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NEW POLYFLUOROALKOXYSULFONYL FLUORIDES.PART IV AROMATIC DERIVATIVES

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SUMMARY

The reactions of $\overline{CF_2CF_2OSO_2}$ and $CF_3\overline{CFCF_2OSO_2}$ with aromatic haloalkanes (RX, X = Br) in the presence of silver fluoride were studied as a means for preparing novel aromatic polyfluoroalkoxysulfonyl fluorides. The following compounds have been prepared and characterized: $ROCF_2CF_2SO_2F$ and $ROCF_2CF(CF_3)SO_2F$, where R is $C_6H_5CH_2$, o-$(CF_3)_2C_6H_3CH_2$, $C_6F_5CH_2$. Infrared, mass and nmr spectra are presented in order to support the assigned structure. In a comparative study, the reaction of $\overline{CFHCF_2OSO_2}$ with benzyl bromide, in the presence of different metal fluorides such as silver fluoride, cesium fluoride and tris(dimethylamino)sulfonium difluorotrimethylsilicate were investigated. In all cases decomposition products such as SO_2F_2, SOF_2 and SO_2 were obtained; no desired alkoxy product was found.

Attempts to prepare the silver alkoxide salt, $AgOCF_2CFHSO_2F$ or the corresponding aromatic alkoxy derivatives were unsuccessful. Apparently the intermediate silver salt is unstable and cannot be recovered or used for nucleophilic displacement reactions.

INTRODUCTION

There is considerable interest in fluorocarbon sulfonyl fluorides ($\mathrm{RSO_2F}$) because of their utilization as ion exchange resin, surface active agents and strong sulfonic acids [1-5]. Previously, we have reported a method which involved the use of metal fluorides (KF, CsF, AgF), sultones ($\overline{\mathrm{CF_2CF_2OS}}\mathrm{O_2}$, $\mathrm{CF_3}\overline{\mathrm{CFCF_2OS}}\mathrm{O_2}$) and aliphatic haloalkane (RX X = Br, I) in preparing fluorocarbon ether containing sulfonyl fluorides [6-8]. In this paper we wish to report our success on reactions of selected aromatic haloalkanes, with $\overline{\mathrm{CF_2CF_2OS}}\mathrm{O_2}$ and $\mathrm{CF_3}\overline{\mathrm{CFCF_2OS}}\mathrm{O_2}$ sultones in the presence of silver fluoride. The new fluorocarbon derivatives not only contain the sulfonyl fluoride grouping but the aromatic grouping as well.

Extension of this preparative route to another fluorosultone, $\overline{\mathrm{CFHCF_2OS}}\mathrm{O_2}$, was also studied under a variety of conditions. In all cases no desired aromatic alkoxy product was obtained.

RESULTS AND DISCUSSION

The reactions of $\overline{\mathrm{CFYCF_2OS}}\mathrm{O_2}$ with aromatic haloalkanes were carried out according to the following equations:

$$\overline{\mathrm{CFYCF_2OS}}\mathrm{O_2} \xrightarrow[\text{Diglyme}]{\text{AgF}} \mathrm{FC(O)CFYSO_2F} \tag{1}$$

$$\mathrm{FC(O)CFYSO_2F} + \mathrm{AgF} \longrightarrow \mathrm{AgOCF_2CFYSO_2F} \tag{2}$$

$$\mathrm{AgOCF_2CFYSO_2F} + \mathrm{RX} \longrightarrow \mathrm{ROCF_2CFYSO_2F} + \mathrm{AgX} \tag{3}$$

where $R = C_6H_5CH_2$, o-$(CF_3)_2C_6H_3CH_2$, $C_6F_5CH_2$

$X = Br$, $Y = F$, CF_3

In general, the reaction occurred in two stages: in the first stage, the sultone, $\overline{CFYCF_2OS}O_2$ undergoes rearrangement (eq. 1), followed by formation of the silver alkoxide (eq. 2). In the second stage, a nucleophilic substitution of RX by $^-OCF_2CFYSO_2F$ occurred (eq. 3) [6-8].

The aromatic haloalkane, $C_6H_5CH_2Br$, o-$(CF_3)_2C_6H_3CH_2Br$ and $C_6F_5CH_2Br$, reacted with sultone, $\overline{CFYCF_2OS}O_2$ ($Y = F$, CF_3) in the presence of metal fluoride giving the corresponding ether sulfonyl fluorides in good yield while the reaction yield varies with the nature of substituted groups adjacent to CH_2Br groups: $C_6F_5 > C_6H_5 >$ o-$(CF_3)_2C_6H_3CH_2$.

