

Anionic derivatives of pentafluoro- λ^6 -sulfanyl (fluorosulfonyl) acetic acid esters

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Abstract

New ester salts $[R_3NH]^+[F_5SC(SO_2F)C(O)OR']^-$ where $R \equiv H, CH_3CH_2$ and $R' \equiv CH_3, (CH_3)_2CH$ have been prepared from corresponding esters and amines. The sodium salt $Na[F_5SC(SO_2F)C(O)OCH(CH_3)_2]$ was used to prepare the following α -substituted derivatives: $SF_5CX(SO_2F)C(O)OCH(CH_3)_2$, $X \equiv Br, Cl$. The crystal structure of $[(C_2H_5)_3NH]^+[F_5SC(SO_2F)C(O)OCH_3]^-$ was determined and is monoclinic: $P2_1/n$; $a = 8.758(2)$ Å, $b = 9.645(2)$ Å and $c = 19.167(4)$ Å; $\beta = 97.92(3)^\circ$; $V = 1603.6$ Å³; $Z = 4$.

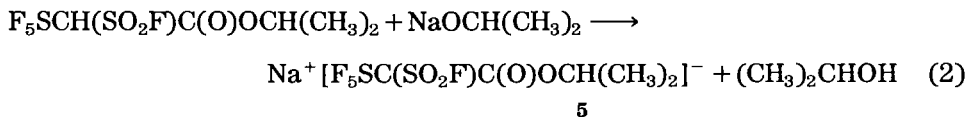
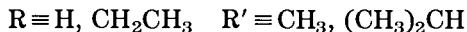
Introduction

Fluorine is particularly effective in stabilizing anionic charges in organic compounds. This is seen, for example, in the increasing pK_a values of fluorinated acetic acids, in the isolation of stable fluoro carbanions, or in the occurrence of products which can only be accounted for by the formation of intermediate fluorocarbanions. Stable anion salts of the methyl ester of 2-*H*-2-fluorosulfonyl trifluoropropionic acid were isolated and used for various substitution reactions [1]. By comparison with a CF_3 group, the charge-stabilizing effect of the SF_5 group [2] should allow one to synthesize and derivatize analogous SF_5 -containing anions. The preparation of such anions should offer a way to introduce carbon substituents α to the SF_5 group. A general method for this is still lacking, and only in selected cases will an SF_5 group be found on a secondary carbon. Some examples are $F_5SCH(CF_3)CF_2Cl$ [3] and $SF_5(CH_3)C=CCl(OCH_3)$ [4] by addition of SF_5Cl to $F_3CCH=CF_2$ and $H_3CC \equiv COCH_3$ or for $F_5SCF(CF_3)CH_2CH_2I$ by addition of $F_5SCF(CF_3)I$ to C_2H_4 [5].

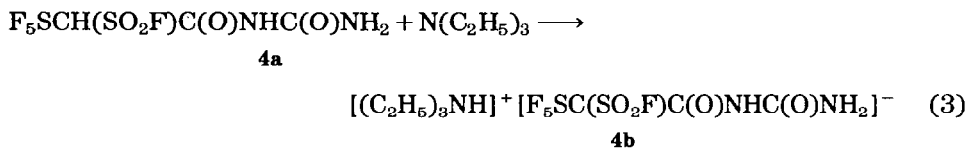
While the acid $F_5SCH(SO_2F)COOH$ is unstable and cannot be isolated, various esters of the acid can be prepared and can be used to prepare new ester salts and α -substituted products.

Results and discussion

We have found that SF₅-containing ester salts are accessible by the following routes:



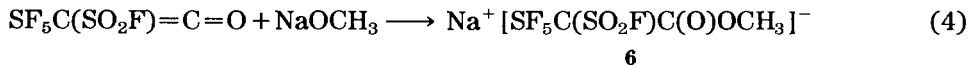
From eqn. (1), the triethylammonium salts of the methyl **1** and isopropyl esters **2** were formed and isolated as solids in nearly quantitative yield. On recrystallization from chloroform the solids were obtained as large irregular crystals; the isopropyl derivative was stored in a closed container for several months at room temperature without decomposition. Other anions that could be isolated but showed only low stability were the ammonium salt of the ester F₅SCH(SO₂F)C(O)OCH(CH₃)₂ (**3**) and the triethylammonium salt **4b** of F₅SCH(SO₂F)C(O)NHC(O)NH₂ (**4a**):



4a was obtained by reaction of the sultone F₅SCHCF₂OSO₂ with urea in ether.

The sodium salt of the isopropyl ester **5** was easily formed when the ester was treated with sodium isopropoxide in ether but attempts to isolate it pure were unsuccessful.

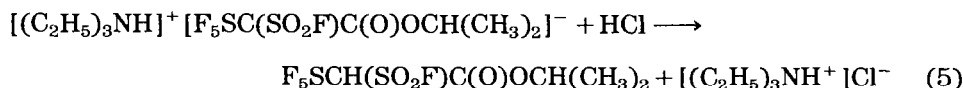
Another route to SF₅-containing ester salts involved the reaction of SF₅C(SO₂F)=C=O with sodium methoxide:



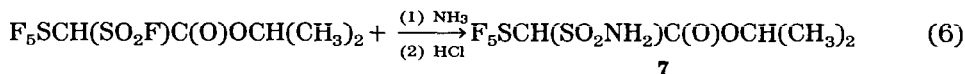
However, while this method clearly showed the formation of an SF₅-containing ester salt **6**, as determined by obtaining a ¹⁹F nuclear magnetic resonance (NMR) spectrum characteristic of SF₅ anions, it did not produce a product of high purity. Previously, stable complexes were formed from SF₅C(SO₂F)=C=O with weaker bases such as caesium fluoride and tetramethylurea [6, 7].

The reaction chemistry of the new amine salt **2** was studied. Acetone solutions of [(C₂H₅)₃NH]⁺ [F₅SC(SO₂F)C(O)OCH(CH₃)₂]⁻ did not change their ¹⁹F NMR spectra upon addition of small quantities of water but the ester was instantaneously formed upon mixing of the salt with concentrated

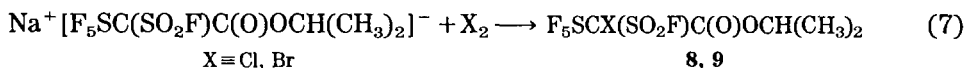
hydrochloric acid; it was recovered in nearly quantitative yield:



The triethylammonium salt **2** was also completely inert to propyl bromide. Refluxing for 1 day in an acetone solution did not produce any change in the ^{19}F NMR spectrum. Interestingly, it was possible to obtain the sulfonamide of the isopropyl ester **7** when an excess of ammonia was added to the ester dissolved in dioxane at temperatures of about 50 °C, followed by recrystallization from diluted HCl; if the ammonia is added too quickly, charring of the ester occurred:



In place of the amine salt, the reaction chemistry of sodium salt ester **5** was studied. Solutions of this salt are sufficiently stable to carry out various studies, and with bromine and chlorine the following reaction was observed:



The chloro product **8** was isolated and characterized; the bromo material could not be purified. It is important to note, however, that α substitution relative to the SF_5 group was found.

