

Letters to the Editor

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

E. E. Nifantiev, E. N. Rasadkina,* and Yu. B. Evdokimenkova

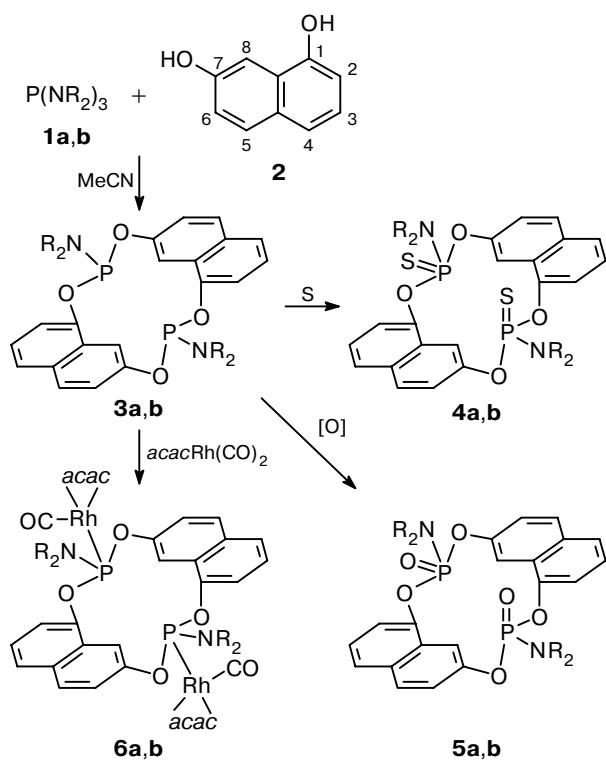
Moscow Pedagogical State University,
3 per. Nesvizhskii, 119021 Moscow, Russian Federation.
Fax: +7 (095) 246 7766. E-mail: chemdept@mtu-net.ru

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 ^1H 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.

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 CDCl₃. ³¹P NMR spectra were recorded on Bruker WP-80 spectrometer with proton decoupling (32.4 MHz) in CH₂Cl₂ with 85% H₃PO₄ 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). ³¹P NMR, δ : 135.1 (s), 135.6 (s). Found (%): C, 61.58; H, 5.24; P, 13.18. C₂₄H₂₄N₂O₄P₂. 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, CH₂Me, $^3J_{H,H}$ = 7.3 Hz); 3.32 (m, 4 H, CH₂, $^3J_{H,P}$ = 9.0 Hz); 3.39 (m, 4 H, CH₂, $^3J_{H,P}$ = 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). ³¹P NMR, δ : 137.4 (br.s). Found (%): C, 64.56; H, 6.24; P, 11.78. C₂₈H₃₂N₂O₄P₂. 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. ³¹P NMR, δ : 67.4 (s). Found (%): C, 54.38; H, 4.44; P, 11.61. C₂₄H₂₄N₂O₄P₂S₂. Calculated (%): C, 54.33; H, 4.56; P, 11.68. Compound **4b**: yield 90%, m.p. 281–282 °C.

³¹P NMR, δ : 66.4 s. Found (%): C, 57.36; H, 5.44; P, 10.61. C₂₈H₃₂N₂O₄P₂S₂. 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(NH₂)₂ · H₂O₂. Compound **5a**: yield 92%, m.p. 249–250 °C. ³¹P NMR, δ : 1.62 (s). Found (%): C, 57.91; H, 4.79; P, 12.37. C₂₄H₂₄N₂O₆P₂. Calculated (%): C, 57.84; H, 4.85; P, 12.43. Compound **5b**: yield 89%, m.p. 268–270 °C.

³¹P NMR, δ : 1.2 (s). Found (%): C, 60.59; H, 5.80; P, 11.22. C₂₈H₃₂N₂O₆P₂. 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. ³¹P NMR, δ : 135.6 (d, $^3J_{P,Rh}$ = 263.0 Hz). Found (%): P, 6.72; Rh, 22.38. C₃₆H₃₈N₂O₁₀P₂Rh₂. Calculated (%): P, 6.69; Rh, 22.22. Compound **6b**: yield 94%, decomp. 233–236 °C. ³¹P NMR, δ : 136.0 (d, $^3J_{P,Ph}$ = 261.5 Hz). Found (%): C, 48.80; H, 4.86; P, 6.28. C₄₀H₄₆N₂O₁₀P₂Rh₂. Calculated (%): C, 48.90; H, 4.72; P, 6.30.

