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SHORT COMMUNICATIONS

Synthesis of Unsymmetrical Phosphorus(III)–Arene Macrocycle Based on 4,4′-Methylenediphenol, 4,4′-(Propane-2,2-diyl)diphenol, and *N*,*N*,*N*′,*N*′-Tetraethyl-*P*-phenylphosphonous Diamide

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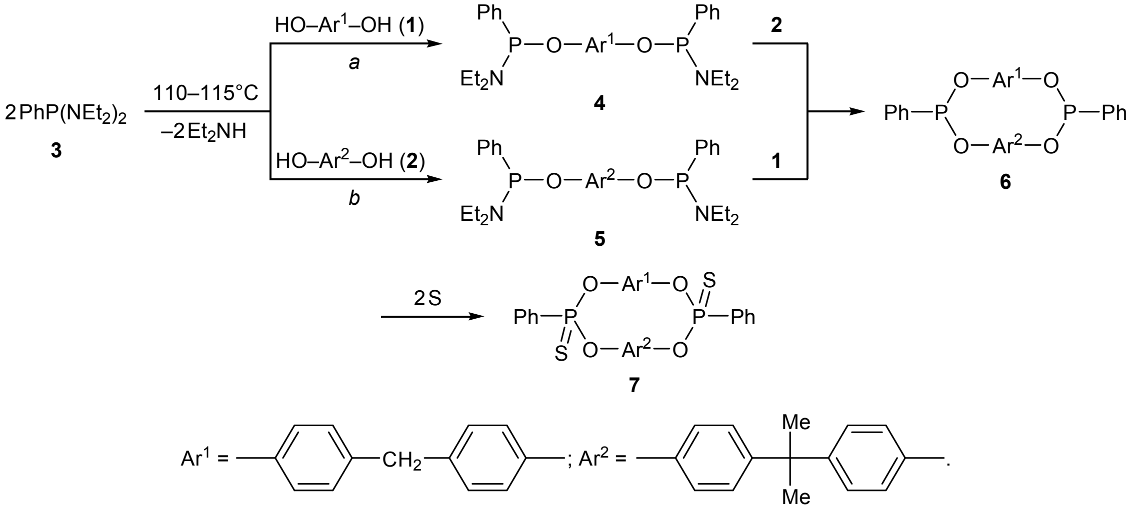
We previously described phosphorylation of bisphenols, 4,4′-methylenediphenol (**1**) and 4,4′-(propane-2,2-diyl)diphenol (**2**), with 2 equiv of *N*,*N*,*N*′,*N*′-tetraethyl-*P*-phenylphosphonous diamide (**3**) and subsequent synthesis of the corresponding symmetrical macrocyclic phenylphosphonites via molecular assembly (as well as by direct phosphorylation) [1–5]. Such macrocyclic compounds are multidentate ligands capable of forming catalytically active complexes with transition metals [4]. They can be used to obtain promising supramolecular systems [6] and are also representatives of a new class of biologically active compounds, in particular those exhibiting antimicrobial and analgesic activity [5].

While developing studies in this line, bisphenols **1** and **2** with spatially separated hydroxy groups were subjected to phosphorylation with 2 equiv of phosphonous diamide **3**, and bis-phosphonoamidites **4** and **5** thus obtained were brought into reaction with bisphenols **2** and **1**, respectively, to obtain new unsymmetrical phosphorus(III)–arene macrocycle **6**. The first phosphorylation step was carried out under solvent-free conditions, and the structure of compounds **4** and **5** was confirmed by ^{31}P NMR, IR, and mass spectra. The IR spectra of **4** and **5** displayed P–N stretching vibration band at 925 and 930 cm^{-1}, respectively, and the phosphorus nuclei resonated in their ^{31}P NMR as a singlet at δ_P 131.1 ppm.



In the second step, macrocycle **6** was assembled from **4** and **2** or from **5** and **1** in a dilute toluene solution at 90–95°C. The IR spectrum of unstable and readily oxidizable oily compound **6** lacked P–N stretching band typical of **4** and **5**. The phosphorus signal appeared in the ^{31}P NMR spectrum of **6** as a doublet at δ_P 165.80 ppm, which was located in a weaker field relative to the signal of the initial compound. Sulfurization of **6** with elemental sulfur enhanced the stability and provided an additional support for the proposed structure. The macrocyclic structure of **6** and **7** followed from the ^{1}H and ^{31}P, IR, and mass spectral data. The IR spectrum of **7** displayed an absorption band at 689 cm^{-1} typical of P=S group, in keeping with our previous data for analogous symmetrical macrocycles [7].

The yields of compound **6** according to pathways *a* and *b* were equally high, which is important from the preparative viewpoint.

Compounds **4** and **5** were synthesized according to the procedures described in [2, 8, 9]. A mixture of 1.8 mmol bisphenol **1** or **2** and 3.6 mmol of **3** was heated for 2 h at 115–120°C until the amount of evolved diethylamine attained nearly theoretical value, and the mixture was kept for 1 h under reduced pressure (1 mm) at that temperature; compounds **4** and **5** were obtained in 96–97% yield as viscous materials.

