(E)-1,2-Difluoro-1-(pentafluoro-\(\alpha\)-sulfanyl)-2-iodoethylene

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1,2,2-Trifluoro-1-(pentafluoro-\(\alpha\)-sulfanyl)ethenyltrimethylphosphonium-tetrafluoroborate, 1,2-Difluoro-1-(pentafluoro-\(\alpha\)-sulfanyl)-2-iodoethylene

The first SF\(_5\)-substituted perfluoroiodo alkene \((E)-\text{F}_5\text{SC}=\text{CFI}\) was synthesized from the phosphonium salt precursor \([\text{(E)}-\text{F}_5\text{SC}=\text{CFPM}e_3]^+\text{BF}_4^-\) and iodine.

**Discussion**

Trimethylphosphine and 1,2,2-trifluoro-1-(pentafluoro-\(\alpha\)-sulfanyl)ethylene (I) reacted at \(-20^\circ\mathrm{C}\) to give the monofluorophosphorane 2 [5], which was not isolated but treated with boron trifluoride-etherate to furnish the thermally stable solid phosphonium tetrafluoroborate 3. Using iodine and sodium carbonate [6] 3 was transformed to (E)-1,2-Difluoro-1-(pentafluoro-\(\alpha\)-sulfanyl)-2-iodoethylene (4), a colorless liquid.

The FAB mass spectrum of 3 exhibits \([\text{F}_5\text{SC}=\text{CFPM}e_3]^+\) and \(\text{BF}_4^-\) ions, whereas the 70 eV El mass spectrum of 4 shows the molecular ion \(\text{M}^+\) (100%) and other characteristic fragments, e.g. \((\text{M}-\text{F})^+, \text{C}_2\text{F}_3^+\), \(\text{C}_2\text{F}_2^+\) and \(\text{SF}_3^+\).

Weak C=C stretching modes are observed in the 1660–1672 cm\(^{-1}\) range of the IR spectra. In \(\text{SF}_5\text{CFCF}_2\) the strong C=C stretching frequency is located at 1782 cm\(^{-1}\) [7], \(\text{F}'(\text{F}_2\text{C})\) resonances appear in the \(19\text{F}\) NMR spectra in the expected regions [4, 8]. The fine structure allows to determine the values for \(3\text{J}_{\text{F-SF}}\) (138.0 (3), 147.3 (4)) which are indicative of the (E)-configuration. Surprisingly, the \(19\text{F}\) signal for \(\text{F}_4\) (4) is found at a much lower field than the respective resonance for 3 and other SF\(_5\) containing phosphorus compounds.

**Experimental**

The appropriate precautions in handling moisture and oxygen-sensitive compounds were observed throughout this work.
Elemental analyses: Mikroanalytisches Laboratorium Beller, Göttingen. MS: MAT 8222 spectrometer, IR: Nicolet 5DX FT spectrometer. Spectra were recorded either as a KBr pellet (3) or as a liquid film between NaCl plates.

NMR: AC 80 Bruker spectrometer, operating at 80.13 MHz (1H, internal standard, TMS), 75.39 MHz (19F, internal standard CCl3F), and 32.44 MHz (31P, external standard 85% H3PO4); d = doublet, p = pentet, dec = dectet. Compound 1 was synthesized via a literature procedure [7],

(E)-1,2-D difluoro-1-(pentafluoro-l6-sulfanyl)-2-iodo-ethylene (3)

In a 100 ml heavy wall glass tube, fitted with a TEFILON® stopcock, weighed 7.6 g (36.5 mmol) 1 and 2.8 g (36.5 mmol) trimethylphosphine were combined at -196 °C using a vacuum line. The reaction mixture was allowed to warm to -20 °C and was kept at this temperature for 24 h. During this period the solution turned from colourless to brown. The product was cooled to -196 °C, 30 ml diethylether was added and 5.2 g (36.5 mmol) boron trifluoride-etherate. The mixture was warmed to -20 °C and kept at this temperature for 72 h. The formation of a brownish-white solid was observed. At 0 °C the solid was washed three times with 10 ml ether. The remaining ether was removed at room temperature.

Yield: 12.0 g (34 mmol) 3 (94%), m.p. 159 °C.

MS (matrix: glycerine): FAB neg.: m/z (%) : 87 (BF4-, 100), 179 (glycerine-H + BF4~, 33), 271 (2glycerine-H + BF4~, 43); FAB pos.: m/z (%) : 265 (F2SCF = CFPM e3 +, 1).

IR: v = 1672 cm^-1 (C = C), 1220 s (CF), 1197 m (CF), 869 vs (SF), 722 m, 670 s, 620 m, 596 s (SF).

NMR: 19F: 6 = +67.3 (F1 multiplet centered at line 6 (see ref. [10]), 3JF1pF1 = 3.9, 4JF1pF1 = 2.2 Hz), +53.1 (F2, multiplet, 4JF1pF1 = 19.3, 2JF1pF1 = 2.9 Hz), -135.1 (F3, dd, 3JF1pF1 = 147.3 Hz), -107.5 (F4, dd).

C5H9BF3PS (351.96)
Calcd  C 17.06  H 2.58  P 8.80
Found  C 17.41  H 2.69  P 9.61.

1,2-Difluoro-1-(pentafluoro-16-sulfanyl)-2-iodo-ethylene (4)

Iodine, 25.0 g (99 mmol) was added to a solution of 11.0 g (31 mmol) 3 in 35 ml dimethylformamide. The solution was cooled to 0 °C and 10.0 g (94 mmol) sodium carbonate was added slowly. When carbon dioxide evolution stopped the mixture was stirred for 15 h at room temperature. All volatiles were distilled at 1 Torr (maximum bath temperature 90 °C) into a receiver (−70 °C), then warmed to room temperature and poured into 50 ml of ice-water. The lower organic layer was washed three times with 10 ml ice-water. The remaining liquid was dried over P4O10. The distillation at 48 °C gave 2.4 g (7.6 mmol) 4 (24%).

MS (inlet temperature 150 °C): m/z (%) : 316 (M+, 100), 297 (M-F, 4), 208 (C,F,1+, 31), 189 (C2F,1+, 48), 158 (CFI+, 8), 127 (SF5+, 1+, 36), 89 (SF3+, 1). High-resolution MS: Found: 315.8660 (C2F7SI+, A0.4 mmu), 207.9005 (C,F,1+, 0.6), 188.9029 (C2F,1+, 1.6), 126.9058 (1+, 1.1), 126.9657 (SF3+, 1.6).

IR: v = 1672 cm^-1 (C = C), 1220 s (CF), 1197 m (CF), 869 vs (SF), 722 m, 670 s, 620 m, 596 s (SF).

NMR: 19F: 6 = +67.3 (F1 multiplet centered at line 6 (see ref. [10]), 3JF1pF1 = 3.9, 4JF1pF1 = 2.2 Hz), +53.1 (F2, multiplet, 4JF1pF1 = 19.3, 2JF1pF1 = 2.9 Hz), -135.1 (F3, dd, 3JF1pF1 = 147.3 Hz), -107.5 (F4, dd).

C2F7IO (315.87)
Calcd  C 7.61  F 42.1
Found  C 7.79  F 42.4.

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