoxyheptafluorocyclopentene (**3**, **X** = **F**). Octafluorocyclopentene (84.8 g, 0.40 mol) was slowly distilled into a stirred solution of 21.6 g (0.40 mol) of sodium methoxide in 500 ml of methanol chilled to −40 °C. After complete addition, the reaction mixture was slowly warmed to room temperature. After standing overnight at room temperature, the reaction mixture was shaken with 2 l. of water, and the separated organic layer was washed with an additional 500 ml of water, dried ($MgSO_4$), and distilled to give 69.7 g (78%) of **3** (X = F): bp 102–103 °C [lit.[7a] bp 100–101 °C]; NMR ($CDCl_3$) ^{1}H δ 4.15 (d, *J* = 3.6 Hz), ^{19}F φ −116.0 (d of m, 2, *J* = 12.7 Hz), −117.0 (d of m, 2, *J* = 11.0 Hz), −130.6 (m, 2), −164.4 (m, 1).

Hexafluorocyclopent-2-en-1-one (**4**, **X** = **F**). Sulfur trioxide (16.0 g, 0.20 mol) was added dropwise to 22.4 g (0.10 mol) of **3** (X = F) chilled to 5 °C. After stirring 2 days at room temperature, the reaction mixture was fractionated (pot temperature <70 °C) to give crude **4**, bp 31–32 °C (200 mm), and 14.0 g (72%) of **5**, bp 43–44 °C (4 mm): IR (neat) 2985 cm^{-1} (C–H); 1480, 1439 cm^{-1} (SO_2O); NMR (CCl_4) ^{1}H δ 4.31 (s), ^{19}F φ +45.0 (s). Crude **4** and the collected cold trap volatiles were treated with sodium fluoride and redistilled to afford 16.0 g (84%) of pure **4** (X = F): bp 66 °C; IR (CCl_4) 1792 cm^{-1} (C═O), 1724 cm^{-1} (C═C), 1400–1150 cm^{-1} (C–F); NMR (CCl_4) ^{19}F φ −122.3 (d of d, 2, *J* = 13.1, 9.4 Hz), −127.1 (d of d, 2, *J* = 4.7, 4.0 Hz), −129.2 (t of t, 1, *J* = 13.1, 4.0 Hz), −143.8 (t of t, *J* = 9.4, 4.7 Hz). Anal. ($CH_3F_6O_6S_2$) (**5**) C, H, F, S; (C_5F_6O) (**4**, X = F) C, F.

2-Chloropentafluorocyclopent-2-en-1-one (**4**, **X** = **Cl**). To 36.7 g (0.157 mol) of **3** (X = Cl) at 0 °C was added 25.6 g (0.32 mol) of sulfur trioxide. After stirring overnight at room temperature, the reaction mixture was distilled (pot temperature <70 °C) to give crude **4** (X = Cl), bp 37–41 °C (100 mm), and 25.3 g (83%) of **5**, bp 43–44 °C (4.5 mm). Crude **4** (X = Cl) and the recovered cold trap volatiles were treated with sodium fluoride and redistilled to give 24.8 g (77%) of pure **4** (X = Cl): bp 58 °C (200 mm) [lit.[3] bp 92–95 °C]; IR (CCl_4) 1786 cm^{-1} (C═O), 1667 cm^{-1} (C═C), 1370–1110 cm^{-1} (C–F), 756 cm^{-1} (C–Cl); NMR (CCl_4) φ −110.0 (t of t, 1, *J* = 19.2, 4.5 Hz), −123.0 (d of t, 2, *J* = 19.2, 1 Hz), −126.0 (d of t, 2, *J* = 4.5, 1 Hz). Anal. (C_5ClF_5O) C, Cl, F.

A similar reaction of 48.1 g (0.20 mol) of **3** (X = Cl) and 35.2 g (0.44 mol) of sulfur trioxide was carried out. In this case, the bath temperature during distillation was raised to 100 °C and resulted in a mixture of **4** (X = Cl) and CH_3OSO_2F, bp 50–59 °C (220 mm), which could not be fractionated apart. Attempts to remove the methyl fluorosulfate by heating the mixture with sodium fluoride or epichlorohydrin failed, but treatment with dimethyl sulfide gave a solid mass which was pyrolyzed to give 11.6 g (26%) of **4** (X = Cl), bp 93 °C.

