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NEW POLYFLUOROALKOXYSULFONYL FLUORIDES (I)

L.F. CHEN, J. MOHTASHAM AND G.L. GARD

Department of Chemistry, Portland State University, Portland, Oregon 97207-0751 (U.S.A.)

SUMMARY

The reaction of $\overline{CF_2CF_2OSO_2}$ with haloalkanes (RX, X = Cl, Br, I) in the presence of metal fluorides, MF (M = K^+, Cs^+, Ag^+) was studied as a means for preparing novel reactive polyfluoroalkoxysulfonyl fluorides. The following compounds have been prepared and characterized: $ROCF_2CF_2SO_2F$ where R = CF_2=$CFCH_2CH_2$, $SF_5CH_2CH_2$, -CH_2-, -CH_2CH_2-, $CH_3CH_2CH_2$, $BrCH_2CH_2$, CH_2=$CHCH_2$, CH_2=CHC(O). Infrared, mass and nmr spectra are presented in order to support the assigned structures.

INTRODUCTION

Fluorocarbon sulfonyl fluorides (R_fSO_2F) are undergoing considerable study. It is known that incorporating a sulfonyl fluoride group (SO_2F) into molecular systems can lead to compounds useful as ion-exchange resins, surface-active agents and strong sulfonic acids [1-3]. In this paper, we wish to report a convenient method for preparing polyfluoroalkoxysulfonyl fluorides that not

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only contain the SO_2F group but other functional groups such as $CF_2=CF-$, $SF_5CH_2CH_2$, $BrCH_2CH_2$, $CH_3CH_2CH_2$, $CH_2=CHCH_2$; we also prepared bis alkoxysulfonyl fluoride compounds.

RESULTS AND DISCUSSION

We have found that the fluorosultone $\overline{CF_2CF_2OS}O_2$, in the presence of metal fluorides, reacts with mono and dihaloalkanes according to the following equations:

$$RX + \overline{CF_2CF_2OS}O_2 + MF \xrightarrow{\text{Diglyme}} ROCF_2CF_2SO_2F + MX \qquad (1)$$

R = $CH_2=CHCH_2$, $CF_2=CFCH_2CH_2$, $SF_5CH_2CH_2$, $BrCH_2CH_2$, $CH_3CH_2CH_2$, $CH_2=CHC(O)$

M = K^+, Cs^+, Ag^+; X = Br, Cl

$$R'X_2 + 2\overline{CF_2CF_2OS}O_2 + 2MF \xrightarrow{\text{Diglyme}} R'(OCF_2CF_2SO_2F)_2 + 2MX \qquad (2)$$

R' = $-CH_2-$, $-CH_2CH_2-$

M = Ag^+

X = I, Br

These reactions are carried out in two steps; the first step involves rearrangement of the sultone followed by formation of the metal alkoxide. In the second step, a nucleophilic substitution of RX by $^-OCF_2CF_2SO_2F$ occurs. This mechanism is summarized as follows:

$$\overline{CF_2CF_2OS}O_2 \xrightarrow{MF} FC(=O)-CF_2-SO_2F \qquad (3)$$

$$FSO_2CF_2C(=O)F + M^+F^- \longrightarrow FSO_2CF_2CF_2O^-M^+ \qquad (4)$$

$$FSO_2CF_2CF_2O^- + RX \longrightarrow FSO_2CF_2CF_2OR + X^- \qquad (5)$$

Previously, the rearranged acylsulfonyl fluoride, $FSO_2CF_2C(O)F$ [4,5] and the potassium alkoxide intermediate have been isolated [5] Also, for Eq (5), a similar reaction involving methyliodide and allyl bromide/iodide have been reported [6]

It was found that the nature of metal fluoride had an important effect on the preparation of polyfluoroalkoxylsulfonyl fluorides Using allyl bromide, $\overline{CF_2CF_2OSO_2}$ and KF in diglyme, the desired product of $CH_2{=}CHCH_2O(CF_2)_2SO_2F$ was formed in 53 5% yield, in this reaction the reactants were heated at 75 °C for 24 h and 90-95 °C for 48 h If cesium fluoride is used in place of KF an almost identical yield of product was formed in only 24 h at 90 °C With AgF, the yield of the reaction increased to 70% even though the reaction temperature was lowered to 30-40 °C (12 h) These results, particularly with alkali metal fluorides, are in close agreement with the general activity order for metal fluorides

