Mendeleev Commun., 2005, 15(2), 53–54

Interaction of 2-diethylamino-5,5-dimethyl-1,3,2-dioxaphosphorinane with *ortho*-hydroxyphenols

Edward E. Nifantiev,*[a] Vera I. Maslennikova,[a] Tatyana V. Guzeeva,[a] Wolf D. Habicher,[b] Ingmar Bauer,[b] Konstantin A. Lyssenko[c] and Mikhail Yu. Antipin[c]

[a] *Moscow State Pedagogical University, 119021 Moscow, Russian Federation. Fax: +7 095 248 0162; e-mail: chemdept@mtu-net.ru*
[b] *Dresden University of Technology, D-01062 Dresden, Germany.*
Fax: +49 351 463 3409; e-mail: Wolf.Habicher@chemie.tu-dresden.de
[c] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation.*
Fax: +7 095 135 5085; e-mail: kostya@xray.ineos.ac.ru

DOI: 10.1070/MC2005v015n02ABEH002098

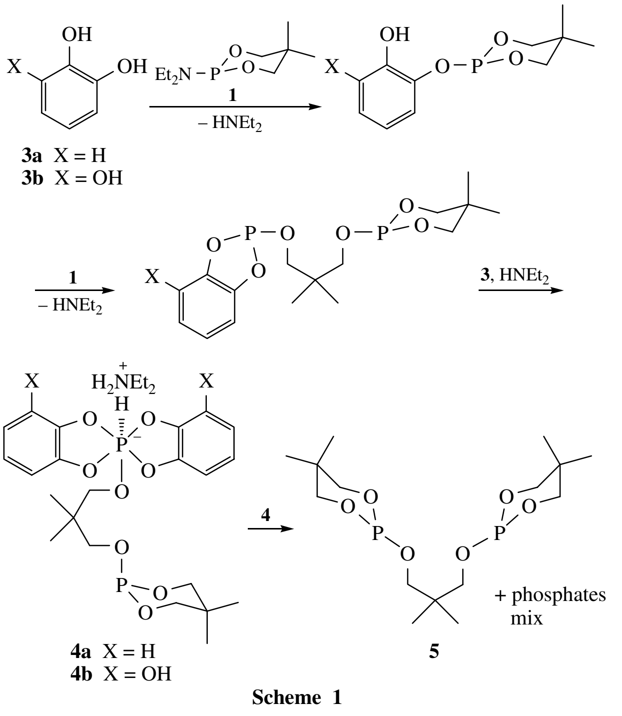
The interaction of 2-diethylamido-5,5-dimethyl-1,3,2-dioxaphosphorinane with pyrocatechol, pyrogallol or pyrogallolarene results in the formation of 1,3-bis(5′,5′-dimethyl-1′,3′,2′-dioxaphosphorinanoxy)-2,2-dimethylpropane; in the case of pyrogallolarene, the second product is a hemicarceplex whose calixarene cups are linked by two phosphoneopentylene bridges.

2-Amino-1,3,2-diheterophosphocyclanes are readily available and have a high phosphorylating capacity of proton-bearing nucleophiles due to the rupture of an exocyclic P–N bond. They are widely used in the design of various organophosphorus compounds,[1] including the phosphorylation of complex polyol systems. In particular, the phosphorylation of resorcinarenes using 2-amino-1,3,2-diheterophosphorinanes gave high yields of individual conformers containing eight specifically oriented phosphorinane fragments on the periphery of the molecule.[2]

Here, we consider a formally similar interaction between 2-diethylamino-5,5-dimethyl-1,3,2-dioxaphosphorinane **1** and pyrogallolarene **2**. It is well known that *ortho*-hydroxyphenols react with diheterophosphocyclanes in a complex manner;[3] therefore, phosphorinane **1** was first introduced into reaction with model compounds **3** (pyrocatechol **3a** and pyrogallol **3b**). The reactions were conducted in dioxane at various reagent ratios and temperatures.