With other reagents, such as $BrCN$, $CH_3CH_2CH_2Br$, $ClC(O)OCH_3$, $CH_2=CHCH_2Br$ and $CH_3C(O)Cl$ the sodium ester salt **5** led only to recovery of the starting ester in about 50% yield, although in all cases the formation of a white precipitate was observed. One can assume that the environment of the α -C is so crowded that an S_N2 reaction is not normally possible, except for chlorine and bromine, where attack can occur along the X-X axis.

When the sodium salt of the isopropyl ester **5** was stirred for several days at room temperature in ether, without any substrate present, slow reversion to the ester occurred, accompanied by the formation of a white precipitate; the ester was finally isolated in about 50% yield. This instability contrasts with the apparent stability of the triethylammonium salt.

The fluorine NMR and IR spectra showed characteristic and significant changes upon going from the neutral compounds to the corresponding salt derivatives. The most striking observation is found in the fluorine resonances in the SF_5 and SO_2F regions, in which significant deshielding (downfield shift) is present; such shifts have been reported for other SF_5 anionic species [8a, b] and fluorocarbanions [9].

This observation is the opposite of what one would expect, i.e. an increase in charge density should lead to stronger shielding about the fluorine. This is observed for the $C(O)F$ groups in the CsF , AgF and NaF adducts of the ketene $F_5SC(SO_2F)C=O$ (Table 1).

TABLE 1

¹⁹F nuclear magnetic resonance and IR spectral data

Structure	Counterion	ϕ_A^a	ϕ_B	ϕ_{SO_2F}	J_B	ν_{CO}^b
F ₅ SC(SO ₂ F)C(O)OC ₃ H ₇ ^{-c}	Na ⁺	95.3	82.8	67.3	150.4	—
F ₅ SC(SO ₂ F)C(O)OC ₃ H ₇ ^{-d}	Na ⁺	93.5	81.7	66.2	—	—
F ₅ SC(SO ₂ F)C(O)OC ₃ H ₇ ^{-e}	(C ₂ H ₅) ₃ NH ⁺	97.0	82.1	66.3	154.0	1615
F ₅ SC(SO ₂ F)C(O)OC ₃ H ₇ ^{-d}	NH ₄ ⁺	96.1	82.0	65.8	151.3	1589
F ₅ SC(SO ₂ F)C(O)OCH ₃ ^{-f}	(C ₂ H ₅) ₃ NH ⁺	95.4	82.1	67.0	154.2	1640
F ₅ SC(SO ₂ F)CO·OC(N(CH ₃) ₂) ₂ ^g	—	89.6	79.7	71.3	154.2	1669
F ₅ SC(SO ₂ F)CONHCONH ₂ ^{-g}	(C ₂ H ₅) ₃ NH ⁺	95.7	82.0	73.1	150.2	1653
F ₅ SC(SO ₂ F)COF ^{-h}	Cs ⁺	92.8	79.2	68.7	148.0	1648
F ₅ SC(SO ₂ F)COF ⁻ⁱ	Ag ⁺	94.0	79.9	69.7	—	1764
F ₅ SC(SO ₂ F)COF ⁻ⁱ	Na ⁺	91.9	78.7	68.3	—	—

^aFor the SF₅ group the axial fluorine atom is designated as A and the four equatorial fluorine atoms as B; for the -C(O)F resonances with MF (M≡Cs, Ag, Na⁺) and F₅SC(SO₂F)C(O)F the upfield shifts are 16.4 ppm, 17.0 ppm and 16.0 ppm, respectively [7].

^bNeat samples.

^cIn isopropanol.

^dIn ether.

^eIn CD₃COCD₃.

^fIn CDCl₃.

^gIn CH₂Cl₂.

^hIn acetone.

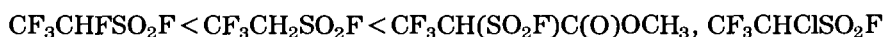
ⁱIn CH₃CN.

For the SF₅ group itself, only a small chemical shift range for A or B resonance is observed for compounds in Table 1. The axial fluorine atom undergoes a larger chemical shift change than the equatorial fluorine atoms. All compounds with the F₅SCH(SO₂F)C(O)R feature (R≡OCH₃, OCH(CH₃)₂, NHC(O)NH₂ and others [10]) show a degenerate AB₄ system at about 70 ppm as a narrow multiplet, whereas the anionic species show a normal AB₄ spectrum with F_A appearing at 89–97 ppm and F_B at 79–82 ppm. For the SO₂F group the ϕ_F values are found in the anions over a somewhat larger range and are also involved in the general deshielding phenomenon; normally the fluorine resonance of the SO₂F group would be in the 50–55 ppm range. This deshielding effect is a general indicator for the formation of these anionic complexes. An even larger deshielding is observed in the absence of a CO group β to an SF₅ group, e.g. as found for Cs[F₅SC(CF₃)₂] [8b].

As expected, the C=O stretching frequency is shifted to a lower frequency in the salts, compared with the neutral compounds. This is to be expected for an enolate-type ion. The lowering is considerable when compared with the respective neutral species (see Table 1), up to 170 cm⁻¹ in NH₄⁺[F₅SC(SO₂F)COOCH(CH₃)₂]⁻. The colour of the SF₅-containing anions ranged from pale yellow to brown in solution; the colour of the anion F₅SC(CF₃)₂⁻ is described as yellow [8b]. Table 1 summarizes the spectroscopic

parameters as discussed above; the silver and sodium salts could be detected, although not obtained in the pure state, and are added for comparison.

The ease of formation of various anionic species were compared under similar conditions. The compounds $F_5SCH_2SO_2F$ [10], $F_5SCH_2C(O)OCH_3$ [11], $F_5SCHFSO_2F$ [12], $F_5SCH(SO_2F)C(O)OCH(CH_3)_2$, $F_5SCH(SO_2NH_2)C(O)OCH(CH_3)_2$ and $F_5SCH(SO_2F)C(O)NHC(O)NH_2$ were dissolved in an NMR tube in acetone and a drop of triethylamine was then added. Only the compounds with the three functional groups SO_2F , SF_5 and $C(O)R$ exhibited the characteristic downfield shift of the SF_5 and the SO_2F fluorine resonances indicative of anion formation. In the case of the remaining compounds, no evidence was found for anion formation. These results parallel the expected acidities and can be compared with the following CF_3 compounds for which CF_3CHFSO_2F was the least acidic member [1]:



Fluorine as a +M, -I substituent should stabilize the anionic site less than chlorine, which is a weaker +M, -I substituent. Tertiary perfluoroalkyl carbanions (e.g. $(F_3C)_3C^-$) are much more stable than secondary and primary perfluorocarbanions or CF_3^- [9]. This is usually attributed to hyperconjugative stabilization.

