

### 3,4,5-Tris(2,4-di-*t*-butyl-6-methoxyphenyl)-3,4,5-triselenoxo-1,2-diselena-3,4,5-triphospholane as a Selenation Reagent

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A new type of phosphorus-selenium containing heterocyclic compound, 3,4,5-tris(2,4-di-*t*-butyl-6-methoxyphenyl)-3,4,5-triselenoxo-1,2-diselena-3,4,5-triphospholane, was prepared and was allowed to react with amides to give the corresponding selenoamides in good yields.

Recently, we have reported the preparation of a transient dithioxophosphorane bearing 2,4-di-*t*-butyl-6-methoxyphenyl group (abbreviated to Mox)<sup>1</sup> and the sulfurization reaction of benzophenone to thiobenzophenone by utilizing the dithioxophosphorane.<sup>2</sup> We now wish to report the preparation and properties of a new type of phosphorus-selenium heterocycle.

2,4-Di-*t*-butyl-6-methoxyphenylphosphine (1) was prepared according to the method reported previously.<sup>1</sup> A solution of 7.12 mmol of 1 in benzene (100 mL) was added to a suspension of elemental selenium (1.68 g, 3 equiv) in pyridine (10 mL) and stirred at room temperature for 1 day. After chromatographic treatment, 2 was obtained in 11% yield based on 1 as a stable compound together with air-sensitive 3 (5%) and 4 (3%).<sup>3</sup> These results on selenium are different from either of those on sulfur<sup>1</sup> or 2,4-di-*t*-butyl-6-dimethylaminophenylphosphine.<sup>4</sup> It should be mentioned that attempts by Guziec and Moustakis to prepare a selenium analog of Lawesson's reagent have failed.<sup>5</sup>

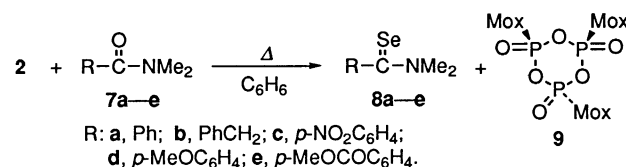
The <sup>31</sup>P NMR spectrum of 2 gave signals of AB<sub>2</sub> pattern (δ<sub>PA</sub> 72.9 and δ<sub>PB</sub> 81.2, <sup>1</sup>J<sub>PP</sub> = 302.1 Hz) and the spin-spin coupling constant (*J*<sub>PP</sub>) is much larger than <sup>2</sup>*J*<sub>PP</sub> for typical >P(Se)-Se-P(Se)< or >P-Se-P< compounds,<sup>6</sup> strongly suggesting that PA is directly bonded to PB. The <sup>31</sup>P NMR spectrum of 3 showed signals of an AX<sub>2</sub> pattern with smaller coupling constant (*J*<sub>PP</sub>) than that for compound 2. Satellite peaks due to <sup>77</sup>Se also supported the structure 3. On the other hand, <sup>31</sup>P NMR of compound 4 showed a singlet signal similar to a sulfur analog, (ArPS)<sub>3</sub>,<sup>7</sup> where Ar = 2,4,6-*t*-Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>.

When 2 (22.5 μmol) was heated in benzene-*d*<sub>6</sub> at 80°C for 5 days in an NMR sample tube under argon, a reaction occurred only to give 3 (8.3 μmol) and 4 (ca. 4 μmol) together with 2 (31% recovery). Although no direct evidence was obtained by

**Table 1.** Reaction of 2 with Amides 7a–e in Benzene at 90 °C

| 7  | Substrate R                                             | Reaction time / h | Reaction product   |                    |
|----|---------------------------------------------------------|-------------------|--------------------|--------------------|
|    |                                                         |                   | 8 / % <sup>a</sup> | 9 / % <sup>b</sup> |
| 7a | Ph                                                      | 220               | 8a 50              | 17                 |
| 7b | PhCH <sub>2</sub>                                       | 185               | 8b 51              | 13                 |
| 7c | <i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> | 186               | 8c 82              | 39                 |
| 7d | <i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>              | 186               | 8d 71              | 26                 |
| 7e | <i>p</i> -MeOCOC <sub>6</sub> H <sub>4</sub>            | 162               | 8e 80              | 16                 |

