1-(Pentafluoro-λ⁶-sulfanyl)-2,2,2-trifluoroethanethione, F₅S(F₃C)C=S, and Related Compounds

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Introduction

Alkylidenesulfur difluorides were isolated for the first time in 1989.[1] So far six examples are known: $(F_3C)_2C=SF_2$,[1] F_5S-$(F_3C)C=SF_2$,[1] and $R_fN=CFC(R_f') = SF_2$[2] ($R_f = C_6F_5$, CF_3; $R_f' = CF_3$, SF_5). This novel class of compounds contains carbon–sulfur multiple bonds, as is established by the short CS bond length[1,2] and by the rigidity of the CS double bond against torsion,[1,2] resulting in *E,Z* isomers. These compounds should therefore not be considered as a kind of sulfur ylides, which have a longer CS bond length[3–6] and obviously free rotation around this bond. Little is known about the chemistry of alkylidene sulfur difluorides, except that some of them undergo a spontaneous 1,2-fluorine shift reaction forming sulfenyl fluorides, R_fSF.[1] The present work will show that these compounds can serve as starting materials for other novel compounds, e.g. $F_5S(F_3C)C=S$ and $F_5S(F_3)C=S=O$.

Experimental Section

Hydrolytically sensitive materials were handled in a glovebox with automatic argon purification and a water content of less than 1 ppm.

Characterization Methods. The ¹⁹F FT NMR measurements were performed on a JEOL FX 90 Q instrument at 84.25 MHz. They were referenced to external CFCl₃. Mass spectra: Varian MAT 711, EI, 80 eV. Mass numbers refer to ³²S, ³⁵Cl, and ⁷⁹Br isotopes, intensities include all isotopes. Infrared spectra: Perkin Elmer 853. UV spectra: Beckman 5240.

Materials. $F_5SCH=CF_2$,[7] $F_5S(F_3C)C=SF_2$ (*E,Z* isomeric mixture),[1] F_3CSF_3,[8] and $F_3CCFClSF_3$[9] were obtained following literature methods. Activated cesium fluoride was obtained by brief melting in a platinum crucible and grinding under anhydrous conditions.

1-(Pentafluoro-λ⁶-sulfanyl)-1,2,2,2-tetrafluoroethanesulfenyl Fluoride, $F_5S(F_3C)CFSF$. $F_5S(F_3C)C=SF_2$ and BF_3 are condensed into a NMR tube at –196 °C. The tube is sealed and slowly warmed from –78 °C to room temperature. The reaction is monitored by ¹⁹F NMR spectroscopy: ab₄c₃de type; δ 66.4 (a, SF), 66.0 (b, SF₄), –73.8 (c, CF₃), –125.0 (d, CF)), –125.0 (d, F), –329.5 (e, SF) ppm; *J*(ab) = 146.3, *J*(bc) = 22.5, *J*(bd) = 5.4, *J*(be) = 3.6, *J*(cd) = 26.0, *J*(ce) = 3.6, *J*(de) = 11.0 Hz. For further physical data on this compound see ref 1.

1-Chloro-1-(pentafluoro-λ⁶-sulfanyl)-2,2,2-trifluoroethanesulfenyl Chloride, $F_5S(F_3C)CCl$-SCl. $F_5S(F_3C)C=SF_2$, 3 g (11 mmol), and BCl₃, 1.5 g (13 mmol), are condensed at –196 °C into a trap. The mixture is stirred at –78 °C for approximately 1 h, followed by fractional condensation in a dynamic vacuum through +25, –32, and –196 °C cold traps. The product is obtained as a yellow liquid in the –32 °C trap: yield 2.3 g (68%); vapor pressure 12 mbar at 25 °C. ¹⁹F NMR: ab₄c₃ type; δ 68.6

(a, SF), 56.9 (b, SF₄), –67.3 (c, CF₃) ppm; *J*(ab) = 141.6, *J*(bc) = 9.2 Hz. Mass spectrum: *m/z* = 310 (M⁺, 3%), 294 (C₂ClF₈S₂⁺, 17%), 202 (C₂Cl₂F₄S⁺, 15%), 183 (C₂ClF₃S⁺, 59%), 167 (C₂ClF₄S⁺, 100%) and smaller fragments. Infrared spectrum: 1205 (s), 1124 (w), 530 (w), 868 (s), 783 (m), 702 (m), 675 (m), 596 (m), 579 (w) cm⁻¹.

