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THE CHEMISTRY OF (PENTAFLUORO- λ^6-SULFANYL) (FLUOROSULFONYL) KETENE. PART II*

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SUMMARY

The reactions of $F_5SC(SO_2F)=C=O$ with electrophilic (SO_3) and nucleophilic (MF, NaN_3, $((CH_3)_2N)_2C=O$) reagents were studied. Halogenation of $Cs[F_5SC(SO_2F)C(O)F]$ produced the following new compounds: $F_5SC(SO_2F)XC(O)F$ (X = Br,Cl), $F_5SC(SO_2F)ClC(O)Cl$ and $F_5SCBr_2SO_2F$. Reaction of $F_5SC(SO_2F)XC(O)F$ (X = Br,Cl) with water gave $F_5SCHXSO_2F$; $F_5SC(SO_2)BrC(O)F$ with ethylene gave $F_5SCH(SO_2F)CH_2CH_2Br$.

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INTRODUCTION

Previously, we discussed the preparation and some reactions of (pentafluoro- λ^6-sulfanyl((fluorosulfonyl) ketene, $F_5SC(SO_2F)=C=O$ 1 [1]. Since we are greatly interested in molecular systems containing the SF_5 and SO_2F groups, additional studies have been carried out. Compounds containing the SO_2F group are precursors to a number of derivatives potentially useful as acid electrolytes, surface active agents and ion-exchange resins [2]. The starting ketene 1 was prepared in high yield and purity by treating the acid fluoride $F_5SCH(SO_2F)C(O)F$, 2, with $F_3B \cdot N(C_2H_5)_3$. It was found that with the comparatively weak base NaF, the sultone 3, $F_5S\overline{CHCF_2OS}O_2$, also underwent rearrangement and partial dehydrofluorination to give a mixture of 1 and 2.

RESULTS AND DISCUSSION

In this study reactions of 1 with electrophiles and with nucleophiles were of interest; with electrophilic reagents, the reaction with SO_3 was particularly interesting, as this would not only allow one to compare the electrophilicity of 1 with $(CF_3)_2C=C=O$ and $F_3CC(SO_2F)=C=O$, but could also possibly lead to a sulfur ylide, by analogy to the reaction of $F_3CC(SO_2F)=C=O$ and SO_3 leading to $F_2C=C(SO_2F)_2$ [3]:

$$F_5SC(SO_2F)=C=O + SO_3 \longrightarrow F_4S=C(SO_2F)_2 + CO_2$$

Essentially no reaction was observed up to 240°C, but at 270°C rather rapid formation of CO_2 occurred, accompanied by the formation of dark material. Therefore, it is possible that the $SF_4{=}C$ product had been formed indeed by a similar mechanism but did not withstand the high temperature. From these results one can suggest the following order of nucleophilicity (reverse order of electrophilicity):

$(CF_3)_2C{=}C{=}O$ (-30°C) > $CF_3(SO_2F)C{=}C{=}O$ (160°C) > <u>1</u> (270°C)

The numbers in parentheses indicate the reaction temperature with SO_3.

In general, fluorinated ketenes show a great tendency to undergo nucleophilic additions. Whereas bis(trifluoromethyl) ketene undergoes F^--catalyzed rearrangement (with NaF) and the intermediate $Na^+ [(CF_3)_2CC(O)F]^-$ is assumed, [4] and a mercury compound, $((CF_3)_2C(C(O)F))_2Hg$, was described in 1972 by Knunyanz <u>et al.</u> [5], the corresponding anion, $[(CF_3)_2CC(O)F]^-$, has only recently been isolated with the counterion $((CH_3)_2N)_3S^+$ [6]. No results are available for trifluoromethyl fluorosulfonyl ketene. We have found in this work that anion formation is the predominant mode of reaction of pentafluorothio(fluorosulfonyl) ketene.

A pertinent observation was made in the NaF-catalyzed rearrangement of <u>3</u> to <u>2</u>. Although both <u>1</u> and <u>2</u> are volatile liquids, it was noticed, that it took a long time (≈ 2 h) and heating (100-120°C) to collect most of the product by vacuum-transfer. From these observations one assumes the formation of a complex between either 1 or 2 and NaF or $NaHF_2$. Such a complex was indeed later observed, when the residual solid of the rearrangement 3 → 2 was extracted with dry CH_3CN; according to ^{19}F n.m.r. data it is likely that the complex was 1·NaF. Nuclear magnetic resonance data are given in tabular form together with other identified complexes of the form 1·MF in Table 1.

With CsF the following sequence of reactions was studied:

$$\underline{1} + CsF \longrightarrow \underset{\underline{4}}{Cs^+[F_5SC(SO_2F)C(O)F]^-} \longrightarrow \underset{\underline{5}}{F_4S{=}C(SO_2F)C(O)F} + CsF$$

Compound 4 was isolated as the sole product in this reaction without any evidence of its rearrangement to 5 occurring.

An intermediate similar to 4 is assumed in the anionotropic rearrangement of the following two ketenes:

$$(CF_3)_2C{=}C{=}O \quad + NaF \longrightarrow CF_2{=}C(CF_3)C(O)F \quad [4]$$

$$F_5SCH{=}C{=}O \quad \{glass\} \longrightarrow F_4S{=}CHC(O)F \quad [7]$$

The additional strong electron withdrawing capability of the SO_2F group is evidenced by the formation of 4. According to an earlier investigation, the SF_5 group has a stronger chargestabilizing effect than a CF_3 group [8]; in <u>1</u>, there are two highly electronegative substituents at an sp^2 carbon, which leads to the likelihood of nucleophilic addition. Compound <u>4</u> was investigated in more detail and will be discussed later.

The reactivity of <u>1</u> towards nucleophiles offered the possibility of several derivitizations. It should have been possible to generate an azide, which by the Curtius degradation might lead to an amine:

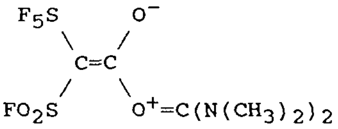
$$\underline{1} + NaN_3 \longrightarrow F_5SC^{-}(SO_2F)C(O)N_3\ Na^{+} \longrightarrow F_5SCH(SO_2F)C(O)N_3$$
$$\longrightarrow F_5SCH(SO_2F)NH_2$$

However, although it was found by ^{19}F n.m.r. that the reaction passed through an anionic intermediate, as evidenced by the characteristic downfield shift of the F-resonances, only $F_5SCH_2SO_2F$ was found as product.

