Notes

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Conversion of an SF_5 Group into an $F_2S(O){=}$ Substituent by a Novel Elimination–Rearrangement Sequence

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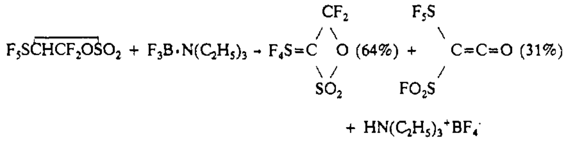
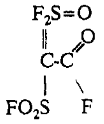
In our investigations of hydrocarbons containing the SF_5 and the SO_2F groups, a new and somewhat novel trifunctional compound was unexpectedly produced.

It was previously shown, that when the sultone $F_5SCHCF_2OSO_2$ is treated with the base $F_3B{\cdot}N(C_2H_5)_3$, HF elimination and partial rearrangement occurs:[1]



(1)

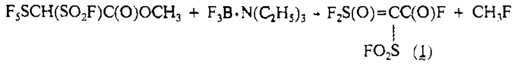
Extension of this unique reaction involving loss of F^- from SF_5 was applied to esters of the composition $F_5SCH(SO_2F)C(O)OR$. Instead of obtaining the expected $F_4S{=}C$ derivative, we found that, in the case of the isopropyl ester, a mixture of gaseous products and a high-boiling liquid were produced. The gas products were tentatively identified as a mixture of propylene and 2-fluoropropane, whereas the spectral and analytical data of the high-boiling liquid were consistent with a composition of the form



(1)

It seemed likely that isopropyl fluoride first was formed as an elimination product of the ester and then underwent HF loss by reaction with the strong HF acceptor $F_3B{\cdot}N(C_2H_5)_3$ to produce propylene as the secondary byproduct.

In order to facilitate the analysis of the gaseous products and to support primary alkyl fluoride formation, the new ester $F_5SCH(SO_2F)C(O)OCH_3$ was synthesized from $F_5SCHCF_2OSO_2$ and CH_3OH. In this case, treatment of the methyl ester with $F_3B{\cdot}N(C_2H_5)_3$ should give as the only volatile product methyl fluoride, since HF elimination would not lead to a stable product. When the ester was treated with $F_3B{\cdot}N(C_2H_5)_3$, CH_3F was produced in high yield as the sole gaseous product along with **1**:



$$F_5SCH(SO_2F)C(O)OCH_3 + F_3B{\cdot}N(C_2H_5)_3 \rightarrow F_2S(O){=}\underset{\substack{|\\FO_2S\ (1)}}{C}C(O)F + CH_3F \qquad (2)$$

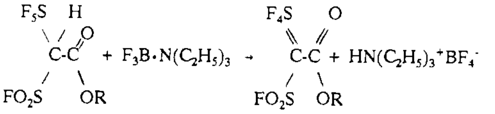
The new trifunctional compound, **1**, is the first of its kind. There is only one other example that contains the C(O)F and $F_2S(O)$ functional groups bonded to the same carbon. This compound, $F_2S(O){=}CHC(O)F$, was obtained by hydrolysis of $F_4S{=}CHC(O)F$ and seems to exist in a number of rotation isomers, as shown by variable-temperature NMR spectroscopy.[2]

The first-order ^{19}F NMR spectrum of **1** at room temperature is very similar to that of $F_2S(O){=}CHC(O)F$.[2] Chemical shifts and splitting patterns are comparable, with the exception that additional large coupling to the SO_2F fluorine has occurred. The coupling constants are similar to the ones found in $F_5SCX(SO_2F)C(O)F$ where X = H, F.[3,4]

The main characteristics of the infrared spectrum include the strong C=O stretch vibration (1825 cm^{-1}) and various S=O stretch vibrations, i.e., $\nu_{as}(SO_2)$ = 1448 cm^{-1} and $\nu(SO)$ = 1419 cm^{-1}.[2] The asymmetric SO_2 stretching mode shows only a small variability and always appears between ≈1440 and 1456 cm^{-1}. The symmetric SO_2 stretching mode frequency occurs normally at ≈1220 cm^{-1}; in the same region (1100–1300 cm^{-1}), one expects the resonance for the S=C double bond. Since there are several bands in this region, an unambiguous assignment is not possible, but the band at 1226 cm^{-1} could correspond to $\nu_{sym}(SO_2)$. In particular, the SF modes (stretching) at 875 and 801 cm^{-1} have a rather unusual appearance, as compared to SF_5 band shapes. The two bands are of about equal intensity and show no further structure, whereas in $SF_5{-}SO_2F$ compounds one finds a multitude of bands of various intensity in the same region.

