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IODOFLUOROALKYLSULFONYL FLUORIDES - SYNTHESIS AND CONVERSION TO NEW DERIVATIVES

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

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

SUMMARY

The thermal reaction of $I(CF_2)_2O(CF_2)_2SO_2F$ $\underset{\sim}{1}$ with unsaturated alkenes and alkynes, in the presence of benzoyl peroxide, was studied as a means for preparing reactive iodofluoroalkylsulfonyl fluorides. The following compounds have been prepared and characterized: $R(CF_2)_2O(CF_2)_2SO_2F$ where R = $I(CH_2)_2$, $I(CH_2)_4$, CH_3CH_2, $-(CH_2)_3-$, $ClCH_2CHICH_2$, ICH=CH (cis and trans), $CF_3CH=CH$ (E and Z). The alcohol, $HO(CH_2)_2(CF_2)_2O(CF_2)_2SO_2F$, and olefin, $H_2C=CH(CF_2)_2O(CF_2)_2SO_2F$, have been also synthesized from the corresponding iodoalkane. Infrared, mass and NMR spectra data are presented in order to support the assigned structures.

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INTRODUCTION

Fluorocarbon sulfonyl fluorides (RSO_2F) are currently the subject of much study; e.g., a sulfonyl fluoride group (SO_2F) incorporated into molecular systems can lead to compounds useful as ion-exchange resins, surface-active agents and strong sulfonic acids [1-4]. It is of interest to study systems containing not only the SO_2F group but other reactive sites such as double bonds, alcohol grouping, and carbon-iodine bonds. The compound used in our study, **1**, octafluoro-5-iodo-3-oxapentanesulfonyl fluoride ($ICF_2CF_2OCF_2CF_2SO_2F$) has been shown by others to be potentially useful for the synthesis of sulfonyl fluorides [5,6].

RESULTS AND DISCUSSION

We have found that $I(CF_2)_2O(CF_2)_2SO_2F$, **1**, in the presence of benzoyl peroxide, adds to ethylene in high yield:

$$\mathbf{1} + H_2C{=}CH_2 \xrightarrow[100\text{-}120^\circ\ 24h]{Bz_2O_2} \underset{\mathbf{2}}{I(CH_2)_2CF_2CF_2OCF_2CF_2SO_2F} \qquad (1)$$

At higher temperatures (120≈140 °C) and with excess ethylene, mixtures of compound **2** and $I(CH_2)_4CF_2CF_2OCF_2CF_2SO_2F$, **3**, were produced:

$$\mathbf{1} + \text{xs. } H_2C{=}CH_2 \xrightarrow[\Delta]{Bz_2O_2} I(CH_2)_nCF_2CF_2OCF_2CF_2SO_2F \qquad (2)$$

$$\begin{array}{ll} n = 2 & (73\%),\ \mathbf{2} \\ n = 4 & (27\%),\ \mathbf{3} \end{array}$$

Previously, reaction (1) has been reported but without the use of benzoyl peroxide, higher temperatures were required; no product **3** however was reported [7]. In an interesting fashion, it was found that at higher reaction temperatures (200-250 °C) the product $CH_3CH_2CF_2CF_2OCF_2CF_2SO_2F$, **4**, was formed in 41% yield. The formation of **4** is attributed to the reaction of HI with **2** [8]:

$$FO_2SCF_2CF_2OCF_2CF_2CH_2CH_2I + HI \longrightarrow FO_2SCF_2CF_2OCF_2CF_2CH_2CH_3 + I_2 \qquad (3)$$

4

The hydrogen iodide is produced from the dehydroiodination of **2**.

With allyl chloride, and benzoyl peroxide, no iodoadduct was found at 140°≈160 °C. However, at 190 °C, the following mixture of compounds **5** and **6** were obtained:

$$\mathbf{1} + ClCH_2CH{=}CH_2 \xrightarrow{190\ ^{\circ}C} CH_2(CH_2CF_2CF_2OCF_2CF_2SO_2F)_2 \; + \qquad (4)$$

