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NEW POLYFLUOROALKOXYSULFONYL FLUORIDES PART III

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SUMMARY

The reaction of $CF_3\overline{CFCF_2OSO_2}$ with haloalkanes (RX, X=I, Br) in the presence of silver fluoride was studied as a means for preparing novel reactive polyfluoroalkoxysulfonyl fluorides. The following compounds have been prepared and characterized: $ROCF_2CF(CF_3)SO_2F$, where R is $CH_2{=}CHCH_2$, $CF_2{=}CFCH_2CH_2$, $(CF_3)_2CFCH_2CH_2$, CH_3, $CH_2{=}CBrCH_2$, $SF_5CH_2CH_2$, $\overline{CH_2CHO}CH_2$, $FSO_2CF(CF_3)CF_2OCH_2$. Infrared, mass and nmr spectra are presented in order to support the assigned structures.

INTRODUCTION

Fluorocarbon sulfonyl fluorides (RSO_2F) continue to be subjects of considerable interest because of their utilization as ion exchange resins, surface active agents and strong sulfonic acids [1-5]. Previously, we have reported on a method involving the use of metal fluorides (KF, CsF, AgF), $\overline{CF_2CF_2OSO_2}$ and RX (X=Br, I) in preparing fluorocarbon ether-containing sulfonyl fluorides [6-7]. In this paper we wish to report our success in

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the reaction of haloalkanes with $CF_3\overline{CFCF_2OS}O_2$ in the presence of silver fluoride. The new fluorocarbon derivatives not only contain the sulfonyl fluoride grouping but other functional groups such as $CH_2{=}CHCH_2$, $CF_2{=}CFCH_2CH_2$, $(CF_3)_2CFCH_2CH_2$, $CH_2{=}CBrCH_2$, CH_3, $SF_5CH_2CH_2$, $\overline{CH_2CHO}CH_2$ and $FSO_2CF(CF_3)CF_2OCH_2$. Our attempts to use KF or CsF in place of AgF with $CF_3\overline{CFCF_2OS}O_2$ were unsuccessful.

RESULTS AND DISCUSSION

The reactions of $CF_3\overline{CFCF_2OS}O_2$ with haloalkanes were carried out according to the following equations:

$$CF_3\overline{CFCF_2OS}O_2 \xrightarrow[\text{Diglyme}]{\text{AgF}} FC(O)CF(CF_3)SO_2F \qquad (1)$$

$$FC(O)CF(CF_3)SO_2F + AgF \longrightarrow AgOCF_2CF(CF_3)SO_2F \qquad (2)$$

$$AgOCF_2CF(CF_3)SO_2F + RX \longrightarrow ROCF_2CF(CF_3)SO_2F + AgX \qquad (3)$$

R is $CH_2{=}CHCH_2$, $CF_2{=}CFCH_2CH_2$, $(CF_3)_2CFCH_2CH_2$, CH_3, $CH_2{=}CBrCH_2$, $SF_5CH_2CH_2$, $\overline{CH_2CHO}CH_2$, $FSO_2CF(CF_3)CF_2OCH_2$.

X=I, Br.

In general, the reaction occurred in two stages: in the first stage, the $CF_3\overline{CFCF_2OS}O_2$ sultone undergoes rearrangement, Eq. (1), followed by formation of the silver alkoxide, Eq. (2). In the second stage, a nucleophilic substitution of RX by $^-OCF_2CF(CF_3)SO_2F$ from $AgOCF_2CF(CF_3)SO_2F$ occurred, Eq. (3). Overall, participation of the solvent may lead to the formation of the by-product $CH_3OCF_2CF(CF_3)SO_2F$ [7].

Monohaloalkanes, such as $CH_2{=}CHCH_2Br$, $CF_2{=}CFCH_2CH_2Br$, $(CF_3)_2CFCH_2CH_2I$, $SF_5CH_2CH_2Br$, $\overline{CH_2CHO}CH_2Br$, reacted with the silver salt, $FSO_2CF(CF_3)CF_2OAg$, to give the corresponding monosubstituted product; with diiodomethane, the disubstituted product was formed. However, when 2,3-dibromopropene was used, only a monosubstituted product, at the allylic position, was obtained.

Previously we reported that reactions of $\overline{CF_2CF_2OSO_2}$ with haloalkanes were carried out in the presence of KF, CsF, and AgF, respectively [6,7]. In these studies it was found that the effectiveness of the metal fluoride decreased according to the following order: AgF >> CsF > KF. In this study when KF or CsF was used in the reactions of $CF_3CFCF_2OSO_2$ with the active haloalkane, $CH_2=CHCH_2Br$, the desired product was not formed. Instead, a large amount of gas was formed. Infrared spectral characterization of the gas showed absorption bands characteristic of SO_2F_2, COF_2, $CF_3CF_2C(O)F$, and $CF_3CHFC(O)F$.

This result clearly demonstrates that the decomposition of $CF_3CFCF_2OSO_2$, in the presence of KF or CsF, is the predominant mode of reaction. It is believed that AgF is effective because alkoxy product formation occurs at temperatures below 40°C. In our studies of $CF_2CF_2OSO_2$ with KF or CsF, higher temperatures (~90-95°) were needed for alkoxy product formation [6,7]. Unfortunately, $CF_3CFCF_2OSO_2$ is not stable at these higher temperatures when KF or CsF is present.