We found that the reaction of model compounds **3** with phosphorinane **1** at 18–22 °C and an equimolar reagent ratio results in the formation of hexacoordinated phosphorus derivatives **4** (Scheme 1).

Reactions proceed rapidly; 10 min after the mixing of reagents, a signal with δ_P 148 ppm due to phosphorinane **1** completely disappeared from the ^{31}P NMR spectra of the reaction mixture, and two signals with equal integral intensities appeared: a singlet with δ_P 121 ppm and a doublet with δ_P –95 ppm and $^1J_{PH}$ 820 Hz. The ^{1}H NMR spectra of compounds **4** are in agreement with the proposed formula.†



Scheme 1

The heating of the reaction mixture (50–55 °C, 2 h) or standing at room temperature for 3 days results in the dismutation of compounds **4** with the formation of 1,3-bis(5′,5′-dimethyl-1′,3′,2′-dioxaphosphorinanoxy)-2,2-dimethylpropane **5** and tetracoordinated phosphorus derivatives (Scheme 1). The structure of compound **5** was supported by NMR spectroscopy,‡ and the structure of its thione derivative **6** was supported by X-ray powder diffraction analysis.§

The bond lengths and angles in **6** are characterised by the expected values for this class of compounds (Figure 1).

The conformation of the six-membered rings is a chair with the P=S bond in the equatorial position and an alkoxy group in the axial one. The conformation of the P(1)O(3)C(11)C(13) and P(2)O(6)C(12)C(13) fragments is practically the same with torsion angles of 175.7° and 169.6°, respectively, while the mutual arrangement of six-membered rings with respect to the C(13)C(14)C(15) fragment is principally different, as illustrated by the pseudotorsion angles S(1)P(1)C(13)C(15) and S(2)P(2)–C(13)C(15) equal to 46.7° and 163.5°, respectively.