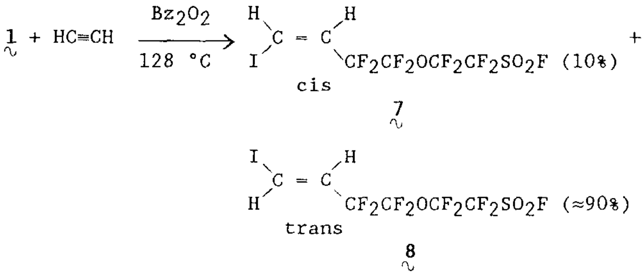
5

$$ClCH_2CHICH_2CF_2CF_2OCF_2CF_2SO_2F$$

6

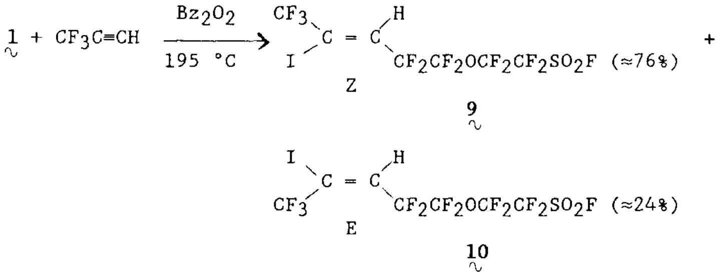
The lack of reactivity of allyl chloride is attributed to the electron withdrawing effect of the chloro group which reduces the electron density at the olefinic site and lowers the rate of addition of the electrophilic free radical, $\cdot CF_2CF_2OCF_2CF_2SO_2F$. However, at higher temperatures (>190 °C), the allyl free radical, produced from the cleavage of carbon chlorine bond, reacts and couples with fluorinated free radicals to form compound **5**.

In an analogous way, the thermal reaction of **1** with acetylene in the presence of benzoyl peroxide was effective in producing the cis and trans iodofluoroolefinic sulfonyl fluorides, $HIC{=}CHCF_2CF_2OCF_2CF_2SO_2F$, in 78% yield:



(5)

In place of acetylene, the asymmetric acetylene $CF_3C{\equiv}CH$ was used to prepare the E and Z iodo(trifluoromethyl)olefinic sulfonyl fluorides:

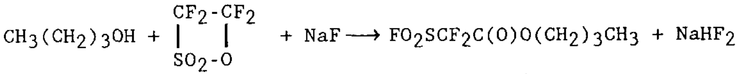


(6)

It was also of interest to investigate the preparation of $H_2C{=}CH(CF_2)_2O(CF_2)_2SO_2F$ via the dehydroiodination of **2** (n=2) with triethylamine. The literature method [7] reported that a molar ratio for **1** to triethylamine of 1.0:2.0 at 90-120 °C gave the olefinic product in 72% yield. However, we could not duplicate these results but did find that when the molar ratio was 1.0:1.3 and the reaction temperature was controlled within 80-85 °C, the olefinic product was formed in 77% yield:

$$FO_2SCF_2CF_2OCF_2CF_2CH_2CH_2I + Et_3N \xrightarrow[80\text{-}85\ ^\circ C]{24\ h} \underset{\mathbf{11}}{FO_2SCF_2CF_2OCF_2CF_2CH{=}CH_2} \qquad (7)$$

There are no reports in the literature of molecular systems containing the sulfonyl fluoride (SO_2F) and an alcohol grouping. The initial attempt involved reduction of an ester containing the sulfonyl fluoride group.



$$CH_3(CH_2)_3OH + \begin{array}{c} CF_2\text{-}CF_2 \\ | \quad\ \ | \\ SO_2\text{-}O \end{array} + NaF \longrightarrow \underset{\mathbf{12}}{FO_2SCF_2C(O)O(CH_2)_3CH_3} + NaHF_2 \qquad (8)$$

The reduction of ester **12** (prepared as in eq. 8) with $LiAlH_4$ failed to produce the desired alcohol but treating compound **2** with oleum (33%), followed by hydrolysis at 90-100 °C, gave the alcoholic sulfonyl fluoride derivative (**13**):

$$\underset{\mathbf{2}}{I(CH_2)_2CF_2CF_2OCF_2CF_2SO_2F} \xrightarrow[\text{oleum (33\%)}]{40\text{-}50\ ^\circ C} [HO_3SO(CH_2)_2(CF_2)_2O(CF_2)_2SO_2F]$$

and

$$[HO_3SOCH_2CH_2CF_2CF_2OCF_2CF_2SO_2F] \xrightarrow[90\text{-}100\ ^\circ C]{H_2O}$$

$$\underset{\mathbf{13}}{HOCH_2CH_2CF_2CF_2OCF_2CF_2SO_2F} \qquad (9)$$

If the reaction of compound 2 with oleum is carried out at elevated temperatures (70-80 °C), the alcohol product was not obtained; it is thought that a dialkylsulfate is formed but undergoes hydrolysis [9]. Also, it was found that higher temperatures are not only needed for the hydrolysis step but actually benefit the yield of the reaction.

