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THE CHEMISTRY OF $F_4S{=}\overline{CCF_2OSO_2}$ - PART II

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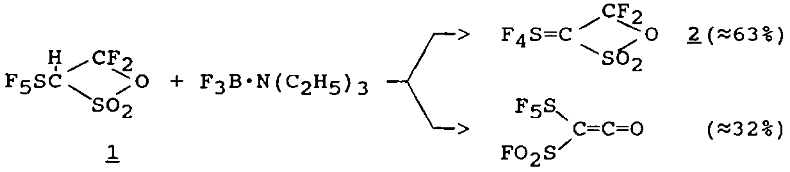
SUMMARY

The reaction of $F_4S{=}\overline{CCF_2OSO_2}$ with ROH (R= CH_3, $CH(CH_3)_2$, $C(CH_3)_3$), ClX (X = F, OCF_3) and $CsOCF_3$ was studied as a means for preparing novel sulfonyl fluorides or sultones. The new β-fluoro sultones $CH_3OSF_4\overline{CHCF_2OSO_2}$ and $F_5S\overline{C(Cl)CF_2OSO_2}$ were prepared and characterized.

INTRODUCTION

We have observed recently that when sultone 1 was treated with $F_3B{\cdot}N(C_2H_5)_3$, a two-directional elimination occurred:



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The reactivity of the ylidic S=C bond and the presence of a sultone ring made it possible to synthesize several derivatives of the sultone $F_5S\overline{CHCF_2OS}O_2$ via the intermediacy of $F_4S=\overline{CCF_2OS}O_2$, $\underline{2}$. We published earlier our initial results from the reactions of $\underline{2}$ with various reagents[1]. It was found that $\underline{2}$ easily added HF to give $\underline{1}$, and added HCl to give a cis-SF_4Cl compound, with the sultone ring intact, and CsF, leading to F^- addition and rearrangement to give Cs^+ $[F_5SC(SO_2F)COF]^-$ occurred.

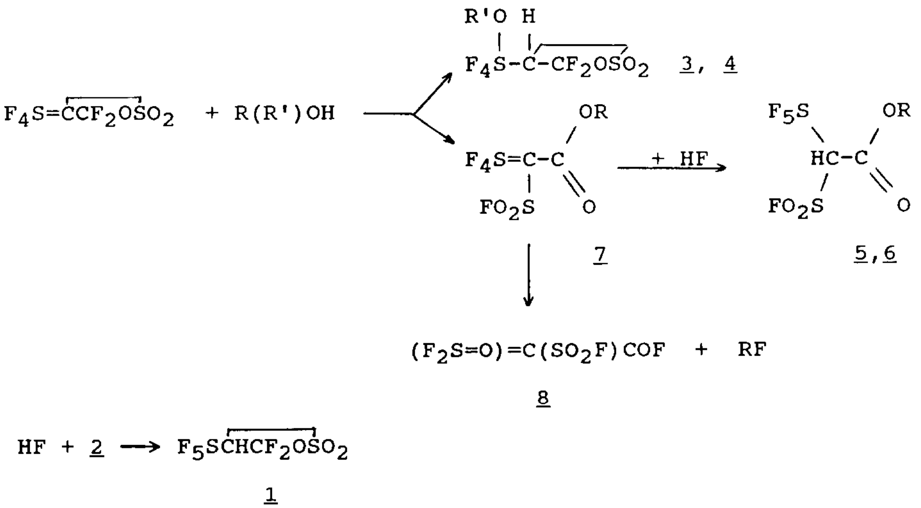
RESULTS AND DISCUSSION

Since we are interested in synthesizing new sultones [2-5] as precursors for sulfonyl fluorides, further studies involving addition to the polar S=C bond in $\underline{2}$ were carried out.