1-(Pentafluoro-λ⁶-sulfanyl)-1,2,2,2-tetrafluoroethanesulfenyl Bromide, $F_5S(F_3C)CF-SBr$. Equimolar amounts of $F_5S(F_3C)C=SF_2$ and BBr₃ are condensed into a trap at –196 °C. This trap is connected to a second trap (–196 °C), and both are connected to a vacuum line, and a pressure of approximately 200 mbar is retained by partial pumping throughout the reaction. The mixture is warmed to –78 °C, held for 0.5 h at this temperature, and then warmed to room temperature. Fractional condensation in a dynamic vacuum through +25, –45, and –196 °C cold traps retains the product in the –45 °C trap. Traces of bromine are extracted by stirring with mercury. The orange liquid product is obtained in 17% yield. The byproduct $F_5S(F_3C)C=S$ is mostly trapped at –196 °C. ¹⁹F NMR: ab₄c₃d type; δ 66.0 (a, SF), 53.5 (b, SF₄), –72.5 (c, CF₃), –114.6 (d, CF) ppm; *J*(ab) = 141.6, *J*(bc) = 22.0, *J*(bd) = 12.2, *J*(ce) = 9.7 Hz. Mass spectrum: *m/z* = 338 (M⁺, 1%), 240 (C₂F₈S₂⁺, 8%), 211 (C₂BrF₄⁺, 4%), 161 (CBrF₂S⁺, 1%), 151 (C₂F₅S⁺, 6%), 132 (C₂F₄S⁺, 83%), 127 (SF₅⁺, 29%), 120 (CF₄S⁺, 1%), 113 (C₂F₃S⁺, 100%), and smaller fragments. Infrared spectrum: 1416 (w), 1326 (m), 1258 (s), 1218 (vs), 1109 (s), 946 (s), 873 (s), 811 (vs), 749 (m), 726 (m), 679 (m), 605 (s) cm⁻¹.

1-(Pentafluoro-λ⁶-sulfanyl)-2,2,2-trifluoroethanethione, $F_5S(F_3C)$-C=S. BI₃, 8 g (20 mmol) is weighed into a trap; $F_5S(F_3C)C=SF_2$, 5 g (18 mmol), is condensed into it at –196 °C. A second trap, cooled to –196 °C, is connected to the reaction trap, and in both a vacuum of approximately 200 mbar is retained. The reaction mixture is warmed to room temperature within 1 h. Subsequently, all volatile products are pumped through a +25, –45, –78, and –196 °C trap system in a dynamic vacuum. The product is retained in the –78 °C cold trap, and elemental iodine is removed by reaction with elemental mercury. Violet F_5S-$(F_3C)C=S$, 1.9 g (42%), is obtained. ¹⁹F NMR: ab₄c₃ type; δ 66.7 (a,SF), 49.9 (b,SF₄), –64.0 (c,CF₃) ppm; *J*(ab) = 141.6, *J*(bc) = 12.2 Hz. Mass spectrum: *m/z* = 239.9314 (M⁺, 2%), calcd 239.9312, 208 (C₂F₈S⁺, 5%), 183 (C₂F₅S₂⁺, 29%), 171 (CF₅S₂⁺, 9%), 164 (C₂F₄S₂⁺, 10%), 151 (C₂F₅S⁺, 11%), 132 (C₂F₄S⁺, 25%), 127 (SF₅⁺, 45%), 119 (C₂F₅⁺, 100%), and smaller fragments. Infrared spectrum: 1743 (w), 1673 (w), 1329 (m), 1276 (s), 1231 (s), 1185 (s), 1150 (s), 1121 (m), 948 (m), 916 (s), 886 (vs), 832 (s), 795 (w), 748 (m), 710 (m), 674 (m), 606 (w) cm⁻¹. UV spectrum (gas): λ_max = 557.6 nm.