The infrared spectra of all new sulfonyl fluoride compounds have several common features. The characteristic SO_2 asym, SO_2 sym and S-F stretching frequencies are found in 1462-1465, 1242-1254, 784-817 cm^{-1} regions respectively. The C-H absorption bands are located in the 2860-3100 cm^{-1} region. The olefinic vibrational bands for $CH_2=CHCH_2OCF_2CF(CF_3)SO_2F$ and $CH_2=CBrCH_2OCF_2CF(CF_3)SO_2F$ are located at 1652 and 1649 cm^{-1}, respectively. These assignments agree with the results obtained previously [6-7].

In the $(CI)^+$ or $(EI)^+$ mass spectra, no molecular ions were obtained except for $CF_2=CFCH_2CH_2OCF_2CF(CF_3)SO_2F$, $CH_2=CBrCH_2OCF_2CF(CF_3)SO_2F$ and $CH_2=CHCH_2OCF_2CF(CF_3)SO_2F$. For all compounds a cracking pattern was found that was supportive of the assigned structure.

The structure of all new products were determined from their respective ^1H and ^{19}F nmr spectra; with most compounds, first order couplings were found. The ^1H nmr chemical shift and coupling constants are listed in Table I. The ^{19}F nmr chemical shifts and coupling constants are reported in Table II. It is found that consistent chemical shift values for similar groupings are maintained for all compounds. For $O\underline{CF}_2$, $\underline{CF}$, $SO_2\underline{F}$, and CF_3, the chemical shift values range from -77.1 to -80.5, -166.0 to -169.0, 52.3 to 54.2 and -72.3 to -74.8 ppm, respectively; in a like manner the following coupling constants: J_{a-c}, J_{b-c}, J_{a-b}, J_{a-d}, J_{b-d} and J_{c-d} range from 8.8 to 11.2 Hz, 6.3 to 6.8 Hz, 8.9 to 11.0 Hz, 10.2 to 12.4 Hz, 3.0 to 3.7 Hz and 11.2 to 13.5 Hz, respectively.

TABLE I

^1H NMR of $ROCF_2CF(CF_3)SO_2F$

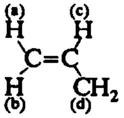
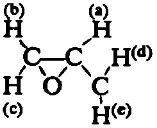
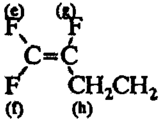
R	Chemical Shift (ppm)	Coupling Constants (Hz)
	H_a = 5.27 (d) H_b = 5.40 (d) H_c = 5.88 (t-d-d) CH_2 = 4.61 (d)	J_{a-b} = 1.1 J_{a-c} = 10.0 J_{b-c} = 16.7 J_{c-d} = 5.4
$\overset{(a)}{C}F_2=\overset{(b)}{C}F\overset{(c)}{C}H_2\underline{\overset{(d)}{C}H_2}$	$CFCH_2$ = 2.78 (d-m) $\underline{CH_2}$ = 4.30 (t)	J_{b-c} = 20.3 J_{c-d} = 6.3
$(\overset{(a)}{C}F_3)_2\overset{(b)}{C}F\overset{(c)}{C}H_2\underline{\overset{(d)}{C}H_2}$	$CFCH_2$ = 3.01 (d-t) $\underline{CH_2}$ = 4.90 (t)	J_{b-c} = 19.8 J_{c-d} = 7.7
$CH_2=CBr\underline{CH_2}$	CH_2 = 6.63 (s) 6.35 (s) $\underline{CH_2}$ = 5.25 (s)	
CH_3	CH_3 = 4.30 (s)	
$SF_5CH_2\underline{CH_2}$	CH_2 = 4.40 (m) $\underline{CH_2}$ = 5.00 (br)	
	H_a = 3.51 (m) H_b = 3.11 (d-d) H_c = 2.93 (d-d) H_d = 4.80 (d-d-d) H_e = 4.32 (d-d-d)	J_{a-b} = 4.3 J_{a-c} = 2.7 J_{a-d} = 2.7 J_{b-c} = 5.4 J_{d-e} = 12.1
$FSO_2CF(CF_3)CF_2OCH_2$	CH_2 = 6.37 (s)	

TABLE II

^{19}F NMR Data of $RO\overset{(a)}{C}F_2\overset{(b)}{C}F(\overset{(c)}{C}F_3)SO_2\overset{(d)}{F}$

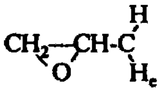
Chemical Shift (ppm) and Coupling Constants (Hz)

R	OCF$_2$	CF$_3$	CF	SO$_2$F
$CH_2=CHCH_2$	-78.2 (d-q-d)	-73.8 (m)	-167.2 (t-q-d)	52.3 (t-q-d)
	$J_{a\text{-}c}$ = 10.5	$J_{b\text{-}c}$ = 6.4	$J_{a\text{-}b}$ = 9.8	$J_{a\text{-}d}$ =11.7
	$J_{b\text{-}d}$ = 3.4	$J_{c\text{-}d}$ = 12.2		
	-80.5 (d-q-d)	-74.8 (m)	-169.0 (t-q-d)	53.0 (t-q-d)
	$J_{a\text{-}c}$ = 10.3	$J_{b\text{-}c}$ = 6.8	$J_{a\text{-}b}$ = 10.7	$J_{a\text{-}d}$ =10.2
	$J_{b\text{-}d}$ = 3.4	$J_{c\text{-}d}$ = 11.9		
	F_e = -107.3 (d-d)	F_f = -127.5 (d-d)	F_g = 183.1 (d-d-t)	
	$J_{e\text{-}g}$ = 33.9	$J_{f\text{-}g}$ = 114.3	$J_{e\text{-}f}$ = 84.7	$J_{g\text{-}h}$ =21.2

(continued)

TABLE II (cont.)

