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## Rearrangement of *O*,*O'*-bis(2-benzylideneaminophenyl) phenylphosphonite into 1,6,7-triphenyl-3,4:9,10-dibenzo-2,11-dioxa-5,8-diaza-1-phosphatricyclo[6.3.0.0<sup>1,5</sup>]undeca-3,9-diene

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Keeping of O,O'-bis(2-benzylideneaminophenyl) phenylphosphonite in a CCl<sub>4</sub> solution for 50 days resulted in its spontaneous rearrangement into 1,6,7-triphenyl-3,4:9,10-dibenzo-2,11-dioxa-5,8-diaza-1-phosphatricyclo[6.3.0.0<sup>1,5</sup>]undeca-3,9-diene, a representative of spirophosphoranes with P–N bonds.

Previously, we were the first to show that P<sup>III</sup> derivatives containing unsaturated electrophilic groups as substituents, such as 2-benzylideneaminophenyl, 3- or 4-oxo(imino)alkyl, react with activated carbonyl compounds under mild conditions with formation of new P–C, P–O and P–N bonds to give cage phosphoranes.<sup>1–7</sup> The interest in the chemistry of pentacoordinate phosphorus derivatives is based on the key role of these compounds as intermediates in phosphorylation and dephosphorylation, *i.e.*, reactions of primary importance for vital activity of cells.<sup>8–16</sup>

Taking into account that unsaturated compounds which are not activated by acceptor substituents, including imines, hardly (if at all) undergo these reactions, we made a first attempt to implement an intramolecular version of cyclisation for PIII derivatives containing two imino groups. One of them, O,O'-bis(2-benzylideneaminophenyl) phenylphosphonite 1, was synthesized using the reaction of dichlorophenylphosphine with two equivalents of 2-benzylideneaminophenol 2 in the presence of triethylamine (Scheme 1). The structure of compound 1 was confirmed by NMR and mass spectra. The protons of the two N=CH groups manifest themselves in the <sup>1</sup>H NMR spectrum as two main singlets with  $\delta$  8.38 and 8.39 in a ~1:4 ratio. The two singlets with  $\delta_{\rm P}$  165.1 and 165.3 in the <sup>31</sup>P-{<sup>1</sup>H} spectrum are present in approximately the same ratio. Apparently, it is a manifestation of the syn/antiisomerism of the two imino groups. The electron impact mass spectrum contains a 500 [M]+ molecular ion peak matching the molecular mass of compound 1.<sup>†</sup>

Monitoring of the behaviour of phenylphosphonite 1 in a CCl<sub>4</sub> solution by means of <sup>31</sup>P-{<sup>1</sup>H} shows that two new peaks at  $\delta_P$ -22.7 and -23.7 appear in the spectrum and gradually grow, whereas the intensity of the signal of compound 1 gradually decreases. The conversion is completed within 50 days and the