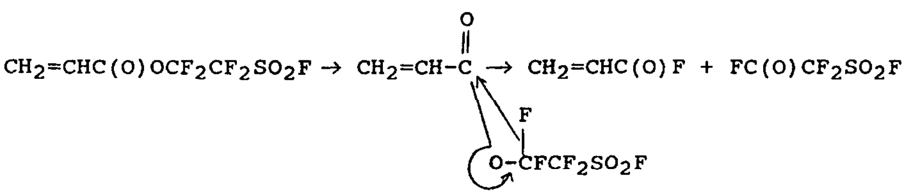
It should be noted [4] that where a mixture of $FSO_2CF_2C(O)F$ and KF, in a molar ratio 0 60 to 0 20 in diglyme, is heated slowly to 40 gas evolution (COF_2) was present and continued for 8 h @ 40-45° and 4 h @ 50 °C However, in our studies we were able to obtain desired reaction products in good yields even at high temperatures (≈ 90-95 °C) and long reaction time

In the presence of cesium fluoride, the alkoxy derivative of n-bromopropane was produced, the cesium fluoride system failed to give the desired products with 4-bromo-1,1,2-trifluorobutene-1 and $SF_5CH_2CH_2Br$ It was possible, however, with the latter two bromides to form the alkoxy derivatives with AgF in place of CsF

When diiodomethane was used with AgF, the corresponding bis alkoxysulfonyl fluoride was formed in good yield (57 6%), with 1,2-dibromoethane, a mixture of the mono and bis alkoxysulfonyl fluorides were formed The reaction of acrylyl chloride with $KOCF_2CF_2SO_2F$ produced the corresponding ester

$$CH_2{=}CHC(O)Cl + KOCF_2CF_2SO_2F \xrightarrow{\text{Diglyme}} CH_2{=}CHC(O)OCF_2CF_2SO_2F + KCl \quad (6)$$

The acrylyl ester is stable for short periods at room temperature but after 7 days was 100% decomposed The decomposition pattern of the ester was obtained from the characteristic ^{19}F nmr spectra, the results are presented in Table I The following rearrangement is offered as a pathway for decomposition



(7)

TABLE I

Decomposition Rate of $CH_2{=}CHC(O)OCF_2CF_2SO_2F$

Temperature (°C)	Time (h)	(%) $CH_2{=}CHC(O)OCF_2CF_2SO_2F$	(%) $F{-}C(O)CF_2SO_2F$	(%) $CH_2{=}CH{-}C(O){-}F$
r t	0 0	100	0	0
55≈70	0 5	33 0	33 5	33 5
60	1 0	27 0	36 5	36 5
90	0 5	0	50 0	50 0

The ınfrared spectra of all new sulfonyl fluorıde compounds have several common features The characteristıc SO_2 asym, SO_2 sym and S-F stretchıng frequencıes are found ın 1460-1455, 1243-1239, 805-781 cm^{-1} regıons, respectıvely These assıgnments agree wıth the results obtaıned wıth other fluorosulfonyl derıvatıves The strong carbon fluorıne absorptıon bands found at 1045-1244 cm^{-1} can be correlated wıth the CF_2 group The C-H absorptıon bands are located ın the 2931-3044 cm^{-1} regıon The olefınıc vıbratıonal bands for $CF_2{=}CF(CH_2)_2O(CF_2)_2SO_2F$ and $CH_2{=}CHC(O)OCF_2CF_2SO_2F$ are found at 1806 and 1631 cm^{-1}, respectıvely, the carbonyl absorptıon band ın the ester ıs located at 1799 cm^{-1}

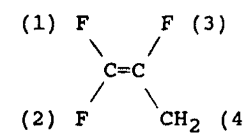
In the $(CI)^+$ mass spectra, no molecular ıons were observed except for $CF_2{=}CFCH_2CH_2OCF_2CF_2SO_2F$ For all compounds a crackıng pattern was found that was supportıve of the assıgned structure

