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NEW POLYFLUOROALKOXYSULFONYL FLUORIDES (II)

LI-FO CHEN, JAVID MOHTASHAM and GARY L GARD

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

SUMMARY

The reaction of $\overline{\mathrm{CF_2CF_2OS}}\mathrm{O_2}$ with haloalkanes (RX, X = I, Br) in the presence of metal fluorides, MF (M = 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 = $\overline{\mathrm{OCH_2C}}\mathrm{HCH_2}$, $(CH_3)_3SiCH_2$, $(CF_3)_2CFCH_2CH_2$, $HC{\equiv}CCH_2$, $BrCH{=}CHCH_2$ (cis and trans), $CH_2{=}CBrCH_2$, $(CH_3CH_2O)_2P(O)CH_2CH_2$, $CH_3CH_2OPF(O)CH_2CH_2$ 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 [1-4] Previously, we have reported on a method involving the use of metal fluorides, $\overline{\mathrm{CF_2CF_2OS}}\mathrm{O_2}$, and RX (X = Br, I) in preparing fluorocarbon ether containing sulfonyl fluorides [5] In this paper we wish to report our success in extending this method to include

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fluorocarbon derivatives that not only contain the sulfonyl fluoride grouping but other functional groups such as $\overline{OCH_2C}HCH_2$, $(CH_3)_3SiCH_2$, $HC{\equiv}CCH_2$, $(CF_3)_3CFCH_2CH_2$, $BrCH{=}CHCH_2$, $CH_2{=}CBrCH_2$, $(CH_3CH_2O)_2P(O)CH_2CH_2$, and $CH_3CH_2OPF(O)CH_2CH_2$

RESULTS AND DISCUSSION

The reactions of $\overline{CF_2CF_2OS}O_2$ with haloalkanes were carried out according to the following equations

$$\overline{CF_2CF_2OS}O_2 \xrightarrow{MF} FC(O)CF_2SO_2F \qquad (1)$$

$$FC(O)CF_2SO_2F + MF \longrightarrow FSO_2CF_2CF_2O^-M^+ \qquad (2)$$

$$FSO_2CF_2CF_2O^- + RX \longrightarrow FSO_2CF_2CF_2OR + X^- \qquad (3)$$

R = $\overline{OCH_2C}HCH_2$, $(CH_3)_3SiCH_2$, $(CF_3)_2CFCH_2CH_2$, $CH{\equiv}C{-}CH_2$,
$BrCH{=}CHCH_2$ (_cis_ and _trans_), $CH_2{=}CBrCH_2$,
$(CH_3CH_2O)PF(O)CH_2CH_2$, $(CH_3CH_2O)_2P(O)CH_2CH_2$

M = Cs^+, Ag^+

X = I^-, Br^-

In general, the reactions involved two stages, in the first stage the rearrangement of the sultone occurs (eqn 1) followed by formation of the alkoxide anion (eqn 2) In the second stage, a nucleophilic substitution of RX by $^-OCF_2CF_2SO_2F$ occurred

We found that silver fluoride was a more efficient reagent for both the catalytic rearrangement of the sultone and the stabilization of $^-OCF_2CF_2SO_2F$ anion We found that using AgF required milder conditions (20-40°C) with better overall yields It was also found that when 1,3 or 2,3-dibromopropene was used, only products attributable to allylic displacement were obtained, no vinyl substituted product was observed For a multi-functional compound such as diethyl-2-bromoethyl phosphonate, a mixture of

$(CH_3CH_2O)_2P(O)CH_2CH_2OCF_2CF_2SO_2F$ and $(CH_3CH_2O)PF(O)CH_2CH_2OCF_2CF_2SO_2$ was formed It was possible to convert the monofluoro derivative the diethoxy product by reaction with absolute ethanol With most of the reactions mentioned above, a by-product, $CH_3OCF_2CF_2SO_2F$, was found This result suggests the possibility that the solvent, diglyme, participated in the reaction and formed CH_3Br Further reaction of CH_3Br with $^-OCF_2CF_2SO_2F$ anion produced the $CH_3OCF_2CF_2SO_2F$

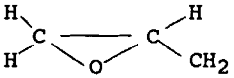
It is worthwhile to note that bromomethyl trimethylsilane reacted to give, as expected, the product $(CH_3)_3SiCH_2OCF_2CF_2SO_2F$ This means that the bulky substituent $(CH_3)_3Si$, at the reaction carbon center, did not prevent the nucleophilic attack of the $^-OCF_2CF_2SO_2$ ion This indicates that a S_N1 mechanism may be involved in this 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 1465-1455, 1244-1210, 803-792 cm^{-1} regions, respectively These assignments agree with the results obtained previously [3-7] The strong carbon fluorine absorption bands found at 1109-1244 cm^{-1} can be correlated with the CF_2 group [8] The C-H absorption bands are located in the 2903-3016 cm^{-1} region The characteristic C-H absorption of $CH\equiv C-$ is found at 3311(s) cm^{-1} region The double bond and triple bond vibrational bands for $BrCH=CHCH_2OCF_2CF_2SO_2F$ and $HC\equiv CCH_2OCF_2CF_2SO_2F$ appeared at 1631 and 2137 cm^{-1}, respectively