One reaction of $\underline{2}$ is the specific addition of methanol, to yield another cis-SF_4-R compound as a white low-melting solid:

$$\underline{2} + CH_3OH \longrightarrow \underset{\underline{3}}{H_3COF_4S\overline{CHCF_2OS}O_2}$$

The reaction of 2 and isopropanol led to a mixture of what was probably the cis-$SF_4(OCH(CH_3)_2)$ 4 derivative of the sultone and the ester $F_5SCH(SO_2F)COOCH(CH_3)_2$ 5. Attempts to isolate the SF_4-derivative failed, as the compound was apparently not stable. The result with $(CH_3)_3COH$ was even more pronounced, as no cis-SF_4OR compound could be detected in the ^{19}F n.m.r. spectrum. What was found was largely the ester $F_5SCH(SO_2F)COOC(CH_3)_3$ 6; the ^{19}F n.m.r. results suggest also initial formation of 1, and later $F_5SCH_2SO_2F$. In order to explain this result, one has to consider the two possible sites of attack at 2:



R' = CH_3 (3), $(CH_3)_2CH$ (4); R = $(CH_3)_2CH$ (5), $(CH_3)_3C$, (6)

It was postulated earlier that an intermediate 7 could have been present in the reaction of $F_5SCH(SO_2F)COOCH(CH_3)_2$ and

$F_3B{\cdot}N(C_2H_5)_3$, leading to the compound $(F_2S{=}O){=}C(SO_2F)COF$, 8, by a rearrangement in a $F_3B{\cdot}N(C_2H_5)_3$ + BF_4^- + $NH(C_2H_5)_3^+$ medium [6]; HF would be first absorbed by $F_3B{\cdot}N(C_2H_5)_3$, and no HF addition to the S=C bond is expected in this case. In the present case, 8 could not be detected. This is not surprising, as neither the $F_2S{=}O$, nor the S=C or the COF moieties are expected to withstand an alcoholic environment. This rearrangement to 8 is also expected to compete with the addition of HF to the S=C bond, and HF addition would need to be much faster than the rearrangement reaction, as concluded from the product distribution (mainly the SF_5-ester 6).

The product distribution is dictated by the alcohol used. The most obvious difference between methanol and t-butanol is the steric bulk, and the fact that with isopropanol an intermediate result is obtained allows one to draw the conclusion that steric factors are responsible for the different course of the reactions of 2 and various aliphatic alcohols.

The preferred attack of CH_3OH at the doubly bonded sulfur shows that the S=C bond is more reactive than the sultone ring, but that this increased reactivity seems to be easily offset by steric demands. It is here also pertinent that 2 failed to react with either C_6F_5OH, CF_3CH_2OH, $(CF_3)_2CHOH$ or $(CF_3)_2(C_2F_5)COH$. In all cases a broad new feature was observed at ≈ 73 ppm, which is also observed as a decomposition product of pure 2, accompanied by the slow disappearance of 2. The t-butyl ester $F_5SCH(SO_2F)COOC(CH_3)_3$ could not be isolated in pure state. When it was obtained from the reaction of $F_5SC(SO_2F){=}C{=}O$ and $(CH_3)_3COH$, attempted purification led always to contamination with $F_5SCH_2SO_2F$; with distillation this was the sole product.

Chlorine monofluoride will add to 2, although not without difficulty: an excess of ClF and several days of reaction time are necessary in order to have complete reaction.

$$2 + ClF \longrightarrow F_5S\overline{C(Cl)CF_2OS}O_2$$

9

This product could not be obtained by the addition of sulfur trioxide to $SF_5CCl{=}CF_2$. The SF_5 group underwent complete degradation.