Based on the NMR and IR results, it was of interest to examine the crystal structure of one of the ester salts. Suitable crystals of the salt **1**, $[(C_2H_5)_3NH]^+ [F_5SC(SO_2F)C(O)OCH_3]^-$, were obtained for X-ray structure analysis. In Table 2 the pertinent crystallographic data are found while in Table 3 the non-hydrogen atomic coordinates and isotropic thermal parameters are presented. Selected non-hydrogen bond lengths and angles are found in Table 4.

As seen in Fig. 1, the ester salt **1** is composed of $[(C_2H_5)_3NH]^+$ cations and $[F_5SC(SO_2F)C(O)OCH_3]^-$ anions. The anion shows some interesting bond lengths and angles when compared with other SF_5 -containing neutral compounds. The bond angles of C_1 (120.2° , 123.5° and 115.4°) shows the anion to be almost flat which is probably due in part to the steric repulsion of

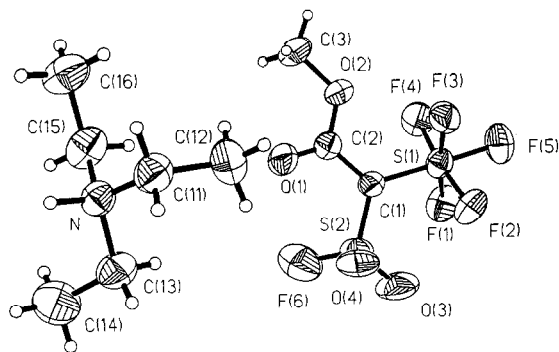


Fig. 1. Thermal ellipsoid view of $[(C_2H_5)_3NH]^+ [F_5SC(SO_2F)C(O)OCH_3]^-$.

TABLE 2

Crystallographic data for $[(C_2H_5)_3NH]^+[F_5SC(SO_2F)C(O)OCH_3]^-$

Formula	$C_9H_{19}F_6NO_4S_1$
<i>a</i>	8.758(2) Å
<i>b</i>	9.645(2) Å
<i>c</i>	19.167(4) Å
β	97.92(3)°
<i>V</i>	1603.6 Å ³
<i>Z</i>	4
<i>F.W.</i>	383.4
Space group	$P2_1/n$
<i>T</i>	293 K
λ	0.710 69 Å
ρ_{calc}	1.588 mg m ⁻³
Absorption coefficient	0.392 mm ⁻¹
Final <i>R</i> indices (observed data)	
<i>R</i>	4.62%
<i>wR</i>	5.88%
<i>R</i> indices (all data)	
<i>R</i>	5.59%
<i>wR</i>	6.75%

the three large substituents and in part to the mesomeric interaction between the anion centre at C₁, the keto group and the SO₂F group. Additional interaction would involve hyperconjugative contributions from the SF₅ group.

The SF₅–C bond length is significantly shorter in **1** (1.770(4) Å) than in a number of other neutral SF₅ systems [11, 13, 14]: (SF₅CH₂CHO)₃ (**10**), SF₅–C = 1.789(6) Å; F₅SCHCF₂OSO₂ (**11**), SF₅–C = 1.854(7) Å; F₅SCH(SO₂F)C(O)N(CH₂CH₃)₂ (**12**), F₅S–C = 1.856(5) Å, (F₅SCH(SO₂F)-CH₂)₂O (**13**), F₅S–C = 1.858(5) Å. The second C–S bond is also shorter (1.679(4) Å) than in **12** (1.801(5) Å) or in **13** (1.789(5)). Further shortening is found for the C₁–C₂ bond in **1** (1.447(4) Å) compared with the values of 1.510(6) Å for **10**, 1.508(8) Å for **11**, 1.544(6) Å for **12** and 1.513(7) Å for **13** and for the C₂–O₂ bond (1.328(4) Å) compared with a C–O single bond of 1.41 Å. It appears that the anion charge is dispersed over the entire molecule with mesomeric and hyperconjugative effects playing a dominant role for bond shortening (Scheme 1(a)–1(d)).

Another possible explanation for these results involves extensive delocalization via conjugation of C₁ (p orbital), F₅S (d orbital), FSO₂ (d orbital) and C₂ (p orbital). Also, an ionic model with increased coulombic interactions due to higher charge density at C₁ would favour shorter F₅C–C, FSO₂–C₁ and C₁–C₂ distances.

Experimental details

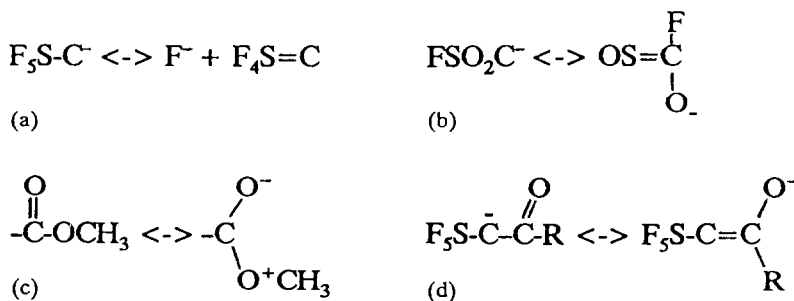
The compounds (CH₃)₂CHOH, (C₂H₅)₃N, CH₃OH, Cl₂, HCl, diethyl ether and P₄O₁₀ were obtained from commercial sources. The compounds

TABLE 3

Non-hydrogen atomic coordinates and equivalent isotropic displacement coefficients for $[(C_2H_5)_3NH]^+[F_5SC(SO_2F)C(O)OCH_3]^-$

	x ($\times 10^4$)	y ($\times 10^4$)	z ($\times 10^4$)	U_{eq}^a ($\times 10^{-1} \text{ pm}^2$)
S(1)	2077(1)	5885(1)	7006(1)	51(1)
F(1)	3068(3)	6996(3)	7466(1)	73(1)
F(2)	3580(2)	4981(3)	6987(1)	69(1)
F(3)	564(3)	6690(3)	7112(1)	70(1)
F(4)	1076(3)	4661(3)	6632(1)	64(1)
F(5)	1902(3)	5116(3)	7728(1)	86(1)
C(1)	2234(4)	6733(4)	6200(2)	44(1)
C(2)	979(4)	6830(4)	5626(2)	45(1)
O(1)	1138(3)	7185(3)	5036(1)	67(1)
O(2)	-406(3)	6523(3)	5790(1)	60(1)
C(3)	-1670(4)	6635(5)	5229(2)	71(2)
S(2)	3969(1)	7211(1)	6004(1)	57(1)
O(3)	5142(3)	7189(4)	6576(2)	94(2)
O(4)	4433(3)	6028(3)	5510(1)	64(1)
F(6)	3870(3)	8370(4)	5544(2)	115(2)
N	2383(3)	2921(3)	1111(1)	43(1)
C(11)	2313(4)	1423(4)	1301(2)	54(1)
C(12)	2324(5)	1117(5)	2070(2)	76(2)
C(13)	3904(4)	3555(5)	1427(2)	59(2)
C(14)	4214(6)	4927(6)	1105(3)	86(2)
C(15)	1037(4)	3753(5)	1287(2)	62(2)
C(16)	-493(4)	3192(6)	975(2)	71(2)

^aEquivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.