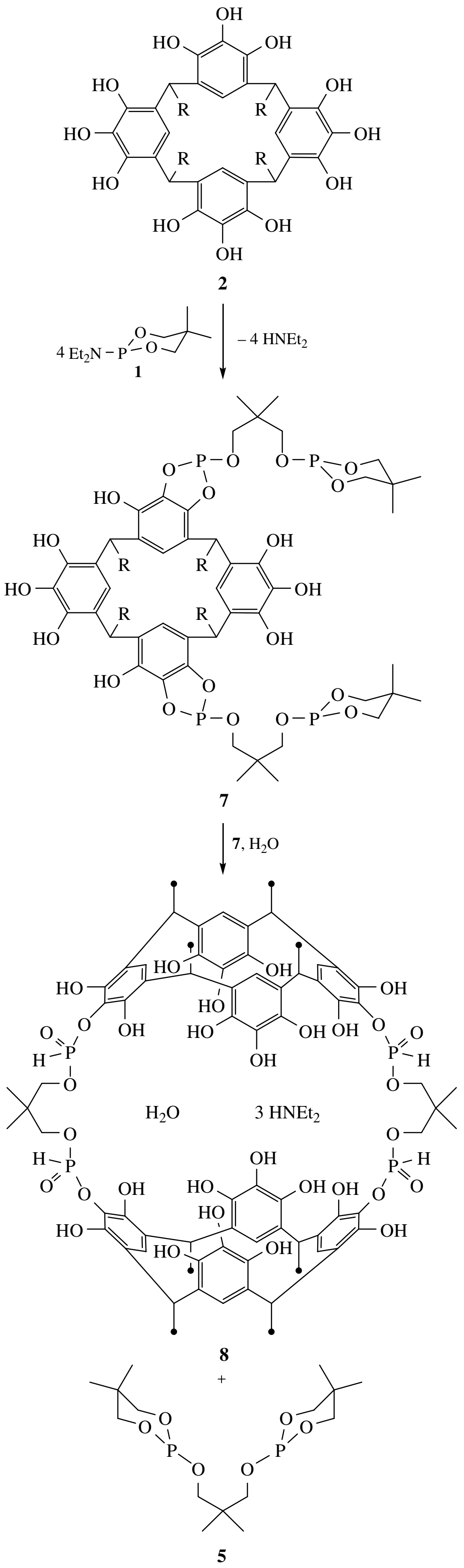
---

† **4a**: ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.64 (s, 6H, Me), 0.88 (s, 3H, Me), 1.01 (t, 6H, NCH_2*Me*, $^3J_{HH}$ 6.6 Hz), 1.14 (s, 3H, Me), 2.1 (q, 4H, $NC\mathit{H}_2$Me, $^3J_{HH}$ 6.6 Hz), 3.2 (dd, 2H, OCH_2^e, $^2J_{HH}$ 10.4 Hz, $^3J_{PH}$ 11.0 Hz), 3.35 (d, 2H, OCH_2, $^3J_{PH}$ 9.9 Hz), 3.48 (d, 2H, OCH_2, $^3J_{PH}$ 6.0 Hz), 4.05 (d, 2H, OCH_2^a, $^2J_{HH}$ 10.4 Hz), 6.42 (d, 1H, PH, $^1J_{PH}$ 820 Hz), 6.48–6.95 (10H, $H_{arom.}$, H_2N).

‡ **5**: ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.72 (s, 6H, Me), 0.97 (s, 6H, Me), 1.24 (s, 6H, Me), 3.29 (dd, 4H, OCH_2^e, $^2J_{HH}$ 10.4 Hz, $^3J_{PH}$ 10.4 Hz), 3.57 (d, 4H, OCH_2, $^3J_{PH}$ 6.0 Hz), 4.13 (d, 4H, OCH_2^a, $^3J_{HH}$ 10.4 Hz). ^{31}P NMR (32.4 MHz, $CDCl_3$) δ: 121.

§ *Crystallographic data for* **6**: crystals of $C_{15}H_{30}O_6P_2S_2$, $M = 432.45$, are triclinic, space group $P\bar{1}$, at 120 K: $a = 8.214(2)$, $b = 12.648(3)$ and $c = 12.880(3)$ Å, $\alpha = 62.290(4)°$, $\beta = 85.762(5)°$, $\gamma = 73.147(5)°$, $V = 1130.8(5)$ Å^3, $Z = 2$ ($Z' = 1$), $d_{calc} = 1.270$ g cm^{-3}, μ(MoKα) = 4.02 cm^{-1}, $F(000) = 460$. Intensities of 8155 reflections were measured with a Smart CCD diffractometer [λ(MoKα) = 0.71072 Å, ω-scans, $2\theta < 52°$], and 4350 independent reflections [$R_{int} = 0.0478$] were used in the further refinement. The structure was solved by the direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. Hydrogen atoms were located from the Fourier synthesis and refined in the isotropic approximation. The refinement converged to $wR_2 = 0.1705$ and GOF = 1.081 for all independent reflections [$R_1 = 0.0710$ was calculated against F for 2747 observed reflections with $I > 2\sigma(I)$] for **6**. All calculations were performed using SHELXTL PLUS 5.0.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 266637. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2005.



