Registry No.—*N-tert*-Butyloxycarbonyl-*O*-benzyl-L-serine cyclohexylammonium salt, 30200-52-3; *N-tert*-butyloxycarbonyl-L-serine, 3262-72-4; benzyl bromide, 100-39-0; *N-tert*-butyloxycarbonyl-*O*-benzyl-L-serine, 23680-31-1.

References and Notes

(1) R. B. Merrifield, *Adv. Enzymol. Relat. Areas Mol. Biol.*, **32**, 221 (1969).
(2) K. Okawa and H. Tani, *J. Chem. Soc. Jpn.*, **75**, 1197 (1950); K. Okawa, *Bull. Chem. Soc. Jpn.*, **30**, 110 (1957).
(3) K. Okawa, *Bull. Chem. Soc. Jpn.*, **29**, 486 (1956).
(4) V. J. Hruby and K. W. Ehler, *J. Org. Chem.*, **35**, 1690 (1970).
(5) All melting points are uncorrected. Thin layer chromatography was performed on silica gel plates (Merck) using chloroform–methanol–acetic acid (95:5:3).
(6) H. Otsuka, K. Inouye, F. Shinozaki, and M. Kanayama, *Bull. Chem. Soc. Jpn.*, **39**, 1171 (1966).

A Novel Reaction of Sulfur Trioxide with Fluoro Olefins

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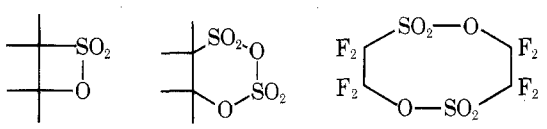
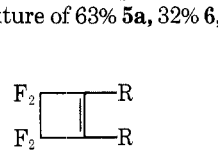
It is well known that sulfur trioxide reacts with fluoro olefins to normally give stable β-sultones (**1**) and β-disultones (**2**).[1] Tetrafluoroethylene is reported to also give the unusual eight-membered ring heterocycle **3**. In some cases, the β-sultone products rearrange to alkenyl fluorosulfates (–C=C–OSO_2F) under the reaction conditions. Polyfluorocyclobutenes are reported here to react in a novel manner with sulfur trioxide to give a new class of products, 3-(fluorosulfato)polyfluorocyclobutenes.

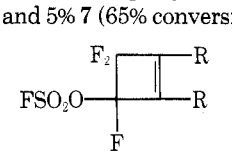


1 **2** **3**

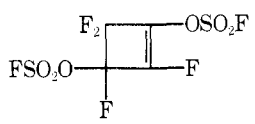
Hexafluorocyclobutene (**4a**) reacts slowly with sulfur trioxide at room temperature and reacts rapidly at 100 °C to give a mixture of 63% **5a**, 32% **6**, and 5% **7** (65% conversion, 91% yield). At 100 °C, **4a** reacts with 2 equiv of sulfur trioxide to give 34% **5a**, 50% **6**, and 16% **7**. Similarly at 100 °C, **4b** gives **5b**. 3,3,4,4-Tetrafluorocyclobutene (**4c**) reacts exothermally with sulfur trioxide at room temperature to give **5c** in 74% yield. There are no appreciable sultone products or 1-cycloalkenyl fluorosulfate monoadducts detected in these reactions.



4a, R = F
b, R = Cl
c, R = H



5a, R = F
b, R = Cl
c, R = H



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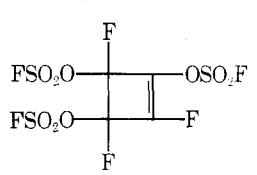

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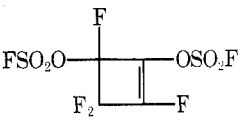
In contrast with **4a** and **4b**, the acyclic analogue octafluoro-2-butene, $CF_3CF{=}CFCF_3$, does not react appreciably with sulfur trioxide at 100 °C,[2] and 2,3-dichlorohexafluoro-2-butene, $CF_3CCl{=}CClCF_3$, is reported to give the β-sultone.[3]

The structures of the reaction products are readily established by ir and NMR analyses. The comparable carbon–carbon double bond vibrational stretching frequencies in **4a–c** and **5a–c** confirm the double bond substitution pattern: **5a** (1792 cm^{-1}), **4a** (1799 cm^{-1}), **5b** (1629 cm^{-1}), **4b** (1620 cm^{-1}), **5c** (1561 cm^{-1}), **4c** (1560 cm^{-1}). The double bond stretching frequencies in **6** and **7** appear at 1762 and 1765 cm^{-1}, respectively, which are comparable to the stretching frequency in 1-methoxypentafluorocyclobutene (1765 cm^{-1}). The NMR spectra of **5a–c** are also consistent with the assigned structures (see Experimental Section).