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 1448-1463, 1237-1251 and 789-828 cm^{-1} regions, respectively. These assignments agree with the results obtained with other fluorosulfonyl derivatives [4,10,11]. The strong carbon fluorine absorption bands found in the 1050-1254 cm^{-1} can be correlated with the CF_2 group [12]. The C-H absorption bands are located in the 2882-3079 cm^{-1} region while the C=C stretching frequency is located in 1617-1652 cm^{-1} region. For $FSO_2(CF_2)_2O(CF_2)_2(CH_2)_2OH$, the OH stretching vibration is found at 3360 cm^{-1}. The carbonyl absorption band for the ester is located at 1785 cm^{-1} and agrees with that found for polyfluoro esters [10,11]. In the $(CI)^+$ mass spectra, parent or (M+1) peaks were found for all of the new compounds except compound 4. For all compounds 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; with most compounds, first order couplings were found. The ^{19}F NMR chemical shifts and coupling constants are reported in Tables I and II. It is found, with the exception of compound 12, that consistent chemical shift values for similar groupings are maintained from compounds 2

TABLE I

^{19}F NMR Data of $RCF_2CF_2OCF_2CF_2SO_2F$

	Chemical Shift (ppm)				
R	RCF_2	CF_2O	OCF_2	CF_2SO_2	SO_2F
ICH_2CH_2	-120.3(t)	-89.0(t,t)	-83.8(m)	-114.0(t,d)	45.5(t-t)
$I(CH_2CH_2)_2$	-120.7(t)	-89.8(t-t)	-84.8(m)	-114.7(t-d)	45.0(t-t)
CH_3CH_2	-122.0(t)	-89.3(t-t)	-84.1(m)	-114.0(t-d)	43.6(t-t)
$CH_2CH_2CH_2$	-119.2(t)	-88.3(t-t)	-82.8(t-d-t)	-113.0(m)	45.7(t-t)
$ClCH_2CHICH_2$	-118.6(t)	-88.8(m)	-82.8(m)	-113.0(m)	45.7(m)
ICH=CH	-117.2(d)	-88.9(t-t)	-83.8(m)	-113.7(t-d)	45.8(t-t)
$CF_3CI{=}CH$ (CF_3,-67.7)	-115.2(d)	-87.4(t-t)	-82.8(m)	-112.9(m)	46.0(t-t)
$CH_2{=}CH$	-120.2(m)	-89.8(t-t)	-84.6(m)	-114.5(m)	44.1(t-t)
$HOCH_2CH_2$	-119.7(t)	-90.4(t-t)	-84.6(m)	-114.6(t-d)	44.2(t-t)
$CH_3CH_2CH_2CH_2OC(O)CF_2SO_2F$				-106.1(d)	39.9(t)

through 13; for $RC\underline{F}_2$, $C\underline{F}_2O$, $OC\underline{F}_2$, $C\underline{F}_2SO_2$ and $SO_2\underline{F}$ the chemical shift values are in -115.2 to -122.0, -87.4 to -90.4, -81.8 to -84.6, -113.0 to -114.7 and +43.6 to 46.0 ppm range, respectively.

The ^1H NMR chemical shifts and coupling constants are given in Table III. For all compounds 2-11 and 13 it was observed from either ^1H or ^{19}F spectra that larger coupling constants were found between proton and fluorine in a $CHCF_2$ unit than in neighboring $-CF_2CF_2-$ units. The proton-proton coupling constants for the cis

TABLE II

^{19}F NMR Data of $R\overset{e'e}{CF_2}\overset{d}{CF_2}O\overset{c}{CF_2}\overset{b}{CF_2}\overset{a}{SO_2F}$

R	Coupling Constant (Hz)					
	$J_{e'-e}$	J_{e-d}	J_{d-c}	J_{c-b}	J_{b-a}	J_{c-a}
ICH_2CH_2	16.08	6.71	13.21	2.03	4.90	7.62
$I(CH_2CH_2)_2$	17.27	6.77	12.70	3.39	5.40	7.28
CH_3CH_2	16.59	4.72	11.52	3.05	5.0	6.60
$CH_2CH_2CH_2$	17.10	overlap	13.16	3.76	5.17	6.58
$ClCH_2CHICH_2$	17.10		13.88			
ICH=CH	10.49	3.39	12.70	3.39	5.08	7.62
CF_3CI=CH	11.85	4.06	13.21	3.39	5.41	6.26
CH_2=CH		3.05	13.71	3.87	5.59	7.97
$HOCH_2CH_2$	18.62	6.00	12.70	3.05	5.08	6.60
$CH_3CH_2CH_2CH_2OC(O)CF_2SO_2F$					5.60	

and trans isomers (**7** and **8**) were determined with the smaller value (7.12 Hz) assigned to the cis isomer and the larger value (15.65 Hz) to the trans isomer [13].