Of special interest would have been the formation of a ketene dimer, which should have been, by analogy to the dimer of bistrifluoromethyl ketene, or the dimer of $F_5SCH=C=O$, a β-lactone [7]. To effect its formation, reaction with a weak base, tetramethyl urea, was tried. No dimer formation was observed, but instead a crystalline, very moisture-sensitive compound was isolated:

$$\underset{\underline{1}}{F_5SC(SO_2F)=C=O} + ((CH_3)_2N)_2C=O \longrightarrow \underset{\underline{6}}{\underline{1}\cdot((CH_3)_2N)_2C=O}$$

Pertinent features of compound <u>6</u> are the relatively low C=O stretching vibrations in the infrared spectrum and the typical chemical shifts of anionic SF_5 compounds (Table 1), i.e., the S-F resonances in the SF_5 and SO_2F group are observed downfield from appropriate model compounds. The C=O resonance frequencies lie very close together, so that it is not possible to make a definite assignment. The methyl protons are observed as a singlet in ^1H n.m.r.spectroscopy. The structure that accounts best for the properties of 6 has the oxygen bonded to the carbonyl group of ketene 1, resulting in an oxonium compound:



The compound is hydrolyzed by water to $F_5SCH_2SO_2F$, CO_2 and tetramethyl urea.

$$6 + H_2O \longrightarrow F_5SCH_2SO_2F + CO_2 + O=C(N(CH_3)_3)_2$$

It is now clear, that 1 could be made by the above dehydrofluorination of 2 only because $F_3B \cdot N(C_2H_5)_3$ is a base of low nucleophilicity, and did consequently not react with the ketene.

A further reaction is the addition of HgF_2 to 1. This should lead to the compound $(F_5SC(SO_2F)C(O)F)_2Hg$. The ^{19}F n.m.r spectrum of the product of this reaction, in which HgF_2 dissolves in CH_3CN in the presence of 1, is indicative of adduct formation (Table 1) and it can be isolated as a white amorphous solid by pumping off the solvent. The i.r. spectrum indicates that there is a $CH_3C{\equiv}N$ complex, and the melting behavior shows gradual softening with final melting at ≈ 80°C. A further indication of complex formation is that weight loss continues after the calculated weight of the complex $HgF_2 \cdot 2(\underline{1})$ is reached, with C-H bands still visible in the i.r.spectrum.

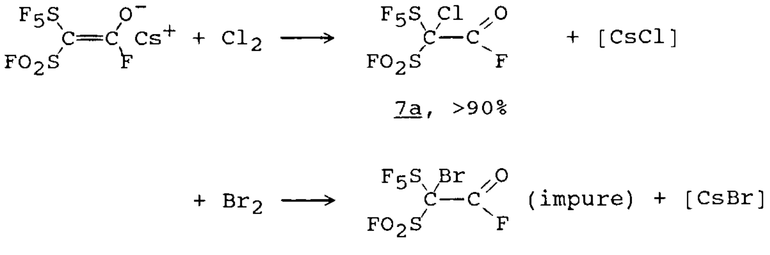
$$2\ \underline{1} + HgF_2 \longrightarrow (F_5SC(SO_2F)C(O)F)_2Hg \cdot\ x\ CH_3CN$$

A similar reaction was observed with silver fluoride, where the fluoride dissolved in a vigorous reaction, forming Ag^+ $[F_5SC(SO_2F)C(O)F]^-$, which was light sensitive and heat sensitive.

$$\underline{1} + AgF \longrightarrow Ag^+\ [F_5SC(SO_2F)C(O)F]^-$$

The cesium salt <u>4</u> can also be obtained by heating <u>1</u> and CsF without solvent; it can then be obtained by extracting the solid residue with acetone. Compound <u>4</u> is of an extraordinary stability and can be heated for hours in the vacuum to > 200°C without significant weight loss, although darkening occurs. The trace of material that distills off is not <u>1</u>, showing the irreversibility of the reaction of <u>1</u> and CsF.

The cesium salt reacted with halogens to give $F_5SCCl(SO_2F)C(O)F$ in very good yield and high purity, $F_5SCBr(SO_2F)C(O)F$ in only fair yield but $F_5SCI(SO_2F)C(O)F$ could not be detected:



7a, >90%

7b, ≈50%

Whereas the reactions with chlorine and bromine were run without solvent, the reaction with iodine was tried with and without the presence of CH_3CN. However, 4 reacts with bromine in a different way in CH_3CN than it does without solvent. When Br_2 is added to a concentrated (to simplify removal of solvent) CH_3CN solution of 4, quick discoloration of the brown Br_2 color is observed, accompanied by the formation of gas bubbles and a white precipitate. The solution can be titrated in this fashion until the brown bromine color persists. The product that is obtained has no CO group (i.r.spectrum), and shows a conspicuous upfield shift in the ^{19}F n.m.r. spectrum. Such a shift is usually observed when electronegative elements are attached to the SF_5-bearing carbon atom. Further characteristics of this compound, a colorless solid, when pure, are its high volatility (it distills with acetonitrile), its halogen-like odor and its low melting point (≈40°C).

This compound has been identified as $F_5SC(Br_2)SO_2F$ (8) via its infrared, ^{19}F n.m.r. and mass spectrum and by elemental analysis.

