New pentafluorothio (SF_5) esters

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Abstract

The addition of either SF_5Br or SF_5Cl to a number of unsaturated esters is discussed. The new SF_5 esters, $SF_5CH_2CHBr(OAc)$, $SF_5CH_2CHBrC(O)OC_2H_5$, $SF_5CH(C(O)OC_2H_5)CHBr(OAc)$ and $SF_5CH_2CHClCH_2OAc$, were prepared from vinyl acetate, ethyl acrylate, β-acetoxyethyl acrylate and allyl acetate, respectively ($OAc = CH_3C(O)O$). The ester $SF_5CH_2C(O)OCH_3$ was prepared by peracid oxidation of the acetal $SF_5CH_2CH(OCH_3)_2$. Base treatment of $SF_5CH_2CHClCH_2OAc$ did not give an epoxide but, unexpectedly, produced the novel $SF_5CH{=}CHCH_2OH$. This alcohol is the first example of an SF_5-containing ene-ol.

Introduction

The introduction of pentafluorothio groups (SF_5, pentafluoro-λ^6-sulfanyl) into molecular systems can bring about substantial changes with regard to their physical, chemical and biological behavior. These new properties are manifested in a multitude of uses, or potential uses, such as surface-active agents, fumigants, thermally and chemically stable systems, solvents for polymers and perfluorinated blood substitutes [1]. On several occasions we have undertaken to prepare SF_5-containing carboxylic esters, where the SF_5 group was contained either in the acid or the alcohol moiety. These compounds were intended to be versatile building blocks in several instances.

SF_5-containing esters have been obtained previously by the reaction of acid chlorides or fluorides with alcohols [2], from sultones and alcohols [3], from a ketene and alcohols [4] and by adding SF_5Cl to vinyl acetate [5]. Furthermore, SF_5-perfluoroacetic esters were obtained by SF_5Cl addition to $CF_2{=}CFOR$; the perhalo ether was converted to the ester with oleum [6].

Results and discussion

In our studies, the first reaction sequence was aimed at obtaining an ester of pentafluorothioacetic acid (SF_5CH_2COOH). Such esters are easily capable of synthesis by bringing together an alcohol and pentafluorothioacetyl chloride; the latter is made by adding SF_5Cl and ketene [7]. In order to avoid the preparation and handling of the noxious ketene, we sought a process that would circumvent its use. In our method, SF_5Cl was added, as described [5], to vinyl acetate:

$$SF_5Cl + CH_2{=}CHOAc \longrightarrow SF_5CH_2CHCl(OAc) \quad (1)$$

Conversion to an acetal was achieved by setting aside the α-chloroacetate with an excess of alcohol, in the same fashion as iodo- and bromo-acetals are obtained [8]. The yields after distillation were >70%:

$$SF_5CH_2CHCl(OAc) + \underset{(R = CH_3,\ C_2H_5)}{ROH\ (\text{excess})} \longrightarrow SF_5CH_2CH(OR)_2 + HCl + ROAc + H_2O \quad (2)$$

Peracid oxidation of the acetal resulted in the formation of a carboxylic ester:

$$SF_5CH_2CH(OR)_2 + m\text{-chloro-perbenzoic acid} \longrightarrow SF_5CH_2C(O)OR \quad (3)$$

($R = CH_3$)

The acetals obtained as depicted in eqn. (2) were only obtained for ethyl and methyl alcohol; CF_3CH_2OH, and benzyl alcohol did not react. Hydrolysis of the acetals to the aldehyde SF_5CH_2CHO was not a useful reaction as the aldehyde decomposed concomitantly under the conditions employed.

In forming the SF_5 ester [eqn. (3)], it was found that after initial formation of a clear liquid mixture, a precipitate was formed that dissolved upon further heating. As speculated by Heywood and Phillips for an analogous case [9], the intermediate could be a hemiacetal *m*-chloroperbenzoate ($SF_5CH_2CH(OR)$-

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$OOC(O)C_6H_4Cl$). This point was not pursued, however. The product, $SF_5CH_2C(O)OCH_3$, was obtained in 66% yield and required no further purification. This method could be a useful alternative to preparing simple aliphatic esters of $SF_5CH_2C(O)OH$. Oxidation of a fluoroacetal was also used by Wakselman and coworkers to synthesize fluorocarboxylic acids [10].

We also studied the addition of SF_5Br to vinyl acetate, but this was only possible on a small scale, with considerable exertion, and lower yields, as compared to the SF_5Cl addition. The more reactive SF_5Br showed partial expulsion of SF_4 and the addition of BrF, which at elevated temperature (> -110 °C) was the sole reaction. The product, most likely $CH_2BrCHFOAc$ according to ^{19}F NMR spectroscopy, decomposed readily and was therefore not characterized further.

$$SF_5Br + CH_2{=}CHOAc \rightarrow \begin{cases} CH_2BrCHF(OAc) & \{>-110\ °C\} \\ SF_5CH_2CHBr(OAc) & \{<-110\ °C\} \end{cases} \quad (4)$$

Qualitatively, we also found that $SF_5CH_2CHBr(OAc)$ is convertible to acetals, as found for $SF_5CH_2CHCl(OAc)$.

In our second sequence, SF_5Br was added to ethyl acrylate; because the double bond in acrylic esters is less reactive than in vinyl acetate, it was possible to use SF_5Br without the expulsion of SF_4 to any extent.

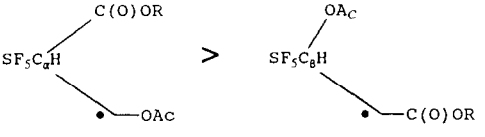
$$CH_2{=}CHC(O)OC_2H_5 + SF_5Br \longrightarrow SF_5CH_2CHBrC(O)OC_2H_5 \quad (5)$$

The above reaction proceeds in the absence of solvent and in a controlled fashion, as opposed to the reaction of vinyl acetate and SF_5Br [eqn. (4)]. It was not possible to dehydrobrominate the adduct as apparently the α-hydrogen atom is more acidic than the β-hydrogen, which therefore leads to the elimination of $\{HSF_5\}$. The ensuing product, α-bromoethyl acrylate [11] was indeed detected.