For the 2:1 adduct, it is not obvious whether **6** or **8** is the correct structure. The NMR spectrum of this adduct was



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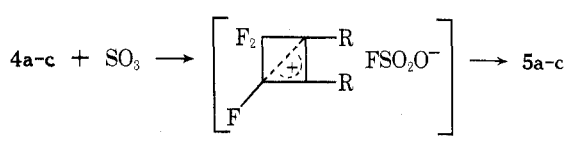
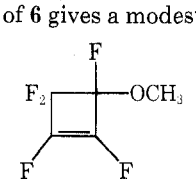
analyzed with computer assistance to obtain the F–F couplings (see Experimental Section). The vinyl fluorine cross couples with the nonequivalent geminal fluorines by 14.4 and 15.2 Hz, while it couples with an adjacent fluorine by 4.4 Hz. When compared with model fluorinated cyclobutenes, the observed couplings are consistent only with structure **6**.[4]

The initial step in the reaction of sulfur trioxide with olefins is normally an electrophilic attack by sulfur trioxide on the double bond to give an intermediate π complex which rearranges to a zwitterionic intermediate (^+C–C–OSO_2^-). Depending upon the fluoro olefin and the reaction conditions, this intermediate usually collapses directly to β-sultone product (**1**) or reacts with an additional 1 equiv of sulfur trioxide, followed by collapse to β-disultone (**2**). For the cyclobutenes **4a–c**, a competitive pathway which involves sulfur trioxide attack on an allylic fluorine to generate an intermediate cyclobutenyl fluorosulfate ion pair is suggested.



In contrast with acyclic alkenyl cations where charge is delocalized only by classical allyl resonance, cyclobutenyl cations can be further stabilized by 1,3-π overlap.[5] This may in part contribute to the increased reactivity of **4a** over its acyclic analogue, octafluoro-2-butene. Similarly, the potential allyl cation generated by attack of sulfur trioxide on an allylic fluorine in 2,3-dichlorohexafluoro-2-butene is less stable than the corresponding cyclobutenyl cation generated from **4b**; therefore, sulfur trioxide preferentially adds to the double bond in the acyclic alkene to give normal β-sultone product.

The cyclobutenyl fluorosulfates **5** are useful alkylating agents. For example, methanolysis of **5a** gives **9** in 80% yield, the only known practical route to this compound.[6] Methanolysis of **6** gives a modest yield (40%) of **10**.



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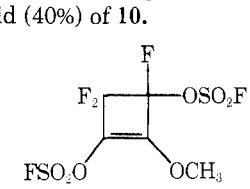

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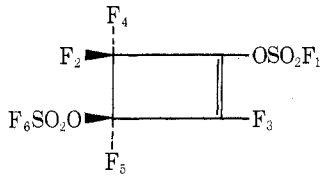
Experimental Section

All NMR spectra were recorded on a Varian Associates XL-100 spectrometer. The ^1H NMR spectra are referenced to internal tetramethylsilane and the ^{19}F NMR spectra are referenced to internal

Table I



	F_1	F_2	F_3	F_4	F_5	F_6
ϕ, ppm	+44.70	−113.14	−113.29	−115.92	−121.26	+48.21

Couplings

Fx,y	J, Hz	Fx,y	J, Hz
1,2	1.5	3,4	14.4
1,3	3.6	3,5	4.4
1,4	1.4	3,6	1.0
2,3	15.2	4,5	−11.8
2,4	188.8	4,6	0.7
2,5	27.4	5,6	9.8
2,6	3.4	1,5; 1,6	0.0

trichlorofluoromethane. Infrared spectra were recorded on a Perkin-Elmer 467 spectrophotometer. Baker and Adams stabilized sulfur trioxide (Sulfan) was employed. All boiling points are uncorrected.