Our attempts to extend this preparation route to another sultone, $\overline{CFHCF_2OS}O_2$, were unsuccessful. When benzylbromide reacted with $\overline{CFHCF_2OS}O_2$ under similar reaction conditions to those previously described, no alkoxy product, $C_6H_5CH_2OCF_2CFHSO_2F$ was formed. Instead gaseous products, SO_2F_2, SOF_2, SO_2, were collected. With cesium fluoride or tris(dimethylamino)sulfonium difluoro trimethylsilicate, no apparent improvement was observed. It was further found that even if the sultone, $\overline{CFHCF_2OS}O_2$, directly reacted with AgF (in diglyme or acetonitrile), the same gaseous products were obtained. This result suggests that the intermediate alkoxide salt of $AgOCF_2CFHSO_2F$ is more unstable than either $AgOCF_2CF_2SO_2F$ or $AgOCF_2CF(CF_3)SO_2F$.

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 1455-1461, 1241-1255, 801-813 cm^{-1} regions, respectively. The C-H absorption bands are located in the 2909-3095 cm^{-1} region. These assignments agree with the results obtained previously [6-8]. Benzene or substituted benzene ring absorption bands appeared at 1501-1660 cm^{-1}, respectively.

In the $(EI)^+$ mass spectra, parent ions for all new compounds were observed. A cracking pattern was found that was supportive of the assigned structure.

The structures of all new products were determined from their respective ^1H and ^{19}F nmr spectra [Tables I-III]; with most compounds, first order couplings were found. In the ^{19}F nmr spectra, consistent chemical shift values for similar groupings are maintained for all compounds. For $RO\overset{a}{C}F_2\overset{b}{C}F_2SO_2\overset{c}{F}$, the chemical shift values of $\underline{OCF_2}$, $\underline{CF_2}$, $\underline{SO_2F}$ range from -85.7 to -87.4, -113.7 to -114.2, and 42.5 to 42.8 ppm, respectively. The coupling constants, J_{a-c}, J_{a-b}, J_{b-c} range from 4.9 to 6.1, 3.6 to 3.9 and 3.6 to 4.6 Hz, respectively. For $RO\overset{a}{C}F_2\overset{b}{C}F(\overset{c}{C}F_3)SO_2\overset{d}{F}$, the chemical shift values of $\underline{OCF_2}$, $\underline{CF}$, $\underline{CF_3}$ and $\underline{SO_2F}$ range from -77.0 to -79.0, -166.9 to -167.8, -72.3 to -73.1, and 54.2 to 54.9 ppm, respectively. The coupling constants of J_{a-c}, J_{a-b}, J_{a-d}, J_{b-c}, J_{c-d} and J_{b-d} range from 9.8 to 10.7, 9.8 to 10.7, 11.3 to 13.0, 6.2 to 6.7, 11.3 to 11.8 and 3.4 to 3.6 Hz, respectively.

TABLE I

^{19}F NMR Data of $RO\overset{a}{C}F_2\overset{b}{C}F_2\overset{c}{S}O_2F$

Chemical Shift (ppm) and Coupling Constants (Hz)

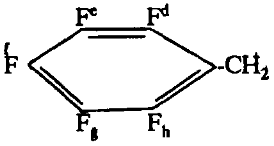
R	OCF_2	CF_2	SO_2F
$C_6H_5CH_2$	-85.7(d-t)	-113.7(d-t)	42.7(t-t)
	$J_{a\text{-}c}$ = 4.9	$J_{a\text{-}b}$ = 3.7	$J_{b\text{-}c}$ = 3.9
o-$(CF_3)_2C_6H_3CH_2$	-87.0(d-t)	-114.1(d-t)	42.5(t-t)
	$J_{a\text{-}c}$ = 5.4	$J_{a\text{-}b}$ = 3.9	$J_{b\text{-}c}$ = 4.6
	ϕ_{CF_3} = -66.0(s)		
	-87.4(m)	-114.2(d-t)	42.8(t-t) [9]
	$J_{a\text{-}c}$ = 6.1	$J_{a\text{-}b}$ = 3.6	$J_{b\text{-}c}$ = 3.6
	$\phi_{d,h}$ = -146.3(m)	ϕ_f = -155.8(t-t)	$\phi_{e,g}$ = -167.0(m)
	$J_{d\text{-}g}$ = 6.9	$J_{d\text{-}e}$ = 18.6	$J_{e\text{-}f}$ = 17.3 $J_{d\text{-}f}$ = 2.7