4,4′-Methylenedi(benzene-4,1-diyl) bis(*N*,*N*-diethyl-*P*-phenylphosphonamidite) (4) [4]. IR spectrum, ν, cm^{-1}: 1436 (P–C), 1186 (O–C), 925 (P–N). ^{31}P NMR spectrum: δ_P 131.1 ppm. Mass spectrum: *m*/*z* 559.63 [*M* + H]$^+$. Found, %: C 70.90; H 7.10; P 11.03. $C_{33}H_{40}N_2O_2P_2$. Calculated, %: C 70.97; H 7.17; P 11.11.

4,4′-(Propane-2,2-diyl)di(benzene-4,1-diyl) bis(*N*,*N*-diethyl-*P*-phenylphosphonamidite) (5) [2]. IR spectrum, ν, cm^{-1}: 1438 (P–C), 1188 (O–C), 930 (P–N). ^{31}P NMR spectrum: δ_P 131.1 ppm. Mass spectrum: *m*/*z* 587.68 [*M* + H]$^+$. Found, %: C 71.58; H 7.60; P 10.51. $C_{35}H_{44}N_2O_2P_2$. Calculated, %: C 71.65; H 7.56; P 10.56.

2,2-Dimethyl-5,11-diphenyl-4,6,10,12-tetraoxa-5,11-diphospha-1,3,7,9(1,4)-tetrabenzenacyclododecaphane (6). Bisphenol **2** or **1**, 2 mmol, was added to a solution of 2 mmol of compound **4** or **5**, respectively, in 50 mL of anhydrous toluene. The mixture was heated for 4 h at 90–95°C, the solvent was removed under reduced pressure (water-jet pump), and the residue was kept for 2 h under reduced pressure (1 mm) at 90–95°C. Yield 83%, unstable oily substance. IR spectrum, ν, cm^{-1}: 1440 (P–C), 1190 (O–C). ^{1}H NMR spectrum, δ, ppm: 1.64 s (6H, CH_3), 3.95 s (2H, CH_2), 6.77 d and 7.04 d (4H, $C_6\mathbf{H}_4CMe_2$), 6.91 d and 6.99 d (4H, $C_6H_4CH_2$), 7.57 m (3H, Ph), 7.94 m (2H, Ph). ^{31}P NMR spectrum: δ_P 165.80 ppm, d. Mass spectrum: *m*/*z* 663.40 [*M* + Na]$^+$.

2,2-Dimethyl-5,11-diphenyl-4,6,10,12-tetraoxa-5λ^5,11λ^5-diphospha-1,3,7,9(1,4)-tetrabenzenacyclododecaphane-5,11-dithione (7). Elemental sulfur, 3 mmol (0.1 g), was added to a solution of 1.5 mmol (1 g) of compound **6** in 20 mL of anhydrous toluene, and the mixture was kept for 24 h at room temperature. The solvent was removed under reduced pressure (water-jet pump), and the residue was purified by silica gel column chromatography using benzene as eluent. The product was dried for 2 h at 20°C under reduced pressure (10 mm). Yield 76%, crystalline solid, mp 240–242°C. IR spectrum, ν, cm^{-1}: 1438 (P–C), 1192 (O–C), 689 (P=S). ^{1}H NMR spectrum, δ, ppm: 1.66 s (6H, CH_3), 3.99 s (2H, CH_2), 6.78 d and 7.03 d (4H, $C_6\mathbf{H}_4CMe_2$), 6.85 d and 7.11 d (4H, $C_6\mathbf{H}_4CH_2$), 7.62 m (3H, Ph), 8.22 m (2H, Ph). ^{31}P NMR spectrum: δ_P 83.63 ppm, d. Mass spectrum: *m*/*z* 705.11 [*M* + H]$^+$. Found, %: C 67.92; H 4.93; P 8.68; S 9.24. $C_{40}H_{34}O_4P_2S_2$. Calculated, %: C 68.17; H 4.86; P 8.79; S 9.10.

The IR spectra were recorded on Perkin Elmer IR-283 (KBr) and Specord 75IR spectrometers (film between KBr plates). The ^{31}P NMR spectra were measured from solutions in $CDCl_3$ on a Bruker AV 300 spectrometer (121.49 MHz) relative to 85% phosphoric acid. The ^{1}H NMR spectra were recorded on a Bruker AV 400 instrument (400 MHz) using $CDCl_3$ as solvent and tetramethylsilane as reference. The mass spectra were obtained on a Bruker Daltonics Ultraflex TOF/TOF mass spectrometer (nitrogen laser, λ 337 nm; positive ion detection). The progress of reactions and the purity of products were monitored by TLC on Silufol plates (hexane–dioxane, 3:1). Ultrapure silica gel (Merck Grade 7734, 60 Å, 70–230 mesh) was used for column chromatography.

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