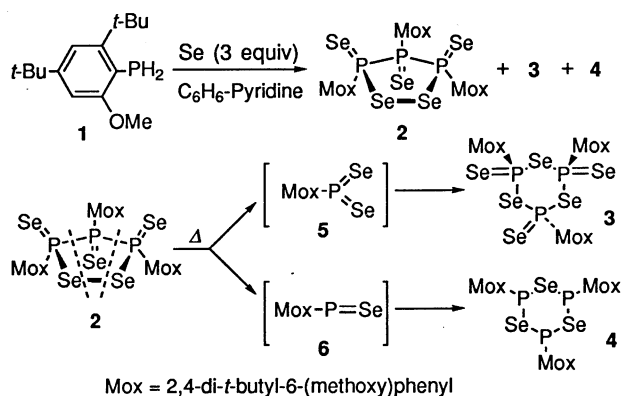
a) Yield based on 7. b) Yield based on the Mox moiety of 2.

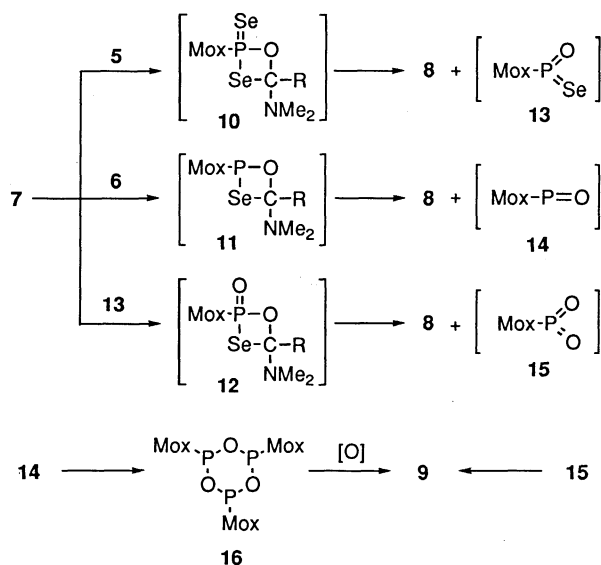


<sup>31</sup>P NMR monitoring during the thermal reaction, the conversion among the compounds 2, 3, and 4 seemed to take intermediacy of 5 and 6, suggesting that selenation of carbonyl compounds might be achieved during the thermolysis of 2.

In fact, when 2 was heated with amides 7, the selenation occurred to give the corresponding selenoamides 8<sup>8</sup> in good yields together with 9.<sup>9</sup> A mixture of *N,N*-dimethylbenzamide 7a (20.5 mg, 137.5 μmol) and 2 (31.5 mg, 27.5 μmol) in benzene (0.8 mL) was heated at 90 °C for 220 h under argon in a sealed tube and then subjected to a silica-gel chromatography to give 14.5 mg of 8a in 50% yield based on 7a together with 9 in 17% yield based on the MoxP moiety of 2. Similarly, selenoamides 8b–d were prepared from 2 and the corresponding amides 7b–d. This method is simple and does not require a tedious separation of the reaction mixtures. Attempts to prepare selenoesters by this method from carboxylic esters such as ethyl benzoate, ethyl phenylacetate, and ethyl *N*-phenylcarbamate failed but the unchanged esters were recovered together with 3 and 4, probably due to the thermolysis of 2 alone. Moreover, when a mixed ester-amide 7e was heated with 2 in benzene, selenoamide 8e was selectively obtained in 80% yield. Table 1 lists the experimental results on this selenation reaction.

This selenation reaction seems to proceed via four-membered ring intermediates 10, 11, or 12 due to the reaction of 5, 6, or 13 with amides. Thus, 5 and 6 due to the thermolysis of 2 react with amide, leading first to 10 and 11, respectively, followed by cleavage of the rings to selenoamides 8 together with 13 and 14. The compound 14 then gives directly trimer 16 and the intermediate 13 reacts further with amide to afford 8 and 15 via 12. The compound 16 was not isolated or detected probably because of its instability. The compound 15 might probably give the corresponding trimer 9, which might also be formed by oxidation of 16.