For the Z-E isomers **9** and **10** the coupling between H and the CF_3 group was too small to measure. However, based on the relative proton chemical shifts values one can assign the proton resonance at 6.95 ppm to the Z isomer and the 7.80 ppm resonance to the E isomer; these assignments agree closely with other CF_3XC=CH- systems [14,15] where X = Cl, Br.

TABLE III

^{1}H NMR Chemical Shift and Coupling Constants of $RCF_2CF_2OCF_2CF_2SO_2F$

R	Chemical Shift (ppm)		Coupling Constant (Hz)
ICH_2CH_2	ICH_2	3.10(t)	$J_{CH_2CH_2}$ = 7.74
	CH_2F_2	2.48(t-t)	$J_{CH_2CF_2}$ = 16.93
$ICH_2CH_2CH_2CH_2$	ICH_2	3.06(m)	
	$(CH_2)_2$	1.73(m)	
	CH_2CF_2	2.77-1.74(m)	
CH_3CH_2	CH_3	1.20(t)	$J_{CH_3CH_2}$ = 7.56
	CH_2CF_2	2.20(t-q)	$J_{CH_2CF_2}$ = 16.59
$CH_2CH_2CH_2$	$CH_2CH_2CH_2$	2.20-2.86(m)	
$ClCH_2CHICH_2$	$ClCH_2$	2.20-2.86(overlap)	
	CH_2CF_2	3.20-3.60(m)	
	CHI	4.95(pent)	$J_{CH_2CH_2CH_2}$ = 6.84
ICH=CH	ICH=	7.84(m)	$J_{cis\ CH=CH}$ = 7.12
			$J_{trans\ CH=CH}$ = 15.66
	=CH	7.15(d-t)	J_{CHCF_2} = 10.49
$CF_3CI=CH$	Z CH	6.95(t)	J_{H-F} = 11.85
	E CH	7.80(t)	J_{H-F} = 11.85
$CH_2=CH$	$CH_2=CH$	5.75-6.30	
$HOCH_2CH_2$	HO	3.95	
	OCH_2	3.61(t)	$J_{CH_2CH_2}$ = 7.20
	CH_2CF_2	2.10(t-t)	$J_{CH_2CF_2}$ = 18.62
$CH_3CH_2CH_2CH_2$	OCH_2	4.58(t)	$J_{OCH_2CH_2}$ = 5.90
	$(CH_2)_2$	1.32-2.05(m)	
	CH_3	1.07(t)	$J_{CH_3CH_2}$ = 5.90

EXPERIMENTAL

The fluorinated sultone $\overline{CF_2CF_2OS}O_2$ and $I(CF_2)_2O(CF_2)_2SO_2F$ were prepared according to literature methods [16] and [6], respectively.

Sodium fluoride (Baker) was dried under vacuum before use. Freon-11 (CCl_3F) was dried with silica gel prior to use. All other chemicals used in this work were obtained from commercial sources and used as received.

General Procedure. Gases were manipulated in a conventional Pyrex glass vacuum apparatus equipped with a Heise-Bourdon tube gauge and a 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 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, F.R.G.

Preparation of $ICH_2CH_2CF_2CF_2OCF_2CF_2SO_2F$ (**2**)

Into a 75 mL stainless steel vessel equipped with a Whitey (20-VF4) stainless steel valve and a Teflon stirring bar were added 15.0 g (35.2 mmol) of $ICF_2CF_2OCF_2CF_2SO_2F$ **1**, 0.45 g benzoyl peroxide and 2.64 g (94.3 mmol) $CH_2=CH_2$. The reaction mixture was heated at 100≈120 °C for 24 h. Distillation of the products gave 13.1 g of **2** (81.4% yield), b.p. 125≈126 °/125 Torr.

Preparation of $I(CH_2)_4CF_2CF_2OCF_2CF_2SO_2F$ (**3**)

Into the same reaction vessel described above were added 10.0g (23.5 mmol) of **1**, 10.29 g (1.2 mmol) of benzoyl peroxide and 65.7 mmol of $CH_2=CH_2$. The mixture was heated at 120-140 °C for 60 h; an additional 0.25 g (1.0 mmol) of benzoyl peroxide and 65.1 mmol of $CH_2=CH_2$ were added and the reaction mixture was heated at 120≈140 °C for an additional 14 h. A ^{19}F nmr analysis (relative integration area) showed the crude product (8.85 g) to contain 73% of 2 and 27% of **3**. Distillation of the crude product gave 6.00 g (13.2 mmol) of **2** and 1.30 g (2.70 mmol) of **3**, b.p. 130≈133 °C/45Torr.

