SYNTHESIS OF S-CATECHOLBORYL (N,N-DIMETHYLAMINOMETHYL)-PHENYLDITHIOPHOSPHINATE

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S-Catecholboryl (N,N-dimethylaminomethyl)phenyldithiophosphinate, the first representative of S-diorganylboric derivatives of phosphonous acid was obtained by the reaction of catecholboryl (N,N-dimethylaminomethyl)phenylphosphine with sulfur.

UDC 542.91:547.1'127'118

N- and O-diorganylboric derivatives of phosphonous acids have been described in the literature [1, 2]. Analogous S-organylboric acids are unknown. We synthesized the first derivative of this type, S-catecholboryl (N,N-dimethylamino)phenyldithiophosphinate (II) in a quantitative yield by the reaction of catecholboryl (N,N-dimethylaminomethyl)phenylphosphine (I) with sulfur in CS₂ at ~20°C.



The structure of (II) was proved by the data of the elemental analysis, ³¹P NMR, PMR, and IR spectroscopy. In the electron impact mass spectrum of (II) there is a peak of molecular ion with m/z 349, and also peaks of fragmentary ions PhPS₂, $C_6H_4O_2BNMe_2$, PhPS, $C_6H_4O_2B$, PhP, PS₂, Ph. The presence in the molecule of (II) of a boron atom as a Lewis acid and a nitrogen atom as a Lewis base presumes the possibility of formation of an intramolecular complex N \rightarrow B bond. In the PMR spectrum of (II), peaks of dimethylamino groups are observed in the form of three bands which may indicate the formation of such a bond.

Compound (II) is unstable in air and on standing in the absence of argon decomposes with the formation of the corresponding disulfide (III) and bis(catecholboryl) oxide (IV). Two variants are possible: oxidation or an initial hydrolysis followed by oxidation.



The hydrolysis of (II) should take place not only at the S-B bond, but also at the catechol fragment of the molecule, although such hydrolysis could be inhibited by the formation of an intramolecular complex $N \rightarrow B$ bond. We did not detect the products of the hydrolysis of the catechol fragment (boric acid and catechol). If the decomposition process of (II) in air were to stop at the dithio acid (V) stage, then this could be distinguished from disul-

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fide (IV) according to the IR spectra by the characteristic vibration of the (S)P-S-H groups in the 2400-2500 cm⁻¹ region [3, 4]. No absorption in the IR spectrum of the decomposition products of (II) was observed in this region, which indicates the oxidation of (II) to disulfide (III). To isolate (III) in an analytically pure state, the decomposition products of (II) were recrystallized from methanol. In the PMR spectrum of (III) the dimethyl groups show an absorption in the form of a singlet at δ 3.03 ppm, the methylene protons are manifested in the form of a doublet at δ 3.61 ppm with $^{2}J_{PH}$ = 9.2 Hz, and the phenyl groups are in the form of a multiplet from 7.33 to 8.53 ppm (DMF- d_7). The absorption in the 2400-2500 cm^{-1} region, characteristic of the vibrations of the dithio acids, was also absent in the IR spectrum of (III). In the electron impact mass spectrum of (III) there are peaks of fragmentary ions (Me₂NCH₂)(Ph)P(S)-S-S-(S)PPh, (Me₂NCH₂)(Ph)P(S)-S-S-PS, (Me₂NCH₂)(Ph)P· (S)-S-S, PhP(S)CH₂NMe₂, PhPS₂, PhPS₂, CH₂NMe₂.

To separate the boric component, the decomposition products of (II) were sublimed in vacuo. In the electron impact mass spectra of (IV), a peak of a molecular ion with m/z 254 is observed, as well as peaks of the fragmentary ions C₆H₄O₂BO, C₆H₄O₂B, C₆H₄O. In the PMR spectrum of (IV) there is absorption of only the catechol protons in the 6.2-6.6 ppm region $(DMF-d_7)$. In the literature is to be found only a brief reference to the synthesis of (IV) from boric anhydride and catechol [5].

The oxidation of (alkylthio)dialkylboranes by bromine [6] and atmospheric oxygen [7] to disulfides is known.

EXPERIMENTAL

The ¹H and ³¹P NMR spectra were measured on "Bruker M-250" and NMR-KGU-4 spectrometers, and the IR spectra on a UR-20 spectrophotometer. The mass spectra were run on an MX-1310 spectrometer with a precision determination of the mass of ions, and their elemental analysis, µ 60 V.

S-Catecholboryl (N,N-dimethylaminomethyl)phenyldithiophosphinate (II). A solution of 0.78 g (24.3 mmoles) of elemental sulfur in 10 ml of CS2 was added (with cooling to -70°C in a dry argon atmosphere) to a solution of 3.47 g (12.1 mmoles) of catecholboryl (N,N-dimetylaminomethyl)phenylphosphine (I) [8] in 5 ml of abs. THF. The reaction mixture was allowed to warm up to room temperature, at which point white crystals of (II) began to separate. The yield of (II) was 3.0 g (70%), mp 93-95°C. ³¹P NMR spectrum 54 ppm (DMF). PMR spectrum of (II) (DMF-d₇, broadened lines, δ , ppm): 2.63 t, 2.80 t, 2.90 t (6H, N(CH₃)₂); 3.23 s (2H, P-CH₂-N); 6.83 s (4H, C₆H₄O₂B); 7.36-8.30 m (5H, Ph). Found, %: C 50.33; H 4.93; N 4.41; P 9.32; S 18.33. C15H17BNO2PS2. Calculated, %: C 51.57; H 4.87; N 4.41; P 8.88; S 18.33.

(N,N-Dimethylaminomethyl)phenylthiophosphine Disulfide (III). Compound (II) was held in air for 2 h and 2 g of oxidation products of (II) were obtained, which were recrystallized from 10 ml of methanol. After filtration, 0.8 g (60%) of (III) was obtained, mp 164-165°C, δ³¹P 56 ppm (DMF). Found, %: C 46.20; H 5.81; N 6.04; P 13.08; S 27.20. C₁₈H₂₆-N₂S₄P₂. Calculated, %: C 46.95; H 5.65; N 6.08; P 13.47; S 27.82.

Bis(catecholboryl) Oxide (IV). A 0.3 g portion of the oxidation products of (II) was sublimed at 140°C (10⁻³ mm) for 4 h. The yield of (IV) was 0.06 g (55%), mp 79°C.

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