Although there have been known several methods of converting the carbonyl group into the selenocarbonyl group using  $(\text{Me}_3\text{Si})_2\text{Se}$ ,<sup>10,11</sup>  $(\text{Me}_2\text{Al})_2\text{Se}$ ,<sup>12,13</sup>  $\text{NaHSe}$ ,<sup>14</sup> and  $\text{Se}_2\text{Br}_2$ ,<sup>5</sup> we have accomplished an additional direct and straightforward selenation reaction of amides using a phosphorus-selenium heterocycle 2.

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## References and Notes

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- M. Yoshifuji, D.-L. An, K. Toyota, and M. Yasunami, *Tetrahedron Lett.*, **35**, 4379 (1994).
- 2: Bright yellow crystals, mp 166 °C (decomp);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.14 (9H, s,  $\text{Bu}^t$ ), 1.20 (18H, s,  $\text{Bu}^t$ ), 1.36 (9H, s,  $\text{Bu}^t$ ), 1.61 (18H, s,  $\text{Bu}^t$ ), 3.82 (6H, s, OMe), 4.32 (3H, s, OMe), 6.62 (1H, d,  $^4J_{\text{HH}}$  = 1.5 Hz, arom.), 6.63 (2H, d,  $^4J_{\text{HH}}$  = 1.5 Hz, arom.), 6.83 (1H, dd,  $^4J_{\text{PH}}$  = 5.5 Hz and  $^4J_{\text{HH}}$  = 1.5 Hz, arom.), and 6.95 (2H, dd,  $^4J_{\text{PH}}$  = 4.5 Hz and  $^4J_{\text{HH}}$  = 1.5 Hz, arom.);  $^{31}\text{P}\{^1\text{H}\}$  NMR (81 MHz,  $\text{CDCl}_3$ ,  $\text{AB}_2$ )  $\delta$  = 72.9 ( $\text{P}^{\text{A}}$ ) and 81.2 ( $\text{P}^{\text{B}}$ ),  $^1J_{\text{PP}}$  = 302.1 Hz; FAB-MS  $m/z$  1149 ( $\text{M}^+ - 1$ ). Found: C, 46.91; H, 5.96%. Calcd for  $\text{C}_{45}\text{H}_{69}\text{O}_3\text{P}_3\text{Se}_5$ : C, 47.17; H, 6.07%. 3:  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.19 (18H, s,  $\text{Bu}^t$ ), 1.24 (9H, s,  $\text{Bu}^t$ ), 1.49 (18H, s,  $\text{Bu}^t$ ), 1.55 (9H, s,  $\text{Bu}^t$ ), 3.89 (6H, s, OMe), 3.93 (3H, s, OMe), 6.65 (2H, d,  $^4J_{\text{HH}}$  = 1.6 Hz, arom.), 6.69 (1H, d,  $^4J_{\text{HH}}$  = 1.6 Hz, arom.), 6.91 (2H, dd,  $^4J_{\text{PH}}$  = 4.7 Hz and  $^4J_{\text{HH}}$  = 1.6 Hz, arom.), and 6.98 (1H, dd,  $^4J_{\text{PH}}$  = 5.1 Hz and  $^4J_{\text{HH}}$  = 1.6 Hz, arom.);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ,  $\text{AX}_2$ )  $\delta$  = 90.2 (satellite,  $J_{\text{PSe}}$  = 98.9 Hz,  $J_{\text{PSe}}$  = 144.9 Hz, and  $J_{\text{PSe}}$  = 228.5 Hz;  $\text{P}^{\text{X}}$ ) and 112.6 (satellite,  $J_{\text{PSe}}$  = 73.6 Hz and  $J_{\text{PSe}}$  = 253.1 Hz;  $\text{P}^{\text{A}}$ ),  $^2J_{\text{PP}}$  = 8.1 Hz; FAB-MS  $m/z$  1229 ( $\text{M}^+ - 1$ ). 4:  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.24 (27H, s,  $\text{Bu}^t$ ), 1.54 (27H, s,  $\text{Bu}^t$ ), 3.89 (9H, s, OMe), 6.69 (3H, d,  $^4J_{\text{HH}}$  = 1.5 Hz, arom.), and 7.00 (3H, dd,  $^4J_{\text{PH}}$  = 4.9 Hz and  $^4J_{\text{HH}}$  = 1.5 Hz, arom.);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 102.8 (satellite,  $J_{\text{PSe}}$  = 270.1 Hz and  $J_{\text{PSe}}$  = 228.9 Hz); FAB-MS  $m/z$  975 ( $\text{M}^+ - \text{Me}$ ).