The structures of all new products were determıned from theır respectıve ^1H and ^{19}F nmr spectra, wıth most compounds, fırst order couplıngs were found The ^{19}F nmr chemıcal shıfts and couplıng constants are reported ın Table II It ıs found that consıstent chemıcal shıft values for sımılar groupıngs are maıntaıned for all compounds For $O\underline{CF}_2$, $C\underline{F}_2$, $SO_2\underline{F}$ the chemıcal shıft values are ın -83 1 to -87 0, -111 5 to -114 0, 43 7 to 45 2 ppm range, respectıvely The ^1H nmr chemıcal shıfts and couplıng constants are found ın Table III

TABLE II

^{19}F NMR Data of $ROCF_2CF_2SO_2F$ Chemical Shift (ppm) and Coupling Constant (Hz)

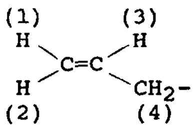
R	OCF_2	CF_2	SO_2F
$CH_2=CHCH_2$	-86 2 (d-t)	-114 0 (d-t)	+42 8 (t-t)
	$J_{OCF_2-SO_2F}$ = 5 74	$J_{OCF_2-CF_2}$ = 4 14	$J_{CF_2-SO_2F}$ = 4 68
$CF_2=CFCH_2CH_2$	-86 1 (d-t)	-113 2 (d-t)	+44 0 (t-t)
	$F_{(1)}$ = -104 0 (d-d)	$F_{(2)}$ = -124 0 (d-d)	$F_{(3)}$ = -180 0 (d-d-t)
	$J_{OCF_2-SO_2F}$ = 5 15	$J_{OCF_2-CF_2}$ = overlap	$J_{CF_2-SO_2F}$ = 4 74
	$J_{(1)(2)}$ = 86 0 $J_{(1)(3)}$ =34 2	$J_{(2)(3)}$ = 118 8	$J_{(3)(4)}$ = 21 1
$SF_5CH_2CH_2$	-86 0 (d-t)	-112 1 (d-t)	+44 8 (t-t)
	SF = +82 1 (m)	SF_4 = +67 0 (complex doublet)	
	$J_{OCF_2-SO_2F}$ = 5 58	$J_{OCF_2CF_2}$ = overlap	$J_{CF_2-SO_2F}$ = 5 04
CH_2	-84 5 (d-t)	-112 0 (d-t)	+45 2 (t-t)
	$J_{OCF_2-SO_2F}$ = overlap	$J_{OCF_2-CF_2}$=overlap	$J_{CF_2-SO_2F}$=overlap



$-CH_2CH_2-$	-84 5 (d-t)	-111 5 (d-t)	+44 5 (t-t)
	$J_{OCF_2-SO_2F}$= 4 87	$J_{OCF_2-CF_2}$= 3 78	$J_{CF_2-SO_2F}$= 4 14
$BrCH_2CH_2$	-84 0 (d-t)	-111 5 (d-t)	+44 5 (t-t)
	$J_{OCF_2-SO_2F}$= 6 43	$J_{OCF_2-CF_2}$= 4 74	$J_{CF_2-SO_2F}$= 5 22
$CH_3CH_2CH_2$	-83 9 (d-t)	-111 6 (d-t)	+44 0 (t-t)
	$J_{OCF_2-SO_2F}$= 5 40	$J_{OCF_2CF_2}$= 4 60	CF_2-SO_2F= 5 04
CH_2=CHC(O)	-87 0 (d-t)	-114 9 (d-t)	+43 7 (t-t)
	$J_{OCF_2-SO_2F}$= 5 64	$J_{OCF_2CF_2}$= 2 82	$J_{CF_2SO_2F}$= 4 52

TABLE III

^1H NMR of $ROCF_2CF_2SO_2F$

R	Chemical Shift (ppm)	Coupling Constant (Hz)
	H_1 = 5 32 (d)	J_{1-2} = 1 10
	H_2 = 5 42 (d)	J_{1-3} = 10 44
	H_3 = 5 95 (t-d-d)	J_{2-3} = 17 10
	CH_2 = 4 61 (d)	J_{3-4} = 5 58
CF_2=$CFCH_2CH_2$	$CFCH_2$ = 3 27 (d-m)	J_{CFCH_2}= 21 2
	CH_2O = 4 78 (t)	$J_{CH_2-CH_2O}$= 6 5
$SF_5CH_2CH_2$	CH_2 = 4 22 (m)	
	CH_2O = 4 75 (br)	
CH_2	CH_2 = 5 84 (s)	
$-CH_2CH_2-$	CH_2 = 4 52 (s)	
$BrCH_2CH_2$	$BrCH_2$ = 3 85 (t)	$J_{CH_2CH_2}$= 5 76
	CH_2O = 4 72 (t)	
$CH_3CH_2CH_2$	CH_3 = 1 55 (t)	$J_{CH_2CH_3}$= 7 38
	CH_2 = 2 13 (t-q)	J_{-CH_2-} = overlap
	CH_2O = 4 61 (t)	$J_{CH_2CH_2O}$ = 5 94
CH_2=CHC(∪)	CH_2 = 5 72, 5 85 (m)	
	-CH = 6 33 (m)	