The mass spectrum shows the molecular ion and appropriate fragment ions; it also shows one rather intense band, which can be accounted for in part if one assumes rearrangement to $F_3OSC(SO_2F){=}C{=}O$ (**2**).

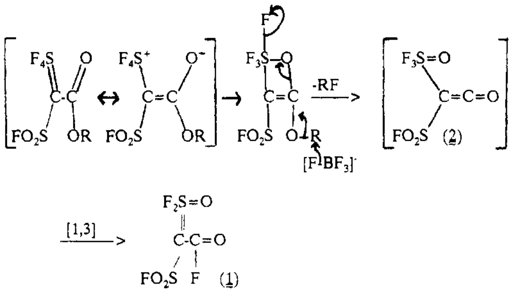
The formation of $F_2S(O){=}C(SO_2F)C(O)F$ and alkyl fluoride can be rationalized by a series of eliminations and rearrangements. In the first step, formation of the HF elimination product is conjectured:



(3)

R = $CH(CH_3)_2$, CH_3

It is assumed that the newly formed $F_4S{=}C$ ester is unstable toward rearrangement. The intermediate $F_4S{=}C$ ester could undergo ring closure, loss of RF, and transformation by a [1,3]-sigmatropic shift to give **1**:



(4)

Alternatively, attack of the alkoxy group at SF_4 is possible, followed by elimination, ring opening, and again a [1,3]-sigmatropic shift. Although a number of other mechanisms can be formulated, which involve migration of F^-, a concerted mechanism in the last step seems more likely for the following reasons: (i) F^- migration is deemed unlikely in the reaction medium, and (ii) in the mass spectrum there is a moderately strong *m*/*e* peak with mass 105. This could indicate the fragment SOF_3^+ from **2**, formed in a reverse reaction from **1** in the mass spectrometer. For the mass 105 the $(MH{-}SOF_4)^+$ fragment is also formulated.

Further reactions of the trifunctional molecule could not be completed successfully. Reaction with diethylamine led to an

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inseparable mixture of many compounds, as evidenced by the ^{19}F NMR spectrum. Reaction with CsF in CH_3CN led to the uptake of 1 equiv of CsF, but the fluorine spectrum showed the presence of at least two C(O)F groups. Separation was not attempted.

While the esters $SF_5CH(SO_2F)C(O)OR$ (R = CH_3, $CH(CH_3)_2$, when treated with the base $F_3B{\cdot}N(C_2H_5)_3$, gave compound **1**, similar treatment of the ester $SF_5CH_2C(O)OCH_3$ resulted in decomposition; only residual material and SF_4 were observed in the ^{19}F NMR spectrum.

Experimental Section

All experiments were done on a conventional Pyrex glass vacuum line equipped with a mercury manometer. $F_5SCH(SO_2F)C(O)OCH(CH_3)_2$ was made as described earlier.[5] Infrared spectra were measured from capillary films on KBr plates with a Nicolet 20DX spectrometer, and NMR spectra were obtained on a Varian Model EM-390 spectrometer at 90.0 (^1H) or 84.67 (^{19}F) MHz. Tetramethylsilane and CCl_3F were used as external standards. The mass spectra were taken on a VG-7070 HS mass spectrometer at 70 eV. Elemental analyses were determined by Microanalytisches Laboratorium Beller, Göttingen, West Germany.

1. $F_5SCH(SO_2F)C(O)OCH(CH_3)_2$ + $F_3B{\cdot}N(C_2H_5)_3$. A 50-mL round-bottom flask equipped with a magnetic stirring bar and containing the ester (5.00 g, 16.1 mmol) and the base $F_3B{\cdot}N(C_2H_5)_3$[6] (6.10 g, 36.1 mmol) was connected via a vacuum transfer line that was attached to another vacuum line with a cold trap held at −196 °C. The pressure in the entire system was lowered to ≈300 mmHg, and heating of the reaction vessel commenced. When the oil bath had reached a temperature of 71 °C, a vigorous reaction occurred. Heating was continued for another 15 min; the reaction vessel was then chilled (−196 °C), the compartment was evacuated, and the remaining volatile materials were transferred at room temperature into a cold trap for containment. A total of 0.4960 g was collected. The high-boiling product was distilled directly from the reaction flask, bp 44.5–45 °C/4–5 mmHg (1.40 g). The foreshot (0.22 g) and the contents of the cold trap (0.23 g) had identical infrared spectra as the main fraction. Yield: 1.40 g (38.1%).