This rather interesting result offered the possibility of synthesizing the compound $F_5SCCl_2SO_2F$ by a similar route. With chlorine, however, a different result was obtained; while the reaction stops at the stage of $F_5SCCl(SO_2F)C(O)F$ without irradiation, it continues with irradiation in a solvent to give a single major product, which is an acyl chloride (<u>9</u>) (see below). This product did not seem to undergo any further changes. The solvent was necessary for the reaction; without CH_3CN present only $F_5SCCl(SO_2F)C(O)F$, even after long irradiation, was formed. The progress of the reaction without solvent could also be conveniently monitored by the drop in chlorine pressure; no further pressure drop was observed after 1 equivalent of Cl_2 was consumed (a dichloro compound should have consumed two equivalents and produced either CO or COClF as a by-product - neither was detected):

$$\underline{4} + Cl_2 \left\langle \begin{array}{lll} \text{hv, no solvent} & \longrightarrow & F_5SCCl(SO_2F)C(O)F \\ \text{hv, } CH_3CN & \longrightarrow & F_5SCCl(SO_2F)C(O)Cl\ \ \underline{9} \\ \text{no hv, } CH_3CN & \longrightarrow & F_5SCCl(SO_2F)C(O)F\ \ \underline{7a} \end{array} \right.$$

According to n.m.r. spectral comparisons, one by-product in the reaction is $F_5SCHClSO_2F$, and another minor-product has an n.m.r. spectrum very similar to $SF_5CBr_2SO_2F$, so that the formation of $F_5SCCl_2SO_2F$, cannot be entirely excluded.

The compounds $F_5SCCl(SO_2F)C(O)F$ and $F_5SCBr(SO_2F)C(O)F$ hydrolyzed slowly in water:

$$F_5SC(Cl,Br)(SO_2F)C(O)F + H_2O \longrightarrow F_5SCH(Cl,Br)SO_2F + HF + CO_2$$

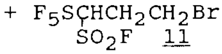
$$Br = \underline{10a},\ Cl = \underline{10b}$$

With SF_5Br, BrF addition occurred:

$\underline{1} + SF_5Br \longrightarrow F_5SCBr(SO_2F)C(O)F \quad (+SF_4)$

It was found that $F_5SCBr(SO_2F)C(O)F$ does react with C_2H_4 in the presence of a free radical initiator, but loss of COF was observed:

$F_5SCBr(SO_2F)C(O)F + C_2H_4 + (\phi COO)_2 \longrightarrow F_5SCH_2SO_2F$ (chiefly)



$$+ F_5S\underset{SO_2F}{C}HCH_2CH_2Br$$

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A further interesting result was obtained with $p\text{-}O_2NC_6H_4N_2^+$ **BF_4^- which did not react with 4. All that** was observed was the very slow conversion of 4 into $SF_5CH_2SO_2F$ (within weeks) when the reaction was run in CH_3CN.

TABLE 1

^{19}F n.m.r.[a] and i.r. table of SF_5-anions

Structure	Counterion	ϕ_A (ppm)	ϕ_B (ppm)	ϕ_X (ppm)	J_{AB} (Hz)	ν_{CO}[b] (cm^{-1})
$F_5SC(SO_2F)C(O)\cdot$urea [c]	-	89.6	79.7	71.3	154.2	1669 1653
$F_5SC(SO_2F)C(O)F^-$ [d]	Cs^+	92.8	79.2	68.7	148.0	1764
" [e]	Ag^+	94.0	79.9	69.7	155.3	- #
$F_5SC(SO_2F)C(O)N_3^-$ [e]	Na^+	95.9	82.6	69.5	151.5	- #
$(F_5SC(SO_2F)C(O)F)_2Hg$ [e]		90.6	79.9	66.1	154.3	1826

[a] Not measured; by convention, resonances appearing downfield from CCl_3F are assigned positive values; upfield resonances are assigned negative values; [b] neat samples; [c] in CH_2Cl_2; [d] in acetone; [e] in CH_3CN.

EXPERIMENTAL

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 n.m.r. spectra were usually run at 90.0 (^1H) and 84.67 (^{19}F) MHz on a Varian EM-390 spectrometer, otherwise they were run on a General Electric QE-300 spectrometer at 300 MHz (^1H), or on a Bruker AMX-400 spectrometer (^{19}F at 376 MHz, ^1H at 400.6 MHz). Infrared spectra were obtained from neat samples between KBr or NaCl plates on a Nicolet DX-20 spectrometer.

The mass spectra were obtained on a VG 7070 mass spectrometer under the conditions indicated with each compound. $F_5S\overline{CHCF_2OS}O_2$ was prepared as previously described [9]. Elemental analyses were carried out by Mikroanalytisches Laboratorium Beller, Göttingen, Federal Republic of Germany.

HgF_2 + 1

Fresh mercury(II)-fluoride (0.4089 g, 1.71 mmol, Aldrich) was kept overnight in a 50 ml pear-shaped flask with a Kontes Teflon valve connector under high vacuum (0.003 torr) at room temperature. A solution of 0.91 g of 1 (3.64 mmol) in 1.0 ml of dry acetonitrile was added via vacuum transfer, and the flask was allowed to warm up slowly with stirring. The mercury fluoride dissolved largely in a vigorous reaction, and the reaction was moderated with cooling. All HgF_2 dissolved after keeping the reaction mixture at room temperature for 66 hours. Excess ketene and solvent were removed at room temperature by pumping on the flask through a -196°C trap for 8 hours. The rate of weight loss slowed down constantly, but never reached zero. After 8 hours, 1.2559 g of a white slightly sticky mass was left behind. Although this corresponds to a ratio $\underline{1}$:HgF_2 = 1.976:1.000, the product contained CH_3CN, as inferred from the melting behavior and the i.r. spectrum. Melting range 40 to ≈80°C, bubbling starts at 104°C. Therefore, an elemental analysis was not obtained.

^{19}F n.m.r.spectrum (CH_3CN, external CCl_3F): AB_4MX spectrum, the relative band areas are indicated. ϕ_A = 90.6 ppm, 9 lines , area = 1.00; ϕ_B = 79.9 ppm, d-m, area = 4.13; ϕ_M = 66.1 ppm, broad singlet, area = 0.97 (SO_2F); ϕ_X = 21.2 ppm, broad singlet, area = 0.97 (CF(O); J_{AB} = 154.3 Hz. All lines are broadened.