In the $(CI)^+$ or $(EI)^+$ mass spectra, the (M+1) or molecular ion peak for most of the compounds was found For all compounds, a cracking pattern was found that was supportive of the assigned structure

TABLE I

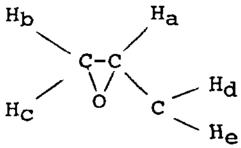
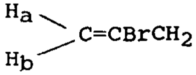
^{19}F NMR Data of $ROCF_2CF_2SO_2F$ Chemical Shift (ppm) and Coupling Constant (Hz)

R	OCF_2	CF_2	SO_2F
	-86 o (d-t)	-113 7 (d-t)	43 0 (t-t)
	$J_{OCF_2-SO_2F}$=4 9	$J_{OCF_2-CF_2}$=3 7	$J_{CF_2-SO_2F}$=4 4
$(CH_3)_3SiCH_2$	-87 7 (d-t)	-112 7 (d-t)	42 6 (t-t)
	$J_{OCF_2-SO_2F}$=5 8	$J_{OCF_2-CF_2}$=4 7	$J_{CF_2-SO_2F}$= 5 4
$(CF_3)_2CFCH_2CH_2$	-87 5 (d-t)	-113 8 (d-t)	42 5 (t-t)
	$J_{OCF_2-SO_2F}$= 6 1	$J_{OCF_2-CF_2}$= 4 2	$J_{CF_2-SO_2F}$= 5 2
	$(CF_3)_2$ = -78 6 (d)	F = -187 2 (t-hept)	
	J_{CF_3-CF}= 6 6	J_{CF-CH_2}= 19 8	
HC C-CH_2	-85 0 (d-t)	-112 0 (d-t)	44 2 (t-t)
	$J_{OCF_2-SO_2F}$= 5 6	$J_{OCF_2-CF_2}$= 3 9	$J_{CF_2-SO_2F}$= 4 6

$BrCH=CH_2CH_2$	-84 2 (d-t)	-113 0 (d-t)	43 8 (overlap)
	$J_{(trans)OCF_2-SO_2F}$= 6 6	$J_{(trans)OCF_2-CF_2}$= 4 9	$J_{(trans)CF_2-SO_2F}$= 5 0
	$J_{(cis)OCF_2-SO_2F}$= 5 2	$J_{(cis)OCF_2-CF_2}$= 4 9	$J_{(cis)CF_2-SO_2F}$= 5 0
$CH_2=CBrCH_2$	-85 2 (d-t)	-112 7 (d-t)	44 2 (t-t)
	$J_{OCF_2-SO_2F}$= 6 4	$J_{OCF_2-CF_2}$= 4 7	$J_{CF_2-SO_2F}$= 5 1
$(CH_3CH_2O)_2P(O)CH_2CH_2$	-84 5 (d-t)	-111 5 (d-t)	44 4 (t-t)
	$J_{OCF_2-SO_2F}$= 5 2	$J_{OCF_2-CF_2}$= 3 7	$J_{CF_2-SO_2F}$= 4 2
$(CH_3CH_2O)PF(O)CH_2CH_2$	-84 9 (d-t)	-111 5 (d-t)	44 2 (t-t) PF 60 7
	$J_{OCF_2-SO_2F}$= 5 2	$J_{OCF_2-CF_2}$= 3 7	$J_{CF_2-SO_2F}$= 4 2
			J_{PF}= 1075