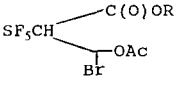
$$SF_5CH_2CHBrC(O)OC_2H_5 \xrightarrow{-HSF_5} \begin{cases} \xrightarrow{X} SF_5CH{=}CHC(O)OC_2H_5 \\ CH_2{=}CBrC(O)OC_2H_5 \end{cases} \quad (6)$$

The greatly different reactivities of vinyl acetate and ethyl acrylate towards SF_5Br should make it possible to introduce the SF_5 group at a secondary carbon atom if β-acetoxyethyl acrylate [12]* were used as the substrate. It has already been seen that SF_5X (X = Br, Cl) adds to vinyl acetate as well as to ethyl acrylate, such that the SF_5 group is attached at the terminal carbon. The addition to vinyl acetate is much more efficient than the addition to ethyl acrylate, as inferred from the almost uncontrollable reaction of the former with SF_5Br and the comparatively mild reaction with the latter.

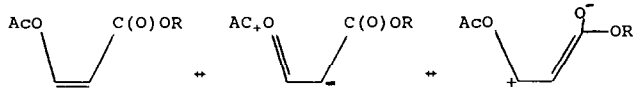
The radical chain-transfer coefficient for a compound parallels the increase in radical reactivity of the radical formed: vinyl acetate > methyl acrylate [13]. Hence, if the SF_5 radical adds at the end of vinyl acetate, a more reactive radical should result than from terminal addition to ethyl acrylate. Assuming that the characteristics of vinyl acetate and ethyl acrylate are retained independently to some degree in β-acetoxyethyl acrylate, addition of $SF_5\cdot$ to C_α should lead to a more reactive radical than addition to C_β:



The addition of SF_5X to C_α should therefore be preferred to addition to C_β with the preponderance of the product shown:

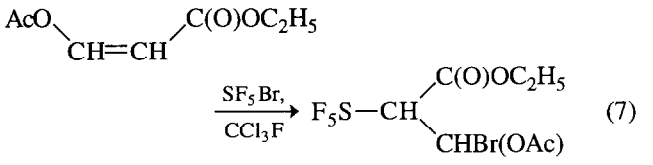


A stronger argument for this orientation of addition comes from a consideration of polar effects: an electrophilic radical such as $SF_5\cdot$ tends to be more reactive with electron-rich rather than electron-poor olefins, as exemplified with vinyl acetate and ethyl acrylate. Mesomeric structures for ethyl acrylate, vinyl acetate and β-acetoxyethyl acrylate show that, in the latter, an increase in charge density is to be expected at the position vicinal from the OAc group and should therefore be the primary position of $SF_5\cdot$ radical attack.



For this reason, our third reaction sequence was concerned with an investigation of the reactivity of β-acetoxyethyl acrylate towards pentafluorothio halides. While β-acetoxyethyl acrylate did not react at all thermally with SF_5Cl or SF_5Br, addition of SF_5Br occurred photochemically at low temperature; the product was sensitive to elevated temperatures. In the dark, no SF_5Br addition was observed at room temperature.

*Both Freeman *et al.* and Salmon *et al.* describe β-acetoxyethyl acrylate as a yellow liquid. It was found that slow distillation resulted in a completely colorless oily product.



(7)

In comparison to ethyl acrylate and vinyl acetate, the reactivity of β-acetoxyethyl acrylate is greatly diminished, as inferred from the reaction conditions. Steric reasons for this were ruled out, as it was possible to react SF_5Cl with β,β-dialkoxyalkyl acrylates. In these cases, only the chloromalonates could be detected (gas chromatography–mass spectroscopy).

A second (minor) product was also present in reaction (7), and it is assumed that it was the reverse SF_5Br addition product, i.e. RO(O)CCHBrCH(SF_5)OAc; this could only be observed via ^{19}F NMR spectroscopy and was difficult to remove by distillation. The assignment was based upon the observation that sulfur-bonded fluorine NMR signals suffer an upfield shift when the SF_5-bearing carbon is substituted with an electronegative element (e.g. $\phi_{B4} = 53$ ppm in F_5SCHCF_2O [14]). This was observed for this minor product with $\phi_{B4} = 52$ ppm, while the major product had a normal (within the realm of expectation for such compounds) shift of $\phi_{B4} = 67.3$ ppm. This product exhibited two C=O bands in the infrared spectrum, at 1783 cm^{-1} similar to $F_5SCH_2CH(Cl, Br)OAc$ (1778 cm^{-1}) and at 1754 cm^{-1}, similar to $F_5SCH_2C(O)OCH_3$ (1757 cm^{-1}).

Unfortunately, the subsequent reaction of the bromoacetate $F_5SCH(C(O)OC_2H_5)CHBr(OAc)$ with an excess of ethanol or methanol did not result in an acetal. Instead, as revealed by ^{19}F NMR spectroscopy, an intricate reaction ensued, with the appearance and disappearance of several SF_5 resonances, and the final establishment of two close-lying resonances of about equal intensity at $\phi_{B4} \approx 72$ ppm. The infrared band at 1783 cm^{-1} disappeared during the course of the reaction. Gas chromatography–mass spectroscopy (DB5 column, 25 m) revealed that a complicated mixture was formed, and the masses of the expected acetals could not be detected. It was found that several of the compounds contained bromine. Further study of this system was abandoned, as distillation resulted in the formation of at least four new SF_5 compounds (^{19}F NMR spectroscopy).

The fourth example concerns the addition of SF_5Cl to allyl acetate; the reaction was very slow (2 weeks, 100 °C, 60% yield) and produced 2-chloro-3-SF_5-propyl acetate:

$$SF_5Cl + CH_2{=}CHCH_2OAc \longrightarrow F_5SCH_2CHClCH_2OAc \quad (8)$$

Treatment with base did not produce an epoxide but rather an allylic alcohol in either aqueous KOH or methanolic CH_3ONa. The reaction in methanol took place with only 1 equiv. of base; the allylic alcohol must have been formed by transesterification of an intermittently-formed $SF_5CH{=}CHCH_2OAc$.

$$F_5SCH_2CHClCH_2OAc \xrightarrow{KOH(aq.)} SF_5CH{=}CHCH_2OH \quad (9)$$

To our knowledge, this is the third alcohol that derives from sulfur hexafluoride, the others being $SF_5CH_2CH_2OH$ [15] and $SF_5(CF_2)_4CH_2OH$ [16]. It should be pointed out that, with $SF_5CH_2CHCl(OAc)$, HCl elimination seems to be the first step in the base-induced conversion to SF_5CH_2CHO. When $SF_5CH_2CHCl(OAc)$ was treated with 1 equiv. of methanolic KOH, $SF_5CH_2CH(OCH_3)OAc$ (probably formed by nucleophilic addition of methanol to an intermittently-formed $SF_5CH{=}CHOAc$) was isolated along with SF_5CH_2CHO and $SF_5CH_2CH(OH)_2$.

