Letters to the Editor

Synthesis of cavity systems by cyclophosphorylation of 1,7-dihydroxynaphthalene with phosphorous triamides

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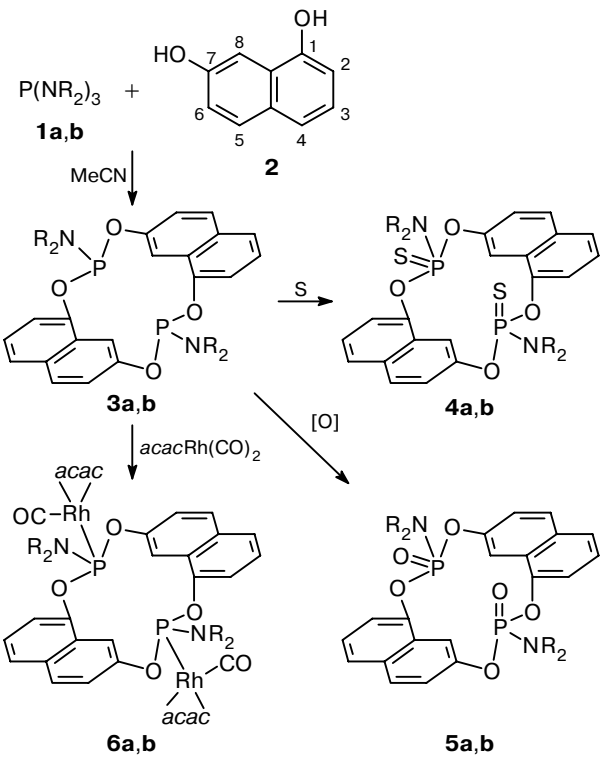
Previously,[1—3] it was shown that macrocyclic systems can be synthesized by the reactions of equimolar amounts of phosphorous amides **1a**,**b** with dihydroxyarenes whose hydroxy groups are symmetrically positioned. Note that there is no problem of regioselectivity in their cyclophosphorylation.

In the present work, an unsymmetrical diatomic phenol, namely, 1,7-dihydroxynaphthalene (**2**), was successfully cyclophosphorylated with phosphamides for the first time. Containing the α- and β-hydroxy groups in the different rings, this diol reacts with equimolar amounts of phosphamides **1a**,**b** in MeCN at 20 °C to give cyclobisamidophosphites **3a**,**b** in 50% yields (Scheme 1).

The products obtained were characterized by ^{1}H and ^{31}P NMR spectroscopy and X-ray diffraction analysis. According to the X-ray data,* compounds **3a** and **4b** include two dinaphthol fragments connected successively *via* the α- and β-O atoms by the phosphamide groups, which are *trans*-oriented to the cavity of the molecule. The ^{31}P NMR spectra of compounds **3a**,**b** each show two singlets with a slight difference in their chemical shifts. We believe that these compounds exist in solutions as two conformers. Compounds **3a**,**b** exhibit the essential chemical properties of amidophosphites.[4] Thus, they can add sulfur to give **4a**,**b**, be oxidized to

Scheme 1



* X-ray studies were carried out by A. I. Stash and V. K. Bel′skii and will be published elsewhere.

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5a,**b**, and form complexes with $Rhacac(CO)_2$ (**6a**,**b**), always retaining its macrocyclic structure. Compounds **3a**,**b**—**6a**,**b** can be regarded as a new type of phosphorus-containing cavity systems, which are of interest for creating supramolecular constructions.

^1H NMR spectra were recorded on Bruker WH-250 spectrometer (250.13 MHz) in $CDCl_3$. ^{31}P NMR spectra were recorded on Bruker WP-80 spectrometer with proton decoupling (32.4 MHz) in CH_2Cl_2 with 85% H_3PO_4 as the standard.