Scheme 1.

$F_5SCH(SO_2F)C(O)OCH(CH_3)_2$ [15] and $F_5SCH(SO_2F)C(O)OCH_3$ [16] were prepared as described.

Volatile materials were manipulated in a conventional Pyrex-glass vacuum line, equipped with a Heise Bourdon tube gauge and a Televac thermocouple unit. IR spectra were obtained from neat liquids or solids between KBr or NaCl plates on a Nicolet 20DX spectrometer. NMR spectra were recorded on a Varian model EM-390 spectrometer operating at 84.67 MHz for ^{19}F ,

TABLE 4

Selected non-hydrogen bond lengths pm and angles for $[(C_2H_5)_3NH]^+ [F_5SC(SO_2F)C(O)OCH_3]^-$

	Bond length (pm)		Bond angle (°)
S(1)–F(1)	157.1(3)	F(1)–S(1)–F(2)	89.6(1)
S(1)–F(3)	157.3(3)	F(1)–S(1)–C(1)	94.1(2)
S(1)–F(5)	159.5(3)	S(1)–C(1)–C(2)	123.5(3)
C(1)–C(2)	144.7(4)	C(2)–C(1)–S(2)	115.4(3)
C(2)–O(1)	120.7(5)	C(1)–C(2)–O(2)	115.4(3)
C(2)–C(3)	143.6(4)	C(2)–O(2)–C(3)	116.2(3)
S(2)–O(4)	157.1(3)	C(1)–S(2)–O(4)	104.6(2)
S(1)–F(2)	158.4(2)	C(1)–S(2)–F(6)	112.1(2)
S(1)–F(4)	158.2(3)	O(4)–S(2)–F(6)	101.3(2)
S(1)–C(1)	177.0(4)	F(5)–S(1)–C(1)	178.9(2)
C(1)–S(2)	167.9(4)	F(2)–S(1)–F(3)	173.0(1)
C(2)–O(2)	132.8(4)	S(1)–C(1)–S(2)	120.2(2)
S(2)–O(3)	139.5(3)	C(1)–C(2)–O(1)	123.8(3)
S(2)–F(6)	141.9(4)	O(1)–C(2)–O(2)	120.8(3)
		C(1)–S(2)–O(3)	114.3(2)
		O(3)–S(2)–O(4)	103.8(2)
		O(3)–S(2)–F(6)	118.4(2)

and at 90 HMz (1H), using CCl_3F and $Si(CH_3)_4$ as external standards respectively (by convention, resonances appearing downfield from CCl_3F are assigned positive values while upfield resonances are assigned negative values). Mass spectra were obtained with a VG 7070 HS spectrometer at 70 eV. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany.

The stable $[(C_2H_5)_3NH]^+ [F_5SC(SO_2F)C(O)OCH_3]^-$ salt formed colourless plates; the size of the crystal used in this study was 0.5 mm \times 0.4 mm \times 0.4 mm. The data collection was carried out on a Siemens-Stoe AED 2 diffractometer employing Mo K_α radiation ($\lambda = 0.71069 \text{ \AA}$) and a graphite monochromator. The number of reflections collected were 2998 with 1991 independent reflections ($R_{int} = 1.81\%$) and 1683 observed reflections ($F > 3.0\sigma(F)$). The structure solution was solved by direct methods. The goodness of fit was 2.03 and the final difference map showed a residual of 0.33 electrons \AA^{-3} . The Shelxtl Plus (PC version) program led to resolution of all atomic positions.

$[NH_4]^+ [F_5SC(SO_2F)C(O)OCH(CH_3)_2]^-$ (3)

Ammonia was bubbled into a solution of 0.55 g (1.80 mmol) of $F_5SCH(SO_2F)C(O)OCH(CH_3)_2$ in 14 ml of anhydrous ether, cooled to $-25^\circ C$, in a 25 ml round-bottomed flask, fitted with a Claisen head, Drierite tube and a gas inlet tube. The temperature was increased to $+15^\circ C$, when a small amount of precipitation was observed. ^{19}F NMR spectroscopy showed that the starting ester was gone, but attempts to isolate the product failed.

When isolated as a solid, the compound decomposed rather quickly upon reaching room temperature but was stable in solution. An IR spectrum was obtained by allowing the ether to evaporate on a KBr disk and immediately recording the spectrum.

^{19}F NMR (in ether, CCl_3F ext.): AB_4X , ϕ 96.1 ppm (9 lines, int. = 1.07, (F_A)); ϕ 82.0 ppm (d-m, int. = 4.00 (F_B)); ϕ 65.8 ppm p, int. = 1.02 (F_X , SO_2F); $J_{\text{AB}} = 151.3$ Hz; $J_{\text{BX}} = 10.9$ Hz.

IR ν_{max} (neat sample, KBr): 3648 (m), 3585 (m), 3400–2900 (s, br), peaks at 3037, 2995, 1743 (w), 1636 (m, sh), 1589 (s), 1543 (s, sh), 1493 (m-s), 1453 (s), 1436 (s, sh), 1399 (s), 1366 (vs), 1292 (s-vs), 1191 (s), 1181 (s), 1145 (m), 1100 (s), 1047 (m), 910 (m-s), 868 (s, sh), 850 (vs), 810 (vs), 760 (vs), 710 (m-s), 668 (s), 620 (s), 582 (s), 573 (m-s), 494 (m), 486 (m), 462 (m), 424 (m-s), 413 (m-s) cm^{-1} .

$F_5\text{SCH}(\text{SO}_2\text{NH}_2)\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2$ (7)

Gaseous ammonia was introduced slowly into a stirred solution of $F_5\text{SCH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2$ (2.40 g, 7.70 mmol) in 5 ml of dioxane contained in a 50 ml round-bottomed flask. Initially, a temperature rise was observed, and the rate of NH_3 introduction was maintained in order that the temperature stayed below 50 °C (charring is possible). When the temperature of the mixture dropped, NH_3 addition was stopped, 2 ml of water was added and most of the solvent was boiled off. Since the product still contained the starting ester, the treatment with NH_3 was repeated. The volume of the solution was further diminished and the product was obtained by recrystallization (twice) from dilute HCl ($\text{H}_2\text{O}:\text{HCl}$, 5:1) with a yield of 1.20 g (dried over P_4O_{10} in desiccator) (50.5%) of a cream-coloured amorphous mass (m.p., 244–246 °C, darkens; at 254 °C, it solidifies and forms shiny flakes; at 270 °C, it melts again; at 280 °C, it darkens).