TABLE II

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 Constant (Hz)

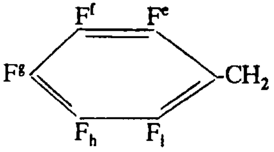
R	OCF_2	CF_3	CF	SO_2F
$C_6H_5CH_2$	-77.0(d-q-t) $J_{a\text{-}c}$ = 10.7 $J_{c\text{-}d}$ = 11.5	-72.7(m) $J_{b\text{-}c}$ = 6.7 $J_{b\text{-}d}$ = 3.4	-167.0(t-q-d) $J_{a\text{-}b}$ = 9.8	54.9(t-q-d) $J_{a\text{-}d}$ = 11.3
o-$(CF_3)C_6H_3CH_2$	-77.5(d-q-d) $J_{a\text{-}c}$ = 10.3 $J_{c\text{-}d}$ = 11.3	-72.3(m) $J_{b\text{-}c}$ = 6.2 $J_{b\text{-}d}$ = 3.6	-166.9(t-q-d) $J_{a\text{-}b}$ = 10.7 ϕ_{CF_3} = -63.8(s)	54.8(t-q-d) $J_{a\text{-}d}$ = 12.7
	-79.0(d-q-d) $J_{a\text{-}c}$ = 9.8 $J_{c\text{-}d}$ = 11.8 $\phi_{e,i}$ = -144.7(m) $J_{e\text{-}h}$ = 6.2	-73.1(m) $J_{b\text{-}c}$ = 6.7 $J_{b\text{-}d}$ = 3.4 ϕ_g = -153.0(t-t) $J_{e\text{-}f}$ = 21.5	-167.8(t-q-d) $J_{a\text{-}b}$ = 10.6 $\phi_{f,h}$ = -163.9(m) $J_{f\text{-}g}$ = 20.3	54.2(t-q-t) $J_{a\text{-}d}$ = 13.0 $J_{e\text{-}g}$ = 3.0

TABLE III

^{1}H NMR Data of $ROCF_2CFXSO_2F$

$ROCF_2CFXSO_2F$	Chemical Shift (ppm)
$C_6H_5CH_2OCF_2CF_2SO_2F$	C_6H_5 = 7.98 (s) CH_2O = 5.68 (s)
$C_6H_5CH_2OCF_2CF(CF_3)SO_2F$	C_6H_5 = 7.85 (s) CH_2O = 5.58 (s)
o-$(CF_3)_2C_6H_3CH_2OCF_2CF_2SO_2F$	C_6H_3 = 8.05 (s) CH_2O = 5.35 (s)
o-$(CF_3)_2C_6H_3CH_2OCF_2CF(CF_3)SO_2F$	C_6H_3 = 8.08 (s) CH_2O = 5.42 (s)
$C_6F_5CH_2OCF_2CF_2SO_2F$	CH_2O = 5.67 (s)
$C_6F_5CH_2OCF_2CF(CF_3)SO_2F$	CH_2O = 5.80 (s)

EXPERIMENTAL

The sultones $\overline{CF_2CF_2OS}O_2$, $CF_3\overline{CFCF_2OS}O_2$ and $\overline{CFHCF_2OS}O_2$ were prepared according to the literature method [10]. Cesium fluoride and silver fluoride were 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 or as solids between KBr disks 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 $C_6H_5CH_2OCF_2CF_2SO_2F$

Into a 125 ml Pyrex-glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar were added 4.70 g (37.0 mmol) of dried silver fluoride and 7.0 ml of diglyme. The β-sultone, $\overline{CF_2CF_2OS}O_2$ (7.70 g, 42.8 mmol), was transferred under vacuum into the reaction vessel cooled to -196°C. The reaction mixture was warmed to room temperature and stirred for 3 h at 35°-40°C. At -196°C, 5.50 g (32.2 mmol) of benzyl bromide was transferred into vessel, and the reaction was maintained at 35°-38°C for 64 h. At -196°C, 1.30 g of volatile materials (mixture of SO_2F_2 and $FC(O)CF_2SO_2F$) were collected. The rest of the reaction mixture was filtered in order to remove AgBr and the filtrate was washed three times with water (25 mL). The oily crude product was separated, dried over P_4O_{10} and distilled to give 5.30 g of product (56.9% yield), b.p. 95-96°C/14 mm.

