NOTIZEN

(E)-1,2-Difluoro-1-(pentafluoro-λ^6-sulfanyl)-2-iodoethylene

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Z. Naturforsch. **46b**, 123–125 (1991); received August 24, 1990

1,2,2-Trifluoro-1-(pentafluoro-λ^6-sulfanyl)-ethylene, [(E)-1,2-Difluoro-2-(pentafluoro-λ^6-sulfanyl)]ethenyltrimethylphosphonium-tetrafluoroborate, 1,2-Difluoro-1-(pentafluoro-λ^6-sulfanyl)-2-iodo-ethylene

The first SF_5-substituted perfluoro iodo alkene (E)-$F_5SCF{=}CFI$ was synthesized from the phosphonium salt precursor [(E)-$F_5SCF{=}CFPMe_3$]$^+BF_4^-$ and iodine.

Introduction

Fluoralkyl iodides are an important class of compounds and are used in preparing large numbers of useful organo and organometallic derivatives [2]. The SF_5 containing perfluoroalkyl iodides, $SF_5(C_2F_4)_nI$ (n = 1, 2, 3) and $SF_5CF(I)CF_3$ have been prepared [3, 4], but no corresponding iodo alkene have been synthesized. We wish to report the first SF_5-substituted iodo perfluoroalkene.

Discussion

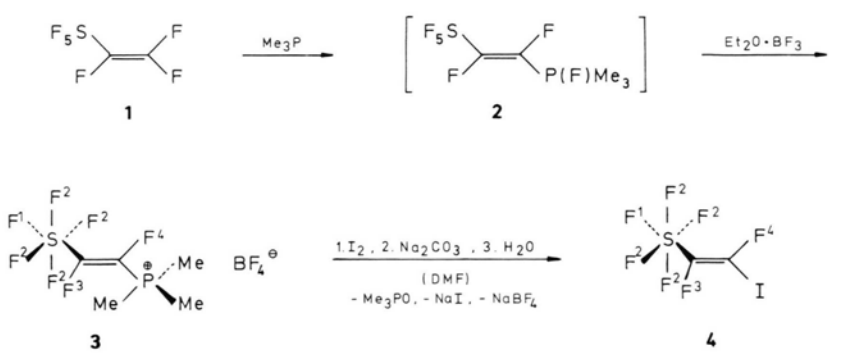
Trimethylphosphine and 1,2,2-trifluoro-1-(pentafluoro-λ^6-sulfanyl)ethylene (**1**) reacted at −20 °C to give the monofluorophosphorane **2** [5], which was not isolated but treated with boron trifluoride-etherate to furnish the thermally stable solid phosphonium tetrafluoroborate **3.** Using iodine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

The FAB mass spectrum of **3** exhibits [$F_5SCF{=}CFPMe_3$]$^+$ and BF_4^- ions, whereas the 70 eV EI mass spectrum of **4** shows the molecular ion M^+ (100%) and other characteristic fragments, *e.g.* $(M-F)^+$, $C_2F_3I^+$, $C_2F_2I^+$ and SF_3^+.

Weak C=C stretching modes are observed in the 1660–1672 cm^{-1} range of the IR spectra. In SF_5CFCF_2 the strong C=C stretching frequency is located at 1782 cm^{-1} [7]. $F^1(F^2_4)S$ resonances appear in the ^{19}F NMR spectra in the expected regions [4, 8]. The fine structure allows to determine the values for $^3J_{F^3F^4}$ (138.0 (**3**), 147.3 (**4**)) which are indicative of the (E)-configuration. Surprisingly, the ^{19}F signal for 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.



Scheme 1

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Verlag der Zeitschrift für Naturforschung, D-7400 Tübingen
0932–0776/91/0100–0123/$ 01.00/0

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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 (^{1}H, internal standard, TMS), 75.39 MHz (^{19}F, internal standard CCl_3F), and 32.44 MHz (^{31}P, external standard 85% H_3PO_4); d = doublet, p = pentet, dec = decet. Compound **1** was synthesized *via* a literature procedure [7].