EXPERIMENTAL

The sultone $\overline{CF_2CF_2OSO_2}$ was prepared according to the literature method [9] Potassium fluoride, cesium fluoride, silver fluoride were dried under vacuum before use All other chemicals were obtained from commercial sources and used as received

<u>General Procedure</u> 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

<u>Preparation of $CH_2=CHCH_2OCF_2CF_2SO_2F$</u>

(a) <u>KF Method</u>

Into a 125 mL Pyrex-glass reaction vessel equipped with a Kontes Teflon valve and a Teflon stirring bar were added 6 5 g (112 0 mmol) of dried potassium fluoride and 10 0 mL of diglyme The reaction vessel was cooled to -196°C and 15 0 g (83 3 mmol) of

$\overline{CF_2CF_2OSO_2}$ was added A clear solution was produced after 1 h at room temperature The reactor was again cooled to -196 °C and 10 0 g (83 3 mmol) allyl bromide was added The reaction was heated at 75 °C for 24 h and 90-95 °C for 48 h The mixture was decanted into 30 mL of water and the oily layer which formed was washed three times with water and dried over P_4O_{10} Distillation gave 10 7 g (44 6 mmol) $CH_2=CHCH_2OCF_2CF_2SO_2F$, 53 5% yield, b p 120-121 °C

(b) CsF Method

In a similar procedure described above, 9 0 g (59 2 mmol) of dried cesium fluoride, 10 0 mL of diglyme, 9 5 g (52 8 mmol) of $\overline{CF_2CF_2OSO_2}$ and 6 4 g (52 8 mmol) allyl bromide were added The reaction was heated at 90 °C for 24 h The products were poured into 30 mL of water, washed, dried and distilled to give 6 38 g of product, 50 4% yield

(c) AgF Method

Using a similar procedure described above, 5 0 g (39 3 mmol) of dried silver fluoride, 7 0 mL of diglyme, 7 0 g (38 8 mmol) of $\overline{CF_2CF_2OSO_2}$ and 4 7 g (39 9 mmol) of allyl bromide were added The vessel was covered by aluminum foil and was heated at 30≈40 °C for 12 h The solution was filtered in order to remove AgBr The filtrate was poured into 15 mL water and the oily layer which formed was washed twice with water and dried over P_4O_{10} The crude product (8 0 g) was analyzed via gas chromatography, 81 8% product (70 4% yield) and 11 5% starting material $CH_2=CHCH_2Br$

Preparation of $CF_2{=}CFCH_2CH_2OCF_2CF_2SO_2F$

Into the same reaction vessel previously described, 7 0 g (55 5 mmol) of silver fluoride was added and dried in vacuo Also added were 10 0 ml of diglyme and 10 6 g (58 9 mmol) of $\overline{CF_2CF_2OSO_2}$ After 3 h at room temperature, the reaction mixture was cooled to -196 °C and 10 9 g (57 8 mmol) of $CF_2{=}CFCH_2CH_2Br$ was added The reaction mixture was stirred at r t for 24 h, after which the AgBr was removed The liquid product was poured into 25 mL of water and the oily layer which formed was washed twice with water and dried over P_4O_{10} Distillation gave 7 0 g of product (41 2% yield), b p 112-114 °C

The infrared spectrum had the following bands (cm^{-1}) 2988 (w), 2931 (w), 1806 (s), 1456 (s), 1340 (m), 1309 (m), 1243 (s), 1203 (s), 1142 (s), 1121 (s), 1045 (m), 1005 (m), 949 (w), 807 (s), 781 (m), 655 (m), 609 (s), 548 (w)