I.r spectrum (neat sample on KBr, cm^{-1}): 3016, w; 2966, w; 2952, w-m; 2629, w; 2423, w; 2385, w; 2347, w-m (CO_2?); 2305, m; 2276, m; 2053, w,vbr; 1826, vs,br; 1414, vs,br; 1288, s; 1233, s-vs; 1195, s-vs; 1126, s-vs; 1078, s,sh; 1040,s; 964, m-s,br; 855, vs,br; 792, sh,s-vs,br; 682, m-s,br; 663, m-s; 618, s; 583, s-vs,br; 493, m-s; 465,s.

AgF + 1

The sample was prepared as described above. Initially, strong reaction was observed which slowed down with time. A colorless liquid was obtained, which left behind a glassy mass when the solvent was pumped off at room temperature; a weight corresponding to a stoichiometric composition was not obtained. Upon warming, a weight corresponding to less than a 1:1 composition of AgF and 1 was obtained. The compound deposited slowly a dark precipitate when exposed to light, which seemed to suppress further decomposition, as the complex could still be detected by ^{19}F n.m.r. spectroscopy. An elemental analysis was not obtained.

^{19}F n.m.r. spectrum (CH_3CN, external CCl_3F): AB_4MX ϕ_A = 94.0 ppm, 9 lines, area = 1.09; ϕ_B = 79.9 ppm, d-m, area = 4.0; ϕ_M = 69.7 ppm, d-p (not well resolved), area = 0.89 (SO_2F); ϕ_X = 17.0 ppm, d-p, area = 0.78 (CF(O)). J_{AB} = 155.3 Hz; J_{BM} = 10.2 Hz; J_{BX} = 19.7 Hz; J_{MX} = 6.3 Hz.

NaN_3 + 1

When a solution of 1 in dry acetonitrile was shaken with a few crystals of NaN_3 at 0°C in an n.m.r. tube, the salt dissolved rapidly, and a pale yellow solution was formed. ^{19}F n.m.r. spectroscopy indicated the complete consumption of 1, with the formation of a single species. When the solution was allowed to warm, it started to bubble, and turned dark yellow.

^{19}F n.m.r. spectrum of Na^+ $[F_5SC(SO_2F)C(O)N_3]^-$ (CH_3CN, external CCl_3F): AB_4M, ϕ_A = 95.9 ppm; ϕ_B = 82.6 ppm; ϕ_M = 69.5 ppm (SO_2F); J_{AB} = 151.5 Hz; J_{BX} = 10.3 Hz.

$F_5SC(SO_2F)=C=O \cdot O=C(N(CH_3)_2)_2$

To 0.68 g of $((CH_3)_2N)_2C=O$ (5.9 mmol) in a 10 ml pear-shaped flask, equipped with a Kontes Teflon valve connector, 1.18g of $F_5SC(SO_2F)=C=O$ (4.7 mmol) were added through vacuum-transfer. The mixture was allowed to attain room-temperature slowly. At room temperature it bubbled slightly and became viscous. After keeping the sample at room temperature for 45 min, volatile materials were removed by pumping them off through a vacuum-line overnight, leading to a loss of 0.24 g. The sample was still oily and was re-crystallized from CH_2Cl_2 (-12°C), to form large colorless, extremely moisture-sensitive crystals. Yield: 0.94 g = 54.5 %. M.p. = 100-102°C (sealed tube).

^1H n.m.r. ($CDCl_3$, $Si(CH_3)_4$ ext.): δ = 3.42 ppm, s.

^{19}F n.m.r. (CH_2Cl_2, CCl_3F ext.): (AB_4X) ϕ = 89.6 ppm, 9 lines, int. 1.0 (F_A); ϕ = 79.7 ppm, d-m, int. = 3.88 (F_B); ϕ = 71.3 ppm, p, int. = 1.0 (F_X, SO_2F); J_{AB} = 154.2 Hz; J_{BX} = 9.1 Hz.

I.r. spectrum (cm^{-1}, neat sample): 2910, w, broad; 1726, s; 1669,s; 1653,s,sh; 1531, m; 1442, m-w; 1414, m-s; 1390, s; 1248, m-s; 1203, s; 1179, s; 1057, m-s; 1049, m-s; 895, m; 858, vs; 842, vs; 777, vs; 729, vs; 713, s; 660, vs; 615, m; 587,m.

Anal. calcd for $C_7H_{12}F_6N_2O_4S_2$: C, 22.96; H, 3.03; F, 31.1; N, 7.65; S, 17.50. Found: C, 22.10; H, 3.46; F, 31.3; N, 8.27; S, 16.70%.

$F_5SC(SO_2F)=C=O$ and SF_5Br

Pentafluorosulfur bromide (0.55 g) and 1 were heated in a 50 ml Carius tube for 2 days to 110°C. After ≈ 1h, large crystals were observed at the colder parts of the tube, but disappeared later. After 2 days, 0.87 g of a brownish liquid was transferred out; its i.r. spectrum was almost identical with the i.r. spectrum of crude $F_5SCBr(SO_2F)COF$. Repeated fractional distillation resulted in 0.12 g of a slightly brown solid. Both the i.r. and the ^{19}F n.m.r. spectrum were consistent with the composition $F_5SCBr(SO_2F)COF$.

$F_5SC(SO_2F)=C=O$ and SO_3

Ketene 1 (0.96 g, 3.8 mmol) was heated with $(SO_3)_3$ (0.31 g, 3.9 mmol) under anaerobic conditions in a 50 ml Carius tube (the lower two thirds were in the upright oven) to 128°C (20 hours) then to 150°C (50 hours). The mixture became slightly darkened. Infrared spectroscopy (gas phase) showed only a weak CO_2 band; the liquid sample showed a very strong ketene band, and ^{19}F n.m.r. indicated chiefly unchanged ketene, and bands at ≈ 73, 61 and 50 ppm (weak). There was no sign of an A_2BC spectrum as would be expected for the compound $F_4S=C(SO_2F)_2$. The product was condensed back into the Carius tube and heated to 235 °C (20 hours). I.r spectroscopy indicated an increase in CO_2, and the presence of 1, SiF_4 and perhaps COF_2 (weak). The mixture was condensed back into the reaction vessel and heated for another 24 h to 270°C. A comparatively strong CO_2 band was present in the i.r.spectrum, but there was also 1 and SF_4 (very strong). The product was condensed out (1.08 g before, 0.36 g after degassing) and its ^{19}F n.m.r.spectrum showed 1, + bands at ≈69, ≈56 (5:1, probably $F_5SCH_2SO_2F$) and 45 ppm.