3-(Fluorosulfato)-1,2,3,4,4-pentafluorocyclobutene (5a), 1,3-Bis(fluorosulfato)-2,3,4,4-tetrafluorocyclobutene (6), and 1,2,3-Tris(fluorosulfato)-2,3,4-trifluorocyclobutene (7). Two 250-ml Carius tubes, one charged with 60 g (0.37 mol) of hexafluorocyclobutene (**4a**) and 24 g (0.30 mol) of sulfur trioxide and the other charged with 63 g (0.39 mol) of **4a** and 0.30 mol of sulfur trioxide, were heated on a steam bath for 16 h. The tubes were opened, and the contents were combined and distilled to give 59.5 g of **4a** and 53 g of **5a:** bp 49–50 °C (150 mm); ir (neat) 1792 cm^{-1} (C=C); NMR (CCl_4) ϕ +47.6 (d of d of m, 1, J = 9.8, 3.1 Hz), −115.4, −118.2 (AB m of m, 2, J_{AB} = 189 Hz), −121.6 (complex m, 1), −125.7 (complex m, 1), −126.2 (complex m, 1).

Further distillation gave 37.7 g of **6:** bp 79–80 °C (50 mm), ir (neat) 1762 cm^{-1} (C=C), and 6.8 g of **7,** bp 85–88 °C (11 mm), ir (neat) 1765 cm^{-1} (C=C).[7]

Anal. Calcd for $C_4F_6O_3S$ (**5a**): C, 19.84; F, 47.08; S, 13.24. Found: C, 19.75; F, 47.06; S, 13.29. Calcd for $C_4F_6O_6S_2$ (**6**): C, 14.91; F, 35.38; S, 19.90. Found: C, 14.80; F, 35.28; S, 20.12. Calcd for $C_4F_6O_9S_3$ (**7**): C, 11.94; F, 28.34; S, 23.91. Found: C, 12.26; F, 28.57; S, 23.95.

Similarly, 0.1 mol of **4a** and 0.1 mol of sulfur trioxide at 100 °C for 2 h gave a mixture of 68% **5a** and 32% **6** (65% conversion, 91% yield).

The NMR spectral parameters for **6** are given in Table I.[8]

3-(Fluorosulfato)-1,2-dichloro-3,4,4-trifluorocyclobutene (5b). A mixture of 19.5 g (0.10 mol) of **4b** and 0.1 mol of sulfur trioxide in a Carius tube was heated on a steam bath for 14 h. The product mixture was fractionated to give 12.2 g of **5b:** bp 77–78 °C (80 mm); ir (neat) 1629 cm^{-1} (C=C); NMR (CCl_4) ϕ +48.6 (d of d, 1, J = 10, 4.5 Hz), −112.9, −115.5 (AB m of m, 2, J_{AB} = 190 Hz; A, d of d, J = 22, 4.5 Hz; B, d, J = 9 Hz), −120.4 (d of t, 2, J = 22, 9 Hz).

Anal. Calcd for $C_4Cl_2F_4O_3S$: C, 17.47; F, 27.63; S, 11.66. Found: C, 16.69; F, 26.83; S, 11.91.

3-(Fluorosulfato)-3,4,4-trifluorocyclobutene (5c). Neat **4c** (12.6 g, 0.10 mol) was treated dropwise with 0.1 mol of sulfur trioxide (exotherm to ca. 40 °C). After stirring for 2 h the mixture was fractionated to give 15.3 g of **5c:** bp 62–63 °C (50 mm); ir (neat) 1561 cm^{-1} (very weak C=C); Raman 1561 cm^{-1} (intense); NMR (CCl_4), ^1H δ 6.90, 6.94 (complex AB m of m, 2, J_{AB} = 3.4 Hz), ^{19}F ϕ + 46.9 (d of d, 1, J_{FF} = 9.8, 2 Hz), −107.5, −119.7 (complex AB m of m, 2, J_{AB} = 198 Hz; A, d of d of m, J_{FF} = 25, 2 Hz; B, d of m, J_{FF} = 6.2 Hz), −112.8 (complex m, 1, J_{FF} = 25, 9.8, 6.2 Hz).

Anal. Calcd for $C_4H_2F_4O_3S$: C, 23.31; H, 0.98; F, 36.88. Found: C, 23.76; H, 1.03; F, 36.87.