R	OCF_2	CF_3	CF	SO_2F
$(\overset{(e)}{CF_3})_2\overset{(f)}{C}FCH_2CH_2$	-79.3 (d-q-d)	-73.8 (m)	-168.7 (t-q-d)	52.5 (t-q-d)
	$J_{a\text{-}c}$ = 10.6	$J_{b\text{-}c}$ = 6.6	$J_{a\text{-}b}$ = 10.1	$J_{a\text{-}d}$ = 11.0
	$J_{b\text{-}d}$ = 3.4	$J_{c\text{-}d}$ = 13.2		
	$(CF_3)_2$ = -79.3(d)	CF_f = -189.4(m)	$J_{e\text{-}f}$ = 6.7	
CH_2=CBrCH_2	-78.3 (d-q-d)	-73.4 (m)	-167.4 (t-q-d)	54.0 (t-q-d)
	$J_{a\text{-}c}$ = 8.8	$J_{b\text{-}c}$ = 6.3	$J_{a\text{-}b}$ = 8.9	$J_{a\text{-}d}$ = 10.2
	$J_{b\text{-}d}$ = 3.4	$J_{c\text{-}d}$ = 11.9		

CH_3	-80.3 (d-q-d)	-72.6 (m)	-166.6 (t-q-d)	54.0 (t-q-d)
	$J_{a\text{-}c}$ = 11.2	$J_{b\text{-}c}$ = 6.4	$J_{a\text{-}b}$ = 11.0	$J_{a\text{-}d}$ = 11.0
	$J_{b\text{-}d}$ = 3.7	$J_{c\text{-}d}$ = 11.2		
$SF_5CH_2CH_2$	-80.2 (d-q-d)	-74.0 (m)	-168.5 (t-q-d)	53.3 (t-q-d)
	$J_{a\text{-}c}$ = 10.3	$J_{b\text{-}c}$ = 6.4	$J_{a\text{-}b}$ = 10.5	$J_{a\text{-}d}$ = 10.2
	$J_{b\text{-}d}$ = 3.4	$J_{c\text{-}d}$ = 11.5	SF_4 = 65.0(m)	SF = 80.0(m)
	-77.1 (d-q-d-d)	-72.3 (m)	-166.0 (t-q-d)	54.2 (t-q-d)
	$J_{a\text{-}c}$ = 10.3	$J_{b\text{-}c}$ = 6.8	$J_{a\text{-}b}$ = 10.5	$J_{a\text{-}d}$ = 12.4
	$J_{b\text{-}d}$ = 3.0	$J_{c\text{-}d}$ = 13.5	$J_{a\text{-}e}$ = 5.9	
$FSO_2CF(CF_3)CF_2OCH_2$	-78.0 (br)	-72.1 (br)	-167.2 (br)	55.5 (br)

EXPERIMENTAL

The sultone $CF_3\overline{CFCF_2OS}O_2$ was prepared according to the literature method [8]. Silver fluoride was dried under vacuum before use. All other chemicals were obtained from commercial sources and used as received.

General Procedure. Gases were manipulated in a conventional Pyrex vacuum apparatus equipped with a Heise-Bourdon tube gauge and televac thermocouple gauge. Infrared spectra were obtained by using a Pyrex-glass cell with KBr windows on a Nicolet 20DX spectrometer. The nmr spectra were recorded with a Varian model EM-390 spectrometer operating at 90.0 MHz for proton and 84.67 MHz for the fluorine resonance. TMS and F-11 were used as external standards. In some cases, compounds were purified via gas chromatography using an Aerograph Autoprep (model A-700) gas chromatograph. The mass spectra were taken on a VG-7070 HS mass spectrometer with an ionization potential of 70 eV. Perfluorokerosene was used as an internal standard.

Elemental analyses were determined by Beller Microanalytical Laboratory in Göttingen, Federal Republic of Germany.

Preparation of $CH_2=CHCH_2OCF_2CF(CF_3)SO_2F$ and $CH_3OCF_2CF(CF_3)SO_2F$

Method A

Into a 125 mL Pyrex-glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar, were added 2.70 g (21.2 mmol) of dried silver fluoride and 5.0 mL of diglyme. The sultone, $CF_3\overline{CFCF_2OS}O_2$, (6.00 g, 26.1 mmol) was transferred under vacuum into the reaction vessel cooled to -196°C. The reaction mixture was warmed to room temperature and stirred at 35~37°C for 3 h. The reaction vessel was again cooled to -196°C and 2.5 g (20.7 mmol) of allyl bromide was added. The reaction mixture was maintained at 0°C for 3 h, at room temperature for 24 h, at 30~35°C for 48 h.

The liquid and gaseous products were vacuum transferred into another 25 mL vessel and cooled to -196°C. The volatile products were washed with water 3 times (total 60 mL) in order to remove the solvent (diglyme); 4.00 g of an oily material was recovered, dried over P_4O_{10}, and distilled to give 2.30 g product, b.p. 105-107°C, 38.3% yield based on allyl bromide, and 0.70 g of a minor product, $CH_3OCF_2CF(CF_3)SO_2F$, b.p. 85~88°C, 12.8% yield.