Experimental

General methods

Volatile materials were handled in conventional Pyrex glass vacuum lines, equipped with either mercury manometers or Heise–Bourdon tube gauges and a Televac vacuum gauge. ^1H and ^{19}F NMR spectra were usually run at 90 MHz (^1H) and 84.67 MHz (^{19}F) on a Varian EM-390 spectrometer, otherwise they were run, as indicated, on a Bruker AMX-400 spectrometer (^1H at 400.6 MHz). The following abbreviations are used to indicate splitting patterns: s = singlet; d = doublet; t = triplet; q = quartet; p = pentet, quintet; m = multiplet.

Infrared spectra were obtained from neat samples placed between KBr or NaCl plates on a Nicolet DX-20 spectrometer. Band intensities are indicated by the following abbreviations: vs = very strong; s = strong; m = medium; w = weak; vw = very weak; br = broad; sh = shoulder.

The mass spectra were obtained on a VG 7070 mass spectrometer under the conditions indicated for each compound. In the mass spectra of bromine or chlorine compounds, the masses of fragments of only one isotope are listed, i.e. for ^{35}Cl and ^{79}Br. The ionization mode is indicated by the following: EI = electron impact; CI = chemical ionization.

Elemental analyses were carried out by Mikroanalytisches Laboratorium Beller, Göttingen, Germany.

Preparation of $F_5SCH_2CHBrOAc$

Into a 300 ml dry glass-vessel containing a stirring bar and equipped with a Kontes Teflon valve, 100 ml of CCl_3F, previously dried over P_4O_{10}, was vacuum-transferred. Then 12.67 g of SF_5Br (61.2 mmol) were

condensed into the solvent. The CCl_3F was allowed to melt and dissolve the SF_5Br. Freshly distilled vinyl acetate (Aldrich, 10.0 g, 116.3 mmol) was added by vacuum-transfer and the reaction vessel was allowed to warm slowly in a cold bath until the solution started to melt; it was then swirled so as to achieve complete mixing. Another 7.8 g (37.7 mmol) of SF_5Br was added by the same method. The reaction mixture was now allowed to attain room temperature slowly with stirring. Only slight bubbling was observed. The solvent was then removed (rotary evaporator) leaving 19.8 g of a lightly yellowish liquid. Distillation through a 12 cm Vigreux column gave 8.5 g of a main fraction, b.p. 45–48 °C/6 mmHg. The foreshot and the 48–49 °C fraction (2.0 g in total) had the same composition (^{1}H NMR spectroscopy) as the main fraction. Yield 10.5 g, 36.2%. The 48–49 °C fraction was used for analysis.

^{1}H NMR ($CDCl_3$, $Si(CH_3)_4$ ext.): $\delta_1 = 2.10$ ppm [s, rel. int. = 3.17 (CH_3)]; $\delta_2 = 4.74$ ppm [m, rel. int. = 1.92 (CH_2)]; $\delta_3 = 7.15$ ppm [d–d, rel. int. = 1.00 (CH)]; $J_{23}(cis) = 9.6$ Hz, $J_{23}(trans) = 3.0$ Hz. ^{19}F NMR (neat sample, CCl_3F ext.): (AB_4), $\phi_A = 81.4$ ppm (9 lines, rel. int. = 0.96); $\phi_B = 65.9$ ppm (d–m, rel. int. = 4.0); $J_{AB} = 146.4$ Hz. IR (NaCl, neat sample) (cm^{-1}): 3042 (w); 3023 (w); 2988 (w–vw); 1778 (vs); 1419 (m); 1377 (m–s); 1358 (w–m); 1312 (w); 1203 (vs); 1193 (vs, sh); 1103 (s–vs); 1040 (vs); 998 (m); 941 (m–s); 879 (vs); 844 (vs); 817 (s–vs); 735 (w); 675 (w); 645 (vw); 614 (w); 602 (m); 577 (w); 564 (vw). Analysis: Calc. for $C_4H_6BrF_5O_2S$: C, 16.39; H, 2.06; Br, 27.27; F, 32.42; S, 10.94%. Found: C, 17.19; H, 2.18; Br, 28.86; F, 30.4; S, 9.90%.

Preparation of $F_5SCH_2CH(OC_2H_5)_2$

To 22.86 g of $F_5SCH_2CHClOAc$ (92.0 mmol) in a 100 ml round-bottom flask, 32.46 g of absolute ethanol (705.6 mmol, 1.56-fold excess) was added at room temperature. The lightly stoppered flask was set aside. After 2 d there was still some $F_5SCH_2CHClOAc$ (IR spectrum), but after another 48 h all the compound had been consumed. The mixture was poured into 200 ml of water, washed again with water (2 × 30 ml), dried (Na_2SO_4) and distilled through a 12 cm Vigreux column. Product (16.47 g, 73.4%) boiling from 66–72 °C/19–20.5 Torr was collected.