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- All new selenoamides **8b–e** showed satisfactory spectral data ( $^1\text{H}$ ,  $^{13}\text{C}$  NMR, MS, and UV). Some selected data are as follows. **8a**:<sup>11</sup> Orange crystals, mp 77–79 °C;  $^{13}\text{C}\{^1\text{H}\}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  = 205.1 ( $\text{C}=\text{Se}$ ). **8b**: Pale yellow crystals, mp 90.5–91.5 °C;  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  = 204.1 (satellite,  $J_{\text{CSe}}$  = 208.9 Hz,  $\text{C}=\text{Se}$ ). Found: C, 52.84; H, 5.63; N, 6.15%. Calcd for  $\text{C}_{10}\text{H}_{13}\text{NSe}$ : C, 53.10; H, 5.79; N, 6.19%. **8c**: Orange crystals, mp 164–166 °C;  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  = 202.1 (satellite,  $J_{\text{CSe}}$  = 209.9 Hz,  $\text{C}=\text{Se}$ ). Found: C, 42.03; H, 3.77; N, 10.79%. Calcd for  $\text{C}_9\text{H}_{10}\text{N}_2\text{O}_2\text{Se}$ : C, 42.04; H, 3.92; N, 10.89%. **8d**: Orange crystals, mp 89–90 °C;  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  = 205.2 (satellite,  $J_{\text{CSe}}$  = 207.5 Hz,  $\text{C}=\text{Se}$ ). Found: C, 49.68; H, 5.24; N, 5.87%. Calcd for  $\text{C}_{10}\text{H}_{13}\text{NOSe}$ : C, 49.60; H, 5.41; N, 5.78%. **8e**: Orange crystals, mp 95–96 °C;  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  = 166.3 (s,  $\text{COOMe}$ ) and 203.9 (s,  $\text{C}=\text{Se}$ ). Found: C, 49.01; H, 4.77; N, 5.19%. Calcd for  $\text{C}_{11}\text{H}_{13}\text{NO}_2\text{Se}$ : C, 48.90; H, 4.85; N, 5.18%.
- 9: Colorless crystals, mp >150 °C (decomp);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.23 (18H, s,  $\text{Bu}^t$ ), 1.27 (9H, s,  $\text{Bu}^t$ ), 1.47 (18H, s,  $\text{Bu}^t$ ), 1.52 (9H, s,  $\text{Bu}^t$ ), 3.12 (6H, s, MeO), 4.12 (3H, s, MeO), 6.50 (2H, bs, arom.), 6.91 (1H, d,  $^4J_{\text{PH}}$  = 4.3 Hz, arom.), 7.16 (1H, d,  $^4J_{\text{PH}}$  = 7.0 Hz, arom.), and 7.19 (2H, bs, arom.);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\text{AB}_2$ )  $\delta$  = -5.3 ( $\text{P}^{\text{A}}$ ) and -6.8 ( $\text{P}^{\text{B}}$ ),  $^2J_{\text{PP}}$  = 47.0 Hz. Found: C, 63.61; H, 8.16%. Calcd for  $\text{C}_{45}\text{H}_{69}\text{O}_9\text{P}_3$ : C, 63.82; H, 8.21%.
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