^1H NMR (D_2O , 300 MHz, $\text{Si}(\text{CH}_3)_4$ int.) δ_1 1.30 ppm, (d, int. = 6.00 $\text{CH}(\text{CH}_3)_2$); δ_2 5.13 ppm (septet, int. = 0.97, $\text{CH}(\text{CH}_3)_2$); δ_3 5.88 ppm (p, int. = 0.77, ($F_5\text{SCH}$)); NH_2 is not observed; $J_{12} = 6.30$ Hz, $J_{\text{HB}} = 5.85$ Hz.

^{19}F NMR (H_2O , CCl_3F ext.): AB_4 , ϕ 79.8 ppm (9 lines, int. = 1.0 (F_A)); ϕ 69.2 ppm (d-m, int. = 3.6 (F_B)); $J_{\text{AB}} = 151.7$ Hz.

IR ν_{max} (KBr, neat): 3184 (m-s), 3087 (m-s), 2986 (m-s), 2880 (m), 1733 (s), 1684 (m, sh), 1460 (m-s), 1440 (m-s), 1393 (m), 1380 (m), 1353 (m), 1310 (m-s), 1265 (s), 1211 (s-vs), 1181 (s, sh), 1149 (m, sh), 1104 (m-s), 1051 (s), 945 (vw), 904 (s), 871 (s), 859 (vs), 810 (s), 783 (m-s), 741 (m-s), 682 (w), 648 (m-s), 610 (w), 592 (m-s), 572 (m), 550 (m), 521 (m), 483 (m-w), 417 (w) cm^{-1} . Mass spectrum (negative ionization, for int. > 1%): m/z 307 (0.14%, M^-), 249 (2.3%, ($\text{M}-\text{C}_3\text{H}_7\text{O}$) $^-$), 180 (1.2%, ($\text{M}-\text{SF}_5$) $^-$), 139 (2.1%, $\text{C}_5\text{HNO}_2\text{S}^-$), 129 (4.0%, $\text{C}_4\text{HO}_3\text{S}^-$), 127 (59.7% SF_5^-); 124 (7.1%, $\text{C}_2\text{HFO}_3\text{S}^-$, C_2HOS_2^- , $\text{CH}_2\text{NO}_2\text{S}_2^-$); 123 (2.4%, $\text{C}_2\text{FO}_3\text{S}^-$, C_2FOS_2^- , $\text{CHNO}_2\text{S}_2^-$); 122 (2.4%, CNO_2S_2^-); 118 (2.2%, $\text{C}_2\text{NO}_3\text{S}^-$); 113 (2.2%, $\text{C}_2\text{F}_3\text{S}^-$); 110 (4.5%, $\text{C}_2\text{F}_2\text{OS}^-$); 108 (100.0%, SF_4^-); 105 (1.6; 98%, ($\text{CCHSO}_2\text{NH}_2$) $^-$); (1.8; 96%, (CCOOC_3H_6) $^-$); (8.1; 95%, CHFS_2^-); (2.5%, CFS_2^-); 94 (9.0, 6.9%, $\text{CH}_2\text{SO}_2\text{NH}_2^- \text{CC}(\text{O})\text{OC}_3\text{H}_2^-$ two fragments), 93 (23.6%,

CHSO₂NH₂⁻; 89 (15.4%, SF₃⁻); 85 (1.0%, C₄H₅O₂⁻); 83 (34.8%, CHSF₂⁻); 82 (7.4%, CSF₂⁻); 80 (2.9%, SO₂NH₂⁻).

Analysis calculated for C₅H₁₀F₅NO₄S₃: C, 19.54; F, 30.9; H, 3.28; N, 4.56; S, 20.87%. Found: C, 19.41; F, 30.2; H, 3.37; N, 4.44; S, 20.62%.

$[(C_2H_5)_3NH]^+[F_5SC(SO_2F)C(O)OCH_3]^-$ (1)

To 0.3385 g (1.20 mmol) of F₅SCH(SO₂F)C(O)OCH₃ in 2.0 ml of anhydrous ether in a 10 ml flask fitted with a Claisen head, Drierite tube and dropping funnel, 0.15 g (1.49 mmol) of N(C₂H₅)₃ in 2.0 ml of anhydrous ether was added dropwise during 30 s with swirling at -45 °C. An immediate separation of a lower pale-yellow layer was observed. The cold bath was removed and the mixture was allowed to attain room temperature slowly with occasional swirling. After removal of the solvent *in vacuo* 0.4288 g (1.12 mmol) or 93% of an amorphous, slightly yellow solid was obtained, which was analytically pure.

¹H NMR (CDCl₃, Si(CH₃)₄ ext.): δ₁ 1.79 ppm (t, int. = 10.1 HN(CH₂CH₃)₃⁺); δ₂ 3.59 ppm (quart., int. = 6.3, HN(CH₂CH₃)₃⁺); δ₃ 4.04 ppm (s, int. = 3.0, (COOCH₃)); δ₄ 7.46 ppm (s, broad, int. = 1.0 (HN(C₂H₅)₃)⁺); J_{H-H} = 7.40 Hz (ethyl).

¹⁹F NMR (CDCl₃, CCl₃F ext.): AB₄X, φ 95.3 ppm (9 lines, int. = 1.0 (F_A)); φ 82.1 ppm (d-m, int. = 4.1 (F_B)); φ 67.0 ppm (p, int. = 1.0 (F_X, SO₂F)); J_{AB} = 154.2 Hz; J_{BX} = 10.2 Hz.

IR ν_{max} (neat sample, KBr): 3093 (m-s), 2995 (m), 2952 (m), 2875 (w-m), 2748 (w), 2495 (vw), 1640 (s-vs), 1523 (vw), 1474 (m-s), 1462 (m), 1442 (s), 1423 (m), 1394 (m-s), 1367 (s, sh), 1355 (s), 1306 (vs), 1289 (vs), 1179 (s), 1093 (m), 1052 (m), 1020 (w-m), 939 (w-m), 900 (vw), 864 (vs), 839 (vs), 805 (vs), 757 (s), 690 (m-s), 666 (s), 615 (s), 579 (s), 572 (m), 538 (vw), 485 (vw), 459 (w), 406 (w-m) cm⁻¹.

