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

De-Lie An, Kozo Toyota, Masafumi Yasunami, and Masaaki Yoshifuji*
Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Sendai 980-77

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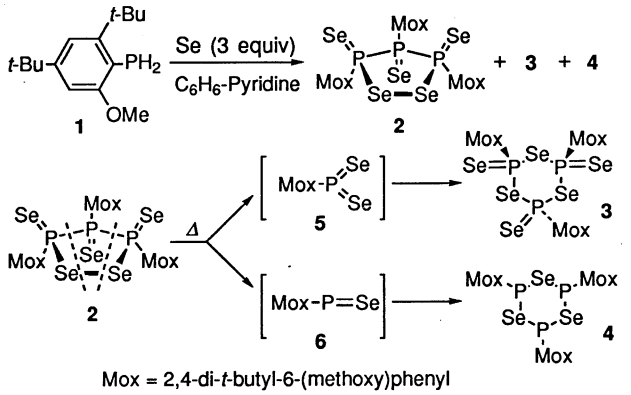
A new type of phosphorus-selenium containing heterocyclic compound, 3,4,5-tris(2,4-di-*t*-butyl-6-methoxyphenyl)-3,4,5-triselenoxo-1,2-diselena-3,4,5-triphospholane, was prepared and was allowed to react with amides to give the corresponding selenoamides in good yields.

Recently, we have reported the preparation of a transient dithioxophosphorane bearing 2,4-di-*t*-butyl-6-methoxyphenyl group (abbreviated to Mox)[1] and the sulfurization reaction of benzophenone to thiobenzophenone by utilizing the dithioxophosphorane.[2] 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.[1] 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%).[3] These results on selenium are different from either of those on sulfur[1] or 2,4-di-*t*-butyl-6-dimethylaminophenylphosphine.[4] It should be mentioned that attempts by Guziec and Moustakis to prepare a selenium analog of Lawesson's reagent have failed.[5]

The ^{31}P NMR spectrum of **2** gave signals of AB_2 pattern (δ_{PA} 72.9 and δ_{PB} 81.2, $^1J_{PP}$ = 302.1 Hz) and the spin-spin coupling constant (J_{PP}) is much larger than $^2J_{PP}$ for typical >P(Se)-Se-P(Se)< or >P-Se-P< compounds,[6] strongly suggesting that P^A is directly bonded to P^B. The ^{31}P NMR spectrum of **3** showed signals of an AX_2 pattern with smaller coupling constant (J_{PP}) than that for compound **2**. Satellite peaks due to ^{77}Se also supported the structure **3**. On the other hand, ^{31}P NMR of compound **4** showed a singlet signal similar to a sulfur analog, $(ArPS)_3$,[7] where Ar = 2,4,6-*t*-Bu$_3$C$_6$H$_2$.

When **2** (22.5 μmol) was heated in benzene-d_6 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

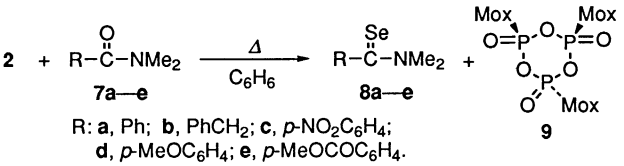


Mox = 2,4-di-*t*-butyl-6-(methoxy)phenyl

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

Substrate		Reaction time / h	Reaction product		
7	R		**8**	/ %[a]	**9** / %[b]
7a	Ph	220	**8a**	50	17
7b	$PhCH_2$	185	**8b**	51	13
7c	*p*-$NO_2C_6H_4$	186	**8c**	82	39
7d	*p*-$MeOC_6H_4$	186	**8d**	71	26
7e	*p*-$MeOCOC_6H_4$	162	**8e**	80	16

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

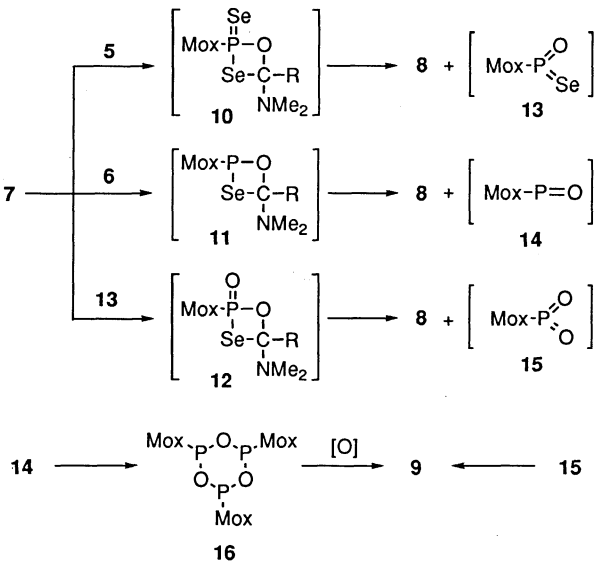


R: **a**, Ph; **b**, $PhCH_2$; **c**, *p*-$NO_2C_6H_4$; **d**, *p*-$MeOC_6H_4$; **e**, *p*-$MeOCOC_6H_4$.

^{31}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**[8] in good yields together with **9**.[9] 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 $(Me_3Si)_2Se$,[10,11] $(Me_2Al)_2Se$,[12,13] NaHSe,[14] and Se_2Br_2,[5] we have accomplished an additional direct and straightforward selenation reaction of amides using a phosophorus-selenium heterocycle **2**.