The infrared spectrum of $C_6H_5CH_2OCF_2CF_2SO_2F$ had the following bands (cm^{-1}): 3095 (v,w), 3075 (vw), 3042 (vw), 2972 (vw), 2909 (vw), 1502 (w), 1456 (vs), 1393 (vw), 1333 (m), 1241 (s), 1204 (s), 1138 (s), 1112 (s), 1026 (w), 993 (m), 906 (w), 805 (vs), 780 (m), 748 (m), 697 (m), 655 (m), 616 (m), 607 (m).

In the $(EI)^+$ mass spectrum, $(M+1)^+$, $(M)^+$ and $(M-1)^+$ peak were found at 291 [$(M+1)^+$, 2.64], 290 [$(M)^+$, 24.27], 289 [$(M-1)^+$, 4.95]. Other main fragments were observed: 140 [$(C_3H_2O_2F_2S)^+$, 3.93], 107 [$(C_7H_7O)^+$, 3.64], 106 [$(C_7H_6O)^+$, 17.36], 105 [$(C_7H_5O)^+$, 17.67], 100 [$(C_2F_4)^+$, 1.53], 92 [$(C_3H_2F_2O)^+$, 6.21], 91 [$(C_7H_7)^+$, 100.00], 90 [$(C_7H_6)^+$, 6.57], 89 [$(C_7H_5)^+$, 3.72], 80 [$(C_2H_2F_2O)^+$, 1.53], 79 [$(CFSO)^+$, 18.03], 78 [$(C_2F_2O)^+$, 3.71], 77 [$(C_6H_5)^+$, 8.75], 67 [$(SOF)^+$, 5.22], 65 [$(C_4HO)^+$, 16.60], 63 [$(CFS)^+$, 6.43], respectively.

Anal. Calcd. for $C_9H_7F_5O_3S$: C, 37.24; H, 2.41; F, 32.8; S, 11.03. Found: C, 37.05; H, 2.46; F, 33.0; S, 10.92%.

Preparation of $C_6H_5CH_2OCF_2CF(CF_3)SO_2F$

In a similar procedure as previously described, 5.80 g (45.7 mmol) of dried silver fluoride, 10.0 mL of diglyme, and 11.70 g (50.9 mmol) of $CF_3\overline{CFCF_2OSO_2}$ were mixed at 35~39°C for 3 h, after which 6.80 g (39.8 mmol) of $C_6H_5CH_2Br$ was transferred into the reactor at -196°C. The reaction was maintained at 35~38°C for 3 d. At -196°C, 1.30 g of volatile materials (SO_2F_2 and $CF(O)CF(CF_3)SO_2F$) were collected. The remaining reaction mixture was filtered in order to remove AgBr solid. The filtrate was washed three times with water (25 mL). The oily crude product was separated and dried over P_4O_{10} and distilled to give 7.3 g of product (54.0% yield), b.p. 100-101°C/14 mm.

The infrared spectrum of $C_6H_5CH_2OCF_2CF(CF_3)SO_2F$ had the following bands: 3098 (vw), 3074 (vw), 3042 (vw), 2973 (vw), 2909 (vw), 1501 (m), 1462 (vs), 1304 (vs), 1225 (vs), 1198 (s), 1154 (s), 1102 (s), 1009 (s), 982 (s), 965 (s), 900 (w), 809 (vs), 780 (m), 748 (m), 735 (s), 696 (s), 615 (s), 588 (w), 544 (m).

In the $(EI)^+$ mass spectrum, $(M+1)^+$, $(M)^+$ and $(M-1)^+$ peaks were observed at 341 [$(M+1)^+$, 2.54], 340 [$(M)^+$, 25.00], 339 [$(M-1)^+$, 4.38]. Other main fragments were found at 131 [$(C_3F_5)^+$, 1.62], 110 [$(C_3HF_3O)^+$, 1.26], 109 [$(C_3F_3O)^+$, 2.64], 107 [$(C_7H_7O)^+$, 11.21], 106 [$(C_7H_6O)^+$, 20.79], 105 [$(C_7H_5O)^+$, 18.77], 100 [$(C_2F_4)^+$, 1.78], 92 [$(C_3H_2F_2O)^+$, 6.42], 91 [$(C_7H_7)^+$, 100.00], 90 [$(C_7H_6)^+$, 12.44], 89 [$(C_7H_5)^+$, 4.30], 79 [$(CFSO)^+$, 30.50], 77 [$(C_6H_5)^+$, 14.38], 69 [$(CF_3)^+$, 9.80], 67 [$(SOF)^+$, 7.11], 66 [$(OCF_2)^+$, 1.37], 65 [$(C_4OH)^+$, 15.21], 63 [$(CFS)^+$, 5.38].