Cyclo[bis(naphthalene-1,7-diyl dialkylamidophosphites)] (3a,b). Phosphorous triamide **1a**,**b** (4.5 mmol) was added to a solution of diol **2** (4.5 mmol) in 20 mL of dry MeCN, and the reaction mixture was stirred at ~20 °C for 4 h. The precipitate that formed was washed with MeCN and then with benzene several times. The residue was recrystallized from methylene chloride. Compound **3a**: yield 50%, m.p. 191—192 °C. ^1H NMR, δ: 2.88 (d, 12 H, NMe, $^3J_{H,P}$ = 9.4 Hz); 7.01 (d, 2 H, H(2), $^3J_{H(2),H(3)}$ = 7.7 Hz); 7.26 (dd, 2 H, H(6), $^3J_{H(6),H(8)}$ = 2.2 Hz, $^3J_{H(6),H(5)}$ = 8.3 Hz); 7.34 (dd, 2 H, H(3), $^3J_{H(3),H(4)}$ = 8.3 Hz, $^3J_{H(3),H(2)}$ = 7.7 Hz); 7.58 (d, 2 H, H(4), $^3J_{H(4),H(3)}$ = 8.3 Hz); 7.82 (d, 2 H, H(5), $^3J_{H(5),H(6)}$ = 8.3 Hz); 8.7 (s, 2 H, H(8), $^4J_{H,H}$ = 2.2 Hz). ^{31}P NMR, δ: 135.1 (s), 135.6 (s). Found (%): C, 61.58; H, 5.24; P, 13.18. $C_{24}H_{24}N_2O_4P_2$. Calculated (%): C, 61.79; H, 5.18; P, 13.28. Compound **3b**: yield 49%, m.p. 173—174 °C. ^1H NMR, δ: 1.23 (t, 12 H, $CH_2\underline{Me}$, $^3J_{H,H}$ = 7.3 Hz); 3.32 (m, 4 H, CH_2, $^3J_{H,P}$ = 9.0 Hz); 3.39 (m, 4 H, CH_2, $^3J_{H,P}$ = 9.0 Hz); 7.10 (d, 2 H, H(2), $^3J_{H(3),H(2)}$ = 7.7 Hz); 7.24 (dd, H(6), $^3J_{H(6),H(5)}$ = 8.5 Hz, $^4J_{H(6),H(8)}$ = 2.6 Hz); 7.28 (dd, 2 H, H(3), $^3J_{H(3),H(4)}$ = 8.1 Hz, $^3J_{H(3),H(2)}$ = 7.7 Hz); 7.56 (d, 2 H, H(4), $^3J_{H(4),H(3)}$ = 8.1 Hz); 7.80 (d, H(5), $^3J_{H(5),H(6)}$ = 8.5 Hz); 8.71 (dd, 2 H, H(8), $^4J_{H,P}$ = 1.7 Hz, $^4J_{H(8),H(6)}$ = 2.6 Hz). ^{31}P NMR, δ: 137.4 (br.s). Found (%): C, 64.56; H, 6.24; P, 11.78. $C_{28}H_{32}N_2O_4P_2$. Calculated (%): C, 64.36; H, 6.17; P, 11.86.

Cyclo-*O*,*O*-[bis(naphthalene-1,7-diyl dialkylamidothiophosphates)] (4a,b) were obtained by the reactions of cyclophosphites **3a**,**b** with sulfur in methylene chloride at ~20 °C. Compound **4a**: yield 91%, m.p. 297—298 °C. ^{31}P NMR, δ: 67.4 (s). Found (%): C, 54.38; H, 4.44; P, 11.61. $C_{24}H_{24}N_2O_4P_2S_2$. Calculated (%): C, 54.33; H, 4.56; P, 11.68. Compound **4b**: yield 90%, m.p. 281—282 °C. ^{31}P NMR, δ: 66.4 s. Found (%): C, 57.36; H, 5.44; P, 10.61. $C_{28}H_{32}N_2O_4P_2S_2$. Calculated (%): C, 57.33; H, 5.50; P, 10.56.

Cyclo[bis(naphthalene-1,7-diyl dialkylamidophosphates)] (5a,b) were obtained by oxidation of cyclophosphites **3a**,**b** with $CO(NH_2)_2 \cdot H_2O_2$. Compound **5a**: yield 92%, m.p. 249—250 °C. ^{31}P NMR, δ: 1.62 (s). Found (%): C, 57.91; H, 4.79; P, 12.37. $C_{24}H_{24}N_2O_6P_2$. Calculated (%): C, 57.84; H, 4.85; P, 12.43. Compound **5b**: yield 89%, m.p. 268—270 °C. ^{31}P NMR, δ: 1.2 (s). Found (%): C, 60.59; H, 5.80; P, 11.22. $C_{28}H_{32}N_2O_6P_2$. Calculated (%): C, 60.65; H, 5.82; P, 11.17.

Bis[acetylacetonatocarbonylrhodium(I)] μ-cyclo[bis(naphthalene-1,7-diyl dialkylamidophosphites)] (6a,b) were obtained by the reactions of compounds **3a**,**b** with two moles of $Rhacac(CO)_2$ in methylene chloride at ~20 °C. Compound **6a**: yield 96%, m.p. 236—240 °C. ^{31}P NMR, δ: 135.6 (d, $^3J_{P,Rh}$ = 263.0 Hz). Found (%): P, 6.72; Rh, 22.38. $C_{36}H_{38}N_2O_{10}P_2Rh_2$. Calculated (%): P, 6.69; Rh, 22.22. Compound **6b**: yield 94%, decomp. 233—236 °C. ^{31}P NMR, δ: 136.0 (d, $^3J_{P,Ph}$ = 261.5 Hz). Found (%): C, 48.80; H, 4.86; P, 6.28. $C_{40}H_{46}N_2O_{10}P_2Rh_2$. Calculated (%): C, 48.90; H, 4.72; P, 6.30.

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