Compound 9 is a reactive compound, as is evident from the formation of $F_5SCCl(SO_2F)COF$ (10) in the reaction of 2 and ClF [7]; the formation of 10 could be mostly avoided only when acid-washed apparatus was used. The conversion of 9 into 10 occurred on the potassium bromide plates (apparently catalyzed by Br^-) that were used for infrared analysis: The rearrangement was easily followed by observing the build-up of the band attributable to the carbonyl group. The conversion of 9 into 10 is part of a general reaction of fluorosultones of the form $R_f\overline{CXCF_2OS}O_2$ (R_f = fluoro radical, X = H or halogen) with bases that results in the opening of the four-membered ring to give an isomeric acyl fluoride.

Furthermore, 2 did not react in the expected fashion with either CF_3OCl or $CF_3O^-Cs^+$. Familiar products were obtained in these cases:

$$\underline{2} + CF_3OCl \longrightarrow F_5S\overline{C(Cl)CF_2OS}O_2$$

9

$$\underline{2} + CF_3O^-\ Cs^+ \longrightarrow Cs^+\ [F_5SC(SO_2F)COF]^- + \{CF_2O\}$$

The addition of ClF instead of CF_3OCl in reactions of CF_3OCl is not uncommon. Trifluoromethyl hypochlorite is assumed to undergo polar addition, rather than a free radical one. This conclusion has been reached from the product distribution in several reactions [8]. Likewise, cesium trifluoromethoxide will usually transfer only F^- in nucleophilic substitutions.

As expected, the ^{19}F n.m.r. spectrum of $F_4S(OCH_3)\overline{CHCF_2OS}O_2$ (3) is of the type ABCDXY. The ^{19}F n.m.r. spectrum of 3 shows three types of fluorine in the ratio of 1:2:1, which identifies it clearly as a cis-SF_4R compound, because for a trans arrangement a singlet is observed for the fluorine resonances, due to their equivalence, whereas the CF_2 group appears as an XY system with asymmetric coupling to the proton, analogous to sultone 1. The coupling within the SF_4 arrangement is complicated. In 3 one observes actually four fluorine resonances. Two of these lie close together, respectively, and are very similar, except that in one of them additional coupling is seen. This suggests that the rotation of the SF_4OCH_3 group is hindered, perhaps through hydrogen bonding between either a fluorine or CH_3O and the hydrogen at C_α of the sultone ring. The assignment of the different fluorines and coupling constants followed the one given for similar compounds[9]. Also, $\phi_Y = -74.3$ ppm, $\phi_X =-80.3$ ppm, $J_{XY} = 102.7$ ppm. The ^{19}F n.m.r. spectrum of the isopropyl derivative, $F_4S(OCH(CH_3)_2)CHCF_2OSO_2$, 4, is very similar. The determination of spectral parameters was somewhat more difficult due to the presence of other compounds.

In the ^{19}F n.m.r. spectrum of $F_5S\overline{C(Cl)CF_2OS}O_2$, the SF_5 group appears as an AB_4 resonance with overlapping A and B parts; a simple interpretation is therefore not possible. The CF_2 group is observed as an AB system, $\phi_A = -77.2$ ppm, $\phi_B = -79.0$ ppm, $J_{AB} = 94.3$ Hz, $J_{ASF4} = 3.6$ Hz. The respective values for the sultone $F_5S\overline{CHCF_2OS}O_2$ are $\phi_A = -72.8$ ppm, $\phi_B = -79.7$ ppm, and $J_{AB} = 103$ Hz [2], and for $ClF_4S\overline{CHCF_2OS}O_2$, $\phi_A = -74.9$ ppm, $\phi_B = -78.9$ ppm, $J_{AB} = 100.8$ Hz[1].

The infrared spectra of 3 and 9 are in accord with the proposed structures. Vibrational bands for the asymmetric and symmetric stretching modes of the SO_2 group are observed in the following regions: 1424-1481 cm^{-1} and 1216-1234 cm^{-1}. The assignment is complicated through the presence of other bands.

The mass spectra of the new β-fluorosultones did not contain molecular ions but appropriate fragments were found: for 3, $(M-CH_3O)^+$, $(M-CH_3O-HF)^+$, $(M-SO_3)^+$, $(M-SO_3-F)^+$, $(CH_3OSF_2)^+$, SF_3^+; for 9, $(M-Cl-SO_2)^+$ and SF_5^+.