^{1}H NMR ($CDCl_3$, $Si(CH_3)_4$ ext.): $\delta_1 = 1.27$ ppm (t, 6H, CH_3, $J_{H-H} = 7.1$ Hz); $\delta_2 = 3.67$ ppm (m, 6H, $H_3CCH_2 + F_5SCH_2$); $\delta_3 = 4.92$ ppm (t, 1H, CH, $J_{H-H} = 5.2$ Hz). ^{19}F NMR (neat sample, CCl_3F ext.): (AB_4), $\phi_A = 83.7$ ppm (9 lines, rel. int. = 1.0); $\phi_B = 66.8$ ppm (m, rel. int. = 4.0); $J_{AB} = 143.8$ Hz. IR (cm^{-1}): 3035 (vw); 2985 (s); 2936 (m); 2904 (m); 2893 (m); 2805 (vw); 1484 (w); 1458 (w, sh); 1448 (w–m); 1417 (m); 1378 (m–s); 1361 (m); 1349 (m); 1300 (w); 1229 (w); 1159 (m, sh); 1125 (s–vs); 1063 (s–vs); 1023 (s, sh); 1000 (w–m, sh); 935 (w–m); 906 (s); 865 (s–vs); 840 (vs); 817 (vs); 737 (w–m); 710 (s); 667 (w); 643 (s); 630 (m); 620 (m); 600 (s); 566 (m); 539 (w). MS. (EI, 70 eV) (mass, species, % > 2): 243, $(M-H)^+$, 0.15; 201, $(M+H-C_2H_5-CH_3)^+$, 5.0; 200, $(M-C_2H_5-CH_3)^+$, 4.9; 199, $(M-C_2H_5O)^+$, 100; 179, $C_4H_7F_4OS^+$, 14.2; 178, $C_4H_6F_4OS^+$, 2.5; 177, $C_4H_5F_4OS^+$, 40.2; 171, $(M-C_2H_5-OC_2H_4)^+$, 26.5; 153, $(M-C_2H_5O-C_2H_5OH)^+$, 3.0; 152, $(M-2C_2H_5OH)^+$, 2.0; 151, $C_2SF_5^+$, 54.3; 127, SF_5^+, 1.2; 107, $C_6H_3O_2^+$, 2.5; 104, $C_6O_2^+$, $CH_3SF_3^+$, 3.5; 103, $CH_2SF_3^+$, 59.7; 92, $C_6H_4O^+$, C_2HFOS^+, 2.7; 91, C_2FOS^+, 57.4; 89, SF_3^+, 19.5; 87, $C_2H_2O_2C_2H_5^+$, 2.4; 79, $FSC_2H_4^+$, 2.9; 77, $FSC_2H_2^+$, 11.8; 75, FSC_2^+, $C_2H_3OS^+$, 8.0; 73, C_2HOS^+, $C_3H_5O_2^+$, 7.9; 72, C_2OS^+, $C_3H_4O_2^+$, 2.9; 70, two fragments, SF_2^+, $C_3H_2O_2^+$, 2.2, 1.9; 69, $C_3HO_2^+$, $C_2OC_2H_5^+$, 3.2; 65, C_4HO^+, 1.5; 64, C_4O^+, 2.0; 63, CFS^+, 71.3; 61, $(SC_2H_3+2H)^+$, 11.4; 59, $SC_2H_3^+$, $CH_2OC_2H_5^+$, 2.3; 57, SC_2H^+, $COC_2H_5^+$, 4.7; 56, SC_2^+, $COC_2H_4^+$, 3.6; 55, $COC_2H_3^+$, 6.8; 54, $COC_2H_2^+$ 1.1 Analysis: Calc. for $C_6H_{13}F_5O_2S$: C, 29.51; H, 5.37; F, 38.9; S, 13.13%. Found: C, 29.50; H, 5.23; F, 39.0; S, 13.03%.

Preparation of $F_5SCH_2CH(OCH_3)_2$

This compound was obtained by a procedure similar to that for $F_5SCH_2CH(OC_2H_5)_2$ with methanol. Yield 81.2%, b.p. 83–84 °C/96 mmHg.

^{19}F NMR (neat sample, CCl_3F ext.):(AB_4), $\phi_A = 83.1$ ppm (9 lines, rel. int. = 1.0); $\phi_B = 66.5$ ppm (d–m, rel. int. = 4.0); $J_{AB} = 144.7$ Hz. IR (neat sample, NaCl) (cm^{-1}): 2960 (vw); 2945 (w); 2847 (vw); 1465 (w); 1451 (w); 1418 (w); 1387 (w); 1387 (w); 1187 (w–m); 1126 (m); 1078 (m); 1060 (w–m, sh); 1023 (w–m); 976 (w–m); 879 (m–s); 840 (vs); 817 (vs); 725 (w–m); 712 (w–m); 641 (w).

Preparation of $F_5SCH_2C(O)OCH_3$

To 2.96 g of $F_5SCH_2CH(OCH_3)_2$ (13.7 mmol) in a 50 ml round-bottomed flask containing a stirring bar, 2.96 g of *m*-chloroperbenzoic acid (*c.* 85%, *c.* 14 mmol, Aldrich) were added and a reflux condenser was attached. The mixture was heated slowly with stirring to 100 °C when a homogeneous melt was obtained. After *c.* 2.5 h the melt solidified, but after heating overnight (16 h) it was liquid again. A ^{19}F NMR spectrum indicated the reaction to be incomplete. Another 1.5 g of peracid was added and heating continued at 96 °C for 20 h. From the mixture, 1.82 g of crude product was collected by vacuum condensation. This product was 99% pure by GC analysis. Yield 66.4%. A sample for elemental analysis was obtained by preparative gas chromatography on an SE-30 column at 100 °C. The ester is a clear, colorless pleasant-smelling liquid.

^{1}H NMR ($CDCl_3$, $Si(CH_3)_4$ ext.): $\delta_1 = 4.58$ ppm [s, rel. int. = 3.0 (CH_3)]; $\delta_2 = 5.08$ ppm [p, rel. int. = 2.0 (CH_2)]; $J_{HF} = 7.7$ Hz. ^{19}F NMR (neat sample, CCl_3F ext.): (AB_4), $\phi_A = 78.2$ ppm (9 lines, rel. int. = 1.02); $\phi_B = 69.0$ ppm (d–m, rel. int. = 4.00); $J_{AB} = 145.7$ Hz. IR (neat sample, NaCl) (cm^{-1}): 3058 (w); 3002 (w); 2966 (w); 2854 (vw); 1757 (vs, C=O); 1441 (s); 1321 (s); 1272 (m); 1166 (s); 1009 (m); 948 (m); 836 (vs); 787 (m); 709 (m); 660 (m); 611 (w); 569 (vw). MS (EI, 70 eV) (mass, species, % > 1): 181, $(M-F)^+$, 1.5; 180, $(M-HF)^+$, 1.2; 171, $C_2H_4F_5OS^+$, 4.0; 170, $(M+-H-CH_3O)^+$, 2.9; 169, $(M-CH_3O)^+$, 81.7; 168, $(M-CH_3OH)^+$, 2.1; 149, $(M-CH_3O-HF)^+$, 2.1; 131, $(M-CH_3O-2F)^+$, 2.3; 127, SF_5^+, 20.8; 122, $FSCCOOCH_3^+$, 3.1; 119, $C_3FO_2S^+$, 2.2; 91, C_2FOS^+, 5.1; 89, SF_3^+, $C_2HO_2S^+$ (two fragments), 100, 30.2; 74, $CH_2COOCH_3^+$ (^{13}C), 1.7; 73, $CH_2COOCH_3^+$ (^{12}C), 46.3; 72, $CH_2COOCH_2^+$, 11.0; 70, SF_2^+, 6.8; 69, $C_3HO_2^+$, 8.6; 65, CH_2FS^+, 3.1; 62, CH_2OS^+ (rearr.), 2.7; 61, $CHOS^+$ (rearr.), 64.6; 60, COS^+, $C_2H_4O_2^+$, 4.3; 59, $C_2H_3O_2^+$, 36.9; 51, SF^+, H_2SO^+ (two fragments), 2.2, 2.1. Analysis: Calc. for $C_3H_5F_5O_2S$: C, 18.00; H, 2.52; F, 47.5; S, 16.02%. Found: C, 18.17; H, 2.58; F, 48.2; S, 15.96%.