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References and Notes

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3 **2**: Bright yellow crystals, mp 166 °C (decomp); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 1.14 (9H, s, Bu^t), 1.20 (18H, s, Bu^t), 1.36 (9H, s, Bu^t), 1.61 (18H, s, Bu^t), 3.82 (6H, s, OMe), 4.32 (3H, s, OMe), 6.62 (1H, d, $^4J_{HH}$ = 1.5 Hz, arom.), 6.63 (2H, d, $^4J_{HH}$ = 1.5 Hz, arom.), 6.83 (1H, dd, $^4J_{PH}$ = 5.5 Hz and $^4J_{HH}$ = 1.5 Hz, arom.), and 6.95 (2H, dd, $^4J_{PH}$ = 4.5 Hz and $^4J_{HH}$ = 1.5 Hz, arom.); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$, AB_2) δ = 72.9 (P^A) and 81.2 (P^B), $^1J_{PP}$ = 302.1 Hz; FAB-MS *m/z* 1149 (M$^+$–1). Found: C, 46.91; H, 5.96%. Calcd for $C_{45}H_{69}O_3P_3Se_5$: C, 47.17; H, 6.07%. **3**: ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.19 (18H, s, Bu^t), 1.24 (9H, s, Bu^t), 1.49 (18H, s, Bu^t), 1.55 (9H, s, Bu^t), 3.89 (6H, s, OMe), 3.93 (3H, s, OMe), 6.65 (2H, d, $^4J_{HH}$ = 1.6 Hz, arom.), 6.69 (1H, d, $^4J_{HH}$ = 1.6 Hz, arom.), 6.91 (2H, dd, $^4J_{PH}$ = 4.7 Hz and $^4J_{HH}$ = 1.6 Hz, arom.), and 6.98 (1H, dd, $^4J_{PH}$ = 5.1 Hz and $^4J_{HH}$ = 1.6 Hz, arom.); ^{31}P{^{1}H} NMR ($CDCl_3$, AX_2) δ = 90.2 (satellite, J_{PSe} = 98.9 Hz, J_{PSe} = 144.9 Hz, and J_{PSe} = 228.5 Hz; P^X) and 112.6 (satellite, J_{PSe} = 73.6 Hz and J_{PSe} = 253.1 Hz; P^A), $^2J_{PP}$ = 8.1 Hz; FAB-MS *m/z* 1229 (M$^+$–1). **4**: ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.24 (27H, s, Bu^t), 1.54 (27H, s, Bu^t), 3.89 (9H, s, OMe), 6.69 (3H, d, $^4J_{HH}$ = 1.5 Hz, arom.), and 7.00 (3H, dd, $^4J_{PH}$ = 4.9 Hz and $^4J_{HH}$ = 1.5 Hz, arom.); ^{31}P{^{1}H} NMR ($CDCl_3$) δ = 102.8 (satellite, J_{PSe} = 270.1 Hz and J_{PSe} = 228.9 Hz); FAB-MS *m/z* 975 (M$^+$–Me).

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8 All new selenoamides **8b**—**e** showed satisfactory spectral data (^{1}H, ^{13}C NMR, MS, and UV). Some selected data are as follows. **8a**:[11] Orange crystals, mp 77—79 °C; ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ = 205.1 (C=Se). **8b**: Pale yellow crystals, mp 90.5—91.5 °C; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ = 204.1 (satellite, J_{CSe} = 208.9 Hz, C=Se). Found: C, 52.84; H, 5.63; N, 6.15%. Calcd for $C_{10}H_{13}NSe$: C, 53.10; H, 5.79; N, 6.19%. **8c**: Orange crystals, mp 164—166 °C; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ = 202.1 (satellite, J_{CSe} = 209.9 Hz, C=Se). Found: C, 42.03; H, 3.77; N, 10.79%. Calcd for $C_9H_{10}N_2O_2Se$: C, 42.04; H, 3.92; N, 10.89%. **8d**: Orange crystals, mp 89—90 °C; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ = 205.2 (satellite, J_{CSe} = 207.5 Hz, C=Se). Found: C, 49.68; H, 5.24; N, 5.87%. Calcd for $C_{10}H_{13}NOSe$: C, 49.60; H, 5.41; N, 5.78%. **8e**: Orange crystals, mp 95—96 °C; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ = 166.3 (s, COOMe) and 203.9 (s, C=Se). Found: C, 49.01; H, 4.77; N, 5.19%. Calcd for $C_{11}H_{13}NO_2Se$: C, 48.90; H, 4.85; N, 5.18%.

9 **9**: Colorless crystals, mp >150 °C (decomp); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 1.23 (18H, s, Bu^t), 1.27 (9H, s, Bu^t), 1.47 (18H, s, Bu^t), 1.52 (9H, s, Bu^t), 3.12 (6H, s, MeO), 4.12 (3H, s, MeO), 6.50 (2H, bs, arom.), 6.91 (1H, d, $^4J_{PH}$ = 4.3 Hz, arom.), 7.16 (1H, d, $^4J_{PH}$ = 7.0 Hz, arom.), and 7.19 (2H, bs, arom.); ^{31}P{^{1}H} NMR (C_6D_6, AB_2) δ = –5.3 (P^A) and –6.8 (P^B), $^2J_{PP}$ = 47.0 Hz. Found: C, 63.61; H, 8.16%. Calcd for $C_{45}H_{69}O_9P_3$: C, 63.82; H, 8.21%.

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