[(E)-1,2-Difluoro-2-(pentafluoro-6-sulfanyl)ethenyl]phosphonates

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For the first time SF₃ containing organic phosphonates, SF₃CF=CFP(O)(OR')₂, have been prepared from trimethylsilylphosphites, (R'O)₂POSiMe₃ (R' = Et, R' = SiMe₃) and trifluorovinylsulfur pentfluoride, SF₃CF=CF₂ in an Arbuzov type reaction.

Introduction

Trialkylphosphites (R'O)₃P react with perfluorinated alkenes, e.g. CF₃C(R')=CF₂ furnishing the phosphonates CF₃C(R')=CFP(O)(OR')₂ (R' = Et, iPr; R'' = F, CF₃) and alkylfluorides R'F via an Arbuzov type reaction [2]. The use of trimethylsilylphosphites, (R'O)₂POSiMe₃ (1a: R' = Et, 1b: R' = SiMe₃) is advantageous because of its greater nucleophilicity and easy formation of fluorotrimethylsilane [3]. It was of interest to determine whether an olefin containing the SF₃ group would undergo reaction with organic phosphites. There are no reports in the literature of organophosphorus compounds containing an SF₃ group.

Discussion

We have found that organic phosphites (1a and 1b) will react with 1,2,2-trifluoro-1-(pentafluoro-6-sulfanyl)ethylene (2) [5] to give the first F₃S group containing alkenylphosphonates, 4a,b, which are moisture-sensitive colorless liquids (Scheme 1). The (E) isomers exclusively were found, derived from the intermediates 3a,b in which there is maximum repulsion between the phosphonium and sulfanyl groupings [4]. The 70 eV EI mass spectra show no parent molecular ion, but for 4a the ion [M+1]⁺ was found; this has been observed in a few cases, for similar compounds [6]. For 4b the [M–CH₃]⁺ fragment was obtained in keeping with results reported for O-trimethylsilylated phosphonates, e.g. for CF₃CF=CFP(O)(OSiMe₃)₂ [7]. In the IR spectra, substitution of one fluorine atom in 2 by the phosphonate groupings decreases considerably (as expected) the C=C stretching frequency [8]; ν = 1782 (2) versus 1666 (4a) and 1665 cm⁻¹ (4b). The same trend [4] was found for CF₃CF=CF₂ and CF₃CF=CFP(O)(OR')₂; ν = 1797 versus 1672 (R' = Et) and 1673 cm⁻¹ (R' = SiMe₃). However, stretching and deformation modes of the F₃S moiety remain unaffected. The presence of (E) isomers is proven by the trans F–F coupling [J = 136.6 Hz (4a), 138.6 Hz (4b)] (see Table I) obtained from the ¹⁹F-NMR spectra. By comparison, the respective values for (Z)–CF₃CF=CFP(O)(OR')₂ are 147.0 and 144.0 Hz [4]. The introduction of the (R'O)₂P(O) group in SF₃CF=CF₂ causes a large high field shift (ca. 50 ppm) for the F₃S nucleus whereas a 25 ppm downfield shift is observed for F₃ [9]. The same trend can be found with CF₃CF=CF₂ and CF₃CF=CFP(O)(OR')₂ [4, 10].
Table 1. $^1$H, $^{19}$F and $^{31}$P NMR data for 4a and 4b (J given in Hz).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>F$^1$</th>
<th>F$^2$</th>
<th>F$^3$</th>
<th>F$^4$</th>
<th>F$^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a$^{ab}$</td>
<td>+65.7c</td>
<td>+52.8d</td>
<td>-136.2e</td>
<td>-154.0f</td>
<td>-1.7f</td>
</tr>
<tr>
<td>4b$^{bc}$</td>
<td>+66.0c</td>
<td>+52.4d</td>
<td>-137.4e</td>
<td>-152.6f</td>
<td>-22.1f</td>
</tr>
</tbody>
</table>

structure (quintuplet) is induced in the resonances of F$^2$ and phosphorus by the coupling with four cis-F$^2$ nuclei of the F$_3$S group. The multiplet signals of F$^1$ and F$^2$ experience a small highfield shift with respect to F$^1$SCF=CF$_2$[9]. It is interesting to note that the F$_3$S and F$_2$C groups obviously have a similar influence on phosphorus in the phosphonates XCF=CFP(0)(0Me)0SiMe$_3$.[9].