The infrared spectrum had bands (cm^{-1}): 2959 (w), 1462 (s), 1321 (m), 1244 (m), 1195 (s), 1152 (s), 1110 (m), 1065 (w), 991 (m), 822 (s), 752 (w), 653 (w), 604 (m).

In the mass spectrum $(EI)^+$: 482 [$(M)^+$, 0.37], 453 [$(M-C_2H_5)^+$, 7.29], 355 [$(M-I)^+$, 42.57], 335 [$(M-HFI)^+$, 42.26], 155 [$(ICH=CH_2)$, 961], 141 [$(ICH_2)^+$, 9.89], 135 [$(CH_2F_3O)^+$, 34.52], 133 [$(CF_2SO_2F)^+$, 7.55], 127 [$(I)^+$, 20.22], 119 [$(C_5H_2F_3)^+$ or $(C_3FSO_2)^+$, 53.84], 115 [$(C_5HF_2O)^+$, 35.01], 105 [$(C_4H_3F_2O)^+$, 28.00], 100 [$(C_2F_4)^+$, 32.18], 95 [$(C_4H_5F_2)^+$, 23.28], 85

[$(C_4H_2FO)^+$, 21.22], 77 [$(C_3H_{32})^+$, 79.55], 69 [$(C_4H_2F)^+$, 20.88], 67 [$(SOF)^+$, 100], 65 [$(C_4HO)^+$, 20.33].

Anal. Calcd. for $C_8H_8F_9O_3IS$: C, 19.92; H, 1.66; F, 35.2; S, 6.64; I, 26.36. Found: C, 20.02; H, 1.68, F, 35.5; S, 6.78; I, 26.44%.

Preparation of $CH_3CH_2CF_2CF_2OCF_2CF_2SO_2F$ (**4**)

Into the same reaction vessel described previously, were added 15.0 g (35.2 mmol) of **1**, 0.45 g (1.8 mmol) of benzoyl peroxide and 93.2 mmol of $CH_2{=}CH_2$. The reaction mixture was heated at 150 °C for 28 h, 200≈250 °C for 12 h; a liquid (3.5 g) was decanted from the black solid in the vessel. The black solid was extracted three times with diethyl ether and washed twice with an aqueous $NaHSO_3$ solution. The ether extracts along with the 3.5 g of liquid were dried (Na_2SO_4) overnight and distilled to give 4.7 g **4** (41.0% yield), b.p. 120≈121 °C.

The infrared spectrum has absorption bands (cm^{-1}) : 2973 (w), 2910 (vw), 1462 (s), 1349 (m), 1310 (m), 1244 (m), 1195 (s), 1152 (s), 998 (m), 822 (s), 780 (m), 710 (w), 667 (w), 618 (m).

In the mass spectrum $(CI)^+$, the molecular ion was not observed, but other appropriate fragment ions were found: 309 [$(M-F)^+$, 0.38], 288 [$(M-HF_2)^+$, 17.29], 183 [$(CF_2CF_2SO_2F)^+$, 7.19], 129 [$(C_2H_5CF_2CF_2)^+$, 7.71], 119 [$(C_5H_5F_2O)^+$, 19.47], 109 [$(C_4H_4F_3)^+$, 100], 100 [$(C_2F_4)^+$, 10.6], 79 [$(C_2H_5CF_2)^+$, $(CFSO)^+$, 72.09], 69 [$(C_4H_2F)^+$, 5.92], 67 [$(SOF))^+$, 15.73], 64 [$(SO_2)^+$, 2.70], 59 [$(C_3H_4F)^+$, 25.24].

Anal. Calcd for $C_6H_5O_3F_9S$: C, 21.95; H, 1.53; F, 52.1; S, 9.76. Found: C, 22.13; H, 1.53, F, 52.1; S, 9.75%.

Preparation of $CH_2(CH_2CF_2CF_2OCF_2CF_2SO_2F)_2$ (**5**) and $ClCH_2CHICH_2CF_2CF_2OCF_2CF_2SO_2F$ (**6**)

In the same apparatus described earlier were added 5.00 g (11.7 mmol) of **1**, 0.15 g (0.60 mmol) of benzoyl peroxide and 1.00 g (13.0 mmol) of $CH_2{=}CHCH_2Cl$ and heated at 190 °C for 24 h. An oily material (4.00 g) was formed; solid materials remaining in the reaction vessel were extracted with diethyl ether and treated with a saturated $NaHSO_3$ solution. The extracts were combined with the above oily material, dried over P_4O_{10} (12 h) and distilled; the fraction (1.42 g mixture) that boiled at 140-162 °C/60 Torr contained 65% **5** and 35% **6** as determined from ^1H and ^{19}F integration areas. Compound **5** was purified via gas chromatography (SE-30, 3m, 170 °C); b.p. 160-162 °C/60 Torr.