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 (^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 (^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 described.

Elemental analyses were carried out by Mikroanalytisches Laboratorium Beller, Göttingen, F.R.G..

$F_5S\overline{C(Cl)CF_2OS}O_2$ by reaction of 2 with ClF

Acid-washed apparatus was used, due to the easy rearrangeability of the product.

An oven-dried 75 ml steel bomb was charged with 2.95 g of CCl_3F (dried over P_4O_{10}), 0.31 g 2 (1.24 mmol) and 0.17 g (3.1 mmol) ClF. The bomb was allowed to warm up slowly and kept at room temperature for two days. Fractional condensation in an acid-washed glass apparatus yielded (-196, -40 °C) 0.23 g of product in the -40°C trap. The ^{19}F n.m.r. spectrum showed still 2 to be present. Both cold trap fractions were transferred back into the bomb, another 0.19 g ClF (3.5 mmol) were added and the bomb kept at room temperature for 6 days. Fractional condensation afforded 0.19 g in the -50°C trap, and after repeating the procedure with the -196°C fraction another 0.06 g were collected. The product was free of 2 but contained some small impurities (71, 53, 48, -70 ppm in ^{19}F n.m.r.spectrum). Yield 0.25g (66.2%). The infrared spectrum was quickly run, because rearrangement to the acyl fluoride took place very readily on the KBr plates, as could be judged from the slow increase of the CO band (1855 cm^{-1}) [9].

^{19}F n.m.r. spectrum (neat sample, CCl_3F ext.): ϕ_{SF5} = 62.8 ppm (m), int. = 5.00; ϕ_{CF2} (AB system): ϕ_A = -77.2 ppm, d-p, int. = 1.04, J_{ASF4} = 3.6 Hz (average); ϕ_B = -79.0 Hz, ≈ d-p-m, irregular spacing, int. = 1.09. J_{AB} = 94.3 Hz.

Infrared spectrum (neat sample, KBr, cm^{-1}): 1481, m; 1461, m,sh; 1437, s-vs; 1351, vw; 1276, m-s; 1234, s, 1202, vs; 1151, m-s; 1129, m-s; 1090, s-vs; 1046, w-m; 970, m-s; 934, s; 890, vs; 836, s-vs; 819, s; 782, m-s; 738, vw; 692, m; 666, m-s; 624, m; 609, m-s; 588, m; 572, m; 551, m; 535, m-s; 503, w; 483, w; 454, m; 434, w-m; 414, w-m.

Mass spectrum (c.i., mass,species, % < 1): 205, $(M-Cl-SO_2)^+$, 1.9; 191, $(M-Cl-CF_2-CO)^+$ (rearr.), 10.6; 163, $C_2H_2F_3OS_2^+$, 1.6; 127, SF_5^+, 2.2; 107, $C_2FO_2S^+$, 1.8; 91, C_2FOS^+, 5.9; 89, SF_3^+, 100.0; 85, CF_3O^+ (rearr.), 3.0; 83, SO_2F^+ (rearr.), 1.8; 81, $C_2F_3^+$ (rearr.), 2.4; 79, $CFOS^+$, 1.6; 73, C_2HOS^+, 2.6; 71, ?, 5.2; 70, SF_2^+, 1.9; 69, CF_3^+ (rearr.), 4.5; 67, , FSO^+, 2.5; 63, CFS^+, 1.9; 61, $CHOS^+$, 1.9.

Anal. calcd for $C_2ClF_7O_3S_2$: C, 7.89; F, 43.7; S, 21.05; Cl, 11.64. Found: C, 7.94; F, 44.2; S, 21.36; Cl, 11.51 %.