Pentafluorothio(fluorosulfonyl)chloroacetylfluoride, $F_5SCCl(SO_2F)C(O)F$, 7a

To 2.0 g of Cs^+ $[F_5SC(SO_2F)C(O)F]^-$ (5.0 mmol) in a 75 ml steel reaction vessel, chlorine (0.551, 210 torr, room temperature, 6.3 mmol) was added via vacuum transfer. The vessel was heated to 85°C for 2h, then kept at room temperature for 18 h. The volatile products (1.25 g), as collected by vacuum transfer, were obtained as a clear liquid. Excess chlorine was removed by shaking with ≈1g of mercury and the product thus obtained by vacuum transfer, a clear and colorless liquid, was analytically pure (1.14 g, 75.3 %).

^{19}F n.m.r. spectrum (pentane, CCl_3F ext.): ϕ_1 = 63.6 ppm, m, int. = 5.1, (SF_5); ϕ_2 = 49.3 ppm, m, int.= 1.0 (SO_2F); ϕ_3 = 31.3 ppm, m, int. = 1.0 (COF).

Infrared spectrum (neat liquid, KBr, cm^{-1}): 1873 (s); 1853 (s); 1458 (vs); 1223 (vs); 1175 (s); 955 (m); 890 (vs); 834 (s); 808 (m); 790 (m); 739 (vw); 700 (m); 694 (m); 669 (vw); 635 (m-w); 623 (m-w); 612 (m-s); 579 (vs); 569 (vs,sh); 504 (w); 496 (w); 472 (w); 417 (w).

Mass spectrum (electron impact, 70 eV, mass, species, >1%): 158, $C_2{}^{35}ClFO_3S^+$, 23.4; 155, $C^{35}ClF_4S^+$, $C_2FO_3S_2{}^+$, 5.5; 129, $C_2{}^{35}ClF_2S^+$, 2.2; 127, $SF_5{}^+$, $CFO_2S_2{}^+$; 125, $CHO_3S_2{}^+$, 1.1; 124, $C_2HFOS_2{}^+$, 2.9; 113, $C_2{}^{35}ClF_2O^+$, 5.2; 108, $SF_4{}^+$, 1.5; 103, $CH_2SF_3{}^+$, 2.0; 101, CF_3S^+, 1.7; 95, $C^{35}ClOS^+$, $CFS_2{}^+$, 7.0; 94, $C_2{}^{35}ClFO^+$, 8.7; 91, C_2FOS^+, $^{34}SF_3{}^+$, 4.8; 89, $SF_3{}^+$, 100.0; 86, $^{35}ClFS^+$, 6.6; 85, $C^{35}ClF_2{}^+$, 8.5; 83, SO_2F^+, 3.4; 81, $C_2F_3{}^+$ (rearr.), 11.2; 79, $CSOF^+$, 1.3; 78, $C_2F_2O^+$ (rearr.), 1.1; 77, CHS_2O^+,$C_2H_2FS^+$ (two fragments), 1.4, 2.5; 76, $CSO_2{}^+$, C_2HFS^+, 1.2; 75, C_2FS^+, 8.0; 73, C_2HOS^+, 1.1; 72, C_2OS^+, 1.2; 70, $SF_2{}^+$, 44.8; 69, $CF_3{}^+$ (rearr.), 8.6; 67, SOF^+, 58.9; 66, $C^{35}ClF^+$, 19.8; 65, SO_2H^+, 5.6; 64, $SO_2{}^+$, 54.3; 63, CFS^+, 17.3; 60, COS^+, 1.8; 51, SF^+, 12.0.

Anal.calcd for $C_2ClF_7O_3S_2$: C, 7.89; Cl, 11.64; F, 43.7; S, 21.05. Found: C, 7.85; Cl, 11.9; F, 44.0; S, 21.23%.

Pentafluorosulfur(fluorosulfonyl)chloromethane, $F_5SCHCl(SO_2F)$, 10b

In a 5.0 ml Pyrex flask 0.74 g of $F_5SCCl(SO_2F)(C(O)F)$ (2.4 mmol) were mixed with 0.65 g water (distilled). The flask was stoppered lightly and kept at room temperature for 21 h. After pipetting off the water layer, adding ≈ 1g of powdered P_4O_{10} in the cold under swirling in small portions, and vacuum transferring away the volatile product, and repeating the drying procedure, 0.61 g (97.1%) of a clear liquid was obtained. The material was analytically pure by gas chromatography (30% SE-30, 2m, 120°C, R_f = 15.3 min.), ^1H and ^{19}F n.m.r.

Infrared spectrum (neat liquid, KBr, cm^{-1}): 2992 (m); 1448 (vs); 1262 (m-w); 1232 (s-vs); 1205 (m-s); 1192 (m-w,sh); 874 (vs); 851 (vs); 811 (s); 774 (m-s); 757 (w,sh); 688 (vw); 669 (m); 612 (m); 581 (s); 571 (s); 566 (s); 499 (vw); 490 (w-m); 463 (m); 453 (vw); 423 (vw); 405 (m).

^1H n.m.r. (neat liquid, CH_2Cl_2 ext. standard): $\delta = 6.14$ ppm, pentet. $J_{BH} = 4.20$ Hz.

^{19}F n.m.r. (neat liquid, ext. CCl_3F): $\phi_1 = 61.5$ ppm, m, int. = 5.0, (degenerate AB_4 spectrum, SF_5); $\phi_2 = 49.8$ ppm, p, int. = 1.0 (SO_2F). $J_{B2} = 9.5$ Hz.