Mass spectrum (electron impact, 70 eV, mass, species, % > 2): 251 (M-N(C₂H₅)₃-CH₃O)⁺, 11.7; 231, (M-N(C₂H₅)₃-HF-CH₃O)⁺, 5.1; 168, (M-N(C₂H₅)₃-SO₂F-CH₃O)⁺, 4.5; 155, (M-N(C₂H₅)₃-SF₅)⁺, 6.5; 149, (M-N(C₂H₅)₃-SO₂F-CH₃O-F)⁺, 2.3; 143, (M-N(C₂H₅)₃-4F-CH₃O-2O)⁺, 5.2; 139, (M-N(C₂H₅)₃-SO₂F-COOCH₃-H)⁺, 3.6; 135, (M-N(C₂H₅)₃-SF₅-HF)⁺, 3.7; 129, (M-N(C₂H₅)₂C₂H₄-5F-COOCH₃)⁺, 2.7; 127, SF₅⁺, 52.1; 125, (M-N(C₂H₅)₂C₂H₄-SF₅-CH₃O)⁺, 19.5; 124, (M-N(C₂H₅)₃-SF₅-CH₃O)⁺, 3.9; 122, (M-N(C₂H₅)₂C₂H₄-SO₂F-F-COOCH₃)⁺, 5.6; 105, (M-N(C₂H₅)₃-SF₅-CH₃O-F)⁺, (C₃H₂FOS)⁺ (two fragments), 8.8, 10.3; 102, HN(C₂H₅)₃⁺, 2.5; 101, N(C₂H₅)₃⁺, 29.1; 100, N(C₂H₅)₂C₂H₄⁺, 11.5; 91, C₂FOS⁺, 2.4; 89, SF₃⁺, 48.3; 87, HN(C₂H₅)₂CH₂⁺, 11.3; 86, N(C₂H₅)₂CH₂⁺, 100.0; 79, CFOS⁺, 4.0; 72, N(C₂H₅)₂⁺, CHCOOCH₃⁺, 7.5; 71, N(C₂H₅)C₂H₄⁺, CCOOCH₃⁺, 2.8; 70, N(C₂H₅)C₂H₃⁺, CCOOCH₂⁺, SF₂⁺ (two fragments), 5.7, 3.7; 69, N(C₂H₅)C₂H₂⁺, CCOOCH⁺, 3.0; 67, FSO⁺, C₄H₅N⁺, 35.1; 63, CFS⁺, 3.3; 62, C₄N⁺, 2.3.

Analysis calculated for C₉H₁₉F₆NO₄S₂: C, 28.19; F, 29.7; H, 5.00; N, 3.65; S, 16.73%. Found: C, 28.40; F, 30.1; H, 4.89; N, 3.78; S, 16.43%.

$$[(C_2H_5)_3NH]^+[F_5SC(SO_2F)C(O)OCH(CH_3)_2]^- \quad (2)$$

To 2.11 g (6.80 mmol) of $F_5SCH(SO_2F)C(O)OCH(CH_3)_2$, dissolved in 3 ml of anhydrous ether, in a 25 ml round-bottomed flask, equipped with a magnetic stirring bar, Claisen head, dropping funnel and Drierite tube, 0.80 g of triethylamine, dissolved in 4.0 ml of anhydrous ether, was added dropwise with stirring at -60 to -50 °C. At -45 °C, two layers were observed; stirring was continued for 2 min, the cold bath was removed and the solvent was pumped away through a cold trap (-196 °C), leaving 2.80 g of an analytically pure amorphous white solid with a yield of 100% (m.p., $94-97$ °C). The solid could be handled in air without difficulty and formed large irregular crystals upon recrystallization from chloroform.

1H NMR (CD_3COCD_3 , $Si(CH_3)_4$ ext.): δ_1 6.45 ppm (s, broad, int. = 0.93 (NH)); δ_2 4.85 ppm (sept., int. = 0.71 ($CH(CH_3)_2$)); δ_3 3.23 ppm (q, int. = 6.00 ($N(CH_2CH_3)_3$)); δ_4 1.24 ppm (t, int. about 8.6 (overlap, $N(CH_2CH_3)_3$)); δ_5 1.09 ppm (d, int. about 6.6 (overlap, $CH(CH_3)_2$)); $J_{25} = 6.36$ Hz; $J_{34} = 7.14$ Hz.

^{19}F NMR (CD_3COCD_3 , CCl_3F ext.): AB_4X , ϕ 97.0 ppm (9 lines, int. = 1.00 (F_A)); ϕ 82.1 ppm (d-m, int. = 4.25 (F_B)); ϕ 66.3 ppm (p, int. = 1.00 (F_X , SO_2F)); $J_{AB} = 154.0$ Hz; $J_{BX} = 10.6$ Hz.

IR ν_{max} (neat, KBr): 3060 (vw), 2992 (vw), 2941 (vw), 2754 (vw), 2677 (vw), 2498 (vw), 1615 (s), 1467 (m), 1401 (m), 1380 (s), 1291 (s), 1194 (s), 1179 (s), 1144 (m), 1111 (m-s), 1093 (s), 1041 (s), 910 (m), 846 (vs), 836 (vs, sh), 806 (s), 755 (vs), 697 (s), 664 (s), 610 (s), 586 (m), 577 (s), 570 (s), 484 (w), 463 (w) cm^{-1} .

Mass spectrum (chemical ionization, mass, species, >2%): 311, $(M-N(C_2H_5)_2C_2H_4)^+$, 4.3; 269, $C_2H_3F_6O_4S_2^+$, 9.8; 251, $(M-N(C_2H_5)_3-C_3H_7O)^+$, 3.3; 219, $CF_3O_3S_2^+$ (rearr.), 3.6; 209, $(M-N(C_2H_5)_3-2F-HF-C_3H_7)^+$, 3.1; 205, $CH_2F_5O_2S_2^+$, 6.4; 143, $(M-N(C_2H_5)_3-SO_2F-2HF-CO_2)^+$; 127, SF_5^+ , 12.4; 125, $C_2H_2FO_3S^+$, 8.9; 105, $C_4H_6FS^+$ (rearr.), 3.1; 103, $C_4H_4FS^+$ (rearr.), 3.3; 102, $NH(C_2H_5)_3^+$, 59.5; 101, $N(C_2H_5)_3^+$, 93.6; 100, $(N(C_2H_5)_3-H)^+$, 75.4; 99, $(N(C_2H_5)_3-2H)^+$, 11.5; 91, C_2FOS^+ , 3.4; 89, SF_3^+ , 76.0; 87, $NH(C_2H_5)_2CH_2^+$, 11.4; 86, $N(C_2H_5)_2CH_2^+$, 100.0; 79, $CFOS^+$, 4.3; 74, C_5N^+ , $(NH_2(C_2H_5)_2)^+$, 4.6; 72, $N(C_2H_5)_2^+$, 11.7; 71, $(N(C_2H_5)_2-H)^+$, 2.2; 70, SF_2^+ , $N(C_2H_5)_2-2H)^+$ (two fragments), 4.2, 4.4; 67, FSO^+ , 11.8; 65, CH_2FS^+ , 21.4; 61, $C_3H_7OH_2^+$, 3.5; 59, $C_3H_7O^+$, 53.7; 58, $C_3H_6O^+$, 31.6; 57, $C_3H_5O^+$, 4.2; 56, $C_3H_4O^+$, 7.4; 55, $C_3H_3O^+$.