The infrared spectrum of $CH_2{=}CHCH_2OCF_2CF(CF_3)SO_2F$ had the following bands (cm^{-1}): 3100(vw), 2966(w), 2910(vw), 2860(vw), 1652(w), 1462(vs), 1377(w), 1307(s), 1244(vs), 1159(m), 1103(m), 1019(m), 984(s), 963(m), 885(w), 815(s), 738(m), 618(s).

In the $(CI)^+$ mass spectrum, $(M+1)^+$, $(M)^+$ and $(M-1)^+$ peak were found at 291 [3.25], 290 [47.80] and 289 [4.29]. Other main fragments were observed: 211 [$(C_4HF_6OS)^+$, 4.82], 187 [$(C_6H_4F_5O)^+$, 8.45], 169 [$(C_4F_3SO_2)^+$, 6.21], 150 [$(C_3F_6)^+$, 8.89], 140 [$(C_3H_2O_2F_2S)^+$, 8.37], 137 [$(C_5H_4F_3O)^+$, 6.21], 131 [$(C_3F_5)^+$, 9.41], 119 [$(C_3FO_2S)^+$, 3.95], 100 [$(C_2F_4)^+$, 11.64], 95 [$(CFSO_2)^+$, 4.71], 83 [$(SO_2F)^+$, 4.14], 81 [$(C_2F_3)^+$, 11.76], 79 [$(CFSO)^+$, 10.72], 69 [$(CF_3)^+$, 39.45], 67 [$(SFO)^+$, 49.51], 65 [$(C_4OH)^+$, 24.48], 61 [$(C_2H_2FO)^+$, 12.14], 59 [$(C_2FO)^+$, 9.56], 57 [$(CH_2{=}CHCH_2O)^+$, 42.05], 56 [$(CH_2{=}CHCHO)^+$, 100], 55 [$(C_3H_3O)^+$, 29.14], 51 [$(SF)^+$, 5.58].

Anal. Calcd. for $C_6H_5F_7O_3S$: C, 24.83; H, 1.72; F, 45.86; S, 11.04. Found: C, 24.88; H, 1.79; F, 46.1; S, 11.04%.

The infrared spectrum of $CH_3OCF_2CF(CF_3)SO_2F$ had the following bands (cm^{-1}): 2973(w), 1462(vs), 1306(m), 1278(m), 1247(vs), 1169(m), 1100(m), 1029(m), 1000(m), 966(m), 929(w), 901(vw), 811(vs), 770(m), 736(m), 617(vs), 546(w).

In the $(CI)^+$ mass spectrum, no molecular ion was observed. Other main fragment ions were formed: 247 [$(M-HO)^+$, 5.48], 246 [$(M-H_2O)^+$, 5.09], 245 [$(M-F)^+$, 100], 199 [$(C_5H_2F_3O_3S)^+$, 0.20], 185 [$(C_4F_3O_3S)^+$, 6.39], 181 [$(M-SO_2F)^+$, 16.07], 163 [$(C_3H_3F_4OS)^+$, 5.73], 162 [$(CH_3OCF_2CF{=}CF_2)^+$, 3.04], 159 [$(C_3H_2O_2F_3S)^+$, 0.65], 150 [$(C_3F_6)^+$, 4.12], 143 [$(C_3F_3OSH_2)^+$, 3.99], 131 [$(C_3F_5)^+$, 12.29], 129 [$(C_3HF_4O)^+$, 1.36], 119 [$(C_3FO_2S)^+$, 5.11], 97 [$(C_2F_3O)^+$, 3.11], 95 [$(CFSO_2)^+$, 3.77], 93 [$(C_3H_3F_2O)^+$, 1.09], 83 [$(SO_2F)^+$, 1.59], 81 [$(C_2F_3)^+$, 11.35], 79 [$(CSFO)^+$, 3.65], 69 [$(CF_3)^+$, 5.25], 67 [$(SOF)^+$, 4.58], 65 [$(C_4OH)^+$, 9.09], 55 [$(C_3F)^+$, 8.89], 51 [$(SF)^+$, 2.28].

Anal. Calcd. for $C_4H_3F_7O_3S$: C, 18.18; H, 1.14; F, 50.4; S, 12.12. Found: C, 18.25; H, 1.16; F, 50.7; S, 12.02%.

Method B

Into the same glass vessel described above were added 4.39 g (28.8 mmol) of dried CsF, 7.0 mL of diglyme and 8.20 g (35.6 mmol) of $CF_3\overline{CFCF_2OS}O_2$. The reaction mixture was stirred at room temperature for 3 h after which 3.40 g (28.1 mmol) of $CH_2{=}CHCH_2Br$ was transferred to the reactor at -196°C. The reaction was heated at 50°C for 4 h, at 85°C for 72 h.

Gas products were collected and separated through trap-to-trap transfer: fractions, (1) 3.60 g at -196°C, (2) 0.63 g at -90°C, (3) 2.61 g at -78°C and (4) 2.0 g at room temperature were collected. Infrared spectrum of fraction (1) showed the presence of SO_2F_2 (major) and COF_2 (minor). Fractions (2) and (3) showed bands characteristic of SO_2F_2, $CF_3CF_2C(O)F$ and $CF_3CHF_2C(O)F$ while fraction (4), based on infrared characterization, contained $CH_2{=}CHCH_2Br$ and diglyme.