[(E)-1,2-Difluoro-2-(pentafluoro-λ⁶-sulfanyl)-ethenyl]trimethylphosphonium-tetrafluoroborate (**3**)

In a 100 ml heavy-wall glass tube, fitted with a TEFLON® stopcock 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 (BF_4^-, 100), 179 (glycerine-H+BF_4^-, 33), 271 (2 glycerine-H+BF_4^-, 43); FAB pos.: *m/z* (%): 265 ($F_5SCF{=}CFPMe_3^+$, 1).

IR: $\tilde{\nu}$ = 2965 cm^{-1} s (CH), 2892 m (CH), 1660 w (C=C), 1425 w (CH), 1299 m (CF), 1261 m (CF, P=O), 1209 vs (CF), 1030 vs (P−O−C), 988 vs, 922 vs, 891 vs, 870 vs (SF), 780 m (BF), 760 s, 690 m, 663 m, 624 m, 598 vs (SF), 562 m, 535 m, 523 m (BF).

NMR: ^{1}H: δ = 2.20 (ddd, $^2J_{PH}$ = 15.2, $^4J_{F^4H}$ = 1.1, $^5J_{F^3H}$ = 1.6 Hz); ^{19}F: δ = +68.4 (F^1, multiplet centered at line 6 (see ref. [10]), $^3J_{F^1F^3}$ = 3.8, $^4J_{F^1F^4}$ = 2.4 Hz), +57.2 (F^2, multiplet, $^4J_{F^2F^4}$ = 21.3 Hz), −126.5 (F^3, ddd dec, $^3J_{F^3F^4}$ = 138.0, $^3J_{F^3P}$ = 8.6, $^5J_{F^3H}$ = 1.7 Hz), −148.6 (F^4, dddp dec, $^2J_{F^4P}$ = 65.0, $^4J_{F^4H}$ = 1.2 Hz); ^{31}P{^{1}H}: δ = 37.8 (dd).

$C_5H_9BF_{11}PS$ (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-λ⁶-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 P_4O_{10}. 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 ($C_2F_3I^+$, 31), 189 ($C_2F_2I^+$, 48), 158 (CFI^+, 8), 127 (SF_5^+, I^+, 36), 89 (SF_3^+, 21).

High-resolution MS: Found: 315.8660 ($C_2F_7SI^+$, Δ 0.4 mmu), 207.9005 ($C_2F_3I^+$, 0.6), 188.9029 ($C_2F_2I^+$, 1.6), 126.9058 (I^+, 1.1), 126.9657 (SF_5^+, 1.6).

IR: $\tilde{\nu}$ = 1672 cm^{-1} w (C=C), 1220 s (CF), 1197 m (CF), 1179 s (CF), 869 vs (SF), 722 m, 670 s, 620 m, 596 s (SF).

NMR: ^{19}F: δ = +67.3 (F^1 multiplet centered at line 6 (see ref. [10]), $^3J_{F^1F^3}$ = 3.9, $^4J_{F^1F^4}$ = 2.2 Hz), +53,1 (F^2, multiplet, $^4J_{F^2F^4}$ = 19.3, $^3J_{F^2F^3}$ = 2.9 Hz), −135.1 (F^3, ddp, $^3J_{F^3F^4}$ = 147.3 Hz), −107.5 (F^4, dpd).

C_2F_7IS (315.87)

Calcd	C 7.61	F 42.1,
Found	C 7.79	F 42.4.

The authors are grateful to the Fonds der Chemischen Industrie for financial support. G. L. G. and R. W. express their appreciation to the U.S. Department of energy (DE-FG 21−88 MC 25142) for support of this work. G. L. G. wishes to thank the Fulbright Commission for a Senior Fulbright Fellowship.

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