^{19}F NMR spectrum (neat sample): $[F^2{}_2S(O){=}C(SO_2F^3)C(O)F^1]$ ϕ_1 = 31.3 ppm (d-t), intensity = 1.00 (C(O)F); ϕ_2 = 59.7 ppm (d-d), intensity = 2.04 ($=SOF_2$); ϕ_3 = 72.3 ppm (d-t), intensity = 1.08 (SO_2F); J_{12} = 12.8 Hz; J_{13} = 7.2 Hz; J_{23} = 9.5 Hz.

IR spectrum (cm^{-1}): 1825 (vs), 1448 (vs), 1419 (vs), 1241 (sh, vs), 1226 (vs), 1138 (s), 1099 (m), 1050 (m–w), 986 (w), 875 (vs), 801 (vs), 739 (m), 725 (m), 715 (m–w), 622 (s), 568 (vs), 534 (m–s), 529 (m–s), 482 (m), 473 (m–w), 463 (m–w).

Mass spectrum (electron impact; *m/e*, species, % abundance): 228, $M(^{32}S)^+$, 100.0; 209, $(M - F)^+$, 13.1; 149, $CF_3OS_2^+$, 3.5; 126, $C_2F_2O_2S^+$, 6.3; 123, $C_2FOS_2^+$, 5.3; 107, $C_2FO_2S^+$, 1.5; 105, SOF_3^+ (rearr), $(MH - SOF_4)^+$, 31.5; 91, C_2FOS^+, 5.1; 89, SF_3^+ (rearr), $(MH - SO_2F_4)^+$, 2.6; 86, SOF_2^+, 4.6; 83, SO_2F^+, 4.1; 72, C_2SO^+, 1.3; 70, SF_2^+, 12.9; 67, FOS^+, 94.5; 64, SO_2^+, 18.1; 63, CFS^+, 10.5; 60, COS^+, 3.2; 59, C_2FO^+, 4.4; 51, SF^+, 7.5.

Anal. Calcd for $C_2F_4O_4S_2$: C, 10.53; F, 33.3; S, 28.11. Found: C, 10.71; F, 33.1; S, 27.95.

The infrared spectrum of the gaseous products showed a band of medium size at 1664 cm^{-1} ($\nu(C{=}C)$ in $CH_3CH{=}CH_2$ = 1647 cm^{-1})[7] and another strong one at 1139 cm^{-1}, assigned to a C–F stretch vibration. There was also a very strong band centered at 2990 cm^{-1} and several weaker ones.

2. $F_5SCH(SO_2F)C(O)OCH_3$. Into 7.20 g (26.7 mmol) of $F_5SCH{-}CF_2OSO_2$ in a 50-mL reaction vessel equipped with a Kontes Teflon valve was condensed 2.00 g (62.5 mmol) of anhydrous CH_3OH at −196 °C. The mixture was warmed to room temperature, and after 20 min with stirring, the product was transferred to a 25-mL flask and the reaction vessel was rinsed twice (0.5 mL) with CH_3OH. The rinse solution was combined with the bulk of the product. Distillation (15–18 mmHg) yielded 1.69 g of a fraction boiling from 65 to 68 °C. The foreshot (0.54 g) was also pure ester. Additional product could be collected from the cold trap after precipitating the ester with water (20 mL) and distillation (0.40 g). Total product: 2.63 g (35%).

^1H NMR ($CDCl_3$): δ_1 = 4.45 ppm (s), intensity = 3.3 (CH_3); δ_2 = 6.26 ppm (m, br), intensity = 1.0 ($CHSF_5$).

^{19}F NMR ($CFCl_3$): ϕ_1 = 71.7 ppm (m), intensity = 5.0; ϕ_2 = 59.7 ppm (m), intensity = 1.0 (SO_2F).

IR spectrum (cm^{-1}): 2971 (m), 1767 (vs), 1443 (vs), 1305 (s), 1277 (s), 1223 (s), 1200 (m–s), 1157 (m–s), 1053 (m–w), 1019 (m), 996 (w, sh), 916 (vs), 869 (vs), 804 (s), 773 (m, sh), 749 (m), 692 (m), 648 (m), 612 (m–s), 571 (vs), 490 (m), 458 (m–w), 417 (w).