Method C

Into the same reaction vessel previously described were added 1.30 g (22.4 mmol) of dried KF, 5.0 mL of diglyme and 6.0 g (26.1 mmol) of $CF_3\overline{CFCF_2OS}O_2$. The reaction mixture was stirred at room temperature for 1 h, after which 2.70 g (22.3 mmol) of $CH_2{=}CHCH_2Br$ was transferred into the reactor at -196°C. The reaction mixture was stirred at room temperature for 4 h, at 85°C for 24 h, and at 95°C for 48 h. Gaseous products (3.0 g) were collected at -196°C. The liquid products in the reactor were filtered in order to remove any solids. The filtrate was washed with water; 1.5 g of starting material $CH_2{=}CHCH_2Br$ was recovered. The infrared spectrum of the gas showed absorption bands characteristic of SO_2F_2 and $CF_3CF_2C(O)F$.

Preparation of $CF_2{=}CFCH_2CH_2OCF_2CF(CF_3)SO_2F$

In a similar procedure as previously described, 3.50 g (27.6 mmol) of dried silver fluoride, 7.0 mL of diglyme, and 6.9 g (30.0 mmol) of $CF_3\overline{CFCF_2OS}O_2$ were heated at 30~35°C for 3 h; 5.5 g (29.1 mmol) of $CF_2{=}CFCH_2CH_2Br$ was added and the reaction mixture was heated at 35°C for 4 d. The crude product was condensed under vacuum into the 25 ml vessel and was washed four times with water (25 mL). The oily product was separated, dried over P_4O_{10}, and distilled to give 3.10 g product (31.4% yield), b.p.

136-137°C and 0.96 g of the minor product, $CH_3OCF_2CF(CF_3)SO_2F$, 13.2% yield.

The infrared spectrum had the following bands (cm^{-1}): 2987(vw), 2924(vw), 1806(vs), 1462(s), 1307(s), 1251(vs), 1209(m), 1152(m), 1124(m), 1103(w), 1045(m), 1022(w), 999(w), 967(m), 939(w), 810(s), 787(m), 737(m), 617(s), 548(w).

In the $(EI)^+$ mass spectrum, a molecular ion at 358 [$(M)^+$, 3.57] was found. Other main fragment ions were observed at: 233 [$(CF_2CF(CF_3)SO_2F)^+$, 2.84], 199 [$(C_5H_2F_3O_3S)^+$, 4.07], 169 [$(C_4F_3SO_2)^+$, 17.85], 150 [$(C_3F_6)^+$, 9.54], 131 [$(C_3F_5)^+$, 7.01], 119 [$(C_3FO_2S)^+$, 12.11], 109 [$(CF_2{=}CFCH_2CH_2)^+$, 38.46], 108 [$(CF_2{=}CFCH{=}CH_2)^+$, 48.20], 100 [$(C_2F_4)^+$, 10.46], 95 [$(CF_2{=}CFCH_2)^+$, 80.28], 89 [$(C_4H_3F_2)^+$, 44.89], 83 [$(SO_2F)^+$, 5.35], 81 [$(CF_2{=}CF)^+$, 2.09], 77 [$(C_5HO)^+$, 5.13], 75 [$(C_3HF_2)^+$, 7.14], 69 [$(CF_3)^+$, 67.52], 67 [$(SOF)^+$, 100], 64 [$(SO_2)^+$, 5.16], 59 [$(C_2OF)^+$, 40.30], 57 [$(C_3FH_2)^+$, 11.98], 51 [$(SF)^+$, 7.07].

Anal. Calcd. for $C_7H_4F_{10}O_3S$: C, 23.46; H, 1.12; F, 53.1; S, 8.94. Found: C, 23.57; H, 1.00; F, 53.2; S, 8.77%.

Preparation of $(CF_3)_2CFCH_2CH_2OCF_2CF(CF_3)SO_2F$

Into the same reaction vessel previously described, 3.50 g (27.6 mmol) of dried silver fluoride, 7.0 mL of diglyme and 7.2 g (31.3 mmol) of $CF_3\overline{CFCF_2OSO}_2$ were heated at 30-35°C for 3 h. The reaction mixture was cooled to -196°C and 8.10 g (25.0 mmol) of $(CF_3)_2CFCH_2CH_2I$ was added. The reaction mixture was maintained at room temperature for 24 h, and at 35°C for 72 h. At room temperature, 1.0 g of $FC(O)CF(CF_3)SO_2F$ was recovered. The product was vacuum transferred into a 25 mL vessel and were washed four times with water (25 mL). The oily product which separated was dried over P_4O_{10} and distilled to give 6.95 g product, b.p. 152-153°C, 62.3% yield.

The infrared spectrum had the following bands (cm^{-1}): 2952(vw), 2924(vw), 1463(vs), 1358(w), 1301(m), 1254(s), 1231(vs), 1166(m), 1111(m), 1069(m), 996(w), 926(w), 811(s), 737(m), 718(w), 676(w), 614(s), 544(w).