Anal. Calcd. for $C_{10}H_7F_7O_3S$: C, 35.29; H, 2.06; F, 39.1; S, 9.41. Found: C, 34.88; H, 2.15; F, 39.3; S, 9.36%.

Preparation of o-$(CF_3)_2C_6H_3CH_2OCF_2CF_2SO_2F$

Into the same reaction vessel previously described were added 3.58 g (28.2 mmol) of dried silver fluoride, 7.0 ml of diglyme and 6.20 g (34.4 mmol) of $\overline{CF_2CF_2OS}O_2$. The reaction mixture was warmed at 35°C for 2 h, after which 6.06 g (19.7 mmol) of 3,5-bis(trifluoromethyl)benzyl bromide was transferred into the reactor at -196°C. The reaction was maintained at 35~37°C for 3 d. The products were filtered in order to remove solid AgBr. The filtrate was washed three times with water (25 mL) in order to remove diglyme. The oily crude product was dried over P_4O_{10} and distilled to give 2.77 g of product (33.0% yield), b.p. 107-110°C/9 mm.

The infrared spectrum of o-$(CF_3)_2C_6H_3CH_2OCF_2CF_2SO_2F$ had the following bands: 3100 (vw), 2980 (vw), 1560 (w), 1455 (s), 1377 (m), 1335 (m), 1286 (s), 1244 (m), 1181 (s), 1138 (s), 998 (w), 913 (w), 885 (m), 843 (w), 801 (ms), 706 (w), 683 (m), 610 (m).

In the $(EI)^+$ mass spectrum, a parent ion was observed at 426 [$(M)^+$, 8.75]. Other main fragments were found at: 407 [$(M-F)^+$, 21.24], 406 [$(M-HF)^+$, 4.41], 357 [$(M-CF_3)^+$, 1.65], 343 [$(C_{11}H_5F_{10}O)^+$, 0.77], 342 [$(C_{11}H_4F_{10}O)^+$, 2.83], 291 [$(C_{10}H_3F_8O)^+$, 3.76], 273 [$(C_{10}H_4F_7O)^+$, 3.01], 243 [$(C_9H_5F_6O)^+$, 1.43], 242 [$(C_9H_4F_6O)^+$, 6.63], 241 [$(C_9H_3F_6O)^+$, 25.44], 228 [$(C_9H_6F_6)^+$, 9.22], 227 [$(C_9H_5F_6)^+$, 93.18], 226 [$(C_9H_4F_6)^+$, 4.32], 223 [$(C_9HF_6)^+$, 8.63], 213 [$(C_8H_3F_6)^+$, 5.74], 195 [$(C_9HF_2OS)^+$, 8.31], 187 [$(C_9H_3F_4)^+$, 6.98], 177 [$(C_3HF_4O_2S)^+$, 16.30], 173 [$(C_8HF_4)^+$, 2.21], 163 [$(C_9HF_2O)^+$, 2.86], 158 [$(C_8H_5F_3)^+$, 10.15], 157 [$(C_8H_4F_3)^+$, 2.74], 156

[$(C_8H_3F_3)^+$, 2.37], 155 [$(C_8H_2F_3)^+$, 2.03], 145 [$(CF_2{=}CFSO_2)^+$, 4.77], 144 [$(C_7H_3F_3)^+$, 1.82], 139 [$(C_8H_5F_2)^+$, 1.64], 138 [$(C_8H_4F_2)^+$, 5.67], 137 [$(C_8H_3F_2)^+$, 3.10], 132 [$(C_8HFO)^+$, 1.27], 125 [$(C_7F_2H_3)^+$, 1.42], 104 [$(C_7H_4O)^+$, 7.94], 100 [$(C_2F_4)^+$, 100.00], 87 [$(C_7H_3)^+$, 2.63], 79 [$(CFSO)^+$, 1.40], 75 [$(C_6H_3)^+$, 4.50], 74 [$(C_6H_2)^+$, 2.86], 69 [$(CF_3)^+$, 8.90], 67 [$(FOS)^+$, 15.49], 63 [$(CFS)^+$, 3.65].