Preparation of $F_5SCH(CHBrOAc)C(O)OC_2H_5$

Into a thoroughly dried 100 ml Pyrex glass Carius tube containing a magnetic stirring bar, 10.01 g of $AcOCH=CHC(O)OC_2H_5$ (63.4 mmol) and 45 ml of CCl_3F (dried over P_4O_{10}) was added. The solution was degassed three times by freeze–pump–thaw–freeze cycles, and then 18.15 g (87.7 mmol) of bromine-free SF_5Br (shaken with Hg) was added via vacuum-transfer. The lower part of the tube (*c.* 3 cm) was immersed in an ice bath, and the solution was stirred and irradiated (GE-250 W sunlamp, 80 cm distance) for 14 h. When the volatile materials were condensed into a very dry cold trap, it was found that the residue still contained some olefin; the volatile materials in the cold trap and an additional 4.36 g of SF_5Br (21.1 mmol) were recondensed into the Carius tube. Irradiation at ice temperature was continued for 7.5 h (50 cm distance). A check of the IR spectrum showed that some olefin was still present. For this reason, the volatile materials were recondensed as above and irradiation was continued for another 10 h (30 cm distance) at 0 °C. The solution was by now distinctly yellow and a precipitate had appeared; no C=C bonds were detected in the IR spectrum of the condensation residue (the Carius tube was stored between operations in an ice bath). After vacuum transfer of the volatile materials, 20.5 g of a light brown oil remained; yield (crude) 88.7%. The ^{19}F NMR spectrum showed that a very small amount of an impurity exhibiting peaks at −120 ppm to −130 ppm was present; when the reaction was not carried out at low temperature, there was much more of this impurity present. Part of this crude product was distilled (5.01 g, 0.017 Torr) when a fraction, boiling range 55–70 °C (1.81 g, first fraction, oil bath temperature = 100 °C), containing some of the C–F impurity ($\phi = -120$ to −130 ppm), showed some enrichment of the $\phi \approx 52$ ppm impurity; the second fraction, b.p. 58–61 °C (1.20 g, oil bath temperature = 90 °C, very slow distillation), a colorless oil, was free of the C–F impurity. The samples were stored in a refrigerator since they turned yellowish at room temperature within hours. Yield (extrapolated) 56%. The purity of the second fraction was estimated from ^{19}F NMR measurements to be 98% with the contaminant being the $\phi_B \approx 52$ ppm SF_5 compound.

^{1}H NMR (neat sample, $Si(CH_3)_4$ ext.): $\delta_1 = 1.68$ ppm [t, rel. area = 3.1 (CH_3CH_2)]; $\delta_2 = 2.55$ ppm [s, rel. area = 3.0 ($CH_3C(O)O$)]; $\delta_3 = 4.74$ ppm [q, rel. area = 2.0 (CH_3CH_2)]; $\delta_4 = 5.53$ ppm [d–p, rel. area = 1.0 ($CHCOOC_2H_5$)]; $\delta_5 = 7.63$ ppm [d, rel. area = 0.9, ($CH_3C(O)OCH$)]; $J_{13} = 7.22$ Hz, $J_{45} = 10.8$ Hz, $J_{4B} = 5.7 \pm 0.2$ Hz (coupling to SF_5, AB_4). All lines were broadened. ^{19}F NMR (neat sample, CCl_3F ext.): $\phi_A = 79.0$ ppm (9 lines, rel. area = 1.0); $\phi_B = 67.3$ ppm (d–m, rel. area = 4.0); $J_{AB} = 149.7$ Hz. IR (neat sample, KBr) (cm^{-1}): 3025 (vw, sh); 2992 (w); 2945 (vw); 1784 (s); 1754 (s); 1470 (w); 1449 (w); 1440 (w); 1373 (m); 1354 (w); 1308 (m); 1262 (m); 1195 (s); 1164 (m, sh); 1116 (m); 1101 (m, sh); 1054 (s); 1034 (m, sh); 969 (vw); 940 (vw); 890 (s); 854 (vs); 795 (m); 735 (vw); 697 (w, br); 671 (w); 665 (w); 621 (w); 599 (m); 570 (m); 525 (w). MS (EI, 70 eV) (mass, species, % > 1%): 285, $(M-Br)^+$, 1.7; 197, $(M-Br-COOC_2H_5-CH_3)^+$, 2.2; 194, $(M-Br-COOC_2H_5-O-2H)^+$, 1.1; 168, F_5SCHCO^+, 1.3; 166, $C_3H_3F_5S^+$, 2.2; 149, $C_2HF_4OS^+$, 7.1; 146, $C_5H_3FO_2S^+$, 1.9; 127, SF_5^+, 1.4; 89, SF_3^+, 6.7; 88, $C_2O_2S^+$, C_3HFS^+, 1.0; 87, C_3FS^+, 3.1; 73, $C_3H_5O_2^+$, 1.1; 71, $C_3H_3O_2^+$, 5.1; 70, SF_2^+, $C_3H_2O_2^+$, 1.9; 69, $C_3HO_2^+$, 3.2; 45, $C_2H_5O^+$, 3.8; 44, $C_2H_4O^+$, 3.9; 43, CH_3CO^+, $C_2H_3O^+$, 100.0. Analysis: Calc. for $C_7H_{10}BrF_5O_4S$: C, 23.03; H, 2.76; Br, 21.88; F, 26.0%. Found: C, 22.77; H, 2.67; Br, 22.21; F, 25.4%.

Preparation of $F_5SCH_2CHBrC(O)OC_2H_5$

SF_5Br (41.42 g, 200.1 mmol) was transferred to a 75 ml steel vessel held at −196 °C, then 19.78 g (197.8 mmol) of ethyl acrylate, dried over $MgSO_4$, was condensed in at the same temperature and the vessel allowed to slowly attain room temperature. When the vessel had reached 10–15 °C, it was noticed that the temperature climbed rapidly to about 50 °C, from where it dropped slowly back to room temperature. The vessel was kept at room temperature for 2 h, then warmed to 55 °C for 19 h. After removing volatile materials from the vessel, 4.72 g of a viscous liquid was obtained.