Synthesis of compound 1. Phenyldichlorophosphine (2.81 g, 15.70 mmol) in 10 ml of CCl<sub>4</sub> was added dropwise with stirring over 30 min (15–20 °C) under dry argon to a mixture of 2-benzylideneaminophenol 2 (6.18 g, 31.37 mmol) and triethylamine (3.17 g, 31.39 mmol) in 60 ml of freshly distilled CCl<sub>4</sub>. After the entire amount of the reagent was added, the reaction mixture was stirred for another 2 h and kept overnignt. Next day, the precipitate of triethylammonium hydrochloride that formed was filtered off and the filtrate was carefully concentrated in vacuo (0.1 Torr). The resulting unstable oil of compound 1 was quickly characterised by spectral methods. <sup>1</sup>H NMR (CCl<sub>4</sub>-CDCl<sub>3</sub>, 4:1) δ: 8.39, 8.37, 8.25 (3 s, N=CHPh, 4:1:0.03), 7.88 (br.dd), 7.67 (br.d), 7.38 (m), 7.32 (m), 7.24 (m), 7.10 (m), 7.04 (m) (PPh, C<sub>6</sub>H<sub>4</sub>, CPh). <sup>13</sup>C NMR (main isomer, CCl<sub>4</sub>–CDCl<sub>3</sub>, 4:1)  $\delta$ : 120.10 [dd (s), C<sup>3</sup>, <sup>1</sup>J<sub>HC<sup>3</sup></sub>160.0 Hz, <sup>3</sup>J<sub>HC<sup>5</sup>CC<sup>3</sup></sub> 8.4 Hz], 121.74 [ddddd (d), C<sup>6</sup>, <sup>1</sup>J<sub>HC<sup>6</sup></sub> 160.4 Hz, <sup>3</sup>J<sub>PCC<sup>6</sup></sub> 7.5 Hz, <sup>3</sup>J<sub>HC<sup>4</sup>CC<sup>6</sup></sub> 7.3 Hz,  ${}^{2}J_{\text{HC}^{5}\text{C}^{6}}$  1.6 Hz,  ${}^{4}J_{\text{HC}^{3}\text{CCC}^{6}}$  1.6 Hz], 124.08 [br. dd (br. s), C<sup>5</sup>,  ${}^{1}J_{\text{HC}^{5}}$  161.4 Hz,  ${}^{3}J_{\text{HC}^{3}\text{CC}^{5}}$  8.4 Hz], 126.83 [dm (s), C<sup>4</sup>,  ${}^{1}J_{\text{HC}^{4}}$  161.5 Hz,  ${}^{3}J_{\text{HC}^{6}\text{CC}^{4}}$  8.4–9.8 Hz], 127.92 [ddd (d), C<sup>14</sup>,  ${}^{1}J_{\text{HC}^{14}}$  160.8 Hz,  ${}^{3}J_{\text{HC}^{14}\text{-}\text{CC}^{14}}$  7.0 Hz,  ${}^{3}J_{\text{PCCC}^{14}}$  5.6 Hz], 128.63 [br. dd (s), C<sup>10</sup>,  ${}^{1}J_{\text{HC}^{10}}$  160.0 Hz,  ${}^{3}J_{\text{HC}^{10}\text{-}\text{CC}^{10}}$  7.6 Hz], 129.35 [dm (s), C<sup>9</sup>,  ${}^{1}J_{\text{HC}^{9}}$  160.0 Hz,  ${}^{3}J_{\text{HC}^{9}\text{CC}^{9}}$  7.2–7.5 Hz,  ${}^{3}J_{\text{HC}^{11}\text{CC}^{9}}$  7.2–7.5 Hz,  ${}^{3}J_{\text{HC}^{7}\text{CC}^{9}}$  3.7 Hz,  ${}^{2}J_{\text{HC}^{10}\text{C}^{9}}$  1.4 Hz], 130.81 [br. dddd (d), C<sup>13</sup>,  ${}^{1}J_{\text{HC}^{13}}$  168.4 Hz,  ${}^{2}J_{\text{PCC}^{13}}$  21.6 Hz,  $^{J}_{HC} ^{HC} ^{HC} ^{I4} H2_{J}^{I}$ , 150.51 [b1.dddd (d), C<sup>12</sup>,  $^{J}_{HC} ^{I3}$  165.4 H2,  $^{J}_{PC} ^{I3}$  21.6 H2,  $^{3}J_{HC} ^{I3} ^{I3} ^{I1} ^{I2} ^{I3} ^{I3}$ , 12 Hz,  $^{3}J_{HC} ^{I5} ^{I2} ^{I3}$ , 12 Hz,  $^{3}J_{HC} ^{I1} ^{I2} ^{I1}$ , 160.0 Hz,  $^{3}J_{HC} ^{I2} ^{C} ^{I1}$ , 7.6 Hz], 136.70 [dtd (s), C<sup>8</sup>,  $^{2}J_{HC} ^{I2} ^{I3}$ , 11.2 Hz,  $^{3}J_{HC} ^{I0} ^{C} ^{g}$ , 7.2 Hz,  $^{4}J_{HC} ^{I1} ^{C} ^{C} ^{g}$ , 10 Hz], 142.00 [dtd (d), C<sup>12</sup>,  $^{1}J_{PC} ^{I2}$ , 18.2 Hz,  $^{3}J_{HC} ^{I4} ^{C} ^{C} ^{12}$ , 6.9 Hz,  $^{2}J_{HC} ^{I3} ^{I2} ^{I2}$ , 10 Hz,  $^{4}J_{HC} ^{I5} ^{C} ^{C} ^{I2}$ , 10 Hz], 143.37 [m (d), C<sup>2</sup>,  $^{3}J_{POC} ^{2}$  2.6 Hz], 149.33 [m (d), C<sup>1</sup>,  $^{2}J_{POC} ^{I4}$ , 4.2 Hz], 160.57 [dt (s), C<sup>7</sup>,  $^{1}J_{HC} ^{I1} ^{I5} ^{I5} ^{I5} ^{I1} ^{I5} ^{I1} ^{I5} ^{I5} ^{I1} ^{I5}$ , 14.5 Hz], 160.57 [dt (s), 165 [m (d), 165 [m  ${}^{3}J_{\text{HC}^{9}\text{CC}^{7}}$  5.0 Hz].  ${}^{31}\text{P}-\{{}^{1}\text{H}\}$  NMR (CCl<sub>4</sub>-CDCl<sub>3</sub>, 4:1)  $\delta$ : 165.1 and 165.3 (1:4). MS, m/z (%): 500 (100) [M]<sup>+-</sup> (C<sub>32</sub>H<sub>25</sub>N<sub>2</sub>O<sub>2</sub>P), 501 (35) [M]<sup>+-</sup>, 502 (6.6) [M]<sup>+·</sup>.