Experimental

The appropriate precautions in handling moisture- and oxygen-sensitive compounds were observed throughout this work. The reactions were carried out in a 100 ml heavy-wall glass tube, fitted with a TEFON$^*$ stopcock. At -196°C compound 2 was condensed to 1 by using a vacuum line. After completion of the reaction the tube was opened in vacuo at -196 °C, and fluorotrimethylsilane and excess of 2 were removed at 0 °C by pumping. The crude products were distilled.

Elemental analyses: Mikroanalytisches Laboratorium Beller, Göttingen. - MS: MAT 8222 spectrometer (EI-ionization, electron energy 70 eV; GC/MS inlet system, inlet temperature 270 °C).

IR: Nicolet 5 DX FT spectrometer, spectra were recorded of liquid films between sodium chloride plates (intensity: vs = very strong, s = strong, m = medium, w = weak).

NMR: AC 80 Bruker spectrometer, operating at 80.13 MHz ($^1$H, internal standard TMS), 75.39 MHz ($^{19}$F, internal standard CCl$_3$F), and 32.44 MHz ($^{31}$P, external standard 85% H$_3$PO$_4$). Compounds 1 and 2 were synthesized by literature procedures [3, 5].

Diethyl[(E)-1,2-difluoro-2-(pentfluoroo- \( \text{S}_{2} \)-sulfanyl)ethenyl]phosphonate (4a)

The mixture of 1.8 g (8.7 mmol) of 1a and 2.0 g (9.6 mmol) of 2 was allowed to warm to room temp. within 6 h and then stirred magnetically for 4 d at 60 °C. After distillation at 38 °C/0.04 Torr 2.2 g (79%) of a colorless liquid was obtained.

MS: m/z (%) = 327 (15) [M$^+$+H$^+$], 325 (13) [M$^+$-H$^-$], 283 (14) [M$^+$+H-OC$_2$H$_5$], 271 (64) [M$^+$+H-2CC$_2$H$_5$], 199 (4) [M$^+$-SF$_3$], 171 (44) [M$^+$-CF$_3$-SF$_3$], 151 (43) [M$^+$-2CF$_3$-SF$_3$], 127 (14) [SF$_3$]+, 121 (48) [P(OC$_2$H$_5$)$_2$]+, 93 (56) [P(OH)OC$_2$H$_5$]+, 65 (97) [P(OH)$_2$]+, 45 (37) [OC$_2$H$_5$]+, 29 (100) [C$_2$H$_4$]+ and other fragments.

IR: $\nu$ = 2995 cm$^{-1}$ (CH), 1666 w (C=C), 1300 vs (CF), 1258 s (CF, P=O), 1026 vs (P=O-C), 871 vs (SF), 604 s (SF) and other absorptions.

C$_6$H$_{10}$F$_2$O$_2$PS (326.17)
Calcd C 22.09 H 3.09 F 40.8 P 9.50
Found C 22.09 H 3.09 F 40.8 P 9.68.

Bis(trimethylsilyl) [(E)-1,2-difluoro-2-(pentfluoro-\( \text{S}_{2} \)-sulfanyl)ethenyl]phosphonate (4b)

The mixture of 2.0 g (9.6 mmol) of 1b and 2.0 g (9.6 mmol) of 2 was allowed to warm up within 6 h and stirred magnetically for 16 h at 5 °C. After distillation at 72 °C/0.1 Torr 3.2 g (81%) of a colorless liquid was obtained.

MS: m/z (%) = 399 (89) [M$^+$+CH$_3$], 287 (19) [M$^+$-SF$_3$], 229 (11) [FC=CFP(0)(0Me)OSiMe$_3$]+, 151 (12) [P(OMe)(OSiMe$_3$)+], 135 (11) [P(OMe)$_2$(OSiMe$_3$)+], 121 (9) [HP(OMe)OSiMe$_3$]+, 89 (11) [OSiMe$_3$]+, 77 (45) [P(O)OC$_2$H$_5$]+ and other fragments.

IR: $\nu$ = 2966 cm$^{-1}$ s (CH), 1665 m, broad (C=C), 1264 vs (CF, P=O), 1201 vs (CF), 955 s (P=O-Si), 871 vs (SF), 604 m (SF) and other absorptions.

C$_8$H$_{18}$F$_2$O$_2$PSSi$_2$ (414.43)
Calcd C 23.18 H 4.38 F 32.1 P 7.48
Found C 23.23 H 4.52 F 31.9 P 7.56.

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