In the $(CI)^+$ mass spectrum, the molecular ion was observed at 308 (M^+, 2 58) Other main fragment ions were formed at 177 [$(C_3HF_4O_2S)^+$, 4 67], 157 [$(C_4H_4F_3OS)^+$, 6 31], 127 [$(C_6H_1F_2O)^+$, 3 08], 119 [$(C_3FO_2S)^+$, 2 77], 111 [$(C_3H_2F_3O)^+$, 6 34], 109 [$(C_4H_4F_3)^+$, 100 00], 108 [$(C_4H_3F_3)^+$, 32 6], 100 [$(C_2F_4)^+$, 4 76], 97 [$(C_2F_3O)^+$, 9 73], 95 [$(CFSO_2)^+$, 26 92], 89 [$(C_4H_3F_2)^+$, 31 51], 81 [$(C_2F_3)^+$, 0 66], 79 [$(C_2HF_2O)^+$, 8 91], 75 [$(C_3H_4FO)^+$, 1 64], 67 [$(SOF)^+$, 19 95], 65 [$(C_4HO)^+$, 2 88], 59 [$(C_3H_4F)^+$, 16 42], 55 [$C_3H_3O)^+$, 4 47], 51 [$(SF)^+$, 4 74]

Anal Calcd for $C_6H_4F_8O_3S$ C, 23,38, H, 1 30, F, 49 35, S, 10 39 Found C, 23 36, H, 1 35, F, 49 0, S, 10 54%

Preparation of $SF_5CH_2CH_2OCF_2CF_2SO_2F$

In a similar procedure previously described, 3 4 g (27 0 mmol) of dried silver fluoride, 5 0 mL of diglyme, 5 5 g (30 5 mmol) of $\overline{CF_2CF_2OSO_2}$ and 6 3 g (26 8 mmol) of $SF_5CH_2CH_2Br$ were respectively added The reaction mixture was heated at 35≈38 °C for 72 h The AgBr precipitate was removed and the liquid was poured into 20 mL of water The oil layer was washed twice with water, dried over P_4O_{10}, and distilled to give 2 9 g of product (30 6% yield), b p 98-99 °C/ 80 mm

The infrared spectrum had the following bands (cm^{-1}) 3044 (vw), 2988(vw), 1460 (s), 1340 (s), 1245 (s), 1209 (s), 1133 (s), 1022 (s), 993 (m), 968 (m), 848 (vs), 782 (s), 654 (s), 608 (s), 555 (m)

In the $(CI)^+$ mass spectrum, no molecular ion was observed The other main fragments were found at 335 [$(M-F)^+$, 5 53], 227 [$(CH_2CH_2OCF_2CF_2SO_2F)^+$, 49 23], 226 [$(CH_2=CHOCF_2CF_2SO_2F)^+$, 2 82], 207 [$(C_4H_3F_4O_3S)^+$, 13 92], 163 [$(C_3H_3F_4OS)^+$, 100], 155 [$(SF_5CH_2CH_2)^+$, 10 17], 143 [$(C_4H_3F_4O)^+$, 11 41], 141 [$(SF_5CH_2)^+$, 8 68], 135 [$(SF_4CH=CH_2)^+$, 11 44], 127 [$(SF_5)^+$, 7 17], 119 [$(C_3FO_2S)^+$, 28 06], 114 [$(SF_3C_2H)^+$, 3 85], 111 [$(CF_2=CFOCH_2)^+$, 7 41], 100 [$(C_2F_4)^+$, 10 78], 99 [$(C_4H_3OS)^+$, 5 34], 97 [$(C_2F_3O)^+$, 9 14], 95 [$(CFSO_2)^+$, 8 21], 89 [$(SF_3)^+$, 50 96], 79 [$(CFSO)^+$, 11 86], 67 [$(SOF)^+$, 52 53], 65 [$(C_4HO)^+$, 11 94]

Anal Calcd for $C_4H_4F_{10}O_3S_2$ C, 13 56, H, 1 13, F, 53 67, S, 18 08 Found C, 13 73, H, 1 20, F, 53 2, S, 18 22%