TABLE II

^1H NMR Date of $ROCF_2CF_2SO_2F$

R	Chemical Shift (ppm)	Coupling Constant (Hz)
	H_a = 3 35 (m)	J_{ac}= 5 0
	H_b = 2 94 (d-d)	J_{ab}= 5 8
	H_c = 2 77 (d-d)	J_{bc}= 4 5
	H_d = 4 50 (d-d)	J_{de}= 11 7
	H_e = 4 05 (d-d)	
$(CH_3)_3SiCH_2$	$(CH_3)_3$ = 0 32 (s)	
	CH_2 = 3 98 (s)	
$(CF_3)_2CFCH_2CH_2$	$CFCH_2$ = 2 80 (d-t)	J_{CF-CH_2}= 19 8
	CH_2O = 4 62 (t)	$J_{CH_2-CH_2}$= 7 2
$HC{\equiv}C-CH_2$	CH = 3 00 (t)	J_{CH-CH_2}= 2 5
	CH_2 = 4 95 (d)	
$BrCH{=}CHCH_2$	CH=CH = 6 90 (m)	
	$CH_{2(trans)}$= 5 25 (d)	$J_{(trans)CH-CH_2}$= 5 04
	$CH_{2(cis)}$= 5 02 (d)	$J_{(cis)CH-CH_2}$= 5 58
	H_a = 6 32 (s)	
	H_b = 6 05 (s)	
	CH_2 = 4 97 (s)	
$(CH_3CH_2O)_2P(O)\underline{CH_2}CH_2$		
	CH_3 = 1 75 (t)	$J_{CH_3-CH_2O}$= 7 38
	$O\underline{CH_2}CH_3$ = 4 37 (d-q)	$J_{P(O)-OCH_2}$= 7 38
	CH_2OCF_2 = 4 63 (t)	$J_{\underline{CH_2}-CH_2}$= 7 56
	PCH_2 = 2 55 (d-t)	$J_{P(O)-\underline{CH_2}}$= 19 80
$(CH_3CH_2O)PF(O)\underline{CH_2}CH_2$		
	CH_3 = 1 78 (t)	$J_{CH_3-CH_2O}$= 5 4
	PCH_2 = 2 90 (d-m)	$J_{P-\underline{CH_2}}$= 18 0
	CH_2O = 4 30≈5 05 (m)	$J_{P(O)-OCH_2}$= overlap

The structures of all new products were determined from their respective ^{1}H 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 Table I It is found that consistent chemical shift values for similar groupings are maintained for all compounds For $OC\underline{F}_2$, $\underline{CF}_2$, $SO_2\underline{F}$, the chemical shift values range from -84 2 to -87 7, -112 0 to -113 8, 42 5 to 44 0 ppm, respectively The ^{1}H nmr chemical shifts and coupling constants are listed in Table II

For $BrCH{=}CHCH_2OCF_2CF_2SO_2F$, both ^{1}H and ^{19}F nmr data confirm the presence of isomers (*trans* 60%, *cis* 40%) In the ^{1}H nmr spectra, the two protons situated at a vinyl position exhibited an overlap pattern in the region of 6 9 ppm However, the CH_2 group, adjacent to the vinyl group, appeared at the following chemical shift values δ 5 02 (*cis*) and δ 5 25 (*trans*) ppm

The reaction of diethyl-2-bromoethylphosphonate with $AgOCF_2CF_2SO_2F$ gave a mixture, which from the ^{19}F nmr spectrum was found to consist of $(CH_3CH_2O)PF(O)CH_2CH_2OCF_2CF_2SO_2F$ (45%) and the expected product $(CH_3CH_2O)_2P(O)CH_2CH_2OCF_2CF_2SO_2F$ (55%) The coupling constant of the P-F bond in $CH_3CH_2OPF(O)CH_2CH_2O(CF_2)_2SO_2F$ was 1075 Hz and the fluorine chemical shift appeared at -60 7 ppm, the chemical shift for $OC\underline{F}_2$ was 0 5 ppm higher than that found for the non-P-F containing product The ^{19}F chemical shift and the coupling constant for the PF group are in agreement with values reported for compounds with a similar molecular structure [9] When treated with absolute alcohol, the P-F bond at -60 7 ppm disappeared and only the pure product, $(CH_3CH_2O)_2P(O)(CH_2)_2(CF_2)_2SO_2F$, was present

EXPERIMENTAL

The sultone $\overline{\text{CF}_2\text{CF}_2\text{OS}}\text{O}_2$ was 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 liquids 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 Gottingen, Federal Republic of Germany

Preparation of $\overline{\text{OCH}_2\text{C}}\text{HCH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$

Into a 125 mL Pyrex-glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar were added 5 0 g (39 0 mmol) of dried silver fluoride and 10 0 mL of diglyme, 9 50 g (52 7 mmol) of $\overline{\text{CF}_2\text{CF}_2\text{OS}}\text{O}_2$ was vacuum transferred into the reaction vessel cooled to -196 C The reaction was warmed to room temperature and stirred at

35°C for 1 5 h During this time a homogenous brown solution was formed The vessel was again cooled to -196°C and 4 9 g (35 7 mmol) of epibromohydrin was added The reaction was warmed to room temperature and heated (35 C) for 3 d The volatile material (5 09g), recovered at room temperature in a trap cooled to -196°C, was found to be $FC(O)CF_2SO_2F$ A second fraction (15 0 g) was collected by heating the reaction vessel under vacuum This fraction was washed four times with water and gave 5 6 g of an oil which was dried with $MgSO_4$ and distilled to give 4 0 g (15 6 mmol) product, in 44% yield, b p 92-93 C/40 mm