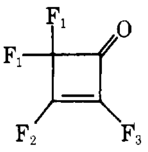
Sulfur trioxide (0.22 mol) and 0.20 mol of **3** (X = Cl) were similarly reacted, then distilled in vacuo at a bath temperature of ca. 70 °C to give 17.4 g (82%) of **5**. The volatile contents of the cold trap indicated a mixture of **3** (X = Cl) and **4** (X = Cl).

2-Methoxypentafluorocyclopent-2-en-1-one (**4**, **X** = $\mathbf{OCH_3}$) **and 6.** To 23.6 g (0.10 mol) of **3** (X = OCH_3) at 0 °C was added dropwise 16.0 g (0.20 mol) of sulfur trioxide. After slowly warming to room temperature, a mild exotherm was controlled at 30 °C or less, and the mixture then was left at room temperature overnight. The mixture was distilled to give 12.4 g (61%) of enone **4** (X = OCH_3), bp 38–39 °C (6 mm), 10.9 g (56%) of crude **5**, and 3.2 g (10%) of sulfate **6**, bp 65 °C (2 mm): IR (CCl_4) 3030, 2976, 2881 cm^{-1} (C–H), 1433 cm^{-1} (SO_2O), 1330–1000 cm^{-1} (C–F, C–O–C, SO_2); NMR (CCl_4) ^{1}H δ 3.83 (d, *J* = 1.1 Hz), ^{19}F φ −123.3, −132.8 (AA′BB′ m of m, 4, J_{AB} = 259 Hz); −127.0–143.6 (AB m of m, 2, J_{AB} = 264 Hz). Enone **4** (X = OCH_3) was redistilled to give an analytical sample: bp 62 °C (30 mm); IR (neat) 3040, 2976, 2874 cm^{-1} (C–H), 1782 cm^{-1} (C═O), 1686 cm^{-1} (C═C), 1430–1000 cm^{-1} (C–F); NMR (CCl_4) ^{1}H δ 4.20 (d, *J* = 3.1 Hz), ^{19}F φ −120.4 (d of m, 2, *J* = 13.7 Hz), −126.7 (d of t, 2, *J* = 5.3, 1.3 Hz), −140.0 (t of t, of q, 1, *J* = 13.7, 5.3, 3.1 Hz). Anal. ($C_6H_3F_5O_2$) (**4**, X = OCH_3) C, H, F; ($C_7H_6F_6O_6S$) (**6**) C, H, F, S.

Perfluorocyclobutenone (**8**, **X** = **F**) **and 3-Fluorosulfato-2,4,4-trifluorocyclobut-2-en-1-one** (**9**, **X** = **F**). Vinyl ether **7** (X = F) (17.4 g, 0.10 mol) was treated dropwise with 16.0 g (0.20 mol) of sulfur trioxide over a 30-min period (exotherm to 50 °C). After the reaction mixture equilibrated to room temperature, it was distilled. No material distilled until the pot temperature reached ca. 90 °C and 3.1 g (22%) of pure **8** (X = F) was collected: bp 45–46 °C; IR (gas) 1845 cm^{-1} (C═O), 1725 cm^{-1} (C═C), mass spect (rel intensity) *m/e* 93 (1000, P − CO, F), 112 (771, P − CO), 140 (285, P), 124 (78), 121 (67), 74 (60), 71 (57), 69 (36). Continued distillation gave 11.1 g (97%) of mostly CH_3OSO_2F, bp 80–88 °C, 52–48 °C (180–160 mm), and 8.4 g (30%) of **9** (X = F), bp 58–62 °C (60 mm), mostly 62 °C; IR (neat) 1838 cm^{-1} (C═O), 1702 cm^{-1} (C═C); NMR (CCl_4) ^{19}F φ +45.1 (d of t, 1, *J* = 3.8, 1.7 Hz), −104.2 (t of d, 1, *J* = 17.8, 3.8 Hz), −112.9

(d of d, 2, J = 17.8, 1.7 Hz). Anal. (C_4F_4O) (**8**, X = F) C; ($C_4F_4O_4S$) (**9**, X = F) C, F.