<sup>&</sup>lt;sup>†</sup> <sup>1</sup>H, <sup>31</sup>P and <sup>31</sup>P-{<sup>1</sup>H} NMR spectra were recorded on a Bruker Avance 400 spectrometer (400 MHz for <sup>1</sup>H; 161.9 MHz for <sup>31</sup>P, <sup>31</sup>P-{<sup>1</sup>H}; 100.6 MHz for <sup>13</sup>C, <sup>13</sup>C-{<sup>1</sup>H}) (20 °C,  $\delta$  scale with reference to Me<sub>4</sub>Si) with signals for the residual protons of the deuterated solvent (CDCl<sub>3</sub>) or the carbon nuclei as the internal standards (<sup>1</sup>H and <sup>13</sup>C) and with H<sub>3</sub>PO<sub>4</sub> as the external standard (<sup>31</sup>P). IR spectra were recorded on a Bruker Vector 22 FTIR spectrometer in Nujol. The EI mass spectra were obtained on a DFS Thermo Electron Corporation instrument (USA); the ionizing electron energy was 70 eV; the ion source temperature was 290 °C. A direct inlet system was used. The evaporator tube was heated in the programmed mode from 100 to 350 °C. The processing of mass spectral data was performed using Xcalibur software.

ratio of the two signals of the final reaction products is 3:1. These reaction products, which are stable in the air, were found to be two diastereomers of 1,6,7-triphenyl-3,4:9,10-dibenzo-2,11-dioxa-5,8-diaza-1-phosphatricyclo[6.3.0.0<sup>1,5</sup>]undeca-3,9-diene **3a,b** [d,l- (6,7-trans) and meso- (6,7-cis) forms].<sup>‡</sup>

Pure samples of the stereoisomers were obtained by column chromatography separation on silica gel. Single crystals of the *d*,*l*-form of compound **3a** suitable for XRD were grown from a  $CCl_4$  solution.<sup>§</sup> Figure 1 shows the geometry of molecule **3a** in a crystal, along with selected parameters. An unusual feature of the molecule is that the phosphorus atom has a distorted depressed square pyramid configuration where two oxygen atoms and two nitrogen atoms are arranged in the base of the pyramid, whereas the phenyl substituent occupies the vertex. The base of the pyramid (N<sup>8</sup>N<sup>5</sup>O<sup>2</sup>O<sup>11</sup>) is planar to within 0.058(2) Å; the P<sup>1</sup> atom deviates by 0.3917(6) Å from this plane. The angle between the N<sup>8</sup>N<sup>5</sup>O<sup>2</sup>O<sup>11</sup> and P<sup>1</sup>C<sup>12–17</sup> planes is ~88.1°. The five-membered P<sup>1</sup>N<sup>8</sup>C<sup>9</sup>C<sup>10</sup>O<sup>11</sup> and P<sup>1</sup>N<sup>5</sup>C<sup>4</sup>C<sup>3</sup>O<sup>2</sup> rings have a depressed envelope conformation [the P<sup>1</sup> atom deviates by 0.289(1) Å from the