2,4-Bis(pentafluoro-λ⁶-sulfanyl)-2,4-bis(trifluoromethyl)-1,3-dithietane, $F_5S(F_3C)CS_2C(CF_3)SF_5$. $F_5S(F_3C)C=S$ 2.4 g (10 mmol) is dissolved in 5 mL of CFCl₃ and irradiated for 24 h at –10 °C with a focusable high pressure mercury lamp until the reaction mixture has become colorless. Fractional condensation in a dynamic vacuum through +25, 0, and –196 °C cold traps retains the product in the 0 °C trap. It is a colorless solid: mp 38 °C; yield 2.3 g (96%). ¹⁹F NMR: mixture of two isomers, ab₄c₃ types; δ 72.9, 73.3 (a, SF) 54.8 (b, SF₄) –66.9, –68.6 (c, CF₃) ppm; *J*(ab) = 141.6, 141.6, *J*(bc) = 7.1, 14.6 Hz. Mass spectrum: *m/z* = 411 (C₃F₁₁S₄⁺, 0.2%), 353 (C₄F₁₁S₃⁺, 96%), 284 (C₃F₈S₃⁺, 2%), 245 (C₄F₇S₂⁺, 10%), 226 (C₄F₆S₂⁺, 100%), 207 (C₄F₇S₂⁺, 7%), 164 (C₄F₄S₂⁺, 6%), and smaller fragments. Infrared spectrum (solid, KBr) 1200 (vs), 972 (w), 881 (s), 862 (s), 805 (m), 777 (m), 771 (m), 705 (m), 679 (m), 595 (m) 543 (w) cm⁻¹. Crystal data: *a* = 711.0, *b* = 1018.6, and *c* = 930.6 pm; b = 109.6°; *P*2₁/*n*, *Z* = 2. Because of low crystal quality the structure could be refined only to *R* = 0.20. Anal. Calcd for C₄S₄F₁₄: C, 10.00; S, 26.71; F, 63.29. Found: C, 9.93; S, 26.62; F, 63.00.

1-(Pentafluoro-λ⁶-sulfanyl)-2,2,2-trifluoroethylidene Sulfoxide, (Pentafluoro-λ⁶-sulfanyl)(trifluoromethyl)sulfine, $F_5S(F_3C)C=S=O$. Silica gel, 15 g (0.25 mmol), is weighed into a reaction vessel, and F_5S-$(F_3C)C=SF_2$, 27.8 g (0.1 mol), is condensed onto it. The reaction mixture is warmed to room temperature and stirred for about 30 h. Then all liquid products are pumped through a frit and distilled with a spinning band column. Sulfine, 18.2 g (71%), is obtained as a colorless liquid, bp 72–74 °C. ¹⁹F NMR (two isomers in the ratio 6:1): a₄bc₃ type, δ 69.9, 81.9, (a, SF₄), 71.7, 74.3 (b, SF), –57.8, –58.5 (c, CF₃) ppm; *J*(bc) = 8.9, 10.7 Hz. Mass spectrum: *m/z* 256 (M⁺, 40%), 237 (C₂F₇S₂O⁺, 3%), 170 (C₂F₆S⁺, 2%), 151 (C₂F₅S⁺, 58%), 127 (SF₅⁺, 35%), 119 (C₂F₅⁺, 42%), 113 (C₂F₃S⁺, 27%), 105 (SF₃O⁺, 5%), 101 (CF₃S⁺, 5%), 100 (C₂F₄⁺ 6%), 94 (C₂F₂S⁺, 5%), 89 (SF₃⁺, 100%), and smaller fragments. Infrared spectrum (gas): 1262 (s), 1230 (m), 1208 (s), 1181 (s), 1087 (m), 978 (m), 894 (s), 847 (s), 723 (w), 692 (w), 611 (w), 611 (w) cm⁻¹.