Reaction of 2 and $CsOCF_3$

In a Carius tube (80 ml), cesium trifluoromethoxide was prepared from 0.171 g of CsF (1.11 mmol) and 0.32 g of COF_2 (4.8 mmol) in 0.93 g of acetonitrile, followed by the vacuum transfer of 0.296 g (1.18 mmol) of 2 at -196°C. The tube was swirled at the melting point of the solid, and a pink coloration was observed. After standing overnight at room temperature, the volatile material was pumped off, leaving behind 0.525 g of a yellowish solid, which was identified as $Cs^+ [F_5SC(SO_2F)COF]^-$ by i.r. and ^{19}F n.m.r. spectroscopy.

Reaction of 2 and CF_3OCl

Trifluoromethyl hypochlorite (0.90 g, 7.3 mmol) and 2 (0.31 g, 1.2 mmol) were vacuum transferred into a 75 ml stainless steel bomb and allowed to warm up in a cold (-196°C) Dewar container; the reaction was then maintained at room temperature for two days. Fractional condensation (-196°C, -47°C, -25°C) yielded 0.37 g of a yellow solid in the -47°C trap. This material consisted (^{19}F n.m.r.) mainly of $F_5S\overline{C(Cl)CF_2OS}O_2$ (9), but contained also weaker signals at + 73 ppm and at - 57.7 ppm. This by-product could not be separated and identified.

2 and CH_3OH

Anhydrous methanol (0.05 g, 1.56 mmol) was added dropwise with swirling to 0.32 g of 2 (1.28 mmol) in a 25 ml pear-shaped flask. The methanol was allowed to flow down the side walls. Heat was liberated. The flask was stoppered and kept at room temperature for 140 minutes. An i.r. spectrum of the heavy yellow oil showed the presence of an ester band (1765 cm^{-1}, medium-strength). Separation was effected by repeated trap-to-trap distillation, first with a -45°C and a -196°C trap, and then, using the material from the -45°C trap, with a -45°C and a -17°C trap. The material in the -17°C trap was subjected again to the same procedure, and after this third process, 0.21 g of a white solid was collected in the -17°C trap. The infrared spectrum of the solid showed that only a very weak ester band was present. Yield = 58.2 %. M.p. = 20.5-22.0 °C (sealed tube).

^1H n.m.r. spectrum ($CDCl_3$, $Si(CH_3)_4$, 300 MHz): δ_1 = 4.11 ppm, s (signs of shoulders), area = 3.00 (CH_3); δ_2 = 6.37 ppm, 8 lines with signs of further splitting, area = 0.96 ($C\underline{H}-CF_2$).

^{19}F n.m.r. spectrum (neat sample, external CCl_3F): ABCDXY system ϕ_A = 68.4 ppm, d-d-d-d, area = 1.00; ϕ_B = 73.6 ppm, d-d-d-d, area = 1.00; ϕ_C = 55.3 ppm, d-d-d, area = 0.93; ϕ_D = 88.2 ppm, d-d-d-d, area = 1.00; ϕ_X = -80.3 ppm, d-m, area = 1.02; ϕ_Y = -74.3 ppm, d, area = 0.97. $J_{AB} \approx J_{AX}$ = 25.1 Hz; $J_{AC} = J_{BC}$ = 137.2 Hz; $J_{AD} = J_{BD}$ = 115.7 Hz; J_{CD} = 149.6 Hz; $J_{AY} = J_{CX} = J_{CY} = J_{DX}$ =

$J_{DY} = J_{CH} \approx J_{YH} = 0.0$ Hz; $J_{AH} = 10.58$ Hz; $J_{BH} = 7.82 \pm 0.39$ Hz; $J_{DH} = 20.21$ Hz; $J_{XY} = 102.7$ Hz; $J_{BX} = 14.47 \pm 0.63$; $J_{XH} \approx 6.8$ Hz.