Preparation of $CH_2(OCF_2CF_2SO_2F)_2$

Using the same procedure previously described, 2 5 g (19 8 mmol) of dried silver fluoride, 5 0 mL of diglyme, 4 3 g (23 8 mmol) of $\overline{CF_2CF_2OSO_2}$, and 2 6 g (9 7 mmol) of diiodomethane were added The reaction mixture was heated at 37≈38 °C for 24 h The AgI precipitate was removed and the solution was poured into 20 mL of water The oil layer isolated was diluted with 20 mL of diethyl ether, then washed twice with water and dried over $MgSO_4$, removal of the diethyl ether gave 2 9 g of crude product Distillation gave 2 3 g of product (57 6% yield), b p 92-95 °C/20-25 mm

The infrared spectrum had the following bands (cm^{-1}) 3022 (vw), 1461 (s), 1329 (s), 1244 (s), 1201 (s), 1138 (s), 1056 (m), 1008 (s), 953 (m), 812 (s), 761 (m), 654 (m), 607 (s)

In the $(CI)^+$ mass spectrum, no molecular ion was found Other fragment ions were observed at 213 [$(C_3H_2O_3F_5S)^+$, 100 0], 149 [$(C_5F_3O_2)^+$, 91 95], 133 [$(CF_2SO_2F)^+$, 4 67], 131 [$(C_5HO_2F_2)^+$, 17 63], 127 [$(C_3H_2F_3O_2)^+$, 64 31], 119 [$(C_3FO_2S)^+$, 46 29], 100 [$(C_2F_4)^+$, 32 61], 99 [$(C_4FO_2)^+$, 83 86], 97 [$(C_2F_3O)^+$, 67 86], 83 [$(SO_2F)^+$, 2 57], 79 [$(C_2HF_2O)^+$, 26 37], 69 [$(C_3HO_2)^+$, 14 62], 67 [$(SOF)^+$, 91 46], 57 [$(C_2HO_2)^+$, 8 64], 51 [$(SF)^+$, 15 60]

Anal Calcd for $C_5H_2F_{10}O_6S_2$ C, 14 56, H, 0 49, F, 46 1, S, 15 53 Found C, 14 78, H, 0 54, F, 46 4, S, 15 56%

Preparation of $(CH_2OCF_2CF_2SO_2F)_2$ and $BrCH_2CH_2OCF_2CF_2SO_2F$

Into the same reaction vessel previously described, 3 3 g (26 2 mmol) of dried silver fluoride, 10 0 mL of diglyme, 5 2 g (28 8 mmol) of $\overline{CF_2CF_2OSO_2}$, 3 2 g (17 0 mmol) of 1,2-dibromoethane were added The reaction mixture was heated at 35≈37 C for 26 h AgBr was removed and the filtrate was decanted into 20 mL water The oily layer which formed was isolated, washed three times with water and dried over P_4O_{10} Distillation gave 3 0 g (9 8 mmol) of $BrCH_2CH_2OCF_2CF_2SO_2F$, (57 5% yield), b p 74≈77 C/25 mm and 1 4 g (3 3 mmol) of $(CH_2OCF_2CF_2SO_2F)_2$ (19 4% yield), b p 106-107 °C/25 mm

The infrared spectrum of $BrCH_2CH_2OCF_2CF_2SO_2F$ had the following bands (cm^{-1}) 2973 (w), 2910 (vw), 1456 (s), 1403 (m), 1338 (s), 1298 (m), 1239 (s), 1206 (s), 1147 (s), 1121 (s), 1068 (m), 1028 (m), 1002 (s), 936 (m), 805 (vs), 654 (s), 608 (s), 581 (m), 542 (m)