In the $(CI)^+$ mass spectrum, no molecular ion was found. Other main fragment ions were observed at 427 [$(M\text{-}F)^+$, 0.15], 407 [$(M\text{-}HF_2)^+$, 1.20], 387 [$(M\text{-}H_2F_3)^+$, 1.42], 363

[$(M\text{-}SO_2F)^+$, 0.63], 263 [$(M\text{-}CF_3CFSO_2F)^+$, 3.03], 233 [$(CF_2CF(CF_3)SO_2F)^+$, 7.35], 231 [$(C_7F_5H_4OS)^+$, 43.81], 213 [$(((CF_3)_2CFCH_2CH_2O)^+$, 2.09], 211 [$(C_4HF_6OS)^+$, 20.36], 199 [$(C_5H_2F_3O_3S)^+$, 7.18], 197 [$(((CF_3)_2CFCH_2CH_2)^+$, 35.16], 178 [$(((CF_3)_2CCH_2CH_2)^+$, 9.50], 177 [$(((CF_3)_2C{=}CHCH_2)^+$, 100], 169 [$(((CF_3)_2CF)^+$, 9.88], 164 [$(CF_2{=}CFSO_2F)^+$, 2.77], 150 [$(C_3F_6)^+$, 9.15], 145 [$(CF_2{=}CFSO_2)^+$, 5.43], 131 [$(C_3F_5)^+$, 3.71], 129 [$(C_3HF_4O)^+$, 8.51], 127 [$(CF_3CFCH_2CH)^+$, 10.66], 119 [$(C_3FO_2S)^+$, 2.48], 113 [$(C_3HF_4)^+$, 4.79], 100 [$(C_2F_4)^+$, 3.41], 97 [$(C_2F_3O)^+$, 1.43], 95 [$(CFSO_2)^+$, 4.72], 79 [$(CFSO)^+$, 5.43], 77 [$(C_5HO)^+$, 7.77], 69 [$(CF_3)^+$, 25.57], 67 [$(SOF)^+$, 24.32], 65 [$(C_4OH)^+$, 11.70], 59 [$(C_2OF)^+$, 3.28], 51 [$(SF)^+$, 7.01].

Anal. Calcd. for $C_8H_4F_{14}O_3S$: C, 21.52; H, 0.89; F, 59.6; S, 7.17. Found: C, 21.62; H, 0.92; F, 59.8; S, 7.25%.

Preparation of $CH_2{=}CBrCH_2OCF_2CF(CF_3)SO_2F$

Into the same reaction vessel previously described were added, 2.85 g (22.4 mmol) of dried silver fluoride, 5.0 mL of diglyme and 5.80 g (25.2 mmol) of $CF_3\overline{CFCF_2OS}O_2$. The reaction mixture was warmed to 30°C for 3 h; 4.30 g (21.5 mmol) of $CH_2{=}CBrCH_2Br$ was then transferred into the reactor cooled to -196°C. The reaction mixture was warmed to 35~37°C for 5 d. At room temperature, 2.3 g of $FC(O)CF(CF_3)SO_2F$ was recovered. The products were filtered in order to remove the AgBr precipitate; the filtrate was washed four times with water (25 mL); 3.90 g of an oily material was separated, dried over P_4O_{10}, distilled to give 1.95 g product, b.p. 121-122°C/165 mm, 24.7% yield and 1.65 g of a minor product, $CH_3OCF_2CF(CF_3)SO_2F$, 28.0% yield.

The infrared spectrum of product had the following bands (cm^{-1}): 2959(w), 1649(m), 1639(m), 1462(s), 1393(w), 1368(w), 1303(s), 1247(vs), 1153(m), 1106(m), 1025(m), 997(m), 963(m), 907(m), 817(vs), 733(m), 667(m), 617(s), 549(w), 505(w).

In the $(EI)^+$ mass spectrum, isotopic molecular ions were found at 370 [$(CH_2{=}C^{81}BrCH_2OCF_2CF(CF_3)SO_2F)^+$, 16.76] and 368 [$(CH_2{=}C^{79}BrCH_2OCF_2\text{-}CF(CF_3)SO_2F)^+$, 18.31]. Other main fragment ions were observed at: 289 [$(M\text{-}Br)^+$, 32.25], 288 [$(M\text{-}HBr)^+$, 21.52], 233 [$(CF_2CF(CF_3)SO_2F)^+$, 2.21], 205 [$(C_4HF_4SO_3)^+$, 4.42], 169 [$(C_4F_3SO_2)^+$, 14.49], 150 [$(C_3F_6)^+$, 4.69], 137 [$(CH_2{=}C^{81}BrCH_2O)^+$, 5.10], 135 [$(CH_2{=}C^{79}BrCH_2O)^+$, 6.25], 136 [$(CH_2{=}C^{81}BrCHO)^+$, 6.54], 134 [$(CH_2{=}C^{79}BrCHO)^+$, 6.18], 131 [$(C_3F_5)^+$, 7.75], 121 [$(CH_2{=}C^{81}BrCH_2)^+$, 32.25], 119 [$(CH_2{=}C^{79}BrCH_2)^+$, 34.16], 100 [$(C_2F_4)^+$, 10.09], 83 [$(SO_2F)^+$, 4.54], 69 [$(CF_3)^+$, 45.46], 67 [$(SOF)^+$, 100], 64 [$(SO_2)^+$, 3.03], 59 [$(C_2OF)^+$, 34.77], 56 [$(C_3H_4O)^+$, 10.09], 55 [$(C_3F)^+$, 20.95], 51 [$(SF)^+$, 2.10].