Mass spectrum (electron impact; *m/e*, species, % abundance): 262, $(M - HF)^+$, 0.8; 253, $(MH - CH_2O)^+$, 1.6; 251, $(M - OCH_3)^+$, 10.4; 250, $(M - CH_3OH)^+$, 1.7; 231, $(M - HF - CH_3O)^+$, 5.4; 168, $(M - SO_2F - OCH_3)^+$, 3.6; 155, $(M - SF_5)^+$, 6.4; 143, $(M - 4F - OCH_3 - 2O)^+$, 4.7; 139, $(M - SO_2F - C(O)OCH_3 - H)^+$, 2.5; 135, $(M - HF - SF_5)^+$, 3.4; 129, $(MH - 5F - C(O)OCH_3)^+$, 2.9; 127, SF_5^+, 48.0; 125, $(MH - SF_5 - OCH_3)^+$, 18.7; 124, $(M - SF_5 - OCH_3)^+$, 2.9; 122, $(MH - SO_2F - F - C(O)OCH_3)^+$, 6.4; 105, $(M - SF_5 - OCH_3 - F)^+$, 9.8; 91, C_2FOS^+, 2.3; 89, SF_3^+, 42.2; 79, $CFOS^+$, 3.8; 70, SF_2^+, 3.3; 67, FSO^+, 27.4; 64, SO_2^+, $CHFS^+$, 2.4; 61, $CHOS^+$, 3.8; 60, COS^+, 3.9; 59, $C(O)OCH_3^+$, 100.0.

Anal. Calcd for $C_3H_4F_6O_4S_2$: C, 12.77; H, 1.43; F, 40.4; S, 22.72. Found: C, 12.83; H, 1.30; F, 40.7; S, 22.58.

3. $F_5SCH(SO_2F)C(O)OCH_3$ + $F_3B{\cdot}N(C_2H_5)_3$. The reaction was conducted as described above for the isopropyl ester derivative with the exception that the volatile materials were collected in a preweighed 50-mL Pyrex glass vessel equipped with a Kontes Teflon valve. $F_5SCH(SO_2F)C(O)OCH_3$ (1.52 g, 5.4 mmol) and 1.12 g of $F_3B{\cdot}N(C_2H_5)_3$ (6.60 mmol) were heated under a pressure of 270 mmHg. At 85 °C (oil bath temperature) a reaction occurred, while at 89 °C foaming had ceased, but heating was continued to a final temperature of 108 °C (12 min). After collection and recondensation (at 0 °C) of the volatile material into another vessel, 0.1600 g was obtained. The infrared spectrum (band positioning) coincided with that of CH_3F.[8] Yield: 87.3%. The spectrum was also identical with that obtained from the product of the reaction of CH_3I + KF in sulfolane at 125 °C/2 days.

The title compound (**1**) was isolated from the reaction mixture by vacuum transfer. The infrared spectrum of this material (1.05 g) was identical with that of the product obtained from $F_5SCH(SO_2F)C(O)OCH(CH_3)_2$. Yield: 85.4%.

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Contribution from the Laboratoire de Chimie Quantique, ER 139 du CNRS Institut Le Bel, F-67000 Strasbourg, France

The Vanadium–Vanadium Double Bond in $(C_5H_5{-}V)_2(C_8H_8)_2$: An Antiferromagnetic Coupling. An ab Initio SCF/CI Study

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Previous work on (cyclooctatetraene)bis(cyclopentadienylvanadium) has proved that the electronic structure of this dinuclear complex of V(II) with a short metal–metal bond was not straightforward. A first study carried out at the ab initio SCF level by Lüthi and Bauschlicher[1] concluded that the two Cp–V moieties were connected through a single metal–metal bond, whereas the four remaining metal electrons were kept localized on the vanadium atoms and involved in stabilizing interactions with the cyclooctatetraene ligand. A subsequent ab initio study[2] including nondynamic correlation completely reversed this picture and showed that all six metal d electrons are involved in a triple metal–metal coupling. One of these bonds, with π character, is delocalized through the C_8H_8 ligand. The two other bonds, with respective σ/δ and π characters, are weak antiferromagnetic V–V couplings with no significant contribution from the ligands. As

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