In the mass spectrum of $BrCH_2CH_2OCF_2CF_2SO_2F$, no molecular ion was observed Other main fragments were found at 227 [$(CH_2CH_2OCF_2CF_2SO_2F)^+$, 0 55], 226 [$(CH_2{=}CHOCF_2CF_2SO_2F)^+$, 0 60], 225 [$(^{81}BrCH_2CH_2OCF_2CF_2)^+$, 3 57], 223 [$(^{79}BrCH_2CH_2OCF_2CF_2)^+$, 4 94], 163 [$(C_5HF_2O_2S)^+$, 1 69], 143 [$(C_4H_3F_4O)^+$, 0 81], 133 [$(CF_2SO_2F)^+$, 0 59], 121 [$(C_3H_2FO_2S)^+$, 0 62], 119 [$(C_3FO_2S)^+$, 2 07], 111 [$(C_3H_2F_3O)^+$, 1 14], 109 [$(^{81}BrCH_2CH_2)^+$, 98 69], 108 [$(^{81}BrCH{=}CH_2)^+$, 16 32], 107 [$(^{79}BrCH_2CH_2)^+$, 100 0], 105 [$(^{79}BrCH{=}CH)^+$, 15 79], 100 [$(C_2F_4)^+$, 3 46], 99 [($C_4FO_2$ or $C_4H_3OS)^+$, 3 51], 97 [$(C_2F_3O)^+$, 5,28], 95 [$(CFSO_2)^+$, 1 88], 93 [$(C_3H_3F_2O)^+$, 2 75], 83 [$(SO_2F)^+$, 1 98], 79 [$(C_2HF_2O)^+$, 4 97], 67 [$(SOF)^+$, 18 66], 65 [$(C_4HO)^+$, 11 80], 55 [$(C_3H_3O)^+$, 14 41], 51 [$(SF)^+$, 5 75]

<u>Anal Calcd</u> for $C_4H_4BrF_5O_3S$ C, 15 64, H, 1 30, F, 30 90, S, 10 42, Br, 26 06 Found C, 15 73, H, 1 35, F, 31 1, S, 10 61, Br, 25 88%

The infrared spectrum of $(CH_2OCF_2CF_2SO_2F)_2$ had the following bands (cm^{-1}) 2979 (w), 1458 (s), 1395 (m), 1337 (s), 1243 (s), 1208 (s), 1114 (s), 1123 (s), 1060 (m), 1029 (m), 987 (s), 815 (s), 794 (s), 658 (s), 611 (s)

In the $(CI)^+$ mass spectrum, no molecular ion was found Other main fragment ions were observed at 407 [$(M-F)^+$, 0 38], 227 [$(CH_2CH_2OCF_2CF_2SO_2F)^+$, 100 00], 226 [$(CH_2{=}CHOCF_2CF_2SO_2F)^+$, 4 46], 213 [$(CH_2OCF_2CF_2SO_2F)^+$, 5 80], 207 [$(C_4H_3F_4O_3S)^+$, 10 73], 183 [$(CF_2CF_2SO_2F)^+$, 8 83], 164 [$(C_5H_2F_2O_2S)^+$, 4 40], 163 [$(C_5HF_2O_2S)^+$, 90 77], 149 [$(C_5F_3O_2)^+$, 8 70], 143 [$(C_4H_3F_4O)^+$, 9 94], 141 [$(C_4H_4F_3O_2)$, 32 30], 133 [$(CF_2SO_2F)^+$, 3 87], 127 [$(C_5H_3O_2S)^+$, 6 02], 121 [$(C_3H_2FO_2S)^+$, 0 90], 119 [$(C_3FO_2S)^+$, 41 22], 111 [$(CF_2{=}CFOCH_2)^+$, 8 09], 100 [$(C_2F_4)^+$, 22 62], 99 [$(C_4FO_2)^+$, 14 55], 97 [$(C_2F_3O)^+$, 26 58], 95 [$(CFSO_2)^+$, 12 14], 93 [$(C_3H_3F_2O)^+$, 11 04], 79 [$(C_2HF_2O)^+$, 21 55], 69 [$(C_3O_2H)^+$, 12 37], 67 [$(SOF)^+$, 76 75], 65 [$(C_4OH)^+$, 39 17], 57 [$(C_2HO_2)^+$, 3 88], 56 [$(C_3H_4O)^+$, 3 72], 55 [$(C_3H_3O)^+$, 9 64], 51 [$(SF))^+$, 20 83]

<u>Anal Calcd</u> for $C_6H_4F_{10}O_6S_2$ C, 16 90, H, 0 94, F, 44 60, S, 15 02 Found C, 16 97, H, 0 99, F, 44 4, S, 15 12%

<u>Preparation of $CH_3CH_2CH_2OCF_2CF_2SO_2F$</u>

To the reaction vessel previously described, 2,6 g (19 5 mmol) of dried cesium fluoride, 5 0 mL of diglyme, 4 0 g (22 2 mmol) of $\overline{CF_2CF_2OSO_2}$, and 2 7 g (22 0 mmol) of $CH_3CH_2CH_2Br$ were added respectively The reaction mixture was heated at 100 °C for 26 h The contents were poured into 20 mL water, the oily layer was isolated, washed twice with water and dried over P_4O_{10}. Distillation gave 1.3 g $CH_3CH_2CH_2Br$ and 1.2 g (5.0 mmol) $CH_3CH_2CH_2OCF_2CF_2OSO_2F$ (25.4% yield); b.p. 112-114 °C.