Analysis calculated for $C_{11}H_{23}F_6NO_4S_2$: C, 32.11; F, 27.7; H, 5.64; N, 3.40; S, 15.59%. Found: C, 32.04; F, 27.5; H, 5.45; N, 3.31; S, 15.80%.

$$[(C_2H_5)_3NH]^+[F_5SC(SO_2F)C(O)OCH(CH_3)_2]^- \text{ and } HCl$$

To 0.70 g (1.7 mmol) of $[(C_2H_5)_3NH]^+[F_5SC(SO_2F)C(O)OCH(CH_3)_2]^-$ in a 5.0 ml pear-shaped flask, 1.60 ml of concentrated HCl was added. The solid liquified immediately and a yellowish oil separated and, after swirling for 2 min, 0.50 g of this oil was pipetted away; its IR spectrum coincided with the spectrum of $F_5SCH(SO_2F)C(O)OCH(CH_3)_2$, except for a few very weak bands at 2500–2700 and 1616 cm^{-1} (yield 94.7%).

$\text{Na}^+[\text{F}_5\text{SC}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2]^-$ (5): *General procedure*

Freshly prepared sodium isopropoxide was stirred in anhydrous ether in a 50 ml flask, equipped with a magnetic stirring bar and fitted with a Claisen head, Drierite tube and a rubber septum. The ester, dissolved in 1.0–2.0 ml of ether was added with a syringe through the septum. The isopropoxide dissolved in a vigorous reaction, causing the ether solution to boil. The addition of the ester was reduced, when necessary, in order to moderate the reaction. When addition was complete, the yellowish-brown solution was stirred for another 0.5–1.0 h at room temperature. The amount of ether used was 5–10 ml for 4.0–7.0 mmol of isopropoxide; the ester was used in about 0.70–0.90 fold quantity. The salt could be prepared by the same method in isopropanol.

^{19}F NMR (in isopropanol, CCl_3F ext.): AB_4X ϕ 95.3 ppm (9 lines, int. = 1.0 (F_A)); ϕ 82.8 ppm (d-m, int. = 4.0 (F_B)); ϕ 67.3 ppm (p, int. = 1.0, (F_X , SO_2F)); $J_{\text{AB}} = 150.4$ Hz; $J_{\text{BX}} = 10.6$ Hz. In ether, ϕ_A 93.5 ppm, ϕ_B 81.7 ppm and ϕ_X 66.2 ppm.

$\text{Na}^+[\text{F}_5\text{SC}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2]^-$ (5): *Stability*

The sodium salt was prepared as described above from 0.33 g (4.00 mmol) of sodium isopropoxide and 1.21 g (3.90 mmol) of $\text{F}_5\text{SCH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2$ in 5.0 ml of ether and stirred at room temperature. ^{19}F NMR spectroscopy showed that the anion signal, which was initially the only observed resonance, disappeared slowly with the reversion to the signal attributable to the starting ester. After 6 days this process was complete, with the formation of a white precipitate. Distillation (room temperature to 60 °C) gave one uniform fraction (0.64 g, 52.3%) which was identified by IR and ^{19}F NMR spectroscopy as the starting ester.

$\text{F}_5\text{SCCl}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2$ (8)

$\text{Na}[\text{F}_5\text{SC}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2]$ was prepared from sodium isopropoxide (0.5745 g, 7.00 mmol) and $\text{F}_5\text{SCH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2$ (1.845 g, 6.00 mmol) in a 50 ml pear-shaped flask as described above. The septum on the Claisen head was replaced by a gas inlet tube that reached just above the liquid level and chlorine gas was introduced at a slow rate. A white precipitate formed instantly; chlorine was added slowly until a greenish-brown color persisted. A distillation unit was then attached to the flask in place of the Claisen head; the ether was removed in a trap-coded -196 °C trap. Distillation of the residue at 2.5 Torr afforded three fractions: room temperature to 48.5 °C (0.360 g), 48.5–49 °C (0.962 g) and 48–28 °C (0.139 g). The last two fractions were 97.7 and 97.0% pure (gas chromatography; 5% QF1; 1 m; 130 °C), whereas fraction 1 was 82% pure chlorinated ester. The impurity was not the starting ester. An analytically pure sample was obtained by preparative gas chromatography. The solid residue in the flask (0.6323 g) was somewhat more than the expected NaCl (0.3482 g) and excess $\text{NaOCH}(\text{CH}_3)_2$ (0.0865 g).

^1H NMR (CDCl_3 , $\text{Si}(\text{CH}_3)_4$, ext.): $\delta = 1.85$ ppm (CH_3 , int. = 6.3); δ 5.80 ppm (CH , int. = 1.0), $J_{\text{H-H}} = 6.47$ Hz.

^{19}F NMR (CDCl_3 , CCl_3F , ext.): AB_4X : ϕ_{A} 68.8 ppm, (9 lines (F_{AX} , int. = 0.95)); ϕ_{B} 63.0 ppm (about d-m (F_{eq} , int. = 4.25)); ϕ_{X} 49.8 ppm (p (SO_2F), int. = 1.0); $J_{\text{AB}} = 150.4$ Hz; $J_{\text{AX}} = 11.6$ Hz.

IR ν_{max} : 2993 (w), 2945 (vw), 1778 (s), 1766 (ms), 1470 (w), 1444 (s), 1393 (w), 1391 (w-m), 1347 (vw), 1256 (s), 1223 (s), 1098 (s), 1035 (vw); 981 (vw), 916 (s), 887 (vs); 877 (vs), 840 (s), 807 (s), 784 (m), 737 (m-w), 689 (w), 673 (vw), 659 (w), 611 (m), 573 (s), 502 (w-vs), 482 (w), 469 (w) cm^{-1} .

Mass spectrum (70 eV, mass, species, %), only the ^{35}Cl signals will be given: 343, (M-H) $^+$, 1.0; 329, (M-CH_3) $^+$, 19.9; 285, ($\text{M-OCH}(\text{CH}_3)_2$) $^+$, 26.5; 231, ($\text{M-Cl-OC}_3\text{H}_7\text{-F}$) $^+$, 2.1; 217, (M-Cl-4F-O) $^+$, 1.2; 209, ($\text{M-Cl-SO}_2\text{F-O-H}$) $^+$, 2.4; 203, ($\text{M-C}_3\text{H}_7\text{-F-Cl-CO}_2$) $^+$, 2.9; 202, (M-Cl-4F-O-CH_3) $^+$, 2.1; 177, ($\text{M-SF}_5\text{-HF-O-4H}$) $^+$ 9.5; 159, ($\text{MH-SF}_5\text{-OC}_3\text{H}_7$) $^+$, 3.8; 158, ($\text{M-SF}_5\text{-OC}_3\text{H}_7$) $^+$, 5.2; 129, ($\text{M-SF}_5\text{-HF-O-5H-C-Cl=C}_4\text{HO}_3\text{S}$) $^+$, 1.3; 127, SF_5^+ , 19.1; 96, C_4OS^+ , 1.6; 94, $\text{C}_2\text{F}_2\text{S}^+$, 6.8; 91, C_2FOS^+ , 89, SF_3^+ , 100.0; 83, SO_2F^+ , 2.7; 79, $\text{C}_5\text{H}_3\text{O}^+$, 1.8; 77, C_5HO^+ , 1.8; 76, C_5O^+ , 3.1; 75, C_2FS^+ , 2.6; 70, SF_2^+ , 8.2; 69, $\text{C}_4\text{H}_5\text{O}^+$, C_3HO_2^+ , 2.4; 1.1 (two fragments); 68, $\text{C}_4\text{H}_4\text{O}^+$, C_3O_2^+ , 3.8; 67, FSO^+ , 39.1; 66, $\text{C}_4\text{H}_2\text{O}^+$, 6.1; 65, C_4HO^+ , 1.8; 64, SO_2^+ , C_4O^+ , 12.1; 63, CFS^+ , 4.0; 61, CHOS^+ , 8.1; 59, $\text{C}_3\text{H}_7\text{O}^+$, 13.3; 58, $\text{C}_3\text{H}_6\text{O}^+$, 2.4; 51, SF^+ , 2.7.