I.r.spectrum (neat sample on KBr, cm^{-1}): 2997, m; 2865, vw; 1459, m; 1424, vs; 1319, s; 1281, s; 1216, vs; 1103, s; 1081, vs; 1020, vs; 975, m; 830, vvs; 744, vs; 671, m; 659, s; 614, m-w; 596, m-w; 583, m-w; 574, w,sh; 556, vw; 529, s; 518, m-w,sh; 492, vw; 453, m.

Mass spectrum (e.i. mass, species, % > 1): 251, $(M-CH_3O)^+$, 3.6; 231, $(M-CH_3O-HF)^+$, 2.8; 227, $(M-2F-H-O)^+$, 1.2; 201, $(M-SO_3)^+$, 9.9; 197, $(M-SO_2-F-2H)^+$, 2.1; 183, $(M-SO_3-F)^+$, 13.0; 182, $(M-SO_3-F-H)^+$, 1.5; 173, $(M-4F-2O-H)^+$, 3.1; 172, $(M-4F-2O-2H)^+$, $(M-5F-CH_3)^+$, 1.6; 171, $(M-4F-2O-3H)^+$, $(M-5F-CH_3-H)^+$, 47.6; 168, $(M-6F)^+$, $(M-SO_3-CH_3-F)^+$, 4.4; 163, $(M-SO_3-2F-H)^+$, 3.5; 149, $(M-SO_3-2F-CH_3)^+$, 9.4; 145, $(M-3F-SO_3)^+$, 3.3; 144, $(M-3F-H-SO_3)^+$, $(M+H-SF_4OCH_3)^+$, 4.3; 139, $SF_4OCH_3^+$, 9.8; 133, $C_2HF_4S^+$, 1.2; 127, $(M+H-4F-SO_3)^+$, 3.1; 124, $CO_3S_2^+$, 15.7; 109, $CHO_2S_2^+$, 1.1; 105, $C_3H_2FOS^+$, $C_2HO_3S^+$ 23.6; 101, $CH_3OSF_2^+$, 12.4; 94, $C_2SF_2^+$, 4.7; 91, C_2FOS^+, 3.4; 89, SF_3^+, 100.0; 85, C_3HOS^+, 1.5; 83, $CHSF_2^+$, 2.6; 82, CSF_2^+, CH_3OSF^+, 2.8; 81, CH_2OSF^+, 2.6; 80, $CHOSF^+$, SO_3^+, 3.5; 79, $COSF^+$, 5.1; 75, CH_3OSC^+, 2.3; 70, SF_2^+, 6.1; 69, CF_3^+ (rearr.), 2.2; 67, FOS^+, 21.0; 66, CF_2O^+, 1.6; 65, $SFCH_2^+$, 9.2; 64, SO_2^+, CH_3OSH^+, $SFCH^+$, 12.8; 63, CFS^+, CH_3OS^+, 9.1; 60, COS^+, 2.0.

Anal.calcd for $C_3H_4F_6O_4S_2^+$: C, 12.77; H, 1.43; F, 40.4; S, 22.72. Found: C, 12.87; H, 1.33; F, 40.0; S, 22.38 %.

2 AND $(CH_3)_2CHOH$

Since attempts to isolate the sultone derivative that was obtained in this reaction failed, the reaction mixture was used to obtain n.m.r. spectral quantities.

Isopropanol (0.0664 g, 1.1 mmol) was vacuum transferred to 2 (0.2767 g, 1.1 mmol) in a 10 ml flask equipped with a Kontes Teflon valve. The flask was allowed to attain room temperature in an initially cold (-196°C) Dewar container and was swirled as soon the contents started to liquefy. After about 15 minutes at room temperature, 2 ml of CCl_3F were added and the ^{19}F n.m.r. spectrum was obtained. The signals from the sultone were partially superimposed by bands originating from unknown compounds. The presence of the ester $F_5SCH(SO_2F)COOCH(CH_3)_2$ (≈ 20 % of the sultone bands) was confirmed by adding a drop of an authentic sample to the original reaction mixture causing its band areas to increase; the increase was measured in both the ^1H and ^{19}F n.m.r spectra. Other compounds were present only in minor amounts.