The infrared spectrum had the following bands (cm^{-1}) 3016(vw), 1457(vs), 1364(w), 1335(m), 1242(s), 1205(s), 1142(s), 1115(s), 1038(w), 1000(m), 948(w), 907(w), 800(vs), 763(w), 655(m), 614(s), 551(w)

In the $(EI)^+$ mass spectrum, the molecular ion was observed at 256 [$(M)^+$, 1 56], other main fragment ions were detected at 226 [$(M-CH_2O)^+$, 5 34], 213 [$(M-C_2H_3O)^+$, 21 14], 149 [$(C_5F_3O_2)^+$, 24 88], 145 [$(CF_2{=}CFSO_2)^+$, 7 66], 133 [$(CF_2SO_2F)^+$, 4 74], 127 [$(C_5H_3O_2S)^+$, 17 58], 119 [$(C_3FO_2S)^+$, 11 81], 100 [$(C_2F_4)^+$, 33 70], 99 [$(C_4O_2F)^+$, 28 25], 97 [$(C_2F_3O)^+$, 63 09], 95 [$(CFSO_2)^+$, 6 77], 93 [$(C_3H_3F_2O)^+$, 47 56], 83 [$(SO_2F)^+$, 2 76], 73 [$(OCH_2CHCH_2O)^+$, 8 66], 71 [$(C_3H_3O_2)^+$, 2 96], 69 [$(C_3HO_2)^+$, 22 22], 67 [$(SOF)^+$, 100], 65 [$(C_4OH)^+$, 5 44], 63 [$(CFS)^+$, 6 02]

Anal Calcd for $C_5H_5F_5O_4S$ C, 23 43, H, 1 95, F, 37 1, S, 12 50 Found C, 23 61, H, 1 94, F, 37 5, S, 12 30

Preparation of $(CH_3)_3SiCH_2OCF_2CF_2SO_2F$

In a similar procedure as previously described, 3 70 g (29 1 mmol) of silver fluoride in 5 0 mL of diglyme with 6 5 g (36 1 mmol) of $\overline{CF_2CF_2OSO_2}$ was heated at 36°C for 26 h to give a homogeneous solution of $AgOCF_2CF_2SO_2F$ and diglyme At -196 C, 4 1 g (24 5 mmol) of $(CH_3)_3SiCH_2Br$ was added by vacuum transfer to the reaction, and then maintained at 37 C for 4 d Only 0 2 g of a low boiling material was recovered The volatile material at room temperature was transferred, washed with water, dried and distilled to give 2 2 g (7 6 mmol) of the product in 33% yield (b p 125-127 C) and 0 30 g of a minor product, $CH_3OCF_2CF_2SO_2F$ in 5 7% yield, b p 83-85°C

The infrared spectrum had the following bands (cm^{-1}) 2964(w), 1459(s), 1344(s), 1293(w), 1257(s), 1238(s), 1206(s), 1137(s), 1109(s), 994(m), 856(vs), 819(w), 792(m), 755(w), 709(w), 649(w), 608(s), 539(w)

In the $(CI)^+$ mass spectrum, no molecular ion was observed Main fragmentations were found at 271 [$(M-CH_3)^+$, 0 37], 187 [$(C_5H_7F_4OSi)^+$, 0 45], 183 [$(CF_2CF_2SO_2F)^+$, 0 56], 145 [$(CF_2{=}CFSO_2)^+$, 1 13], 137 [$(C_4H_7F_2OSi)^+$, 1 87], 135 [$(C_4H_5F_2OSi)^+$, 1 87], 134 [$(C_4H_4F_2OSi)^+$, 0 88], 133 [$(CF_2SO_2F)^+$, 0 81], 123 [$(C_3H_5F_2OSi)^+$, 1 39], 120 [$(C_3H_2F_2OSi)^+$, 1 18], 119 [$(C_3HF_2OSi)^+$, 1 66], 107 [$(C_2HF_2OSi)^+$, 1 67], 100 [$(C_2F_4)^+$, 8 50], 97 [$(C_2F_3O)^+$, 7 86], 95 [$(CFSO_2)^+$, 2 18], 92 [$(C_3H_2F_2O)^+$, 3 65], 91 [$(C_3HF_2O)^+$, 27 15], 89 [$(C_2H_2FOSi)^+$, 4 47], 88 [$(C_2HFOSi)^+$, 9 31], 87 [$(CH_3)_3SiCH_2{}^+$, 100], 83 [$(SO_2F)^+$, 2 13], 81 [$(C_2F_3)^+$, 2 65], 79 [$(C_2HF_2O)^+$, 6 37], 73 [$(CH_3)_3Si^+$, 71 70], 67 [$SOF)^+$, 4 51], 65 [$(C_4OH)^+$, 2 83], 63 [$(CFS)^+$, 2 31]

