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LETTERS TO THE EDITOR

Reaction of 6-Bromo-2-hydroxy-4-tributylphosphonium Naphthyl-1-ate with Chlorobis(phenylenedioxy)spirophosphoranes

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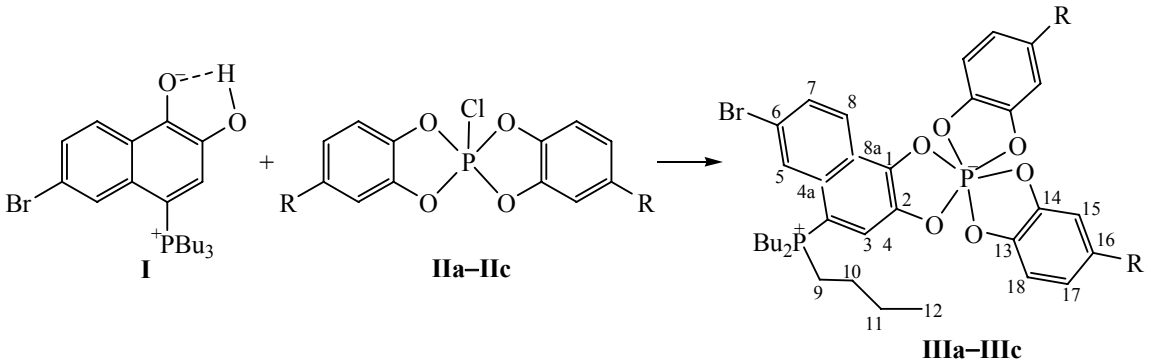
The P(VI) derivatives usually obtained from phosphoranes are interesting in the theoretical aspect as a model in the nucleophilic substitution reactions at the pentacoordinated P atom, and from the practical viewpoint as various reagents, ionic liquids, etc. [1–4]. In this report, we first suggest to use the reaction of P(IV)-containing betaines, such as 6-bromo-2-hydroxy-4-tributylphosphonium naphthyl-1-ate **I**, with bis(phenylenedioxy)chlorophosphoranes **IIa**–**IIc** in the synthesis of the P(VI)-derivatives. These reactions result in the betaine structures **IIIa**–**IIIc** in a high yield. In their structure the positive charge on a phosphonium center and the negative charge on a fragment with the hexacoordinated phosphorus atom are at a considerable distance from each other in a spatially rigid frame. The betaines of this structure are of considerable interest due to the wide synthetic use (reagents in the Wittig reaction, reagents for creating C–C and C–X bonds, where X = O, N, S, as organocatalysts, etc.) [5–10].



R = H (**a**), Me (**b**), *t*-Bu (**c**).

The phosphorates **III** have a very different solubility depending on the nature of R. Compounds **IIIa** and **IIIb** are insoluble in organic solvents, so their structure was proved by the solid-state NMR (CPMAS NMR). In the ^{31}P NMR spectra of compounds **IIIb** and **IIIc** there are two signals in the regions characteristic of P(IV) and P(VI), which indicates the formation of isomeric phosphorates. The introduction of *tert*-butyl substituent increases the solubility of the phosphonium phosphorate **IIIc** in organic solvents, which made it possible to characterize it by the spectral methods used in the liquid phase.

The ^{13}C NMR spectrum of compound **IIIc** contains seven signals of the carbon nuclei connected with protons and 9 signals of the *ipso*-carbons in the aro-

matic region. The carbon nuclei bonded with the oxygen resonate in the weak field at δ_C 145.98 (C^1), 143.75 (C^2), 141.72 (C^{13}), and 147.07 ppm (C^{14}). The alkyl carbon atoms at the phosphonium center and the *tert*-butyl carbon atoms resonate in the strong field.

Compound (IIIa). To a solution of 0.61 g (2.16 mmol) of spirophosphorane **IIa** in 10 ml of CH_2Cl_2 was added dropwise a solution of 0.95 g (2.16 mmol) of betaine **I** [11] in 15 ml of CH_2Cl_2 under argon atmosphere. The reaction mixture became pink, and two minutes latter the color of the reaction mixture changed to green, therewith, HCl release was observed (litmus test). After 2 h the formed fine crystalline precipitate was filtered off under argon atmosphere and dried in a vacuum (12 mm Hg). Yield 1.09 g (74 %), mp 310–312°C. IR spectrum, ν, cm^{-1}: 2724, 2358, 1727, 1658, 1581, 1565, 1378, 1354, 1312, 1207 (P–O–Ar), 1159, 1119, 1100, 1075, 1026, 1014, 968, 912, 874, 826, 742, 721, 695, 646, 630, 555, 534, 498, 403. $^{13}C–\{^1H\}$ CPMAS spectrum (100.6 MHz), δ_C, ppm (*J*, Hz): 146.94 s (C^1), 143.23 s (C^{13}), 140.31 s (C^2), 128.51 s, 124.57 s, 123.92 s, 122.02 s, 118.16 s, 117.43 s, 115.39 s, 110.91 s, 107.30 s, 92.00 d ($^1J_{PC}$ 58.6), 21.17 br.s (C^9, C^{10}, C^{11}), 11.19 s (C^{12}, $^1J_{HC}$ 139.3). $^{31}P–\{^1H\}/^{31}P$ CPMAS spectrum (162.0 MHz), δ_P, ppm: 28.8 (s/br.s) (P^{IV}, 1P), –79.6 (s/br.s) (P^{VI}, 1P).