Mass spectrum (electron impact, 70eV, mass, species, >1%): 175, $(M-SO_2F)^+$, 1.8; 131, $(M-SF_5)^+$, 2.7; 129, $(M+H-5F-Cl)^+$, 2.5; 127, SF_5^+, 53.1; 108, SF_4^+, 2.2; 91, C_2FOS^+, 2.1; 89, SF_3^+, 45.7; 83, SO_2F^+, 2.6; 79, $CFOS^+$, 1.8; 70, SF_2^+, 7.9; 69, H_2SOF^+, CF_3^+, 16.7; 68, $HSOF^+$, 1.6; 67, SOF^+, 100.0; 64, SO_2^+, 8.1; 63, CFS^+, 1.2; 51, SF^+, 4.8

Anal.calcd. for $CHClF_6O_2S_2$: C, 4.64; H, 0.39; Cl, 13.71; F, 44.1, S, 24.80. Found: C, 4.72; H, 0.34; Cl, 13.74; F, 44.3; S, 24.84%.

$F_5SCBr(SO_2F)C(O)F$, 7b

Bromine (0.37 g, 2.31 mmol) and 1 (0.95 g, 2.36 mmol) were gently heated in a 30 ml Carius tube under anaerobic conditions, when most of the bromine was consumed rapidly;

heating was continued at 82°C (1 h), but a brownish color persisted. The product was vacuum transferred out (0.67 g), treated with mercury (≈ 2 g) to remove excess bromine, after which 0.42 g of crude $F_5SCBr(SO_2F)C(O)F$ was collected. This material could not be purified by fractional condensation or distillation and was used as such in subsequent reactions.

I.r. spectrum of the crude material (neat sample, KBr, cm^{-1}): 2985, vw; 2674, vw; 1868, s,sh; 1846, vs; 1455, s-vs; 1290, w; 1230, s; 1171, s; 1103, w; 946, m-s; 881, vs; 835, s,sh; 814, s; 791, s; 692, s; 650, m; 610, s; 579, s; 568, s,sh; 497, m; 492, m; 466, m; 458, m.

^{19}F n.m.r. ($CCCl_3$, external CCl_3F): ϕ = 74 ppm, int. = 4 (impurity); ϕ = 67.6 ppm, m, int. = 30 (SF_5); ϕ = 60-62, several lines, int. = 4 (impurity); ϕ = 50.6 ppm, m; int. = 6 (SO_2F); ϕ = 35.3 ppm, m, int. = 6 (COF).

$F_5SCHBrSO_2F$, 10a

To 1.31 g of crude $F_5SCBr(SO_2F)C(O)F$ in a 4.0 ml conical vial 5 drops of water were added, and the flask was lightly stoppered; no visible reaction occurred. The mixture was kept at room temperature for 18 hours and occasionally swirled. Phosphorus pentoxide was added with cooling and the volatile materials were transferred out (0.84 g); a light, slightly yellow liquid was obtained. Gas chromatography (20% SE-30, on Chromosorb W, 3m, 120°C): 2 bands, R_f = 5.6 minutes, area = 14.6 % (same R_f as $F_5SCH_2SO_2F$), R_f = 12 minutes, area = 85.6 % ($F_5SCHBr(SO_2F)$). Preparative g.c. (20% SE-30, 3m, 115°C) afforded 0.24 g (23.5 %) of a colorless liquid.

^1H n.m.r. spectrum ($CDCl_3$, $Si(CH_3)_4$, 300 MHz): δ = 6.40 ppm, p, 4.58 Hz.

^{19}F n.m.r.spectrum ($CDCl_3$, external CCl_3F): ϕ = 64 - 74 ppm, distorted AB_4 spectrum, maximum at 66.7 ppm, int. = 5.2 (SF_5); ϕ = 53.3 ppm, m, int. = 1.0 (SO_2F).

Infrared spectrum (neat sample, KBr, cm^{-1}): 2997, m; 2922, vw; 1445, s; 1256, w-m; 1225, m-s; 1166, w; 1072, w, broad; 871, vs; 820, s; 785, m; 761, m-s; 690, w; 663, m; 612, m-s; 578, s; 569, s; 564, s,sh; 490, m; 463, w; 456, w; 404, m.

Mass spectrum (e.i., m/e, fragment, % > 1, only ^{79}Br listed): 219, $(M-SO_2F)^+$, 1.6; 175, $(M-SF_5)^+$, 20.5; 129, $^{34}SF_5^+$, 1.9; 127, $^{32}SF_5^+$, 52; 111, $CHBrF^+$, (rearr.), 30.0; 108, SF_4^+, 2.2; 97, $CH_2FS_2^+$, 4.0; 95, CSO_2F^+, CFS_2^+, 1.6; 93, CH_2Br^+, 2.4; 92, $CHBr^+$, 11.8; 91, two fragments, CBr^+, ?, 2.4, 2.5; 89, SF_3^+, 61.5; 83, SO_2F^+, $CHSF_2^+$, 1.3; 80, HBr^+, 3.6; 79, Br^+, 4.4; 70, SF_2^+, 10.2; 69, CF_3^+, 5.0; 68, $FSOH^+$(?), 1.1; 67, FSO^+, 100.0; 64, $CHSF^+$, SO_2^+, 7.5; 63, CSF^+, 1.2; 51, SF^+, 6.3.

Anal.calcd for $CHBrF_6O_2S_2$: C, 3.96; H, 0.33; F, 37.6; S, 21.16; Br, 26.37. Found: C, 4.02; H, 0.37; F, 38.0; S, 21.26; Br, 26.28%.

$F_5SCH(SO_2F)CH_2CH_2Br$, 11

A 75 ml stainless steel bomb was charged with 0.24 g of benzoyl peroxide (1.0 mmol, Aldrich), 1.73 g of crude $F_5SCBr(SO_2F)COF$ (≈ 5 mmol) and 0.57 g of ethylene (21.9 mmol) and heated at 95°C for 24 hours. At room temperature, a colorless liquid (1.01 g after degassing) was transferred out; its i.r. and ^{19}F n.m.r. spectra was virtually identical with the spectra of authentic $F_5SCH_2SO_2F$. The residue in the bomb (0.78 g), a brown partially crystalline mass was dissolved in ether, and both the i.r. and ^{19}F spectra indicated the absence of a C(O)F group in the crude product; present was a C=O band at 1690 cm^{-1}. The material that caused this band could not be removed by vacuum distillation, but stirring a CH_2Cl_2 solution of the collected impure fraction, the pot residue and the rinse of the distillation head with dilute $NaHCO_3$ solution for circa 15 min caused its disappearance. The CH_2Cl_2 solution was pipetted off, dried (Na_2SO_4) and transferred to a 10 ml flask. Distillation (1 mm Hg) afforded a small amount of colorless liquid (45-46°C), but lowering the pressure ($\approx$ 0.5 mm Hg), and heating the distillation head yielded some more product (0.23 g, 14.0%).