Anal Calcd for $C_6H_{11}F_5O_3SiS$ C, 25 17, H, 3 85, F, 33 2, S, 11 19 Found C, 25 41, H, 3 88, F, 33 5, S, 11 39

Preparation of $(CF_3)_2CFCH_2CH_2OCF_2CF_2SO_2F$

In a similar procedure as previously described, 3 50 g (27 5 mmol) of dried silver fluoride, 5 0 mL of diglyme and 6 80 g (37 8 mmol) of $\overline{CF_2CF_2OS}O_2$ were reacted at room temperature (24 h) to give a homogenous clear solution of $AgOCF_2CF_2SO_2F$ and diglyme The mixture was cooled and 8 0 g (24 7 mmol) of $(CF_3)_2CFCH_2CH_2I$ was added The reaction mixture was warmed and maintained at room temperature for 3 d The products were transferred under vacuum and washed with water 8 10 g of an oily material was collected, dried over P_4O_{10} and distilled to give 5 1 g (12 9 mmol) of product in 52 1% yield, b p 150-152°C

The infrared spectrum had the following bands (cm^{-1}) 2945(vw), 2853(vw) 1462(vs), 1335(m), 1314(m), 1237(vs), 1166(s), 1145(s), 1117(s), 1068(m), 1005(m), 934(w), 801(vs), 723(m), 653(v), 612(s), 541(w)

In the $(CI)^+$ mass spectrum, no molecular ion was observed Main fragment ions were found at 377 [$(M-F)^+$, 0 77], 357 [$(M-HF_2)^+$, 3 72], 337 [$(M-H_2F_3)^+$, 2 67], 213 [$(CF_3)_2CFCH_2CH_2O^+$, 3 51], 197 [$(CF_3)_2CFCH_2CH_2^+$, 47 50], 183 [$(CF_3)_2CFCH_2^+$, 5 09], 181 [$(C_4F_7)^+$, 27 88], 178 [$(C_5H_4F_6)^+$, 12 44], 177 [$(C_5H_3F_6)^+$, 100], 175 [$(C_5HF_6)^+$, 4 14], 161 [$(C_2F_3O_3S)^+$, 7 05], 157 [$(C_3F_3O_2S)^+$, 8 01], 155 [$(C_5H_3F_4O)^+$, 5 45], 149 [$(C_6H_4F_3O)^+$, 6 79], 145 [$(CF_2{=}CFSO_2)^+$, 3 19] 133 $(CF_2SO_2F)^+$, 5 36], 127 [$(C_5H_3O_2S)+$, 24 99], 119

[$(C_3FO_2S)^+$, 11 15], 115 [$(C_4H_3O_2S)^+$, 28 86], 113 [$(C_4HO_2S)^+$, 10 48], 109 [$(C_5HOS)^+$, 5 89], 100 [$(C_2F_4)^+$, 25 65], 97 [$(C_2F_3O)^+$, 17 11], 95 [$(CFSO_2)^+$, 11 81], 93 [$(C_3H_3F_2O)^+$, 2 30], 87 [$(C_4H_4FO)^+$, 9 32], 83 [$(SO_2F)^+$, 1 03], 81 [$(CF_2{=}CF)^+$, 15 6], 79 [$(C_2HF_2O)^+$, 19 51], 77 [$(C_5HO)^+$, 11 26], 67 [$(SOF)^+$, 37 20], 65 [$(C_4OH)^+$, 12 76]

<u>Anal Calcd</u> for $C_7H_4F_{12}O_3S$ C, 21 12, H, 1 01, F, 57 6, S, 8 08 Found C, 21 36, H, 1 12, F, 58 0, S, 7 90

<u>Preparation of $HC{\equiv}C\text{-}CH_2OCF_2CF_2SO_2F$</u>

Into the same reaction vessel previously described, 6 70 g (52 7 mmol) of dried silver fluoride, 10 0 mL diglyme and 18 0 g (100 mmol) of $\overline{CF_2CF_2OSO_2}$ were added at -196°C A clear, slightly blue solution of $AgOCF_2CF_2SO_2F$ was obtained after heating at 30-35 C for 2 h At -196 C, 8 10 g of a solution containing toluene (20%) and $HC{\equiv}CCH_2Br$ (80% and 54 6 mmol) was added into the reaction vessel

The reaction mixture was maintained at 5-8°C for 2 h, and at 18-20 C for another 16 h All volatile materials (27 60 g) were distilled to give 4 0 g of $FC(O)CF_2SO_2F$, b p 32-34 C, 6 20 g of $CH_3OCF_2CF_2SO_2F$, 55% yield, b p 78-87°C, and 3 5 g of a mixture The G C indicated that the mixture contained 50% $HC{\equiv}CCH_2OCF_2CF_2SO_2F$ (14% yield) and 40% toluene The pure $HC{\equiv}CCH_2OCF_2CF_2SO_2F$ can be separated from G C (SE-30, 3M, 150°C), b p 107°C