**3a**: <sup>1</sup>H NMR (CDCl<sub>3</sub>–CCl<sub>4</sub>, 3:1)  $\delta$ : 4.64 (dd, 1H, NCHPh, <sup>3</sup> $J_{PNCH}$  2.9 Hz, <sup>3</sup> $J_{HCCH}$  5.3 Hz), 4.83 (dd, 1H, NCHPh, <sup>3</sup> $J_{PNCH}$  11.6 Hz, <sup>3</sup> $J_{HCCH}$  5.3 Hz), 6.04 (d, 1H, H<sup>21</sup>, <sup>3</sup> $J_{H^{20}CCH^{21}}$  7.8 Hz), 6.15 (d, 1H, H<sup>34</sup>, <sup>3</sup> $J_{H^{35}CCH^{34}}$  7.7 Hz), 6.59 (dd, 1H, H<sup>19</sup>, <sup>3</sup> $J_{H^{18}CCH^{19}}$  7.7 Hz, <sup>3</sup> $J_{H^{20}CCH^{19}}$  7.5 Hz), 6.69 (dd, 1H, H<sup>36</sup>, <sup>3</sup> $J_{H^{37}CCH^{36}}$  7.9 Hz, <sup>3</sup> $J_{H^{35}CCH^{36}}$  7.5 Hz), 6.73 (dd, 1H, H<sup>20</sup>, <sup>3</sup> $J_{H^{21}CCH^{20}}$  7.7 Hz, <sup>3</sup> $J_{H^{19}CCH^{20}}$  7.5 Hz), 6.83 (dd, 1H, H<sup>35</sup>, <sup>3</sup> $J_{H^{34}CCH^{35}}$  7.8 Hz, <sup>3</sup> $J_{H^{36}CCH^{37}}$  7.9 Hz), 6.88 (d, 1H, H<sup>18</sup>, <sup>3</sup> $J_{H^{19}CCH^{18}}$  7.7 Hz), 6.94 (d, 1H, H<sup>37</sup>, <sup>3</sup> $J_{H^{36}CCH^{37}}$  7.9 Hz), 7.20–7.40 (m, 14 H, 2Ph, H<sup>15</sup>), 7.39 (td, H<sup>16</sup>, <sup>3</sup> $J_{H^{15}CCH^{16}}$  7.2 Hz, <sup>5</sup> $J_{PCCCCH^{16}}$ 1.7 Hz), 7.54 (br. dd, H<sup>13</sup>, <sup>3</sup> $J_{PCCH^{13}}$  16.0 Hz, <sup>3</sup> $J_{H^{14}CCH^{13}}$  7.1 Hz). <sup>31</sup>P NMR (CDCl<sub>3</sub>–CCl<sub>4</sub>, 3:1)  $\delta$ : –22.7. MS, *m*/*z* (%): 500 (100) [M]<sup>++</sup> (C<sub>32</sub>H<sub>25</sub>N<sub>2</sub>O<sub>2</sub>P), 501 (35) [M]<sup>++</sup>, 502 (6.6) [M]<sup>++</sup>.