Analysis calculated for $\text{C}_5\text{H}_7\text{ClF}_6\text{O}_4\text{S}_2$: C, 17.42; Cl, 10.28; F, 33.1; H, 2.05; S, 18.60%. Found: C, 17.56; Cl, 10.50; F, 33.2; H, 2.24; S, 18.55%.

$F_5\text{SCBr}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2$ (9)

The sodium salt of the ester was prepared as described above from 0.517 g of $\text{NaOCH}(\text{CH}_3)_2$ (6.30 mmol) in 10.0 ml ether and 1.37 g of $\text{F}_5\text{SCH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2$ (4.40 mmol). Bromine was added dropwise with a syringe through the septum until a yellow colour persisted. A white precipitate was immediately formed upon addition of Br_2 . An NMR spectrum (^{19}F) showed that only one fluoro compound was present. The ether was pumped away from the reaction flask through a cold trap and distillation at 3 Torr afforded one fraction, room temperature to 83 °C (1.18 g), a slightly brownish heavy liquid. It was a mixture (^{19}F NMR) of $\text{F}_5\text{SCH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2$ (12 parts) and the alleged $\text{F}_5\text{SCBr}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2$ (88 parts). No separation was achieved by repeated distillation.

^{19}F NMR spectrum of $\text{F}_5\text{SCBr}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2$: ϕ 64.9 ppm (degenerate AB_4 spectrum, m, int. = 5.18 (SF_5)); ϕ 49.0 ppm (p, int. = 1.00 (SO_2F)); $J_{\text{BX}} = 12.3$ Hz).

IR ν_{max} , impure product (neat, KBr): 2995 (m), 2945 (w), 2889 (vw), 1764 (vs), 1470 (m), 1441 (vs), 1393 (m), 1361 (m), 1334 (w), 1296 (m), 1254 (vs), 1222 (vs), 1185 (m), 1148 (m), 1097 (vs), 972 (w), 889 (vs), 860 (vs), 838 (s), 821 (s-vs), 807 (s-vw), 793 (s-vs), 785 (s, sh), 742 (w),

688 (m), 648 (m), 611 (s), 574 (vs), 497 (w-m); 463 (w-m), 415 (w-m) cm^{-1} .

$F_5\text{SCH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{NHC}(\text{O})\text{NH}_2$ (**4a**)

A solution of $F_5\text{SCHCF}_2\text{OSO}_2$ (2.09 g, 7.80 mmol) in 15.0 ml of dry ether was added dropwise to a suspension of urea (0.460 g, 7.70 mmol) in 50 ml of anhydrous ether at 0 °C. The solution quickly turned cloudy and a sticky precipitate formed. It was stirred at room temperature for 2 h and then kept at room temperature for 3 days. The ether was decanted and evaporated, leaving 1.78 g of a white amorphous mass with an acidic odour. It was dissolved in the minimum amount of hot ether and allowed to reprecipitate upon cooling with a yield of 1.54 g (60.3%) (m.p., 168–172 °C).

^{19}F NMR (in ether, CCl_3F ext.): ϕ 71.0 ppm (m, int. = 5.0 (SF_5)); ϕ 59.3 ppm (m, int. = 1.1 (SO_2F)).

IR ν_{max} (neat sample, NaCl): 3400, 3300, 3341, 3254 (br), 2967 (w), 1729 (m-s), 1701 (s), 1627 (m), 1560 (m), 1434 (m-s), 1386 (m), 1301 (m), 1250 (w), 1219 (m-s), 1178 (m), 1099 (m-s), 1052 (w), 976 (m), 952 (w), 891 (s), 863 (vs), 850 (s), 822 (m), 792 (w-m), 783 (m), 744 (m), 736 (m), 685 (w), 645 (w), 610 (w), 600 (w), 571 (m) cm^{-1} .

Analysis calculated for $\text{C}_3\text{H}_4\text{F}_6\text{N}_2\text{O}_4\text{S}_2$: C, 11.62; F, 36.8; H, 1.30; S, 20.7; N, 9.03%. Found: C, 11.89; F, 35.3; H, 1.30; S, 18.81; N, 8.81%.

$[(\text{C}_2\text{H}_5)_3\text{NH}]^+[\text{F}_5\text{SC}(\text{SO}_2\text{F})\text{C}(\text{O})\text{NHC}(\text{O})\text{NH}_2]^-$ (**4b**)

To 1.3085 g of $F_5\text{SCH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{NHC}(\text{O})\text{NH}_2$ (4.20 mmol) in 12 ml of anhydrous ether in a 50 ml pear-shaped flask, fitted with a Claisen head, dropping funnel and a Drierite tube, 0.5187 g of $\text{N}(\text{C}_2\text{H}_5)_3$ (5.10 mmol) in 10 ml of anhydrous ether was added dropwise at -70 °C with stirring. At about 0 °C an oily layer was formed, while the ureide disappeared slowly. Removal of the solvent *in vacuo* left 1.714 g of an almost white solid (theoretical, 1.735 g), which contained a small amount of impurities (^{19}F NMR). Attempts to recrystallize the material resulted in decomposition.

^{19}F NMR (acetone, CCl_3F , ext.): ϕ 95.7 ppm (AB_4X , 9 lines with doublet splitting) ($J=4.9$ Hz), (F_A), int. = 0.94; ϕ 82.0 ppm (d-m, int. = 4.00 (F_B)); ϕ 73.1 ppm (not resolved, int. = 0.99 (F_X , SO_2F)).

IR ν_{max} of the solid obtained above (neat, KBr): 3367 (s, br), 3220 (m, br), 2980 (s), 2938 (m, sh), 2882 (m), 2671 (m, br), 2495 (w, br), 2185 (w-m), 1688 (vs), 1652 (vs), 1567 (s), 1478 (s), 1459 (s, sh), 1370 (vs), 1232 (s-vs), 1167 (vs), 1116 (s), 1036 (m), 945 (w-m), 889 (m), 854 (vs), 834 (vs), 754 (s-vs), 734 (s), 663 (s), 626 (m-s), 580 (s, br), 480 (m-s) cm^{-1} .

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Supplementary material available

Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52857 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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