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Anal. Calcd for $C_2S_2OF_8$: C, 9.38; S, 25.04; F, 59.34. Found: C, 9.41; S, 24.74; F, 59.20.
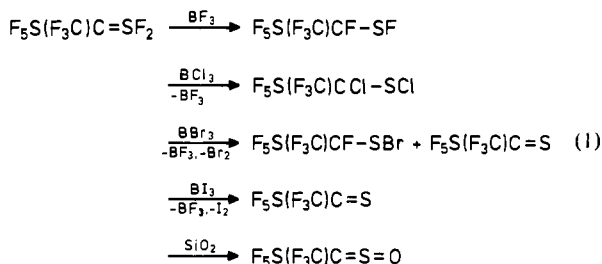
1-(Pentafluoro-λ⁶-sulfanyl)-1,2,2,2-tetrafluoroethyl Trifluoromethyl Sulfide, $F_5S(F_3C)CFSCF_3$. A stainless steel autoclave of 90-mL volume is charged with dry, powdered cesium fluoride, 9 g (59 mmol), and F_5-SCH=CF_2, 3.8 g (20 mmol), and F_3SCF_3, 3.16 g (20 mmol), are condensed into it at –196 °C. The reaction mixture is stirred for 4 h at room temperature. Fractional condensation in a dynamic vacuum of the volatile products through +25, –78, and –196 °C cold traps gives 5.6 g (85%) of the pure sulfide in the –78 °C trap as a colorless liquid. ^{19}F NMR spectrum: $ab_4c_3d_3e$ type; δ 64, (a, SF) 48.5 (b, SF_4) –36.6 (c, SCF_3), –77.2 (d, CCF_3), –122.9 (e, CF) ppm; J(ab) = 141.4, J(bc) = 2.7, J(bd), = 20.5, J(be) = 8.9, J(cd) = 5.4, J(ce) = 17.0, J(de) = 8.9 Hz. Mass spectrum: m/z = 328 (M^+, 0.04%), 309 ($C_8F_{11}S_2^+$, 0.03%), 278 ($C_2F_{10}S_2^+$, 1%), 259 ($C_2F_9S_2^+$, 1%), 201 ($C_3F_7S^+$, 65%), 190 ($CF_6S_2^+$, 7%), 183 ($C_2F_5S_2^+$, 2%), 171 ($CF_5S_2^+$, 6%), 151 ($C_2F_5S^+$, 2%), 132 ($C_2F_4S^+$, 11%), 127 (SF_5^+, 25%), 119 ($C_2F_5^+$, 5%), 113 ($C_2F_3S^+$, 72%), 108 (SF_4^+, 2%), 101 (CF_3S^+, 5%), 100 ($C_2F_4^+$, 3%), 95 (CFS_2^+, 1%), 94 ($C_2F_2S^+$, 4%), 89 (SF_3^+, 60%), 82 (CF_2S^+, 6%), 76 (CS_2^+, 1%), 70 (SF_2^+, 9%), 69 (CF_3^+, 100%), and smaller fragments. Infrared spectrum (gas): 1742 (m), 1673 (w), 1352 (w), 1268 (m), 1225 (s), 1140 (m), 1102 (s), 1012 (w), 946 (m), 883 (vs), 847 (w), 818 (s), 767 (w), 727 (w), 606 (m) cm⁻¹.

1-(Pentafluoro-λ⁶-sulfanyl)-1,2,2,2-tetrafluoroethyl 1-Chloro-1,2,2,2-tetrafluoroethyl Sulfide, $F_5S(F_3C)CFSCFClCF_3$. F_5SCH=CF_2, 3.8 g (20 mmol), $F_3SCFClCF_3$, 4.48 g (20 mmol), and CsF, 9 g (59 mmol), are stirred for 5 h at room temperature in a 90-mL stainless steel autoclave. Fractional condensation of the volatile products in a dynamic vacuum through +25, –78, and –196 °C cold traps produces the sulfide in the –78 °C trap. The colorless liquid is further purified by distilled on a 1-m spinning band column, resulting in a product of bp 114–116 °C, yield 5.6 g (70%). ^{19}F NMR spectrum (mixture of two diastereomers): $ab_4c_3d_3ef$ type; δ 66.6, 66.4 (a, SF), 50.0, 49.6 (b, SF_4), –75.7, –76.0 (c, CF_3), –79.7, –80.0 (d, CF_3), –97.9, –103.2 (e, CF), –121.7, –123.6 (f, CF) ppm; J(ab) = 142.9, 146.4, J(bc) = 21.4, 21.4, J(bf) = 2.3, 4.5, J(cd) = 10.7, J(ce) = 4.1, 2.7, J(cf) 11.6, 12.5, J(de) = 22.3, 24.1, J(df) = 2.7, 8.0, J(ef) = 12.5, 8.9 Hz. Mass spectrum: m/z 359 (M^+-Cl, 2), 318 (C_4-$ClF_8S_2^+$, 3), 302 ($C_4F_{10}S_2^+$, 1), 283 ($C_4F_9S_2^+$, 2), 278 ($C_2F_{10}S_2^+$, 1), 267 ($C_4ClF_8S^+$, 16), 259 ($C_2F_9S_2^+$, 1), 167 ($C_2ClF_4S^+$, 1), 151 ($C_2F_5S^+$, 1), 135 ($C_2ClF_4^+$, 100), and smaller fragments. Infrared spectrum (liquid): 1485 (w), 1410 (w), 1223 (vs), 1159 (s), 1101 (m), 924 (s), 872 (s), 804 (s), 735 (m), 723 (s), 680 (m), 603 (s), 575 (m) cm⁻¹. **Anal.** Calcd for $C_4S_2ClF_{13}$: C, 12.18; S, 16.25; Cl, 8.98; F, 62.59. Found: C, 12.28; S, 16.02; Cl, 9.25; F, 62.50.