Infrared spectrum of **5** had bands (cm^{-1}): 2973 (vw), 1462 (s), 1352 (w), 1321 (m), 1272 (m), 1244 (s), 1202 (s), 1152 (s), 1117 (s), 991 (m), 822 (s), 738 (vw), 646 (w), 611 (s).

Mass spectrum (CI^+) of **5**: 601 [$(M-HF_2)^+$, 6.53], 581 [$(M-H_2F_3)^+$, 21.84], 517 [$(M-2HF-SO_2F)^+$, 5.75], 421 [$(M-HF-OCF_2CF_2SO_2F)^+$, 37.58], 401 [$(M-2HF-OCF_2CF_2SO_2F)^+$, 52.08], 371 [$(CF_2(CH_2)_3CF_2CF_2OCF_2CF_2SO_2F)^+$, 10.70], 351 [$(CF_2{=}CH(CH_2)_2CH{=}CFCF_2OCF_2CF_2SO_2F)^+$, 12.69], 241 [$(C_7H_5F_8)^+$, 16.74], 221 [$(C_7H_4F_7)^+$, 17.66], 199 [$(OCF_2CF_2SO_2F)^+$, 3.17], 191

[$(C_7H_5F_6)^+$, 44.42], 183 [$(CF_2CF_2SO_2F)^+$, 45.98], 171 [$(C_6H_4F_5)^+$, 29.39], 169 [$(C_4F_3O_2S)^+)^+$, 8.77], 151 [$(C_6H_3F_4)^+$, 3.50], 141 [$(C_5H_5F_4)^+$, 19.30], 133 [$(CF_2SO_2F)^+$, 8.13], 127 [$(C_4F_4H_3)^+$, 37.70], 121 [$(C_5H_4F_3)^+$, 14.41], 119 [$(C_3FO_2S)^+$, $(C_5F_3H_2)^+$, 100.0], 100 [$(CF_2{=}CF_2)^+$, 31.02], 95 [$(CF_2{=}CFCH_2)^+$, 14.09], 79 [$(CFSO)^+$, 21.72], 77 [$(CH_2{=}CHCF_2)^+$, 39.29], 69 [$(C_4H_2F)^+$, 17.67], 67 [$(SOF)^+$, 78.87], 65 [$(C_5H_5)^+$, 35.89], 59 [$(C_3H_4F)^+$, 8.31], 57 [$(C_3H_2F)^+$, 8.07], 55 [$(C_3F)^+$, 14.70], 51 [$(SF)^+$, 14.93].

Anal Calcd. for $C_{11}H_6F_{18}O_6S_2$: C, 20.62; H, 0.94; F, 53.4; S, 10.00. Found: C, 20.34; H, 0.93; F, 52.9; S, 10.47%.

Preparation of $ICH{=}CH(CF_2)_2O(CF_2)_2SO_2F$ (**7**,**8**)

Into a 75 mL stainless steel vessel equipped with a Whitey (20-VF4) stainless steel valve and a Teflon stirring bar were added 15.09 g (35.2 mmol) of **1**, 0.45 g (1.9 mmol) of benzoyl peroxide and 98.7 mmol of $CH\equiv CH$. After the reaction mixture was heated at 130 °C for 18 h, an additional 0.35 g (1.5 mmol) of benzoyl peroxide and 98.7 mmol of $CH\equiv CH$ were added. The reaction mixture was then heated at 128 °C (18 h). The crude product was transferred under vacuum into a 15 mL flask and distilled to give 12.4 g (27.4 mmol) of a mixture containing cis and trans isomers, 78.0% yield, b.p. 82≈83 °C/25 Torr.

The infrared spectrum had bands (cm^{-1}): 3079 (vw), 2903 (vw), 1617 (m), 1463 (s), 1348 (m), 1310 (m), 1210 (w), 1249 (s), 1209 (s), 1149 (s), 1116 (s), 1042 (m), 995 (m), 942 (m), 828 (s), 802 (s), 735 (w), 662 (w), 632 (m), 609 (m).