**3b**: <sup>1</sup>H NMR (CDCl<sub>3</sub>–CCl<sub>4</sub>, 3:1)  $\delta$ : 5.25 (d, 2H, NCHPh, <sup>3</sup> $J_{PNCH}$  3.1 Hz, <sup>3</sup> $J_{HCCH}$  0 Hz), 6.29 (d, 2H, H<sup>21</sup>, <sup>3</sup> $J_{H^{20}CCH^{21}}$  7.4 Hz), 6.74 (dd, 2H, H<sup>19</sup>, overlaps with H<sup>23</sup>), 6.75 (br. d, 4H, H<sup>23</sup>, <sup>3</sup> $J_{H^{20}CCH^{23}}$  7.7 Hz), 6.84 (dd, 2H, H<sup>20</sup>, <sup>3</sup> $J_{H^{21}CCH^{20}}$  7.9 Hz, <sup>3</sup> $J_{H^{19}CCH^{20}}$  7.5 Hz), 6.91 (m, 4H, H<sup>24</sup>, <sup>3</sup> $J_{H^{23}CCH^{24}}$  7.7 Hz, <sup>3</sup> $J_{H^{25}CCH^{24}}$  7.0 Hz), 6.95 (m, 2H, H<sup>25</sup>, <sup>3</sup> $J_{H^{24}CCH^{25}}$  7.0 Hz), 7.09 (d, 2H, H<sup>18</sup>, <sup>3</sup> $J_{H^{19}CCH^{18}}$  7.8–7.9 Hz), 7.40 (m, 2H, H<sup>14</sup>, <sup>3</sup> $J_{H^{15}CCH^{14}}$  7.5 Hz, <sup>3</sup> $J_{H^{13}CCH^{14}}$  7.2 Hz, <sup>4</sup> $J_{PCCCH^{14}}$  5.4 Hz), 7.51 (td, 1H, H<sup>15</sup>, <sup>3</sup> $J_{H^{14}CCH^{15}}$  7.5 Hz, <sup>5</sup> $J_{PCCCCH^{15}}$  1.7 Hz), 7.68 (br. dd, 2H, H<sup>13</sup>, <sup>3</sup> $J_{PCCH^{13}}$  16.4 Hz, <sup>3</sup> $J_{H^{14}CCH^{13}}$  7.2 Hz). <sup>31</sup>P NMR (CDCl<sub>3</sub>–CCl<sub>4</sub>, 3:1)  $\delta$ : –23.7. MS, *m*/*z* (%): 500 (100) [M]<sup>++</sup> (C<sub>32</sub>H<sub>25</sub>N<sub>2</sub>O<sub>2</sub>P), 501 (35) [M]<sup>++</sup>, 502 (6.6) [M]<sup>++</sup>.

Crystal data. Crystals of **3a** ( $C_{32}H_{25}N_2O_2P$ , M = 500.51) are orthorhombic, space group *Pna2*<sub>1</sub>. At 293 K: *a* = 11.809(1), *b* = 22.751(3) and c = 9.344(1) Å, V = 2510.4(5) Å<sup>3</sup>, Z = 4,  $d_{calc} = 1.324$  g cm<sup>-3</sup>,  $\mu = 0.143$  mm<sup>-1</sup>, F(000) = 1048. Data were collected on a Bruker Smart APEX II CCD automatic diffractometer [graphite monochromator,  $\lambda$ (MoK $\alpha$ ) = 0.71073 Å,  $\omega\text{-scanning}$ ],  $2\theta < 52^\circ,$   $R_{\rm int} = 0.0509.$  18198 reflections were measured, 4495 of them were independent, the number of observed reflections with  $I > 2\sigma(I)$  was 3547, R = 0.0388,  $R_w = 0.0874$ , GOF = 1.028, the number of refined parameters is 334. An absorption correction was performed using SADABS program.17 The structure was solved by direct method using SIR program<sup>18</sup> and refined by the full matrix least-squares using SHELXL-97 program.<sup>19</sup> Absolute structure was established [Flack parameter 0.05(9)]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed into the geometrically calculated positions and refined as riding atoms. All calculations were performed using WinGX<sup>20</sup> and APEX2<sup>21</sup> programs. All the figures and analysis of intermolecular interactions were performed using PLATON<sup>22</sup> and ORTEP<sup>23</sup> programs.

CCDC 840832 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data\_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2012.



Figure 1 Molecular structure and atom-labeling scheme for 3a (30% thermal ellipsoids). Selected bond lengths (Å), bond and torsion angles (°): P(1)-O(2) 1.673(2), P(1)-O(11) 1.694(2), P(1)-N(5) 1.720(2), P(1)-N(8) 1.698(2), P(1)-C(12) 1.807(3), O(2)-C(3) 1.379(3), O(11)-C(10) 1.375(3), N(5)-C(4) 1.397(3), N(5)-C(6) 1.452(3), N(8)-C(7) 1.461(3), N(8)-C(9) 1.402(3), C(3)-C(4) 1.387(4), C(9)-C(10) 1.390(3); O(2)-P(1)-O(11) 84.10(9), O(2)-P(1)-N(5) 89.2(1), O(2)-P(1)-N(8) 149.1(1), O(2)-P(1)-C(12) 102.3(1), O(11)-P(1)-N(5) 157.4(1), O(11)-P(1)-N(8) 88.43(9), O(11)-P(1)-C(12) 98.53(9), N(5)-P(1)-N(8) 86.27(9), N(5)-P(1)-C(12) 104.0(1), N(8)-P(1)-C(12) 108.5(1), P(1)-O(2)-C(3) 114.2(2), P(1)-O(11)-C(10) 113.3(2), P(1)-N(5)-C(4) 113.9(2), P(1)-N(5)-C(6) 121.1(2), P(1)-N(8)-C(9) 114.4(2), N(5)-C(4)-C(3) 109.4(2), N(8)-C(7)-C(6) 104.9(2); N(5)-P(1)-O(2)-C(3) 7.6(2), O(2)-P(1)-O(11)-C(10) -164.9(2), N(8)-P(1)-O(11)-C(10) -14.9(2), O(2)-P(1)-N(5)-C(4) -6.0(2), N(8)-P(1)-N(5)-C(6) 5.8(2), N(5)-P(1)-N(8)-C(7) -11.0(2), C(9)-N(8)-C(7)-C(6)-171.9(2), P(1)-N(8)-C(7)-C(6) 12.6(3), N(5)-C(6)-C(7)-N(8) -6.9(3).