^1H n.m.r. (in a CCl_3F + $CDCl_3$ mixture, 400 MHz): δ = 6.33 ppm, area = 0.96 ($C\underline{H}-CF_2$) ; δ = 5.15 ppm, area = 1.00 ($(CH_3)_2C\underline{H}$); δ = 1.44 ppm, area = 6.7 (partially superimposed by other bands), ($(C\underline{H}_3)_2CH$).

^{19}F n.m.r. spectrum (in CCl_3F + $CDCl_3$, 376 MHz): ABCDXY system, ϕ_A = 74.32 ppm, d-d-d-d, area = 1.00; ϕ_B = 82.39 ppm, d-d-d-d, area = 1.00; ϕ_C = 60.37 ppm, d-d-d, area = 1.07; ϕ_D = 87.48 pp,. d-d-d-d, area = 1.00; ϕ_X = -73.55 pp, d, area = 0.97;

ϕ_Y = -79.15 ppm, d-m, area = 1.03. $J_{AB} = J_{AY}$ = 27.1 Hz (average); $J_{AC} = J_{BC}$ = 138.2 Hz (av.); $J_{AD} = J_{BD}$ = 115.0 Hz (av.); J_{BY} = 12.1 Hz; J_{CD} = 147.9 Hz (av.); J_{XY} = 113.0 Hz; J_{AH} = 11.2 Hz; J_{BH} = 7.0 Hz (av.); J_{DH} = 20.6 Hz.

2 and $(CH_3)_3COH$

The reaction was run either in a solvent (CCl_3F) or with the pure reactants; in neither case could an ABCD spectrum (^{19}F) be detected. It was not possible to separate the constituents by fractional condensation, and the apparent instability of $F_5SCH(SO_2F)C(O)OC(CH_3)_3$ excluded other methods. Inferences are thus made from ^{19}F n.m.r. and i.r. data.

To 0.067 g of $(CH_3)_3COH$ (0.91 mmol) in a 50 ml pear-shaped flask with a Kontes Teflon valve connector, 0.22 g of 2 (0.88 mmol) was vacuum transferred. The bulb was allowed to attain room temperature slowly in a cold Dewar container (initially -196°C), and swirled when the constituents started to melt. After complete mixing, the vessel was kept at room temperature for one more hour. An i.r. spectrum of this crude material showed a strong ester band at 1760 cm^{-1}, and was otherwise very similar to the i.r. spectrum of $F_5SCH(SO_2F)COOC(CH_3)_3$. The ^{19}F n.m.r. spectrum (in CCl_3F) showed bands corresponding to $F_5SCH(SO_2F)COOC(CH_3)_3$ and probably 1 ($F_5S\overline{CHCF_2OS}O_2$). When the solution was kept at room temperature for several days, the bands corresponding to 1 diminished, while bands corresponding to $F_5SCH(SO_2F)COOC(CH_3)_3$, 6, (major product) and most likely $F_5SCH_2SO_2F$ increased.

$F_5SCH(SO_2F)COOC(CH_3)_3$ (6)

To 0.10 g of tertiary butanol (1.35 mmol), in a 50 ml pear-shaped flask with a Kontes Teflon valve connector, 0.36 g (1.36 mmol) of $F_5SC(SO_2F)=C=O$ in 2.5 ml CCl_3F was vacuum transferred. The flask was swirled while it warmed up, and when all $(CH_3)_3COH$ had dissolved, the mixture was cooled again by dipping the flask into liquid nitrogen, and was then allowed to warm up slowly in a cold Dewar container. The material that was obtained was used as such, as attempts to isolate it earlier by distillation resulted in the formation of $F_5SCH_2SO_2F$; trap-to-trap distillation was also unable to give pure ester. In this case, an originally colorless product was collected that assumed a purple color within hours at room temperature.