In the mass spectrum $(CI)^+$, 452 (M^+, 30.17), other fragment ions were found: 433 [$(M-F)^+$, 58.12], 253 [$(ICH=CHCF_2CF_2)^+$, 12.71], 242 [$(C_6H_2F_8O)^+$, 16.07], 204 [$(C_6H_2F_6O)^+$, 22.38], 203 [$(ICH=CHCF_2)^+$, 100], 127 [$(I)^+$, 18.31], 119 [$(C_3FSO_2)^+$, 38.55], 100 [$(C_2F_4)^+$, 18.60], 79 [$(CFSO)^+$, 16.93], 78 [$(C_5H_2O)^+$, 30.76], 77 [$(C_5HO)^+$, 26.80], 76 [$(C_3H_2F_2)^+$, $(C_5O)^+$, 12.42], 75 [$(C_3HF_2)^+$, 32.31], 69 [$(C_4H_2F)^+$, 18.05], 67 [$(SOF)^+$, 52.92], 65 [$(C_4HO)^+$, 16.88].

Anal Calcd. for $C_6H_2F_9O_3IS$: C, 15.93; H, 0.44; F, 37.83; S, 7.08; I, 28.10. Found: C, 16.40; H, 0.52; F, 37.3; S, 6.93; I, 28.28%.

Preparation of $CF_3CI=CH(CF_2)_2O(CF_2)_2SO_2F$ (9, 10)

Into the same vessel previously described, were added 5.00 g (11.7 mmol) of 1, 0.15 g (0.54 mmol) of benzoyl peroxide and 43.9 mmol of 1,1,1-trifluoropropyne. The reaction mixture was heated at 195 °C for 24 h; the mixture was distilled and gave 2.4 g of the adduct (E and Z isomers). B.P. 64-67 °C/4Torr; 76% Z and 24% E isomers according to ^{19}F nmr integration area.

Infrared spectrum had bands (cm^{-1}): 3065 (w), 1652 (m), 1462 (s), 1349 (m), 1314 (m), 1251 (s), 1209 (s), 1145 (s), 1117 (s), 1047 (m), 991 (m), 920 (m), 824 (s), 798 (s), 745 (m), 681 (m), 645 (w), 611 (s).

In the mass spectrum $(CI)^+$: 520 (M^+, 42.85), 501 [$(M-F)^+$, 59.80], 321 [$(CF_3CI=CHCF_2CF_2)^+$, 15.35], 271 [$(CF_3CI=CHCF_2)^+$, 100], 221 [$(CF_3CI=CH)^+$, 2.35], 194 [$(C_5F_7H)^+$, 18.97], 183

[$(CF_2CF_2SO_2F)^+$, 24.32], 145 [$(C_2F_2SO_2F)^+$, 13.78], 144 [$(CF_3C{\equiv}CCF_2H)^+$, 28.87], 143 [$(CF_3C{\equiv}C{-}CF_2)^+$, 4.93], 133 [$(CF_2SO_2F)^+$, 4.61], 128 [$(C_3F_4O)^+$, 12.04], 127 [$(I)^+$, 19.50], 119 [$(C_3FO_2S)^+$, 82.02], 100 [$(C_2F_4)^+$, 23.77], 83 [$(SO_2F)^+$, 2.85], 79 [$(CFSO)^+$, 14.77], 75 [$(CF_2C{=}CH)^+$, 34.63], 69 [$(CF_3)^+$, 31.53], 67 [$(SOF)^+$, 67.64], 65 [$(C_4HO)^+$], 18.74].

Anal. Calcd for $C_7HF_2O_3SI$: C, 16.15; H, 0.19; F, 43.85; S, 6.15; I, 24.42. Found: C, 16.30; H, 0.22; F, 43.8; S, 6.08; I, 24.77%.

Preparation of $CH_2{=}CH(CF_2)_2O(CF_2)_2SO_2F$ (**11**)

Into four 5 mL glass tubes were added 2.00 g (4.40 mmol) of **1**, 0.54 g (5.3 mmol) of triethylamine. The tubes were sealed and heated at 80-85 °C (20 h). To each of four glass tubes 2.5 mL of water was added; the oily layer was separated, dried over Na_2SO_4, vacuum transferred and distilled; 1.10 g (3.38 mmol) of product **11** was obtained (76.7% yield). B.P. 115-116 °C.

Preparation of $FSO_2CF_2COOC_4H_9$ (**12**)

Into a 100 mL Pyrex glass reaction vessel equipped with a Kontes Teflon valve and a Teflon stirring bar were added 4.68 g (111 mmol) of dried NaF, 4.50 g (60.8 mmol) of n-butyl alcohol, 12.8 g (70.9 mmol) of $\overline{CF_2CF_2OSO_2}$. Upon warming to room temperature an exothermic reaction occurred. The reaction mixture was maintained at room temperature (7 h). The volatile products were transformed in vacuo and distilled; 10.9 g (46.6 mmol) of a colorless liquid, **12** (76.6% yield) was obtained. B.P. 88 °C/84 Torr.

