O-ETHYL S,S-bis(o-CARBORAN-9-YL) DITHIOPHOSPHITE

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UDC 542.91:547.1'127'118

O-Ethyl S,S-bis(o-carboran-9-yl) dithiophosphite was prepared. The reactions of this product with sulfur, selenium, methyl iodide, and chloral were studied.

Keywords: O-ethyl S,S-bis(o-carboran-9-yl) dithiophosphite, trithiophosphate, dithiophosphonate, dithiophosphate

We have recently synthesized the first o-carboran-9-yl ester of a trivalent phosphorus thioacid, namely, O,O-diethyl S-(o-carboran-9-yl) thiophosphite and studied some of its chemical transformations [1]. In a continuation of this work, we attempted to obtain a phosphite containing two bulky carboranyl substituents and test the possibility of using such a reagent as the starting compound in the synthesis of the corresponding biscarboranyl esters of pentavalent phosphorus acids.

O-Ethyl S,S-bis(o-carboran-9-yl) dithiophosphite (1) was obtained from ethyl dichlorophosphite and o-carboran-9-yl mercaptan in ether in the presence of triethylamine in 68% yield.

\[
\text{EtOPCl}_2 + 2 \text{B}_9\text{H}_8\text{SH} \rightarrow \text{HC} = \text{CH} \quad \text{Et}_3\text{N} \quad \text{HC} = \text{CH} \quad \text{B}_9\text{H}_8\text{S}_2\text{POEt} \quad \text{(1)}
\]

In contrast to alkyl and aryl analogs [2], dithiophosphite 1 is a crystalline compound stable in the air. The PMR spectrum of 1 has a group of signals (δ 2.0-3.5 ppm) corresponding to carboranyl group protons and multiplets at δ 1.23 and 4.20 ppm related to the ethyl group. The \(^{31}\text{P}\) NMR spectrum of dithiophosphite 1 is a very broad singlet at 166 ppm (154 Hz). The strong broadening of the signal in the \(^{31}\text{P}\) NMR spectrum is apparently a consequence of spin-spin coupling of the phosphorus nucleus with the two carboranyl substituents containing magnetoactive boron atoms.

Dithiophosphite 1 reacts with sulfur upon heating in benzene to give the corresponding trithiophosphate (2). On the other hand, the reaction with selenium leads to the formation of a product mixture, which could not be separated.

\[
\text{HC} = \text{CH} \quad \text{B}_9\text{H}_8\text{S}_2\text{POEt} \quad \text{(1)} \quad \rightarrow \quad \text{HC} = \text{CH} \quad \text{S} \quad \text{B}_9\text{H}_8\text{S}_2\text{POEt} \quad \text{(2)}
\]

Heating 1 and methyl iodide in benzene at reflux gave S,S-bis(o-carboran-9-yl) methyldithiophosphonate (3), while the analogous reactions with trialkyl phosphites require heating in the alkyl iodide at reflux [3].

\[
\text{HC} = \text{CH} \quad \text{B}_9\text{H}_8\text{S}_2\text{POEt} \quad \text{(1)} \quad \rightarrow \quad \text{HC} = \text{CH} \quad \text{MeI} \quad \text{HC} = \text{CH} \quad \text{B}_9\text{H}_8\text{S}_2\text{PMe} \quad \text{(3)}
\]
<table>
<thead>
<tr>
<th>Compound</th>
<th>(T_p, ^\circ C)</th>
<th>Yield, %</th>
<th>Empirical formula</th>
<th>Found/Calculated, %</th>
<th>(\delta ^{31}P, ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>164-166</td>
<td>68</td>
<td>(C_6H_{12}B_2OOPS_2)</td>
<td>7.17/7.27</td>
<td>50.41/50.55</td>
</tr>
<tr>
<td>2</td>
<td>189-192</td>
<td>93</td>
<td>(C_6H_{12}B_2OOPS_2)</td>
<td>6.65/6.76</td>
<td>47.05/47.16</td>
</tr>
<tr>
<td>3</td>
<td>293-297 [4]</td>
<td>75</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>266-268</td>
<td>65</td>
<td>(C_6H_{12}B_8O_2PS_2)</td>
<td>-</td>
<td>48.76/48.86</td>
</tr>
</tbody>
</table>

In contrast to 0,0-diethyl S-(o-carboran-9-yl) thiophosphite [1], dithiophosphite 1 reacts with chloral to give only its oxidation product. This reaction proceeds upon heating in benzene at reflux and 0-ethyl S,S-bis(o-carboran-9-yl) dithiophosphate (4) was isolated in 65% yield.

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The IR spectra of 1-4 have strong bands at 2590-2600 cm\(^{-1}\) (B-H). Characteristic bands for the P=O bond are found for 3 and 4 in the vicinity of 1200 cm\(^{-1}\).

**EXPERIMENTAL**

The IR spectra were taken on a UR-20 spectrometer in KBr pellets. The \(^{31}P\) NMR and PMR spectra were obtained on a Bruker WP-200 spectrometer at 81.01 and 200.13 MHz, respectively. Silpearl silica gel manufactured in Czechoslovakia was used for the chromatography.

**O-Ethyl S,S-bis(o-Carboran-9-yl) Dithiophosphite (1).** A sample of 3.5 ml (0.025 mole) triethylamine was added to 4.2 g (0.024 mole) o-carboran-9-yl mercaptan in 50 ml abs. ether in an argon atmosphere. After stirring for 0.5 h, a sample of 1.34 ml (0.012 mole) ethyl dichlorophosphite in 20 ml abs. ether was added dropwise to the mixture obtained at -5°C. The reaction mixture was gradually brought to ~20°C and stirred for 12 h. Triethylamine hydrochloride was filtered off and ether was evaporated. The residue was subjected to column chromatography using 4:1 hexane-acetone as the eluent to give 1.

**O-Ethyl S,S-bis(o-Carboran-9-yl) Trithiophosphate (2).** A sample of 0.13 g (0.004 mole) sulfur was added to a solution of 1.57 g (0.0035 mole) 1 in 30 ml benzene in an argon atmosphere. The mixture was heated at reflux for 8 h, benzene was distilled off, and 2 was isolated from the residue by chromatography using 4:1 hexane-acetone as the eluent.

**S,S-bis(o-Carboran-9-yl) Methyl Dithiophosphonate (3).** A sample of 0.8 ml (0.013 mole) methyl iodide was added to 2.23 g (0.0051 mole) 1 in 10 ml benzene in an argon atmosphere. The reaction mixture was heated for 6 h at reflux to give 3 as a precipitate insoluble in benzene. This product was additionally purified by crystallization from 2-propanol.

**O-Ethyl S,S-bis(o-Carboran-9-yl) Dithiophosphate (4).** A sample of 0.41 ml (0.004 mole) chloral was added to 1.62 g (0.004 mole) 1 in 30 ml abs. benzene. The mixture was heated at reflux in an inert atmosphere for 5 h. The solvent was evaporated and the residue was subjected to column chromatography using 2:2:1 hexane-benzene-acetone as the eluent to give 4.

The physical constants and yields of the compounds obtained are given in Table 1.