^1H n.m.r. spectrum (neat sample, external $Si(CH_3)_4$): δ_1 = 5.79 ppm, m, partially resolved, probably a septet, $J \approx 5.4$ Hz, intensity = 0.97 ($F_5SC\underline{H}$); δ_2 = 3.23 ppm, m, intensity = 2.03 ($C\underline{H}_2CH_2Br$); δ_3 = 3.94 ppm, t, J_{23} = 6.0 Hz, intensity = 2.00 ($C\underline{H}_2Br$). All lines are broadened.

^{19}F n.m.r. spectrum (neat liquid, external CCl_3F): AB_4X ϕ_A = 75.3 ppm, d of nine line pattern (the doublet is poorly resolved), intensity = 1.00; ϕ_B = 66.0 ppm, d-m, intensity = 4.00; ϕ_X = 54.8 ppm, $\approx$ pentet, intensity = 0.94 (SO_2F). J_{AB} = 149.6 Hz; J_{BX} = 11.3 Hz; $J_{AH^1} \approx 4.2$ Hz.

I.r.spectrum (neat liquid on KBr, cm^{-1}): 3062, vw; 2960, w; 2940, w,sh; 1428, s-vs; 1364, vw; 1318, w; 1268, m,sh; 1252, m; 1216, s; 1179, w; 1158, vw,sh; 989, w,br; 970, vw,sh; 941, w; 871, vs; 820, m-s; 809, m-s,sh; 775, m-s; 756, m,sh; 672, m; 645, vw; 613, m; 589, s; 579, s,sh; 563, m-s,sh; 512, vw; 495, vw; 475, w; 448, w.

Mass spectrum (e.i., 70 eV, m/e, fragment, % > 1, only ^{79}Br): 330, M^+, 0.5; 253, ($C_3H_2{}^{81}BrF_2O_2S_2$ = M-3H-4F)$^+$, 6.6; 252, (M+H-Br)$^+$, 3.4; 251, (M-Br)$^+$, $C_3H_2{}^{79}BrF_2O_2S_2{}^+$, 71.0; 246, (M-$SO_2$F-H)$^+$, 6.2; 202, (M-$SF_5$-2H)$^+$, 7.4; 167, (M-Br-$SO_2$F-H)$^+$, 4.2; 135, (M-$CH_2$Br-$SO_2$F-F)$^+$, 1.7; 127, $SF_5{}^+$, 20.3; 123, $C_2FOS_2{}^+$, 5.2; 122, $C_2H_2O_2S_2{}^+$, 1.9; 119, $C_3H_3Br^+$, 46.1; 113, $C_2F_3S^+$, 1.4; 111, $CFOS_2{}^+$, 1.9; $CHO_2S_2{}^+$, 2.3; 108, $CO_2S_2{}^+$, $SF_4{}^+$, 1.1; 107, $C_2FS_2{}^+$, 1.8; 97, $CH_2SO_2F^+$, 4.7; 93, CH_2Br^+, 16.7; 91, $C_3H_4FS^+$, 3.4; 89, $SF_3{}^+$, 47.4; 87, C_3FS^+, 1.2; 83, SO_2F^+, 2.9; 81, CH_2SOF^+, 1.5; 79, $CSOF^+$, 2.7; 71, $C_3H_3S^+$, 1.4; 70, $SF_2{}^+$, 6.5; 69, C_3HS^+, $CF_3{}^+$, 4.6; 68, C_3S^+, 1.3; 67, FOS^+, 25.5; 65, CH_2SF^+, 3.1; 64, $SO_2{}^+$, $CHSF^+$, 2.0; 60, $C_2H_4S^+$, 7.9; 59, $C_2H_3S^+$, 100.0; 57, C_2HS^+, 7.9; 55, C_3F^+, 8.7; 51, SF^+, 5.9.

Anal.calcd for $C_3H_5BrF_6O_2S_2$: C, 10.88; H, 1.52; Br, 24.13; F, 34.43; S, 19.37. Found: C, 10.85; H, 1.50; Br, 24.17; F, 34.5; S, 19.33%.

$F_5SCBr_2SO_2F$, 8

Bromine was added dropwise to a stirred solution of 4 (2.00 g, 5.0 mmol) in a 25 ml flask in 0.5 ml of acetonitrile at room temperature. A white precipitate was formed instantly, and after some time bubbling and foaming ensued with the loss of the bromine color. More bromine was added occasionally until a faint red color persisted and no more bubbles were observed (≈ 15 min). Stirring was continued for 5 min. ^{19}F n.m.r. indicated only one product, without a C(O)F group present. Because of the failure to separate the product from the solvent by distillation, the reaction mixture was subjected to fractional condensation (-20, -78, -196°C traps), where the material in the -20°C trap was further purified by three successive trap-to-trap distillations. This resulted in 0.73 g (38.4 %) of an almost colorless, glassy, partially crystalline material, m.p. 39-43°C. The material of the -78 °C trap was subjected to repeated fractional condensations, but it was not possible to obtain a solid material. The product (-10 °C trap, 0.56 g) showed an almost similar i.r. spectrum to the solid, while the -78 °C trap (0.59 g) contained sizable amounts of CH_3CN. The - 196 °C trap (0.64 g) was almost free of any SF_5 containing product.

^{19}F n.m.r. spectrum (CH_3CN, CCl_3F ext.): AB_4X spectrum, ϕ_A = 67.0 ppm, 9 lines, int. = 1.00; ϕ_B = 58.0 ppm, d-m, int. = 4.11; ϕ_X (SO_2F) = 39.9 ppm, ≈ s (not resolved); J_{AB} = 149.0 Hz.