Compound (IIIb). To a solution of 0.52 g (1.67 mmol) of spirophosphorane **IIb** in 5 ml of CH_2Cl_2 was added dropwise a solution of 0.73 g (1.67 mmol) of betaine **I** in 10 ml of CH_2Cl_2 under argon atmosphere. The color of the reaction mixture changed to crimson, and HCl release was observed (litmus test). As the hydrogen chloride release ceased, the reaction mixture became green. After 1 day, the solvent was evaporated. The light yellow precipitate was washed with chloroform under argon atmosphere. The resulting white precipitate was dried in a vacuum (12 mm Hg). Yield 1.00 g (84 %), mp 115–116°C. IR spectrum, ν, cm^{-1}: 1583, 1430, 1321, 1276, 1253, 1217 (P–O–Ar), 1163, 1142, 1112, 1074, 1026, 970, 944, 911, 839, 805, 784, 726, 633, 593, 496, 417. $^{13}C–\{^1H\}$ CPMAS spectrum (100.6 MHz), δ_C, ppm (*J*, Hz): 145.49 s and 145.45 s (C^1), 141.19 s and 140.17 s (C^2), 128.65 s, 126.69 s, 122.75 s, 118.01 s, 107.52 s, 21.32 br.s, 19.79 s, 9.88 s (C^{12}). $^{31}P–\{^1H\}/^{31}P$ CPMAS spectrum (162.0 MHz), δ_P, ppm: 28.4 and 27.7 (two s/two m) (P^{IV}, 1P), –78.0 and –79.4 (two s/two m) (P^{VI}, 1P).

Compound (IIIc). To a solution of 0.28 g (0.71 mmol) of spirophosphorane **II** in 5 ml of CH_2Cl_2 was added dropwise a solution of 0.31 g (0.71 mmol) of betaine **I** in 10 ml of CH_2Cl_2 under argon atmosphere. The reaction mixture became lilac, and HCl release was observed (litmus test). As the hydrogen chloride release ceased, the reaction mixture became green-brown. After 1 day, the solvent was evaporated. The light yellow precipitate was washed with hexane under argon atmosphere. The resulting precipitate was dried in a vacuum (12 mm Hg). Yield 0.47 g (84%), mp 137–140°C. IR spectrum, ν, cm^{-1}: 1582, 1377, 1365, 1314, 1284, 1258, 1241–1207 (P–O–Ar), 1122, 1094, 1074, 1023, 970, 936, 851, 823, 783, 691, 650, 580, 504. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 6.92 d (H^3, $^3J_{PCCH}$ 12.3), 7.28 s (H^5), 8.20 d (H^7, $^3J_{HCCH}$ 8.9), 7.55 d (H^8, $^3J_{HCCH}$ 9.2), 1.17–1.26 m (H^{10}, H^{11}), 0.80 br.t (H^{12}), 6.69 d (H^{16}, $^3J_{HCCH}$ 8.2), 6.80 d (H^{17}, $^3J_{HCCH}$ 7.8), 1.38 br.s (H^{20}). ^{13}C NMR spectrum ($CDCl_3$) δ_C, ppm (*J*, Hz): 145.98 br.m (d) (C^1, $^4J_{PCCCC}$ 2.2), 143.75 d.d (d) (C^2, $^3J_{PCCC}$ 5.5, $^2J_{HCC}$ 3.3), 128.10 d.d (d) (C^3, $^1J_{HC}$ 159.5, $^2J_{PCC}$ 9.2), 98.74 br.d (d) (C^4, $^1J_{PC}$ 84.0), 129.62 d (d) (C^{4a}, $^2J_{PCC}$ 8.8), 124.01 d (d) (C^5, $^1J_{HC}$ 154.4, $^3J_{PCCC}$ 4.7, partially overlapped with the signal of C^{8a}), 120.64 d.d (s) (C^6, $^2J_{HCC}$ 4.0), 129.08 s (d.d) (C^7, $^1J_{HC}$ 169.5, $^3J_{HCCC}$ 5.1), 125.91 s (d) (C^8, $^1J_{HC}$ 166.9), 124.74 m (d) (C^{8a}, $^3J_{PCCC}$ 11.7, partially overlapped with the signal of C^5), 20.92 br.d.t (d) (C^9, $^1J_{HC}$ 130.6, $^1J_{PC}$ 49.5), 23.83 br.d.t (d) (C^{10}, $^1J_{HC}$ 129.1, $^2J_{PCC}$ 3.7), 23.47 t (d) (C^{11}, $^1J_{HC}$ 128.4, $^3J_{PCCC}$ 15.0), 13.20 br.q (s) (C^{12}, $^1J_{HC}$ 125.4), 141.72 d.d (s) (C^{13}, $^3J_{HCCC}$ 8.8, $^2J_{HCC}$ 2.2), 147.07 br.s (br.s) (C^{14}), 115.15 d (s) (C^{15}, $^1J_{HC}$ 158.1), 148.45 m (s) (C^{16}), 116.99 d.d (s) (C^{17}, $^1J_{HC}$ 154.4, $^3J_{HCCC}$ 8.1), 113.17 d.d (s) (C^{18}, $^1J_{HC}$ 154.4, $^3J_{HCCC}$ 8.1), 34.03 m (s) (C^{19}), 31.50 q (s) (C^{20}, $^1J_{HC}$ 125.4). $^{31}P–\{^1H\}/^{31}P$ ($CDCl_3$), δ_P, ppm: 28.0 and 27.0 (two s/two m) (P^{IV}, 1P), –78.5 and –79.8 ppm (two s/two m) (P^{VI}, 1P).

The CPMAS NMR spectra were recorded on a Bruker AC-400 spectrometer. The NMR spectra of compound **IIIc** were recorded on a Bruker Avance-400 spectrometer relative to the signal of residual protons or carbons of the solvent (^1H and ^{13}C) or to external H_3PO_4 (^{31}P). The IR spectra were registered on a Bruker Vector-22 spectrometer from mulls in mineral oil.

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