Anal. Calcd. for $C_6H_4F_7O_3SBr$: C, 19.51; H, 1.08; F, 36.1; S, 8.67; Br, 21.68. Found: C, 19.59; H, 1.07; F. 36.4; S, 8.58; Br, 21.75%.

Preparation of $SF_5CH_2CH_2OCF_2CF(CF_3)SO_2F$

Into the same reaction vessel previously described were added 5.80 g (45.7 mmol) of dried silver fluoride, 8.0 mL of diglyme and 14.0 g (60.9 mmol) of $CF_3\overline{CFCF_2OSO_2}$. The reaction mixture was heated at 35°C for 3h, and then cooled to -196°C. At -196°C, 9.2 g (39.2 mmol) of $SF_5CH_2CH_2Br$ was transferred into the reactor. The reaction mixture was kept at 25°C for 2 d, and heated to 35~37°C for 2 d. At room temperature, 2.0 g of $FC(O)CF(CF_3)SO_2F$ was recovered. The liquid product was transferred under vacuum to a 25 mL vessel cooled to -196°C. The product was washed four times with water (25 mL) and the oily material which separated was dried over P_4O_{10} and distilled to give 1.5 g of $SF_5CH_2CH_2Br$ and 2.5 g product, b.p. 135-137°C/190 mm, 15.8% yield.

The infrared spectrum had the following bands (cm^{-1}): 2988(vw), 1463(vs), 1346(w), 1335(w), 1301(s), 1251(vs), 1154(m), 1112(m), 1034(m), 1019(m), 992(m), 965(s), 853(vs), 784(m), 737(m), 710(vw), 675(w), 648(w), 614(s), 556(m).

In the $(CI)^+$ mass spectrum, no molecular ion was found. Other main fragment ions were observed at: 385 [$(M\text{-}F)^+$, 6.04], 277 [$(M\text{-}SF_5)^+$, 100], 276 [$(M\text{-}SF_5H)^+$, 4.94], 258 [$(M\text{-}SF_6)^+$, 4.01], 257 [$(M\text{-}SF_5\text{-}HF)^+$, 57.83], 233 [$(CF_2CF(CF_3)SO_2F)^+$, 1.99], 231 [$(C_4H_2F_7SO)^+$, 2.86], 213 [$(M\text{-}SF_5\text{-}SO_2)^+$, 8.66], 211 [$(C_4HF_6OS)^+$, 6.60], 199 [$(C_3H_2F_3O_3S)^+$, 3.28], 195 [$(SF_5C_4H_4O)^+$, 3.26], 185 [$(C_4F_3SO_3)^+$, 6.24], 175 [$(SF_4C_4H_3O)^+$, 5.18], 169 [$(C_4F_3SO_2)^+$, 7.18], 155 [$(SF_5CH_2CH_2)^+$, 22.71], 150 [$(C_3F_6)^+$, 4.60], 135 [$(SF_4CH{=}CH_2)^+$, 15.73], 131 [$(C_3F_5)^+$, 2.96], 129 [$(C_3HF_4O)^+$, 7.04], 127 [$(SF_5)^+$, 3.56], 119 [$(C_3FSO_2)^+$, 3.76], 111 [$(CH_2OCF{=}CF_2)^+$, 1.43], 108 [$(SF_4)^+$, 1.60], 100 [$(C_2F_4)^+$, 2.48], 97

[$(C_2F_3O)^+$, 3.58], 95 [$(CFSO_2)^+$, 3.94], 93 [$(C_3H_3F_2O)^+$, 2.38], 89 [$(SF_3)^+$, 41.05], 87 [$(C_3SF)^+$, 17.80], 83 [$(SO_2F)^+$, 3.11], 81 [$(C_2F_3)^+$, 2.82], 79 [$(CFSO)^+$, 5.96], 70 [$(SF_2)^+$, 2.93], 69 [$(CF_3)^+$, 18.17], 67 [$(SFO)^+$, 50.51], 65 [$(C_4OH)^+$, 22.92], 59 [$(C_2OF)^+$, 5.15], 57 [$(C_2SH)^+$, 10.48], 55 [$(C_3F)^+$, 15.59].

Anal. Calcd. for $C_5H_4F_{12}O_3S_2$: C, 14.85; H, 0.99; F, 56.4; S, 15.84. Found: C, 14.87; H, 1.02; F, 56.2; S, 15.74%.

Preparation of $CH_2CHOCH_2OCF_2CF(CF_3)SO_2F$

Into the same reaction vessel previously described were added 3.10 g (24.4 mmol) of dried silver fluoride, 7.0 mL of diglyme and 6.30 g (27.4 mmol) of $CF_3CFCF_2OSO_2$. The reaction mixture was heated at 30-35°C for 2.5 h and cooled to -196°C; 3.00 g (21.9 mmol) of CH_2CHOCH_2Br was then transferred into the vessel. The reaction mixture was heated at 35-37°C for 4 d. At room temperature, 2.0 g of $FC(O)CF(CF_3)SO_2F$ was recovered. The products were filtered to remove the AgBr precipitate. The filtrate was washed four times with water (25 mL), dried over P_4O_{10} and distilled to give 3.5 g product, b.p. 115-116°C/90 mm, 52.2% yield.