The combined products from the bomb were distilled using a 12 cm Vigreux column (3 Torr), yielding one fraction (21.55 g) boiling at 66.5–67.8 °C. Upon raising the temperature, the residue turned yellow; the pressure was lowered to 0.005–0.020 Torr (dynamic vacuum) and 3.07 g of a fraction boiling >110 °C was collected. The cold trap contained 1.08 g of a material which was mainly ethyl acrylate (^{1}H NMR spectroscopy). Yield 35.5% of theory.

^{1}H NMR (neat sample, $Si(CH_3)_4$ ext.): $\delta_1 = 1.33$ ppm [t, rel. area = 3.00 (CH_3)]; $\delta_2 = 4.30$ ppm [q, (CH_3CH_2), $J = 7.2$ Hz]; $\delta_3 = 3.6$–5.0 ppm [m, total area (quartet + multiplet) = 5.04 ($SF_5CH_2CH + CH_3CH_2$)]. ^{19}F NMR ($CHCl_3$, $CFCl_3$ ext.): (AB_4), $\phi_A = 81.49$ ppm; $\phi_B = 65.83$ ppm (d–m, $J_{AB} = 147.4$ Hz). ^{19}F NMR (neat sample, $CFCl_3$ ext.): $\phi_A = 81.00$ ppm; $\phi_B = 65.17$ ppm. IR (neat sample, KBr) (cm^{-1}): 3042 (w); 2988 (w–m); 2946 (w–vw); 2912 (vw); 2881 (vw); 1750 (vs); 1477 (w, sh); 1469 (w–m); 1456 (w–m); 1417 (m); 1398 (m); 1378 (m–s); 1356 (m); 1311 (m–s); 1262 (m–s); 1241 (s); 1206 (w, sh); 1187 (m–s); 1158 (m–s); 1116 (w, sh); 1097 (w); 1089 (w, sh); 1034 (m); 1018 (m); 988 (m); 965 (w–vw); 926 (w); 877 (s–vs); 851 (vs); 832 (vs); 802 (m–s); 740 (w, br); 698 (vw); 673 (vw); 648 (vw); 623 (vw); 602 (m); 577 (s); 564 (m); 481 (w). MS (EI, 70 eV) (mass, species, % > 1): 179, $C_5H_7BrO_2^+$, 6.3; 155, $SF_5C_2H_4^+$, 18.6; 153, $SF_5C_2H_2^+$, 28.1; 151, $F_5SC_2^+$, 2.1; 135, $C_2{}^{79}BrO_2^+$, 3.2; 135, $SF_4C_2H_3^+$, 2.9; 127, SF_5^+, 13.5; 126, $SF_3C_3H^+$, 1.5; 125, $SF_3C_3^+$, 15.0; 109, $C_3H_3F_2S^+$, 9.1; 108, SF_4^+, 66.2; 107, $C_3H_4FOS^+$, 12.5; 106, $C_3H_3FOS^+$, 65; 105, $C_3H_2FOS^+$, 10.2; 99, $C_5H_7O_2^+$, 9.2; 89, SF_3^+, 32.7; 85, $C_4H_5O_2^+$, 2.1; 73, $C_3H_5O_2^+$, 10.6; 71, $C_3H_3O_2^+$, 2.5; 70, SF_2^+, 5.3; 67, $C_4H_3O^+$, 3.6; 56, $C_3H_4O^+$, C_2S^+ (two fragments), 4.9, 3.7; 30.9; 55, $C_3H_3O^+$, 100.0; 54, $C_3H_2O^+$, 5.2; 53, C_3HO^+, 6.3; 51, SF_2^+, 2.1. Analysis: Calc. for $C_4H_8BrF_5O_2S$: C, 16.28; H, 2.73; Br, 27.08; F, 32.2; S, 10.87%. Found: C, 20.10; H, 2.58; Br, 28.68; F, 29.4; S, 9.86%.

Attempted dehydrohalogenation of $F_5SCH_2CHBrC(O)OC_2H_5$

No tractable products were obtained from the reaction with aqueous potassium hydroxide. Both Br^- and F^- were detected in the solution. The course of the reaction both with *N,N*-dimethylaniline and diazabicyclononane was similar; with the latter, charring occurred at room temperature and the ^{19}F NMR spectrum of the reaction mixture showed a singlet at 73.6 ppm, which is probably SF_4 (δ 72.7 ppm for SF_4 in $CDCl_3$). The reaction was finally carried out at −78 °C in the following manner.

In a 50 ml round-bottomed flask equipped with a magnetic stirring bar, 1.0 g of $SF_5CH_2CHBrC(O)OC_2H_5$ (3.26 mmol) was dissolved in 15 ml of anhydrous ether. A dropping funnel containing 0.40 g of diazabicyclononane (Aldrich) (3.26 mmol) in 2 ml of ether (anhydrous) equipped with a Drierite tube was fitted onto the flask and the latter cooled in an acetone/Dry Ice bath to −78 °C. The base solution was added dropwise during 10 min. A white precipitate formed immediately upon addition of the base. When addition was completed, the mixture was allowed to slowly attain room temperature (*c.* 45 min). The white precipitate dissolved during the warming-up process, leaving an almost colorless clear solution. This was kept in a refrigerator overnight (+4 °C) when a light brown oil had separated out by the next morning (IR spectrum: no SF_5, 0.22 g). The remaining solution was freed from solvent by distillation, leaving 0.82 g of a brownish oil. This exhibited only a weak SF_5 band in its IR spectrum and traces of starting material in the ^{19}F NMR spectrum. No other fluorine compound was found. The ^{1}H NMR spectrum indicated as the sole product that which was obtained earlier in the attempted dehydrohalogenation with *N,N*-dimethylaniline together with some diethyl ether. This material was identified as 2-bromoacrylic ester by comparison of its spectra with an authentic sample (^{1}H NMR and IR spectroscopies). The product polymerized quite readily to a rubbery translucent mass.

Preparation of $F_5SCH_2CHClCH_2OC(O)CH_3$

$CH_2{=}CHCH_2OC(O)CH_3$ (Aldrich) (6.50 g, 65 mmol), 11.69 g of SF_5Cl (PCR, 72 mmol) and 25 ml of CCl_3F were heated in a 75 ml steel bomb at 95 °C for 15 d. After venting and bleeding 11.69 g of the gaseous products, the CCl_3F was distilled off at atmospheric pressure and vacuum distillation (1–2 Torr) resulted in four fractions: 1, 20–55 °C (1.54 g); 2, 55–58 °C (3.36 g); 3, 58–61 °C (4.78 g); 4, 61–62 °C (1.54 g). Fraction 1 was *c.* 95% pure adduct, the remainder being allyl acetate. Fractions 2, 3 and 4 exhibited the same ^{1}H NMR spectrum and indicated that only a trace of allyl acetate was present. The cold trap contained 1.96 g of liquid which was largely allyl acetate. Yield of 2+3+4 9.68 g (56.8%).