I.r. spectrum (neat samples, on KBr, cm^{-1}): 1441 (vs); 1268 (vw,sh); 1222 (vs); 1215 (m); 1100 (m,sh); 1087 (w,sh);

1049 (vw); 972 (w); 882 (vs); 857 (vs); 831 (vs); 787 (m-s); 767 (m-s); 749 (m,sh); 715 (m-s); 703 (m-s); 685 (s); 654 (vw); 618 (m-s); 605 (s); 566 (vs); 498 (m); 489 (m); 471 (m); 463 (m).

Mass spectrum (e.i., 70 eV, mass, fragment, % > 10): 299, $F_5SC^{79}Br^{81}Br^+$, 53.4 (triplet, 1:2:1); 281,; 255, $C^{81}Br^{79}BrSO_2F^+$, 54.3 (triplet); 191, CBr_2F^+ (rearr.), 24.8 (triplet); 172, $C^{81}Br^{79}Br^+$, 19.4 (triplet;)159, $CH^{79}BrSOF^+$, 11.0; 127, SF_5^+, 33.9; 92, $C^{79}Br^+$, 26.0; 89, SF_3^+, 92.6; 80, $H^{79}Br$, 15.7; 79, ^{79}Br, $CFSO^+$, 14.2; 70, SF_2^+, 20.7; 67, FSO^+, 100.0; 64, SO_2^+, 64.8; 48, SO^+, 30.1; 44, CS^+, 22.1.

Anal.calcd for $CBr_2F_6O_2S_2$: C, 3.14; Br, 41.84; F, 29.8; S, 16.79. Found: C, 3.32; Br, 40.95; F, 29.4; S, 16.65%.

$F_5SCCl(SO_2F)C(O)Cl$, 9

2.12 g of Cs^+ $[F_5SC(SO_2F)C(O)F]^-$ (5.3 mmol) and 1.31 g Cl_2 (18.5 mmol) in a 300 ml Pyrex-quartz vessel were irradiated with a 250 W GE sunlamp from a distance of 5 cm (4h) and 10 cm (12h). The pressure in the reaction vessel dropped by 1/3, indicating the consumption of 1 equivalent of chlorine; an i.r. spectrum (100 torr, 10 cm path length, KBr windows) showed a C(O)F group, but neither CO nor COClF bands. Irradiation was continued for 24 h with no change in the i.r. spectrum. Dry acetonitrile (1 ml) was then added by vacuum transfer, and irradiation (12h, 10cm) was continued. After 12h, the chlorine color had faded and another 0.84 g of Cl_2 (11.8 mmol) were added. After another 17 h of irradiation (20 cm), the chlorine color had faded again. The product was subjected to fractional condensation (-30, -78, -196°C). The material in the -30°C trap (0.31 g) was (g.c. 5 % QF-1 on Chromosorb W, 1m, 70 °C) 79 % $F_5SCCl(SO_2F)C(O)Cl$, 6.5 % $F_5SCCl(SO_2F)C(O)F$, 7.8 % CH_3CN and 7.5 % of an unknown material. The contents of the -78°C trap were again subjected to fractional condensation (-45, -78,-196°C). The -45°C trap contained 0.77 g of a product that contained (g.c.) 45 % $F_5SCCl(SO_2F)C(O)Cl$ and 14 % $F_5SCCl(SO_2F)C(O)F$. Almost no product was in the -78°C trap and the material in the -19°C (0.39 g) contained no $F_5SCCl(SO_2F)C(O)Cl$. The two products from the trap-to-trap distillations were combined and subjected to preparative gas chromatography (QF-1, 1m, 70 °C). A total of 0.20 g of a clear colorless liquid were collected. Yield: 12 %. When the above procedure was carried out with CH_3CN from the very beginning, the initial formation of $F_5SCCl(SO_2F)C(O)F$ was observed (^{19}F n.m.r.), which upon successive irradiation and chlorine addition decreased, and $F_5SCCl(SO_2F)C(O)Cl$ became the major product. There were other minor SF_5 products, which could not be collected in sufficient quantity so as to allow their identification. One product could have been $F_5SCHClSO_2F$ and another $F_5SCCl_2SO_2F$, as concluded from the similar n.m.r. spectral values of $F_5SCBr_2SO_2F$ ($\phi_A \approx 66$ ppm; $\phi_B \approx 54$ ppm; $\phi_X = 39.5$ ppm, X = SO_2F). The product in this case was washed with water, dried and also subjected to preparative gas chromatography, which allowed the collection of 0.16 g of $F_5SCHClSO_2F$ (12.9 %), apparently formed by the hydrolysis of $F_5SCCl(SO_2F)C(O)Cl$.

^{19}F n.m.r. spectrum (neat sample, CCl_3F ext.): ϕ = 64.5 ppm, m, int. = 5.3 (SF_5); ϕ = 50.6 ppm, m, int. = 1.0 (SO_2F).

Mass spectrum: (negative c.i., isobutane, mass, species,> 5%): 257, $C^{35}ClF_6O_2S_2^-$, 10.9; 223, $F_5SCHSO_2F^-$, 46.9; 167, $C_2F_5OS^-$, 6.6; 165, $CF_3O_2S_2^-$, 9.6; 146, $CF_2O_2S_2^-$, 32.0; 130, $CF_2OS_2^-$, 9.5; 127, SF_5^-, 100.0; 83, SO_2F^-, 37.5.

Infrared spectrum (neat, KBr, cm^{-1}): 1793(s), 1769 (m-s,sh); 1454(vs); 1229(vs); 1022(s); 919(vssh); 890(vs); 878(vssh); 836(s); 798(s); 754(s); 737(s-m); 691(m); 665(vw); 615(s); 599(s); 577(s); 563(s); 515(w); 501(w); 491(w-m); 464(m).

Anal.calcd.: for $C_2Cl_2F_6O_3S_2$: C, 7.48; Cl, 22.08; F, 35.1. Found: C, 7.59; Cl, 22.30; F, 35.2%.

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