This work was financially supported by the Program "Fundamental Research of High Schools into Natural and Humanitarian Sciences. Russian Universities" (Project No. 990986).

References

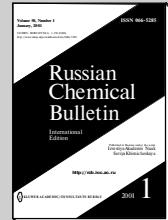
1. C. Bonningue, D. Houalla, and R. Wolf, *J. Chem. Soc., Perkin Trans. 2*, 1983, 773.
2. E. E. Nifantiev, E. N. Rasadkina, I. V. Yankovich, L. K. Vasyanina, V. K. Bel'skii, and A. I. Stash, *Zh. Obshch. Khim.*, 1999, **69**, 36 [*Russ. J. Gen. Chem.*, 1999, **69** (Engl. Transl.)].
3. E. N. Rasadkina and E. E. Nifantiev, *Zh. Obshch. Khim.*, 1999, **69**, 510 [*Russ. J. Gen. Chem.*, 1999, **69** (Engl. Transl.)].
4. E. E. Nifantiev, *Khimiya fosfororganicheskikh soedinenii [Organophosphorus Chemistry]*, MGU, Moscow, 1970, 90 (in Russian).

Received December 13, 2000;
in revised form February 23, 2001

Russian Chemical Bulletin

Do you plan to submit a paper to an international journal?

- You have the material for a high quality paper.
- You want your paper to be published in a prestigious world-class journal.
- You want your paper to be published as rapidly as possible.
- You want your foreign colleagues to know of your paper without any delay.



DO YOU KNOW THAT

Russian Chemical Bulletin,
International Edition

Is All You Need?

- The journal is abstracted or indexed in *Chemical Abstracts*, *Chemical Titles*, *Current Contents/Physical, Chemical and Earth Sciences*, *Reaction Citation Index*, *Science Citation Index*, *Science Citation Index Expanded*, *The ISI Alerting Services*, *Chemistry Citation Index*, and *Energy Research Abstracts*.
- The contents of all issues with graphical and text abstracts as well as annual subject and author indices are available through the Internet.
- The printed edition is complemented by full-text access to the electronic version.
- Papers dealing with topical problems of chemical science are accepted regardless of the country of origin of the author.
- Manuscripts may be submitted in English or in Russian.
- The journal publishes papers containing the results of original studies as well as analytical reviews and reviews covering studies carried out mostly by the author(s) and devoted to a common topic.
- Every article is peer-reviewed by two independent referees.
- Perfectly prepared regular articles are published 4 months after submission to the editorial office; for Letters to the Editor this period is even shorter (2 months).

**Detailed information concerning the journal and the articles
published in it can be found in the Internet at <http://rcb.ioc.ac.ru>**

http://rcb.ioc.ac.ru

Do you know what makes the

Russian Chemical Bulletin

International Edition

worth reading

and different from other chemical journals?

The *Russian Chemical Bulletin* is prepared by chemical professionals who have practical experience in the field and know what information is important for the scientific results to be reproducible by others. We make every effort to ensure that our authors provide every relevant experimental detail in their manuscripts. We feel it very important to include such details in the printed version of the journal rather than publish them as supplementary material to be ordered separately or viewed on-line. We believe it is these details that make a scientific article valuable.

For your convenience, the printed edition is complemented
by **full-text** access to the **electronic version** available
by subscription on Kluwer Online at <http://www.wkap.nl>

Alternatively, you can search Author and Subject on-line indices for FREE, view the latest table of contents including graphical and text Abstracts on the Journal's Home Page at <http://rcb.ioc.ac.ru>

The **scope** of the *Russian Chemical Bulletin* is reflected in its section headings:

- **General and Inorganic Chemistry**
- **Physical Chemistry**
- **Organic Chemistry**
- **Organometallic Chemistry**
- **Chemistry of Natural Compounds, Bioorganic and Biomolecular Chemistry**

Papers on **polymer chemistry** or those dealing with **interdisciplinary topics** can be found in the respective sections.

Nearly 500 scientific manuscripts containing the results of original studies are published annually as full papers, brief communications, and letters to the editor. Additionally, every issue contains one or two review articles as well as information concerning current affairs in the Russian Academy of Sciences, chemistry-related research institutes and centers, international chemistry conferences, and symposia held in Russia.

The main contributors to the *Russian Chemical Bulletin* are scientists from research institutes of the Russian Academy of Sciences and other research centers and universities of Russia. In addition, in the past five years scientists from more than 20 countries have contributed to our journal.

Follow the trend of Russian chemistry research most expediently
by reading the *Russian Chemical Bulletin*.

For more information, visit <http://rcb.ioc.ac.ru>