The infrared spectrum had the following bands (cm^{-1}): 3015(vw), 2966(vw), 1462(vs), 1360(m), 1306(s), 1242(vs), 1157(m), 1105(m), 1020(m), 993(m), 965(m), 935(w), 899(w), 855(w), 812(s), 765(w), 735(m), 614(s).

In the $(CI)^+$ mass spectrum, the molecular ion was found at 306 [$(M)^+$, 0.61]. Other main fragment ions were observed at: 290 [$(M\text{-}O)^+$, 0.61], 289 [$(M\text{-}HO)^+$, 0.84], 287 [$(M\text{-}F)^+$, 0.17], 276 [$(M\text{-}OCH_2)^+$, 26.11], 263 [$(M\text{-}OCH_2CH)^+$, 6.47], 257 [$(M\text{-}CH_2OF)^+$, 42.38], 233 [$(CF_2CF(CF_3)SO_2F)^+$, 2.94], 231 [$(C_4H_2F_7SO)^+$, 6.56], 211 [$(C_4HF_6OS)^+$, 16.75], 199 [$(C_5H_2F_3O_3S)^+$, 10.74], 185 [$(C_4F_3SO_3)^+$, 1.52], 169 [$(C_4F_3SO_2)^+$, 10.13], 150 [$(C_3F_6)^+$, 3.28], 147 [$(C_6H_5O_2F_2$ or $C_5H_4FSO_2)^+$, 4.11], 131 [$(C_3F_5)^+$, 3.13], 129 [$(C_3HF_4O)^+$, 4.97], 123 [$(CH_2CHOCH_2OCF_2)^+$, 0.65], 119 [$(C_3FO_2S)^+$, 5.34], 100 [$(C_2F_4)^+$, 3.57], 97 [$(C_2F_3O)^+$, 3.11], 93 [$(C_3H_3F_2O)^+$, 4.01], 79 [$(CHOCF_2)^+$, 2.35], 77 [$(C_3HO)^+$, 5.88], 73 [$(CH_2CHOCH_2O)^+$, 2.91], 69 [$(CF_3)^+$, 15.45], 67 [$(SOF)^+$, 37.93], 65 [$(C_4OH)^+$, 21.81], 59 [$(C_2OF)^+$, 31.24], 57 [$(C_3H_5O)^+$, 100], 51 [$(SF)^+$, 3.54].

Anal. Calcd. for $C_6H_5F_7O_4S$: C, 23.53; H, 1.63; F, 43.5; S, 10.46. Found: C, 23.72; H, 1.68; F, 43.5; S, 10.37%.

Preparation of $CH_2[OCF_2CF(CF_3)SO_2F]_2$

Into the same reaction vessel previously described were added 4.30 g (33.9 mmol) of dried silver fluoride, 7.0 mL of diglyme and 8.50 g (37.0 mmol) of $CF_3\overline{CFCF_2OSO_2}$. The reaction was maintained at room temperature for 3 h; 4.20 g (15.7 mmol) of diiodomethane was then vacuum transferred into the reactor cooled to -196°C. The reaction mixture was heated at 35~36°C for 3 d. At room temperature, 2.6 g of $FC(O)CF(CF_3)SO_2F$ was recovered. The liquid product was vacuum transferred into a 25 mL vessel cooled to -196°C; this product was then washed with water, dried over P_4O_{10}, and distilled to give 1.46 g of the minor product $CH_3OCF_2CF(CF_3)SO_2F$, 16.4% yield and 1.26 g product, b.p. 92-94°C/22 mm, 15.7% yield.

The infrared spectrum had the following bands (cm^{-1}): 3023(vw), 1465(s), 1295(m), 1243(vs), 1153(s), 1045(w), 1000(m), 969(m), 938(w), 917(vw), 816(s), 761(w), 730(m), 612(s), 543(w).

In the $(CI)^+$ mass spectrum, no molecular ion was found. Other main fragment ions were observed at: 263 [$(CH_2OCF_2CF(CF_3)SO_2F)^+$, 100], 233 [$(CF_2CF(CF_3)SO_2F)^+$, 3.66], 211 [$(C_4HF_6OS)^+$, 9.30], 199 [$(C_5H_2F_3O_3S)^+$, 54.83], 185 [$(C_4F_3O_3S)^+$, 2.99], 181 [$(C_6HF_4O_2)^+$, 7.88], 169 [$(C_4F_3SO_2)^+$, 8.94], 161 [$(CH_2OCF_2CCF_3)^+$, 6.64], 150 [$(C_3F_6)^+$, 11.84], 131 [$(C_3F_5)^+$, 9.08], 129 [$(C_3HF_4O)^+$, 5.39], 119 [$(C_3FO_2S)^+$, 5.34], 100 [$(C_2F_4)^+$, 4.58], 97 [$(C_2F_3O)^+$, 3.15], 95 [$(CFSO_2)^+$, 2.45], 79 [$(CFSO)^+$, 5.42], 69 [$(CF_3)^+$, 15.52], 67 [$(SOF)^+$, 34.33], 65 [$(C_4OH)^+$, 30.11], 59 [$(C_2OF)^+$, 6.26], 57 [$(C_2HO_2)^+$, 9.31], 55 [$(C_3F)^+$, 12.02].

Anal. Calcd. for $C_7H_2F_{14}O_6S_2$: C, 16.41; H, 0.39; F, 51.9; S, 12.50. Found: C, 16.85; H, 0.43; F, 51.7; S, 12.38%.

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