^1H n.m.r. spectrum (400 MHz, CCl_3F, $Si(CH_3)_4$): δ = 1.58 ppm, s, int. = 9.94 ($COOC(CH_3)_3$); δ = 5.88 ppm, m, int. = 1.00 (SF_5CH); an impurity at δ = 1.29 and δ = 2.06 was identified as $(CH_3)_3COH$ by adding a drop of an authentic sample to the original sample; this addition led to a large proportional increase in these two bands. $(CH_3)_3COH$ accounted for 17.3 % of the t-butyl concentration in the crude ester.

^{19}F n.m.r. spectrum (CCl_3F): ϕ_{SF5} = 71.7 ppm, narrow multiplet, area = 5.00; ϕ_{SO2F} = 59.8 ppm, m, area = 0.93.

Infrared spectrum (neat sample, on KBr, cm^{-1}) of the crude product: 2990, m; 2954, w,sh; 1760, s-vs; 1481, w; 1442, s-vs; 1401, w; 1377, m-s; 1299, s; 1266, m-s; 1222, m-s; 1149, s-vs; 1040, vw; 965, w; 879, vs; 835, s; 801, m-s; 788, m-s; 773, m-s; 698, w-m,br; 664, w; 643, w,br; 612, m; 571, s-vs; 490, w-m; 458, w; 452, w-m; 446, w-m.

G.C. mass spectrum (e.i., 70 eV, mass, species, % > 1): 251, $(m-(CH_3)_3CO)^+$, 0.4; 231, $(M-(CH_3)_3CO-HF)^+$, 2.7; 127, SF_5^+, 15.4; 105, $C_2HO_3S^+$, 1.1; 97, CFO_2S^+, $C_6H_9O^+$, 1.0; 91, C_2FOS^+, 1.1; 89, SF_3^+, 17.3; 70, SF_2^+, 2.0; 67, FSO^+, 11.5; 64, SO_2^+, 3.5; 60, COS^+, 3.3; 59, $C_3H_7O^+$, 100.0; 58, $C_3H_6O^+$, 6.2; 57, $C_3H_5O^+$, 68.6; $C_3H_4O^+$, 21.0; 55, $C_3H_3O^+$; 53, C_3HO^+; 51, SF^+, 1.9.

Note: By convention, resonances appearing downfield from CCl_3F are assigned positive values; upfield resonances are assigned negative values.

REFERENCES

1 R.Winter , D.H.Peyton and G.L.Gard, Inorg.Chem., 28, (1989) 3766.

2 R.J.Terjeson, J.Mohtasham and G.L.Gard, J.Fluorine Chem., 27, (1988) 2916.

3 J.Mohtasham, M.Brennen, Z.Yu, J.L.Adcock and G.L.Gard, J.Fluorine Chem. 43 (1989) 349.

4 J.Mohtasham, Z.Yang, D.J.Burton and G.L.Gard, J.Fluorine Chem., 50 (1990) 31.

5 J.Mohtasham, F.Behr and G.L.Gard, J.Fluorine Chem., 49, (1990) 349.

6 R.Winter and G.L.Gard, Inorg.Chem., 29 (1990) 2386.

7 In house work performed at Portland State University.

8 K.K.Johri and D.D.DesMarteau, J.Org.Chem., 48 (1983) 242.

9 G.Kleemann and K.Seppelt, Chem.Ber., 116 (1983) 645 [cis-SF_4BrCH_3, cis-SF_4ClCH_3]. J.S.Thrasher, J.L.Howell, M.Clark and A.F.Clifford, J.Am.Chem.Soc., 108 (1988) 3526 [cis-$CH_3OSF_4N{=}C{=}O$, cis-$CH_3OSF_4NHC(O)OCH_3$].