Anal. Calcd. for $C_{11}H_5F_{11}O_3S$: C, 30.98; H, 1.17; F, 49.06; S, 7.51. Found: C, 30.97; H, 1.14; F, 49.3; S, 7.40%.

Preparation of o-$(CF_3)_2C_6H_3CH_2OCF_2CF(CF_3)SO_2F$

Into a similar reaction vessel previously described were added 3.30 g (26.0 mmol) of dried silver fluoride, 7.0 mL of diglyme and 5.90 g (25.6 mmol) of $CF_3\overline{CFCF_2OS}O_2$. The reaction was heated at 30-35°C for 3 h, after which 5.90 g (19.2 mmol) of 3.5-Bis(trifluoromethyl)benzyl bromide was transferred in vacuo into the reaction vessel at -196°C. The reaction was maintained at 30-32°C for 48 h. At -196°C, 0.5 g of volatile material (SO_2F_2, $FC(O)CF(CF_3)SO_2F$) were collected. The remaining products were filtered in order to remove AgBr. The filtrate was washed three times with water (25 mL). The crude product was dried over P_4O_{10} and distilled to give the 4.30 g of product, 47.1% yield, b.p. 112-114°C/8 mm.

The infrared spectrum of o-$(CF_3)_2C_6H_3CH_2OCF_2CF(CF_3)SO_2F$ had the following bands: 3094 (vw), 2912 (w), 1629 (w), 1461 (s), 1403 (w), 1374 (m), 1284 (vs), 1248 (vs), 1182 (vs), 1142 (vs), 1113 (s), 1017 (m), 996 (m), 914 (m), 884 (ms), 846 (m), 813 (vs), 735 (m), 705 (m), 683 (ms), 618 (s), 544 (w).

In the $(EI)^+$ mass spectrum, a molecular ion was observed at 476 [$(M)^+$, 11.88]. Other main fragment peaks were found at 457 [$(M\text{-}F)^+$, 20.61], 456 [$(M\text{-}HF)^+$, 7.46], 243 [$(C_9H_5F_6O)^+$, 20.56], 242 [$(C_9H_4F_6O)^+$, 36.41], 241 [$(C_9H_3F_6O)^+$, 83.10], 227 [$(C_9H_5F_6)^+$, 100.00], 226 [$(C_9H_4F_6)^+$, 5.59], 223 [$(C_9HF_6)^+$, 16.64], 213 [$(C_8H_3F_6)^+$, 8.68], 195 [$(C_9HF_2OS)^+$, 18.94], 187 [$(C_9H_3F_4)^+$, 7.09], 177 [$(C_3HF_4O_2S)^+$, 11.80], 173 [$(C_8HF_4)^+$, 6.54], 163 [$(C_9HF_2O)^+$, 3.73], 158 [$(C_8H_5F_3)^+$, 6.32], 150 [$(CF_3CF{=}CF_2)^+$, 6.76], 145 [$(CF_2{=}CFSO_2)^+$, 5.08], 138 [$(C_8H_4F_2)^+$, 5.69], 104 [$(C_7H_4O)^+$, 5.19], 100 [$(C_2F_4)^+$, 5.29], 87 [$(C_7H_3)^+$, 2.23], 81 [$(C_2F_3)^+$, 1.50], 75 [$(C_6H_3)^+$, 4.41], 69 [$(CF_3)^+$, 20.69], 67 [$(FOS)^+$, 25.02], 63 [$(CFS)^+$, 4.62].

Anal. Calcd. for $C_{12}H_5F_{13}O_3S$: C, 30.25; H, 1.05; F, 51.9; S, 6.72. found: C, 30.50; H, 1.11; F, 52.1; S, 6.55%.

Preparation of $C_6F_5CH_2OCF_2CF_2SO_2F$

Into the same reaction vessel previously described were added 5.40 g (42.5 mmol) of dried silver fluoride, 8.0 mL of diglyme and 10.0 g (55.6 mmol) of $\overline{CF_2CF_2OS}O_2$. The reaction was stirred at 35°C for 3 h, after which 9.00 g (34.5 mmol) of $C_6F_5CH_2Br$ was transferred in vacuo into the reactor at -196°C. The reaction mixture was heated at 35°C for 3 d. At -196°C, 1.50 g of volatile materials (SO_2F_2 and $FC(O)CF_2SO_2F$) were collected. The reaction mixture was filtered in order to remove AgBr. The filtrate was washed three times with water (25 mL). The oily crude product was dried over P_4O_{10} and distilled to give 8.50 g of product, 64.9% yield, b.p. 104-105/20 mm.