3-Methoxy-1,2,3,4,4-pentafluorocyclobutene (9). A solution of 12.1 g (0.05 mol) of **5a** in 50 ml of methanol was refluxed for 30 min. The reaction mixture was carefully fractionated to give 7.0 g (80%) of **9:** bp 45–46 °C; ir (neat) 1785 cm^{-1} (C=C); NMR (CCl_4), ^1H δ 3.63 (d, $J \simeq 1$ Hz), ^{19}F ϕ −118.5, −120.3 (AB m of m, 2, J_{AB} = 188 Hz), −129.3 to −128.4 (complex m, 2), −135.3 (complex m, 1).

Anal. Calcd for $C_5H_3F_5O$: F, 34.50. Found: F, 34.61.

1,3-Bis(fluorosulfato)-2-methoxy-3,4,4-trifluorocyclobutene (10). To 50 ml of methanol chilled in an ice bath was added dropwise 16.1 g (0.05 mol) of **6.** After slowly warming to room temperature, the reaction mixture was quenched in 100 ml of cold water. The organic layer was taken up in methylene dichloride, washed with water and saturated sodium chloride, and dried ($MgSO_4$) and fractionated to give 6.3 g (40%) of **10:** bp 60 °C (1 mm); ir (neat) 1740 cm^{-1} (C=C); NMR (CCl_4), ^1H δ 4.20 (s), ^{19}F ϕ +48.3 (d of d, 1, J = 8.8, 5 Hz), +42.0 (t, 1, J = 5 Hz), −108.9, −111.5 (AB m of m, 2, J_{AB} = 188 Hz; A, d of t, J = 22, 5 Hz; B, d of d, J = 11, 5 Hz), −123.0 (d of d of d, 1, J = 22, 11, 8.8 Hz).

Anal. Calcd for $C_5H_3F_5O_7S_2$: C, 18.87; H, 0.95; F, 29.87. Found: C, 18.59; H, 1.16; F, 29.77.

Registry No.—**4a,** 697-11-0; **4b,** 377-93-5; **4c,** 2714-38-7; **5a,** 59034-67-2; **5b,** 59034-68-3; **5c,** 59034-69-4; **6,** 59034-70-7; *cis*-**7,** 59034-71-8; *trans*-**7,** 59034-72-9; **9,** 59034-73-0; **10,** 59034-74-1; sulfur trioxide, 14265-45-3.

References and Notes

(1) See I. L. Knunyants and G. A. Sokolski, *Angew. Chem., Int. Ed. Engl.*, **11,** 583 (1972), and references cited therein for a review of sulfur trioxide additions to fluoro olefins.
(2) C. G. Krespan, unpublished results.
(3) Y. H. Kwei, *Acta Chim. Sinica*, **26,** 330 (1957).
(4) Vinyl and allyl fluorine cross couplings are typically 16–19 Hz, while vinyl and adjacent allyl couplings are 4–8 Hz; see K. Jones and E. F. Mooney, *Annu. Rep. NMR Spectrosc.*, **4,** 414 (1971).
(5) See G. A. Olah et al., *J. Am. Chem. Soc.*, **97,** 3489 (1975), and references cited therein for a discussion of 1,3 interactions in cyclobutenyl cations.
(6) Hexafluorocyclobutene reacts with methoxide ion to give 1-methoxypentafluorocyclobutene and 1,2-dimethoxytetrafluorocyclobutene but only a trace of **9;** see J. D. Park, R. J. McMurtry, and J. H. Adams, *Fluorine Chem. Rev.*, **2,** 60–61 (1968).
(7) The NMR spectrum of **7** is exceedingly complex and indicates a mixture of cis and trans isomers. The absence of typical 180–200 Hz geminal fluorine couplings rules out the possible 1,3,3-tris(fluorosulfato)-2,4,4-trifluorocyclobutene product.
(8) This molecule was analyzed as a six-spin ABCDMX system using a LAOCOON III program. The agreement between the observed and calculated spectra is within 0.1 Hz. The solution is unique and the negative sign for J_{45} is correct. The estimated uncertainties in the chemical shifts and coupling constants are 0.001 ppm and 0.1 Hz, respectively. The assistance of Dr. G. S. Reddy is gratefully acknowledged for this analysis.