The infrared spectrum had the following bands (cm^{-1}) 3311(s), 2966(vw), 2903(vw), 2137(m), 1459(vs), 1383(w), 1334(m), 1280(m), 1242(s), 1204(s), 1144(s), 1123(s), 1036(m), 1004(s), 917(w), 803(vs), 766(m), 695(w), 657(m), 608(s)

In the $(CI)^+$ mass spectrum, the $(M+1)^+$ ion was observed at 239 [$(M+1)^+$, 19 14], other main fragment ions were detected at 237 [$(M-1)^+$, 2 24], 155 [$(C_5H_3OF_4)^+$, 5 93], 154 [$(C_5H_2OF_4)^+$, 4 54], 153 [)$C_5HOF_4)^+$, 2 81], 127 [$(C_5H_3O_2S)^+$, 60 19], 126 [$(C_5H_2O_2S)^+$, 24 23], 125 [$(C_5HO_2S)^+$, 13 51], 123 [$(C_4H_2OF_3)^+$, 8 20], 119 [$(C_3FO_2S)^+$, 16 58], 105 [$(C_4H_3OF_2)^+$, 5 96], 103 [$(C_4HF_2O)^+$, 7 77], 100 [$(C_2F_4)^+$, 81 34], 97 [$(C_2F_3O)^+$, 6 43], 95 [$(CFSO_2)^+$, 3.84], 94 [$(C_2F_2S)^+$, 8 86], 91 [$(C_3HOF_2)^+$, 3 26], 90 [$(C_3OF_2)^+$, 3 28], 83 [$(SO_2F)^+$, 3 22], 79 [$(C_2HOF_2)^+$, 38 79], 78 [$(C_5H_2O)^+$, 2 13], 77 [$(C_5HO)^+$, 65 62], 75 [$(C_2FS)^+$, 10 22], 71 [$(C_3OF)^+$, 22 53], 67 [$(SOF)^+$, 43 43], 65 [$(C_4OH)^+$, 22 53], 63 [$(CFS)^+$, 5 84], 59 [$(C_2OF)^+$, 100], 55 [$(C_3H_3O)^+$, 32 81], 54 [$(C_3H_2O)^+$, 29 60], 53 [$(C_3HO)^+$, 21 09]

Anal Calcd for $C_5H_3O_3F_5S$ C, 25 21, H, 1 26, F, 39 9, S, 13 44 Found C, 25 30, H, 1 29, F, 39 8, S, 13 48

Preparation of $BrCH{=}CHCH_2OCF_2CF_2SO_2F$

(A) AgF Method Into a similar reaction vessel previously described, 4 20 g (33 0 mmol) of dried silver fluoride, 7 0 mL of diglyme and 7 70 g (42 7 mmol) of $\overline{CF_2CF_2OSO_2}$ were added The reaction mixture was stirred at room temperature for 5 h, followed by the addition of 6 00 g (30 0 mmol) of $BrCH{=}CHCH_2Br$ The mixture was maintained at 0°C for 1.5 h and at 35-37°C for 24 h The mixture was filtered in order to remove the AgBr The filtrate was washed three times with water to give 7 0 g of a crude product which was dried over P_4O_{10} and distilled to give 0 40 g (6 2% yield) of $CH_3OCF_2CF_2SO_2F$, b p 45-46°C/143 mm, and 5 2 g (16 3 mmol) of product (trans 60%, cis 40%) in 54% yield, b p 119-122°C/143 mm

The infrared spectrum had the following bands (cm^{-1}) 3100(vw), 2966(vw), 2903(vw), 1631(m), 1455(vs), 1335(m), 1300(w), 1244(s), 1202(s), 1138(s), 1117(s), 1033(w), 998(m), 934(m), 801(vs), 725(w), 681(w), 653(m), 612(s), 548(w)

In the $(EI)^+$ mass spectrum, the molecular ion was observed at 320 [($H^{81}BrC{=}CHCH_2OCF_2CF_2SO_2F$), 2 47] and 318 [($H^{79}BrC{=}CHCH_2OCF_2CF_2SO_2F$), 3 88] The other main fragments were found at 239 [$(M-HBr)^+$, 100 0], 155 [$(C_4H_2F_3OS)^+$, 6 05], 134 [$(C_5HOF_3)^+$, 5 98], 133 [$(C_5OF_3)^+$, 4 12], 123 [$(C_4H_2OF_3)^+$, 8 33], 121 [$(^{81}BrCH{=}CHCH_2)^+$, 55 28], 119 [$(^{79}BrCH{=}CHCH_2)^+$, 51 31], 100 [$(C_2F_4)^+$, 20 54], 97 [$(C_2F_3O)^+$, 4 57], 95 [$(CFSO_2)^+$, 5 06], 93 [$(C_3H_3F_2O)^+$, 4 89], 67 [$(SOF)^+$, 65 28], 59 [$(C_2FO)^+$, 81 77], 55 [$(C_3H_2O)^+$, 24 52]