The infrared spectrum of $C_6F_5CH_2OCF_2CF_2SO_2F$ had the following bands: 3048 (vw), 1661 (w), 1525 (s), 1513 (s), 1456 (ms), 1330 (m), 1318 (ms), 1243 (s), 1201 (s), 1137 (s), 1055 (s), 1030 (w), 999 (m), 936 (m), 802 (vs), 677 (w), 654 (w), 610 (s), 570 (w), 543 (w).

In the $(EI)^+$ mass spectrum, molecular ion and $(M+1)^+$ ion peaks were identified at 381 [$(M+1)^+$, 1.53], 380 [$(M)^+$, 12.13]. Other main fragments were found at 197 [$(C_6F_5CH_2O)^+$, 2.11], 196 [$(C_6F_5CHO)^+$, 19.95], 195 [$(C_6F_5CO)^+$, 8.62], 181 [$(C_6F_5CH_2)^+$, 100.00], 180 [$(C_6F_5CH)^+$, 1.19], 167 [$(C_6F_5)^+$, 1.49], 162 [$(C_7F_4H_2)^+$, 1.50], 161 [$(C_7F_4H)^+$, 5.87], 150 [$(C_3F_6)^+$, 3.11], 131 [$(C_3F_5)^+$, 2.15], 112 [$(C_3F_4)^+$, 2.21], 100 [$(C_2F_4)^+$, 10.69], 91 [$(C_3HF_2O)^+$, 7.08], 81 [$(C_2F_3)^+$, 4.48], 67 [$(SFO)^+$, 8.50].

Anal. Calcd. for $C_9H_2F_{10}O_3S$: C, 28.42; H, 0.53; F, 50.0; S, 8.42. Found: C, 28.49; H, 0.57; F, 49.8; S, 8.42%.

Preparation of $C_6F_5CH_2OCF_2CF(CF_3)SO_2F$

Into the same reaction vessel previously described were added 6.00 g (47.2 mmol) of dried silver fluoride, 7.0 mL of diglyme and 10.0 g (43.5 mmol) of $CF_3\overline{CFCF_2OS}O_2$. The reaction was stirred at 35°C for 2 h, after which 8.60 g (33.0 mmol) of $C_6F_5CH_2Br$ was transferred in vacuo into the reactor cooled to -196°C. The reaction mixture was heated at 35~37°C for 3 d. At -196°C, 1.00 g of volatile materials (SO_2F_2, $CF(O)CF(CF_3)SO_2F$) were collected. The reaction mixture was filtered in order to remove AgBr. The filtrate was washed three times with water (25 mL). The oily crude product was dried over P_4O_{10}; distillation gave 10.8 g of the product, 76.1% yield, b.p. 99-100°C/10 mm.

The infrared spectrum of $C_6F_5CH_2OCF_2CF(CF_3)SO_2F$ had the following bands: 3001 (vw), 1660 (m), 1526 (s), 1514 (s), 1460 (s), 1397 (w), 1318 (s), 1296 (s), 1245 (vs), 1152 (m), 1138 (s), 1118 (m), 991 (m), 981 (m), 967 (m), 937 (ms), 810 (vs), 735 (m), 669 (m), 622 (s), 610 (s), 547 (w).

In the $(EI)^+$ mass spectrum, a molecular ion was found at 430 [$(M)^+$, 12.65]. Other main fragments were observed at 197 [$(C_7H_2F_5O)^+$, 8.74], 196 [$(C_7HF_5O)^+$, 31.26], 195 [$(C_7F_5O)^+$, 13.54], 181 [$(C_7H_2F_5)^+$, 100.00], 167 [$(C_6F_5)^+$, 2.0], 162 [$(C_7H_2F_4)^+$, 1.41], 161 [$(C_7HF_4)^+$, 5.85], 150 [$(CF_3CF{=}CF_2)^+$, 3.49], 143 [$(C_7F_3H_2)^+$, 1.48], 131 [$(C_3F_5)^+$, 1.79], 119 [$(C_3FO_2S)^+$, 1.68], 112 [$(C_3F_4)^+$, 2.57], 100 [$(C_2F_4)^+$, 2.02], 91 [$(C_3HF_2O)^+$, 3.48], 81 [$(C_2F_3)^+$, 3.91], 80 [$(CH_2OCF_2)^+$, 1.37], 69 [$(CF_3)^+$, 9.59], 67 [$(SFO)^+$, 9.30].