Perfluorocyclobutenone gave a complex second-order NMR spectrum which was analyzed to give the following parameters:



ϕ_1 = −116.2
ϕ_2 = −101.3
ϕ_3 = −112.9

J_{12} = −6.5 Hz
J_{13} = +19 Hz
J_{23} = −4.8 Hz

A second reaction with the above stoichiometry was worked up by evacuating the system to 120 mm through an attached −78 °C trap after the sulfur trioxide was added. No product was collected until the reaction mixture was warmed to ca. 80 °C and finally to 90-100 °C. The trap content was fractionated to give 3.8 g (27%) of **8** (X = F), bp 46-47 °C.

When 1 equiv of sulfur trioxide was employed in the above reaction, approximately half of the starting material and 0.5 equiv of methylfluorosulfate were recovered. The yield of **8** (X = F) was also halved.

2-Chloro-3,4,4-trifluorocyclobut-2-en-1-one (8, X = Cl) and 2-Chloro-3-fluorosulfato-4,4-difluorocyclobut-2-en-1-one (9, X = Cl). Sulfur trioxide (16.0 g, 0.20 mol) was added dropwise to 19.0 g (0.10 mo) of **7** (X = Cl) over a 30-min period (exotherm to 58 °C). The dark reaction mixture was distilled (pot temperature to 120 °C) to give 2.7 g of a mixture containing ca. 30% **8** (X = Cl) (GLC), bp 63-65 °C, 4.7 g of 20% **8** (X = Cl), 80% CH_3OSO_2F, bp 80-82 °C, 8.0 g of mostly CH_3OSO_2F, bp 85-87 °C, 48-52 °C (180 mm), and 10.7 g (45%) of **9** (X = Cl), bp 75-80 °C (60 mm) (mostly 78-80 °C): IR (neat) 1823 cm^{-1} (C=O), 1630 cm^{-1} (C=C); NMR (CCl_4) ϕ +46.5 (t, 1, J = 2.5 Hz), −109.5 (d, 2, J = 2.5 Hz). Anal. ($C_4ClF_3O_4S$) C, F.

The enone **8** (X = Cl) was identified spectroscopically: IR (neat) 1822 cm^{-1} (C=O), 1668 cm^{-1} (C=C); NMR (CCl_4) ^{19}F ϕ −88.6 (t, 1, J = 5.2 Hz), −113.9 (d, 2, J = 5.2 Hz).

A similar reaction with 0.2 mol of sulfur trioxide and 0.1 mol of **7** (X = Cl) was stirred 2 h at room temperature and quenched in 100 ml of vigorously stirred ice-cold water. The organic layer was drawn off, washed with saturated aqueous NaCl, dried ($MgSO_4$), and distilled to give 2.5 g of a mixture of 33% CH_3OSO_2F and 67% **8** (X = Cl), bp 42-45 °C (160 mm), and 3.1 g of 80% CH_3OSO_2F, 20% **8** (X = Cl), bp 46-47 °C (160 mm).

3-Fluorosulfato-4-fluorocyclobutene-1,2-dione (10). Sulfur trioxide (32.0 g, 0.40 mol) was added dropwise to 18.6 g (0.10 mol) of **7** (X = OCH_3) while keeping the temperature below 50 °C. After stirring overnight, the colorless mixture was distilled to give 25.4 g of mostly CH_3OSO_2F: bp 46-52 °C (180-160 mm). The pot residue became progressively more viscous and darkened as the distillation proceeded (no material collected in an intervening −78 °C trap). Continued distillation in vacuo gave 1.5 g of unidentified purple material, bp 47-57 °C (3.6-2 mm), and 5.8 g of mostly **10**, bp 57-59 °C (2 mm): IR (neat) 1810 cm^{-1} (br, C=O), 1665 (br C=C); NMR (neat, ext) +46.3 (d, 1, J = 2.6 Hz), −72.9 (d, 1, J = 2.6 Hz). The remaining dark viscous pot residue failed to distill at 1.5 mm (pot temperature 130 °C). Product **10** rapidly hydrolyzed to squaric acid on atmospheric exposure.