Anal Calcd for $C_5H_4F_5O_3BrS$ C, 18 81, H, 1 25, F, 29 8, S, 10 03, Br, 25 08 Found C, 18 97,, H, 1 30, F, 29 8, S, 9 88, Br, 24 85

(B) CsF Method In a similar procedure as reported above, 4 80 g (31 5 mmol) of dried CsF, 7 0 mL diglyme, 6 80 g (37 7 mmol) of $\overline{CF_2CF_2OSO_2}$ were stirred at room temperature for 4 h, followed by reaction with 5 00 g (25 0 mmol) of $BrCH{=}CHCH_2Br$ at 100-105°C for 48 h The liquid product was washed with water in order to remove any solvent The crude product was dried over $MgSO_4$ and distilled to give 1 90 g product (24% yield) with a b p 76-78 C/20 mm

Preparation of $CH_2{=}CBrCH_2OCF_2CF_2SO_2F$

(A) AgF Method In a similar procedure as previously described, 3 90 g (30 7 mmol) of dried AgF, 6 0 mL of diglyme and

7 30 g (40 5 mmol) of $\overline{CF_2CF_2OSO_2}$ were mixed together The mixture was stirred at room temperature for 5 h, and then 6 0 g (30 0 mmol) of $CH_2{=}CBrCH_2Br$ was added The reaction mixture was stirred at 0 C for 2 h, and at room temperature for 16 h The AgBr was removed by filtration and the liquid filtrate was washed, dried over P_4O_{10} and distilled to give 3 00 g (9 4 mmol) of the olefinic product (33 1% yield) with a b p 107-109 C/130 mm and 1 6 g of $CH_3OCF_2CF_2SO_2F$, 26% yield

The infrared spectrum had the following bands (cm^{-1}) 2985(vw), 1655(m), 1640(m), 1465(s), 1405(w), 1375(vw), 1337(m), 1300(s), 1210(s), 1145(s), 1125(s), 1040(w), 1005(m), 965(w), 915(m), 821-795(vs), 655(m), 610(s), 546(w)

In the $(CI)^+$ mass spectrum, the molecular ion was observed at 320 [($H_2C{=}C^{81}BrCH_2OCF_2CF_2SO_2F$), 7 95] and 318 [($H_2C{=}C^{79}BrCH_2OCF_2CF_2SO_2F$), 7 90] The other main fragments were found at 239 [$(M-Br)^+$, 12 89], 238 [$(M-HBr)^+$, 11 73], 155 [$(C_4H_2F_3OS)^+$, 5 01], 137 [$(CH_2{=}C^{81}BrCH_2O)^+$, 1 34], 135 [$(CH_2{=}C^{79}BrCH_2O)^+$, 1 17], 134 [$(C_5HOF_3)^+$, 1 52], 133 [$(C_5OF_3)^+$, 129], 121 [$(CH_2{=}C^{81}BrCH_2)^+$, 94 72], 119 [$(CH_2{=}C^{79}BrCH_2)^+$, 100 0], 100 [$(C_2F_4)^+$, 12 82], 97 [$(C_2F_3O)^+$, 4 70], 94 [$(CFSO_2)^+$, 2 69], 93 [$(C_3H_3F_2O)^+$, 2 43], 79 [$(C_2HF_2O)^+$, 6 57], 67 [$(SOF)^+$, 32 57], 65 [$(C_4HO)^+$, 15 43], 59 [$(C_2FO)^+$, 30 92], 55 [$(CH\ CCH_2O)^+$, 10 86]

Anal Calcd for $C_5H_5F_5O_3BrS$ C, 18 81, H, 1 25, F, 29 78, S, 10 03, Br, 25 08 Found C, 18 87, H, 1 22, F, 30 3, S, 10 03, Br, 24 97

(B) CsF Method In a similar way as reported above, 4 80 g (31 5 mmol) of dried cesium fluoride, 7 0 mL diglyme and 5 40 g

(30 0 mmol) of $\overline{CF_2CF_2OS}O_2$ were added in order to prepare the cesium salt, $CsOCF_2CF_2SO_2F$ The cesium salt was then reacted with 6 00 g (30 0 mmol) of $CH_2=CBrCH_2Br$ at 90-97°C for 24 h The CsBr which formed was filtered and the filtrate was washed with water, dried over P_4O_{10} and distilled to give 1 15 g product in 12% yield

Preparation of $(CH_3CH_2O)_2P(O)CH_2CH_2OCF_2CF_2SO_2F$ and $(CH_3CH_2O)PF(O)CH_2CH_2OCF_2CF_2SO_2F$