Anal. Calcd. for $C_{10}H_2F_{12}O_3S$: C, 27.91; H, 0.47; F, 53.0; S, 7.44. Found: C, 27.97; H, 0.49; F, 52.9; S, 7.45%.

The Reaction of $\overline{CFHCF_2OSO_2}$

AgF method

In a similar reaction vessel previously described, a mixture of 4.20 g (33.1 mmol) of dried AgF, 7.0 mL of diglyme, 6.00 g (37.0 mmol) of $\overline{CFHCF_2OSO_2}$ were mixed with 5.10 g (29.8 mmol) of benzyl bromide and heated at 35~37°C for 72 h. At -196°C, 0.95 g of gaseous products were collected. An IR spectrum showed the presence of SO_2F_2 and SO_2. No products were isolated.

CsF method

In a similar manner as noted above, 5.1 g (33.6 mmol) of dried CsF, 7.0 mL of diglyme and 7.00 g (43.2 mmol) of $\overline{CFHCF_2OSO_2}$ were mixed with 5.00 g (29.2 mmol) of benzylbromide at room temperature for 24 h, and at 35°~37°C for 48 h. At -196°C, 1.5 g of gaseous products were collected. An IR spectrum showed the presence of SO_2F_2, COF_2 and SOF_2. No other products were obtained.

$[(CH_3)_2N]_3S[(CH_3)_3SiF_2]$ method

In the same procedure given above, 5.00 g (18.2 mmol) of tris(dimethylamino) sulfonium difluorotrimethylsilicate, 7.0 mL of diglyme and 3.51 g (21.7 mmol) of $\overline{CFHCF_2OSO_2}$ were mixed with 3.00 g (17.5 mmol) of benzylbromide at 0-10°C for 2 h, at room temperature for 12 h, and at 35°C for 48 h. At -196°C, 0.65 g of gaseous products were collected. An IR spectrum showed the presence of SO_2F_2, SO_2 and COF_2. No other products were obtained.

The reaction of AgF with $\overline{CFHCF_2OSO_2}$ in diglyme

In a similar procedure previously described, 3.25 g (25.6 mmol) of dried AgF, 5.0 mL of diglyme were mixed with 5.10 g (31.5 mmol) of $\overline{CFHCF_2OSO_2}$ and heated at 33-39°C for 3 d. The gas products were collected and separated via trap-to-trap distillation. In the -196°C trap, 2.0 g of a mixture of SO_2F_2, SOF_2, SO_2 and a little of COF_2 was collected. In the -60°C trap, 0.70 g of SO_2 was collected.

The reaction of AgF with $\overline{CFHCF_2OSO_2}$ in CH_3CN

In a similar procedure described above, 4.10 g (32.3 mmol) of dried AgF, 7.0 mL of CH_3CN were mixed with 5.40 g (33.3 mmol) of $\overline{CFHCF_2OSO_2}$ and heated at 35-

39°C for 3 d. The gas products were collected and separated via trap-to-trap distillation. In the -196°C trap, 1.53 g of SO_2F_2 and SO_2 were present. In the -95°C trap, SO_2 (0.70 g) was collected.

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REFERENCES

1 G.A. Olah, P.S. Iyer and P. Surya, Synthesis, (1982) 513.

2 C. Bunyagdj, H. Plotrowka and M.H. Aldridge, J. Chem. Eng. Data, 26, (1981) 344.

3 J.M. Canich, M.M. Ludvig, G.L. Gard and J.M. Shreeve, Inorg. Chem., 23, (1984) 4403.

4 C.G. Krespan, J. Fluorine Chem., 16, (1980) 966.

5 R.J. Terjeson, J. Mohtahsam and G.L. Gard, Inorg. Chem., 27, (1988) 2916.

6 L.F. Chen, J. Mohtasham and G.L. Gard, J. Fluorine Chem., 46, (1990) 21.

7 L.F. Chen, J. Mohtasham and G.L. Gard, J. Fluorine Chem., 46, (1990) 39.

8 L.F. Chen, J. Mohtasham and G.L. Gard, J. Fluorine Chem., 48 (1990) 107.

9 M.E. Peach and A.M. Ritcey, J. Fluorine Chem., 21, (1982) 401.

10 D.C. England, M.A. Dietrich, R.V. Linsey, J. Am. Chem. Soc., 82, (1960) 6181.