The infrared spectrum had the following bands (cm^{-1}): 2973 (m), 2945 (w), 1455 (s), 1335 (s), 1244 (s), 1202 (s), 1138 (s), 1110 (s), 991 (s), 822 (m), 787 (s), 653 (m), 611 (s).

In the $(CI)^+$ mass spectrum, no molecular ion was found. Other main fragment ions were observed at: 227 [$(M-CH_3)^+$, 6.29], 163 [$(C_5HF_2O_2S)^+$, 5.93], 158 [$(C_5H_6F_4O)^+$, 29.93], 149 [$(C_4H_2FO_3S)^+$, 2.90], 133 [$(CF_2SO_2F)^+$, 0.98], 121 [$(C_3H_2FO_2S)$, 0.92], 119 [$(C_3FO_2S)^+$, 12.42], 100 [$(C_2F_4)^+$, 100.00], 99 [$(C_4H_3OS)^+$, 26.17], 97 [$(C_2F_3O)^+$, 37.22], 95 [$(CFSO_2)^+$, 2.75], 93 [$(C_3H_3F_2O)^+$, 9.73], 91 [$(C_3HF_2O)^+$, 3.62], 79 [$(C_2HF_2O)^+$, 52.15], 69 [$(C_4H_5O)^+$, 19.25], 67 [$(SOF)^+$, 85.74], 65 [$(C_4HO)^+$, 53.23], 61 [$(C_2H_2FO)^+$, 77.71], 59 [$(C_2FO)^+$, 28.11], 58 [$(C_3H_6O)^+$, 72.67], 57 [$(C_3H_5O)^+$, 35.50], 56 [$(C_3H_4O)^+$, 9.92], 55 [$(C_3H_3O)^+$, 21.04], 51 [$(SF)^+$, 20.81].

Anal. Calcd. for $C_5H_7F_5O_3S$: C, 24.79; H, 2.89; F, 39.26; S, 13.22. Found: C, 24.94; H, 3.03; F, 39.10; S, 13.34%.

Preparation of CH_2=$CHC(O)OCF_2CF_2SO_2F$

Into a similar vessel previously described were added 3.43 g (59 mmol) of dried KF, 15.0 mL of diglyme, 0.0540 g of hydroquinone and 0.049 g of copper powder. The sultone, $\overline{CF_2CF_2OS}O_2$ (13.07 g), was vacuum transferred into the reactor at -196 °C; at room temperature a clear solution of $KOCF_2CF_2SO_2F$ was formed. The reaction was cooled to -196 °C and 6.7 g (74.3 mmol) of acrylyl chloride was added. A white precipitate was formed while the reaction mixture was stirred at 40-50 °C for 4 5 h The mixture was poured into ice water, shaken and the oily layer which formed was isolated, dried over Na_2SO_4 and distilled to give 1 98 g of CH_2=CHC(O)OCF_2CF_2SO_2F in 13 2% yield, b p 65 °C/103 mm

The infrared spectrum had the following bands (cm^{-1}) 1799 (vs), 1631 (w), 1454 (vs), 1413 (m), 1321 (m), 1243 (s), 1208 (s), 1145 (s), 1089 (s), 1061 (s), 1011 (m), 991 (s), 801 (vs), 632 (w), 611 (s)

Decomposition of CH_2=CHC(O)OCF_2CF_2SO_2F

Samples (0 5 g) of CH_2=CHC(O)OCF_2CF_2SO_2F were added into three nmr tubes The first sample was heated at 55≈70 °C for 0 5 h, the second sample at 60 °C for 1 h, and the third sample at 90 °C for 1 h The ^{19}F nmr spectra of these samples showed that for sample one, 67% of CH_2=CHC(O)OCF_2CF_2SO_2F was transformed to CH_2=CHCOF and F(O)CCF_2SO_2F, for sample 2, 73% and for sample 3, 100%

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