N<sup>8</sup>C<sup>9</sup>C<sup>10</sup>O<sup>11</sup> plane; the O<sup>2</sup> atom deviates by 0.105(2) Å from the P<sup>1</sup>N<sup>5</sup>C<sup>4</sup>C<sup>3</sup> plane; the O<sup>2</sup>C<sup>3</sup>C<sup>4</sup>N<sup>5</sup> torsion angle is 2.7(3)°]. The diazaphospholane P<sup>1</sup>N<sup>5</sup>C<sup>6</sup>C<sup>7</sup>N<sup>8</sup> ring has an envelope conformation [the N<sup>8</sup> atom deviates by -0.170(2) Å from the P<sup>1</sup>N<sup>5</sup>C<sup>6</sup>C<sup>7</sup> plane; the N<sup>5</sup>C<sup>6</sup>C<sup>7</sup>N<sup>8</sup> torsion angle is  $-6.9(3)^{\circ}$ ]. The phenyl groups in the 1,3,2-diazaphospholane moiety are in a *trans*-configuration (*d*,*l*-form) [the C<sup>22</sup>C<sup>6</sup>C<sup>7</sup>C<sup>28</sup> torsion angle is 104.5(2)°]. It is interesting to note that the aromatic protons of the two oxazabenzophosphole rings in the <sup>1</sup>H NMR spectrum of this molecule are pairwise nonequivalent, which is apparently due to the different anisotropic effect of the phenyls at C<sup>6,7</sup> and at P<sup>1</sup> and to the presence of chiral centres (C<sup>6,7</sup>). The *cis(meso)* form **3b** shows a more symmetric picture, *i.e.*, these protons are pairwise equivalent (the anisotropic effects of the phenyls at C<sup>6,7</sup> and at P<sup>1</sup> on all protons of both oxazabenzophosphole rings are the same).

The mechanism of this rearrangement remains an open issue. A heterolytic mechanism can be suggested (Scheme 2) involving an intramolecular attack of the phosphorus atom on one imino group nitrogen followed by the formation of bipolar ion **A**. Attack of the carbanion on the carbon atom of the second imino group and formation of the second P–N bond result in the final reaction product **3**.

Thus, the discovered rearrangement of O,O'-bis(2-benzylideneaminophenyl) phenylphosphonite may be considered as a new



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<sup>&</sup>lt;sup>‡</sup> *Preparation of compound* **3**. A solution of compound **1** (7.85 g) in CCl<sub>4</sub> (50 ml) was kept for 50 days at 20 °C under dry argon. The solvent was removed *in vacuo*; the residue was washed with 10 ml of a diethyl etherpentane mixture (1:1) and 10 ml of pentane, then kept under reduced pressure (0.1 Torr) to give 7.25 g (92%) of a white powder as a mixture of *d*,*l*- (**3a**) and *meso*- (**3b**) forms in 2.57:1 ratio. A sample of **3a**,**b** was chromatographed on silica gel in a benzene–hexane system (1:1). The compounds were eluted in the order: *d*,*l*-form, *meso*-form. Individual samples of both stereoisomers were isolated, mp 247–249 °C (**3a**) and 345–346 °C (**3b**).

convenient and rather facile access to spirophosphoranes with  $\ensuremath{\text{P-N}}$  bonds.

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