^{1}H NMR (neat sample, $Si(CH_3)_4$ ext.): $\delta_1 = 2.50$ ppm [s, rel. int. = 3.0 (CH_3)]; $\delta_2 = 4$–5.4 ppm (m, rel. int. = 5.5). ^{19}F NMR (neat sample, CCl_3F ext.): (AB_4), $\phi_A = 83.2$ ppm (9 lines, rel. int. = 1.02); $\phi_B = 67.7$ ppm (d–m, rel. int. = 4.00); $J_{AB} = 154.1$ Hz. IR (neat sample, NaCl) (cm^{-1}): 3029 (w); 2973 (w); 2855 (vw); 1752 (vs); 1460 (w–m); 1430 (m, sh); 1420 (m); 1385 (m–s); 1369 (m–s); 1318 (vw); 1302 (vw); 1232 (s–vs); 1111 (w); 1063 (m, sh); 1045 (m); 1026 (m); 945 (m); 873 (s); 846 (vs); 828 (vs); 728 (w); 715 (w–vw); 696 (vw); 636 (vw); 621 (w); 599 (m); 565 (w). MS (CI) (mass, species, %): 263, $[M(^{35}Cl)+H]^+$, 100; 181, $[M(^{35}Cl)-CH_3COOH-2H-F]^+$, 11.5; 136, $[M(^{35}Cl)H-SF_5]^+$, 1.5; 135, $[M(^{35}Cl)-SF_5]^+$, 29.9; 113, $(M+2H-Cl-3F-CH_3COO)^+$, 1.9; 102, SF_3CH^+, 2.8; 101, SF_3C^+, 62.9;

89, SF_3^+, 1.6; 85, $CH_3COOCH_2C^+$, $SCCCHO^+$, 6.4; 83, $CH_3COOC_2^+$, SF_2CH^+, 4.4; 81, $CHCOOC_2^+$, 6.3; 79, $C_5H_3O^+$, 3.3; 73, $CH_3COOCH_2^+$, 9.5; 71, CH_3COOC^+, 10.8; 70, SF_2^+, $C_3H_2S^+$, 4.4; 69, $CHCOOC^+$, 12.0; 67, $C_4H_3O^+$, 6.9. Analysis: Calc. for $C_5H_8ClF_5O_2S$: C, 22.87; H, 3.07; Cl, 13.50; F, 36.2; S, 12.21%. Found: C, 23.10; H, 3.19; Cl, 13.61; F, 36.5; S, 12.00%.

Preparation of $F_5SCH{=}CHCH_2OH$ by aqueous hydrolysis

$F_5SCH_2CHClCH_2C(O)OCH_3$ (4.00 g, 15.2 mmol) was stirred at room temperature with 9.0 g of a 23% KOH solution for 20 h. According to the ^{19}F NMR spectrum, all the starting material reacted. Accordingly, the lower layer was pipetted off (2.59 g, 92.3%). There was apparently no significant amount of water (as had been suggested by the IR spectrum), since drying over K_2CO_3 or CaO did not alter the IR spectrum which exhibited a broad feature at 1640 cm^{-1}. Vacuum distillation (39–42 °C/2.5 mmHg) also did not lead to an altered IR spectrum. A sample for ^1H NMR spectroscopy was prepared by preparative gas chromatography (5% QF-1 on Chromosorb W, 1 m, 120 °C).

^1H NMR ($CDCl_3$, 400 MHz, $Si(CH_3)_4$ ext.): (ABM_2X), $\delta_A = 6.67$ ppm (m, $SF_5CH{=}$); $\delta_B = 6.55$ ppm (m, $SF_5CH{=}CH$) (area A + B = 2.00); $\delta_M = 4.34$ ppm (s, CH_2, area = 2.04); $\delta_x = 1.75$ ppm (s, OH, area = 1.13); $J_{AB} = 14.8$ Hz. ^{19}F NMR (neat sample, CCl_3F ext.): (AB_4), $\phi_A = 83.1$ ppm (9 lines with doublet splitting, area = 1.0); $\phi_B = 62.3$ ppm (asymmetric doublet, area = 4.0): $J_{AB} = 151.3$ Hz, $J_{AH} = 4.2$ Hz. IR (neat sample, film on KBr plates) (cm^{-1}): 3664 (w); 3353 (m–s, br); 3103 (w–m); 2923 (w); 2879 (w); 1644 (w, br); 1449 (w–m); 1434 (w, sh); 1370 (w); 1300 (w); 1229 (w–m); 1208 (w, sh); 1097 (m–s); 1030 (m); 1009 (w–m); 984 (w–m); 940 (s); 902 (s–vs); 837 (vs); 764 (s); 726 (m); 661 (m); 648 (m); 602 (m); 571 (m); 540 (m); 441 (w–m). MS (EI, 70 eV) (mass, species, % > 2): 183, $(M-H)^+$, 0.2; 135, $(M-F-CH_2O)^+$, 48.7; 127, SF_5^+, 16.1; 116, $SF_3C_2H_3^+$, 2.4; 97, $SF_2C_2H_3^+$, 5.7; 91, $C_3H_4FS^+$, 3.7; 89, SF_3^+, $C_3H_5OS^+$, 100.0; 75, C_2FS^+, 11.1; 73, $(M+H-5F-OH)^+$, 2.1; 70, SF_2^+, 16.5; 59, $C_2H_3S^+$ $(M+H-5F-CH_2OH)^+$, 6.5; 58, $C_2H_2S^+$, 4.9; 57, $C_3H_5O^+$, 79.4; 55, $C_3H_3O^+$, 22.8; 53, C_3HO^+, 3.5; 51, SF^+, 3.4. Analysis: Calc. for $C_3H_5F_5OS$: C, 19.57; H, 2.74; F, 51.6; S, 17.41%. Found: C, 19.69; H, 2.79; F, 51.5; S, 17.48%.