Scheme 2

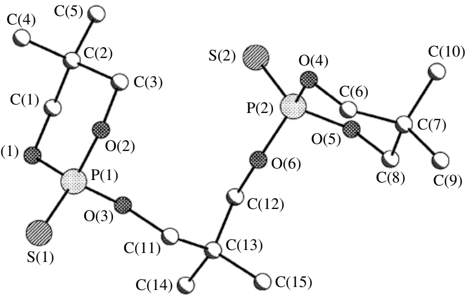


Figure 1 General view of **6**. Selected bond lengths (Å): P(1)–O(1) 1.558(3), P(1)–O(3) 1.572(3), P(1)–O(2) 1.573(3), P(1)–S(1) 1.903(2), P(2)–O(4) 1.565(3), P(2)–O(6) 1.577(2), P(2)–O(5) 1.577(3), P(2)–S(2) 1.901(1); selected bond angles (°): O(1)–P(1)–O(3) 101.4(1), O(1)–P(1)–O(2) 105.3(1), O(3)–P(1)–O(2) 105.5(1), O(1)–P(1)–S(1) 114.9(1), O(3)–P(1)–S(1) 116.3(1), O(2)–P(1)–S(1) 112.1(1), O(4)–P(2)–O(6) 101.3(1), O(4)–P(2)–O(5) 105.9(1), O(6)–P(2)–O(5) 105.9(1), O(4)–P(2)–S(2) 114.6(1), O(6)–P(2)–S(2) 116.5(1), O(5)–P(2)–S(2) 111.5(1).

The reaction of phosphorinane **1** with pyrogallolarene **2** was performed at the reagent ratio **2**:**1** = 1:4 in the temperature range 20–130 °C. Phosphorinane rings introduced into pyrogallolarene opened in all cases, regardless of the reaction temperature, and the resulting peripheral hydroxyl group was phosphorylated (Scheme 1). Intermolecular interaction of intermediates **7**, which was accompanied by the opening of phospholane rings, resulted in the formation of compound **5** and a phosphorus-containing macromolecular system (Scheme 2).

This system was removed from the reaction because of its low solubility in organic solvents, and it was not subjected to further transformations. Data of elemental analysis and NMR spectroscopy¶ suggest that compound **8** is a hemicarceplex, whose molecule calixarene cups are linked by two phosphoneopentylene bridges.

This work was supported in part by the Russian Foundation for Basic Research (grant no. 03-03-32390a), INTAS (grant no. 01-2044) and BMBF (grant no. RUS 00/216).

References

1 E. E. Nifantiev, M. K. Grachev and S. Yu. Burmistrov, *Chem. Rev.*, 2000, **100**, 3755.

2 V. I. Maslennikova, O. S. Serkova, M. Gruner, S. Goutal, I. Bauer, W. D. Habicher, K. A. Lyssenko, M. Yu. Antipin and E. E. Nifantiev, *Eur. J. Org. Chem.*, 2004, **23**, 4884.

3 J. J. Van Lier, R. J. Hermans and H. M. Buck, *Phosphorus Sulfur*, 1984, **19**, 173.

Received: 3rd December 2004; Com. 04/2422

¶ **8**: ^{1}H NMR (200 MHz, DMSO[^{2}H$_6$]) δ: 0.78 (s, 6H, CMe), 0.84 (s, 6H, CMe), 1.16 (t, 18H, NCH$_2$*Me*, $^3J_{\mathrm{HH}}$ 7.2 Hz), 1.44 (d, 24H, CH*Me*, $^3J_{\mathrm{HH}}$ 7.2 Hz), 2.88 (q, 12H, NC*H*$_2$Me, $^3J_{\mathrm{HH}}$ 7.2 Hz), 3.12 (d, 4H, OCH$_2$, $^3J_{\mathrm{PH}}$ 6.6 Hz), 3.44 (d, 4H, OCH$_2$, $^3J_{\mathrm{PH}}$ 6.6 Hz), 4.52 (q, 8H, C*H*Me, $^3J_{\mathrm{HH}}$ 7.2 Hz), 6.68 (s, 8H, H$_{\mathrm{arom.}}$), 6.9 (d, 4H, PH, $^1J_{\mathrm{PH}}$ 680 Hz), 7.92 (br. s, 5H, NH, OH). ^{31}P NMR (32.4 MHz, [^{2}H$_6$]DMSO) δ: 9.2 (d, $^1J_{\mathrm{PH}}$ 680 Hz). Found (%): C, 55.42; H, 6.53; N, 2.23; P, 6.65. Calc. for $C_{74}H_{84}O_{32}P_4 \cdot 3HNEt_2 \cdot H_2O$ (%): C, 55.39; H, 6.54; N, 2.25; P, 6.64.