Into the reaction vessel previously described were added 4 10 g (32 3 mmol) of dried silver fluoride, 5 0 mL diglyme and 7 70 g (42 7 mmol) of $\overline{CF_2CF_2OS}O_2$ at -196°C The mixture was stirred at room temperature for 16 h and 4 50 g (18 3 mmol) of diethyl-2-bromoethyl-phosphonate was then added at low temperature (-90 to -100°C) The reaction mixture was warmed and maintained at 35°C for 4 d The volatile $FC(O)CF_2SO_2F$ (2 50 g) was recovered The AgBr precipitate was filtered in a dry atmosphere and the AgBr was washed twice with anhydrous diethyl ether The washings were combined with the filtrate and then distilled to give a mixture of $(CH_3CH_2O)_2P(O)(CH_2)_2(CF_2)_2SO_2F$ (55%) and $(CH_3CH_2O)PF(O)(CH_2)_2O(CF_2)_2SO_2F$ (45%) Subsequently, this mixture was reacted with an excess of absolute alcohol at room temperature for 14 h and distilled to give 3 30 g of $(CH_3CH_2O)_2P(O)(CH_2)_2O(CF_2)_2SO_2F$, b p 127-129°C/0 7 mm in 54% yield

Anal Calcd for $C_8H_{14}F_5O_6PS$ C, 26 37, H, 3 85, F, 26 1, S, 8 79 Found C, 26 39, H, 3 75, F, 27 1, S, 8 96

The infrared spectrum of $(CH_3CH_2O)_2P(O)CH_2CH_2OCF_2CF_2SO_2F$ had the following bands (cm^{-1}) 2987(w), 2924(w), 1455(s), 1398(w), 1335(m), 1244(s), 1195(m), 1138(m), 1110(m), 1033(s), 998(m), 955(w), 864(w), 800(vs), 737(w), 611(m)

In the $(CI)^+$ mass spectrum of $(CH_3CH_2O)_2P(O)CH_2CH_2OCF_2CF_2SO_2F$, the $(M+1)^+$ peak was observed at 365 [$(M+1)^+$, 47 80], the other main fragments were found at 311 [$(M-CH_3F_2)^+$, 43 49], 291 [$(M-CH_4F_3)^+$, 18 57], 227 [$(CH_2CH_2OCF_2CF_2SO_2F)^+$, 6 26], 225 [$(C_2H_2COCF_2CF_2SO_2F)^+$, 10 35], 205 [$(C_4HF_4O_3S)^+$, 9 46], 181 [$(CH_3CH_2O)_2P(O)CH_2CH_2O\ ^+$, 4 31], 165 [$(CH_3CH_2O)_2P(O)CH_2CH_2{}^+$, 25 05], 151 [$(CH_3CH_2O)_2P(O)CH_2{}^+$, 2 14], 137 [$(CH_3CH_2O)_2P(O)^+$, 25 05], 123 [$(C_4H_2OF_3)^+$, 9 32], 113 [$(C_4HO_2S)^+$, 16 13], 112 [$(C_4O_2S)^+$, 5 04], 97 [$(C_2F_3O)^+$, 5 10], 93 [$(C_3H_3F_2O)^+$, 18 75], 91 [$(C_2H_4O_2P)^+$, 12 56], 83 [$(SO_2F)^+$, 4 00], 81 [$(C_2F_3)^+$, 15 79], 79 [$(C_2HF_2O)^+$, 5 18], 77 [$(CH_2O_2P)^+$, 7 57], 67 [$(SOF)^+$, 12 90], 65 [$(C_4OH)^+$, 18 33]

It was very difficult to obtain a pure sample of $CH_3CH_2OPF(O)CH_2CH_2OCF_2CF_2SO_2F$ However, it was possible to assign some characteristic fragments and the $(M+1)^+$ ion from mass spectrum patterns of a mixture of $(CH_3CH_2O)_2P(O)CH_2CH_2OCF_2CF_2SO_2F$ and $CH_3CH_2OPF(O)CH_2CH_2OCF_2CF_2SO_2F$ The $(M+1)^+$ ion of $CH_3CH_2OPF(O)CH_2CH_2OCF_2CF_2SO_2F$ appeared at 339 [$(M+1)$, 14 37], other main fragment ions were 337 [$(M-1)^+$, 36 22], 323 [$(M-CH_3)^+$, 4 99], 309 [$(M-C_2H_5)^+$, 19 74], 139 [$(CH_3CH_2OPF(O)CH_2CH_2)^+$, 9 99], 138 [$(CH_3CH_2OPF(O)CH=CH_2)^+$, 27 58], 125 [$(CH_3CH_2OPF(O)CH_2)^+$, 16 99], 109 [$(CH_2=CHOP(O)F)^+$, 38 78]

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