Preparation of $F_5SCH{=}CHCH_2OH$ in methanolic methoxide (anhydrous conditions)

To a solution of $SF_5CH_2CHClCH_2OAc$ (2.10 g, 8.0 mmol) in 2.0 g of anhydrous CH_3OH (Mallinckrodt) contained in a 10 ml flask equipped with a magnetic stirring bar, Claisen head, Drierite tube and dropping funnel, was added a solution consisting of 0.23 g of sodium (0.01 mol) in 5.0 ml of anhydrous methanol dropwise at −20 °C (acetone/Dry Ice). No obvious reaction occurred, so the cold bath was removed and the reaction flask allowed to attain room temperature. When this temperature had nearly been reached, a white precipitate quickly formed. Addition of further CH_3ONa solution caused the formation of more precipitate. After *c.* 0.8-times the total volume of methoxide solution had been added, stirring was stopped and the precipitate allowed to settle. Addition of another drop of CH_3ONa to the clear colorless supernatant solution caused no further turbidity. After maintaining the mixture for an additional 3 h at room temperature, the methanol was removed by stirring the solution at *c.* 50 Torr for 1 h (the methanol was collected in a −196 °C trap). Distillation at 6–6.5 Torr afforded two fractions (54.5–57 °C, 0.54 g; 57–57.5 °C, 0.84 g) as colorless viscous liquids which exhibited identical IR spectra. Yield 1.38 g (93.8%). The material was identical in all respects to the product obtained by aqueous hydrolysis.

Preparation of $F_5SCH_2CH(OCH_3)OC(O)CH_3$

To 7.92 g of $F_5SCH_2CHClOC(O)CH_3$ (31.9 mmol) in 10 ml of anhydrous CH_3OH, contained in a 100 ml round-bottomed flask equipped with a magnetic stirring bar, Claisen head, Drierite tube and dropping funnel, was added 2.15 g of 85% KOH dissolved in 10 ml of anhydrous methanol (32.6 mmol). (A slight excess was necessary because the starting material and the product could not be separated by distillation when the reaction was incomplete.) The base solution was added within 20 min at −78 °C and the solution then brought slowly to room temperature. The methanol was distilled off at atmospheric pressure. A small amount of water was then added and the precipitate removed (5.50 g). No starting material was present. Distillation (30–37 °C 3–4 Torr) gave 1.58 g of $F_5SCH_2CH(OCH_3)OC(O)CH_3$. The contents of the cold trap (−196 °C) were distilled to give 2.85 g of a mixture ($F_5SCH_2CH(OH)_2$ + F_5SCH_2CHO). Yield 1.58 g (45%) together with some $F_5SCH_2CH(OCH_3)OC(O)CH_3$ (0.36 g). Total yield (1.58 + 0.36) g = 1.94 g (24.8%). An analytically pure sample was obtained by preparative GC on a Carbowax (20%) column, 3 ft., 100 °C, 1 ml He s^{-1} gas flow.

^1H NMR ($CDCl_3$, $Si(CH_3)_4$ ext.): $\delta_1 = 2.65$ ppm [s, 3.00H (OCH_3)]; $\delta_2 = 4.03$ ppm [s, 3.00H ($C(O)CH_3$)]; $\delta_3 = 4.37$ ppm [d–p, 2.07H (SF_5CH_2)]; $\delta_4 = 6.70$ ppm [t, 0.98H (CH)]; $J_{CH_2-B} = 8.23$ Hz, $J_{H-H} = 5.13$ Hz. ^{19}F NMR ($CDCl_3$, CCl_3F ext.): (AB_4), $\phi_A = 83.67$ ppm (9 lines, 1.07F); $\phi_B = 68.79$ ppm (d–m, 4.00F); $J_{AB} = 147.4$ Hz. IR (neat sample, KBr) (cm^{-1}): 3041 (vw); 3013 (vw); 2973 (w); 2948 (w); 2858 (w); 1755 (s); 1453 (w–m); 1420 (w–m); 1377 (m); 1360 (w, sh); 1300 (vw); 1255

(m, sh); 1230 (s); 1190 (m–s); 1142 (m); 1128 (m); 1083 (m, sh); 1078 (m); 1050 (m); 1014 (s); 992 (m); 941 (m, br); 879 (s); 842 (vs); 824 (s–vs); 714 (w–m); 655 (w, sh); 641 (m); 604 (m); 581 (w); 564 (w–m); 558 (w–m); 549 (w, sh); 581 (vw); 566 (w); 557 (w); 550 (vw). MS (EI, 70 eV) (mass, species, % > 1): 185, $(M-CH_3COO)^+$, 90.7 [+peaks at 187 (3.8) and 186 (4.9), S+C isotope peaks]; 184, $(M-CH_3COOH)^+$, 19.7; 169, $(M-CH_3COOH-CH_3)^+$, 1.6; 165, $(M-CH_3COO-HF)^+$, 12.3; 163, $(M-CH_3O-CH_3-O-F)^+$, 3.0; 153, $(M-CH_3COOH-CH_3O)^+$, 5.3; 149, $(M-CH_3COOH-CH_3-HF)^+$, 2.3; 127, SF_5^+, 12.0; 122, $C_3F_2OS^+$, 3.4; 103, $C_4H_7O_3^+$, 1.4; 101, $C_4H_5O_3^+$, 2.5; 96, $F_2SC_2H_2^+$, 1.1; 91, $FSCCO^+$, 1.9; 89, SF_3^+, 43.6; 87, $C_3H_3O_3^+$, 2.3; 83, $C_4H_3O_2^+$, F_2SCH^+, 1.3; 81, $C_4HO_2^+$, 1.9; 78, $C_2H_3FS^+$, 3.7; 77, $C_2H_2FS^+$, 74.5; 76, C_2HFS^+, 11.9; 75, $C_2H_3OS^+$, C_2FS^+, 8.7; 74, $C_2H_2OS^+$, 7.6; 73, C_2HOS^+, 3.3; 70, $C_3H_2O_2^+$, SF_2^+, 6.2; 69, $C_3HO_2^+$, 1.1; 65, CH_2FS^+, 3.9; 64, $CHFS^+$, 1.0; 63, CFS^+, 100.0; 61, $(CH_3CO_2H_2)^+$, 13.2; 60, CH_3COOH^+, 18.5; 59, CH_3COO^+, 1.2; 58, CH_2COO^+, 17.0; 57, $CHCOO^+$, 17.2. Analysis: Calc. for $C_5H_9F_5O_3S$: C, 24.59; H, 3.72; F, 38.9; S, 13.13%. Found: C, 24.66; H, 3.75; F, 39.4; S, 13.24%.

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