Results and Discussion

The reaction of $F_5S(F_3C)C$=SF_2 with boron halides was carried out with the intention to test the Lewis basicity of the former. BF_3, however, catalyzes the 1,2-fluorine shift reaction resulting in the sulfenyl fluoride. Reaction with BCl_3 is somewhat similar: The possibly formed intermediate $F_5S(F_3C)C$=SCl_2 rearranges as well to the sulfenyl chloride. In the reaction with BBr_3 the possible intermediate $F_5S(F_3C)C$=$SFBr$ rearranges to the sulfenyl bromide, whereas $F_5S(F_3C)C$=SBr_2 eliminates bromine to give $F_5S(F_3C)C$=S. The latter is the only product in the reaction of $F_5S(F_3C)C$=SF_2 with BI_3.
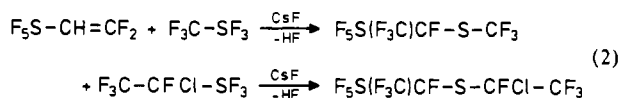
The production of $F_5S(F_3C)C$=S is immediately apparent by its intense blue-violet color. The stability of this new thioketone is without doubt a result of the SF_5 protective group. The related $(F_3C)_2C$=S can be prepared also, but it is known to dimerize spontaneously.[10] The protective effect of a SF_5 group has been observed already. Thus, SF_5 containing olefins or acetylenes like SF_5CH=CH_2, F_5SC≡CH, and F_5SC≡CSF_5 are considerably

$$F_5S(F_3C)C=SF_2 \xrightarrow{BF_3} F_5S(F_3C)CF-SF$$

$$\xrightarrow[-BF_3]{BCl_3} F_5S(F_3C)CCl-SCl$$

$$\xrightarrow[-BF_3, -Br_2]{BBr_3} F_5S(F_3C)CF-SBr + F_5S(F_3C)C=S \quad (1)$$

$$\xrightarrow[-BF_3, -I_2]{BI_3} F_5S(F_3C)C=S$$

$$\xrightarrow{SiO_2} F_5S(F_3C)C=S=O$$

more inert compared to the typical chemical reactivity of an olefin or acetylene. The protective effect seems to be mainly a steric one. Nevertheless it is possible to dimerize the thioketone to the 1,3-dithietane that is present in two isomeric forms. This is apparent from the ^{19}F NMR spectrum of the dimer. An assignment of the isomeric forms to the different ab_4c_3 spectra is not possible with NMR techniques alone. The expectation that the more highly symmetric *E* isomer will have a higher melting point proves to be correct. An imperfect crystal structure analysis showed the existence of a crystallographic inversion center in the center of the four-membered ring. This is only compatible with the *E* structure, if disorder is not taken into consideration.

Surprisingly $F_5S(F_3C)C$=SF_2 does not react with water at room temperature; above 100 °C complete hydrolytic decomposition is observed. However a sulfine, which is the product similar to the one expected from a hydrolysis reaction, is obtained with SiO_2. Such sulfines have been known for a long time, and they are stable compounds if the carbon substituents are chosen properly.[11,12] Here the occurrence of two isomers, as established by ^{19}F NMR, clearly establishes again the overall planar structure of such sulfines. Since the starting material $F_5S(F_3C)C$=SF_2 is not isomerically pure, it cannot be said which isomeric sulfine is formed from which isomeric alkylidene sulfur difluoride. Such information would allow speculation about the reaction mechanism. The ratio of isomers 8:1 before and 6:1 after the reaction along with an overall yield of 71% would allow both possibilities, namely a regiospecific or a nonregiospecific reaction.

The method of preparation of $F_5S(F_3C)C$=SF_2 implies that similar addition–elimination reactions might be possible. The olefinic component has been varied already.[1] Here the substituted sulfur fluorides F_3CSF_3 and $F_3CCFClSF_3$ have been tested instead of SF_4. In these case reactions occur; however, the subsequent 1,2 fluorine shift reaction cannot be supressed. Products are sulfides with no special properties. Because of the existence of two chiral centers, $F_5S(F_3C)CFSCFClSF_3$ is found to exist in two diastereomeric isomers.

$$F_5S-CH=CF_2 + F_3C-SF_3 \xrightarrow[-HF]{CsF} F_5S(F_3C)CF-S-CF_3$$

$$+ F_3C-CFCl-SF_3 \xrightarrow[-HF]{CsF} F_5S(F_3C)CF-S-CFCl-CF_3 \quad (2)$$

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