2-Carboxydifluoroethylenesulfonic Acid γ-Sultone (12). A slurry of 6.2 g (0.05 mol) of **11**[17] in 50 ml of dry 1,1,2-trichlorotrifluoroethane (Freon 113) chilled to −50 °C was treated dropwise with 8.0 g (0.50 mol) of sulfur trioxide. After slowly warming to room temperature, a pale-yellow organic layer separated. The mixture was then distilled to remove the $CFCl_2CF_2Cl$ solvent (no low boiler or difluorocyclopropenone detected), and the residue was fractionated (pot temperature to 120 °C) to give 2.7 g of CH_3OSO_2F, bp 43 °C (120 mm) and 5.6 g (66%) of **12**, bp 72-73 °C (70 mm), mp 42-45 °C; IR (mull) 1845 cm^{-1} (C=O), 1743 cm^{-1} (C=C); NMR (CCl_4) ^{19}F ϕ −133.8 (d, 1, J = 14.8 Hz) −146.3 (d, 1, J = 14.8 Hz), mass spec (rel intensity) m/e 90 (100, P − SO_3), 106 (994, P − SO_2), 62 (351, P − SO_2, CO), 87 (P − SO_2, F), 31 (223), 63 (124), 48 (80), 71 (76), 93 (71), 170 (21, P). Anal. ($C_3F_2O_4S$) C, F, S.

References and Notes

(1) C. G. Krespan, B. E. Smart, and E. G. Howard, preceding paper in this issue.
(2) K. Jones and E. F. Mooney *Annu. Rep. NMR Spectrosc.*, **4**, 414 (1971).
(3) A sample of **14** was prepared for NMR analysis by the procedure of G. Scherer, G. Hörlein, and H. Millauer, *Chem. Ber.*, **99**, 1966 (1966).
(4) B. E. Smart, *J. Org. Chem.*, **41**, 2353 (1976).
(5) J. B. Sieja, *J. Am. Chem. Soc.*, **93**, 2481 (1971).
(6) D. C. England, *J. Am. Chem. Soc.*, **83**, 2205 (1961).
(7) (a) R. F. Stockel, M. T. Beachem, and F. H. Megson, *Can. J. Chem.*, **42**, 2880 (1964), (b) R. J. DuBois and B. Veldbuis, U.S. Patent 3 310 584, 3 310 585 (1967).
(8) See I. L. Knunyants and G. A. Sokolskii, *Angew. Chem., Int. Ed. Engl.*, **11**, 583 (1972), and references therein for a review of sulfur trioxide additions to fluoroolefins.
(9) G. A. Olah, P. W. Westerman, and D. A. Forsyth, *J. Am. Chem. Soc.*, **97**, 3419 (1975).
(10) B. E. Smart and G. S. Reddy, *J. Am. Chem. Soc.*, **98**, 5593 (1976).
(11) P. Vast and J. Heubel, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **267**, 236 (1968).
(12) In the case of **3** (X = OCH_3), the minor product **6** results from trapping of the relatively stable zwitterionic intermediate with sulfur trioxide, followed by irreversible loss of sulfur dioxide. See ref 1 for a description of this mechanism.
(13) L. G. Anello, A. K. Price, and R. F. Sweeney, *J. Org. Chem.*, **33**, 2692 (1968).
(14) J. T. Barr, K. E. Rapp, R. L. Pruett, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, Jr., *J. Am. Chem. Soc.*, **72**, 4480 (1950).
(15) J. D. Park, C. M. Snow, and J. R. Lacher, *J. Am. Chem. Soc.*, **73**, 2342 (1951).
(16) J. D. Park, S. M. Sharrah, and J. R. Lacher, *J. Am. Chem. Soc.*, **71**, 2337 (1949).
(17) B. E. Smart, *J. Org. Chem.*, **41**, 2377 (1976).