The infrared spectrum had the following bands (cm^{-1}): 2966 (m), 2882 (w), 1785 (s), 1448 (s), 1314 (s), 1237 (s), 1195 (m), 1159 (s), 1019 (m), 927 (w), 836 (m), 801 (s), 639 (s), 597 (w), 574 (m), 491 (w).

In the mass spectrum $(CI)^+$: 235 [$(M+1)^+$, 0.05], 219 [$(M-CH_3)^+$, 0.35], 205 [$(M-C_2H_5)^+$, 0.63], 151 [$(C_6H_9F_2O_2)^+$, 2.55], 133 [$(CF_2SO_2F)^+$, 0.79], 119 [$(C_3FO_2S)^+$, 0.54], 100 [$(C_3O_2S)^+$, 0.78], 87 [$(C_4H_7O_2)^+$, 3.44], 86 [$(C_4H_6O_2)^+$, 4.94], 85 [$(C_4H_5O_2)^+$, 5.52], 84 [$(C_4H_4O_2)^+$, 7.82], 83 [$(SO_2F)^+$, 1.18], 79 [$(C_5H_3O)^+$, 14.50], 78 [$(C_2F_2O)^+$, $(C_5H_2O)^+$, 4.94], 67 [$(SOF)^+$, 14.71], 65 [$(C_2H_3F_2)^+$, 24.70], 58 [$(C_3H_6O)^+$, 50.40], 57 [$(C_3H_5O)^+$, or $(C_4H_9)^+$, 100], 56 [$(C_4H_8)^+$, 100], 55 [$(C_4H_7)^+$, 80.36].

Anal. Calcd for $C_6H_9F_3O_4S$: C, 30.77; H, 3.85;, F, 24.4; S, 13.76. Found: C, 30.83; H, 3.99; F, 24.7; S, 13.51%.

Preparation of $HOCH_2CH_2CF_2CF_2OCF_2CF_2SO_2F$ (**13**)

Into a 50 mL round bottom three neck flask equipped with a Teflon stirring bar, a thermometer, a dropping funnel, and a condenser to which was attached a drying tube, were added 13.5 g oleum (33% SO_3, 55.6 mmol SO_3); 3.60 g (7.90 mmol) of **2** was added via the dropping funnel during a 10 min period. After heating the reaction mixture at 40-50 °C for 1 h 15.0 mL of a saturated $NaHSO_3$ solution was added; the brown oily material was separated from the aqueous phase. The aqueous phase was extracted three times using

30 mL of CH_2Cl_2. The extracts were combined with the oily layer, dried over $MgSO_4$ and distilled; 2.10 g (6.10 mmol) of product, 13, was obtained (77.8% yield). B.P. 92-93 °C/18 Torr.

The infrared spectrum had bands (cm^{-1}): 3360 (s), 2973 (w), 2910 (w), 1462 (s), 1349 (m), 1321 (m), 1249 (s), 1202 (s), 1155 (s), 1119 (s), 996 (ms), 819 (s), 613 (ms).

In the mass spectrum $(CI)^+$: 345 [$(M+1)^+$, 3.26], 327 [$(M-OH)^+$, 1.01], 307 [$(M-H_2FO)^+$, 15.45], 305 [$(M-HF_2)^+$, 6.68] 275 [$(CH_2CF{=}CFOCF_2CF_2SO_2F)^+$, 6.77], 183 [$(CF_2CF_2SO_2F)^+$, 5.28] 127 [$(I)^+$, 20.77], 125 [$(OCH_2CH_2CF{=}CF_2)^+$, 100], 119 [$(C_5F_3H_2)^+$, 20.95], 105 [$(C_4H_3F_2O)^+$, 40.63], 100 [$(C_2F_4)^+$, 15.09], 95 [$(HOCH_2CH_2CF_2)^+$, 18.36], 77 [$(CH_2{=}CHCF_2)^+$, 33.96], 69 [$(C_4H_2F)^+$, 14.45], 67 [$(SOF)^+$, 33.50], 64 [$(SO_2)^+$ or $(CH_2{=}CF_2)^+$, 14.38].

Anal. Calcd for $C_6H_5F_9O_4S$: C, 20.93; H, 1.45; F, 49.7; S, 9.30. Found: C, 20.98; H, 1.39; F, 49.5; S, 9.30%.

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