# 1,2,3,5,7-Pentaselena-4,6,8-triphosphocane as the Revised Structure for "3,4,5-Triselenoxo-1,2-diselena-3,4,5-triphospholane" Determined by X-Ray Analysis

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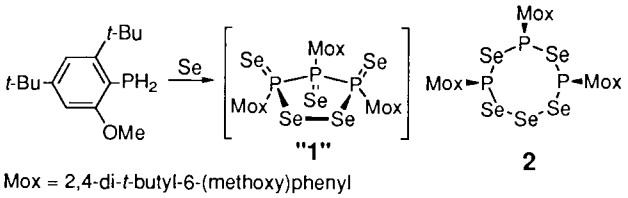
(Received September 3, 1997; CL-970678)

The structure of a new type of phosphorus-selenium containing eight-membered heterocyclic compound, 1,2,3,5,7-pentaselena-4,6,8-triphosphocane, was unambiguously determined by the X-ray analysis as the revised structure for the 3,4,5-triselenoxo-1,2-diselena-3,4,5-triphospholane, which had been previously proposed as a selenation reagent of amides to selenoamides.

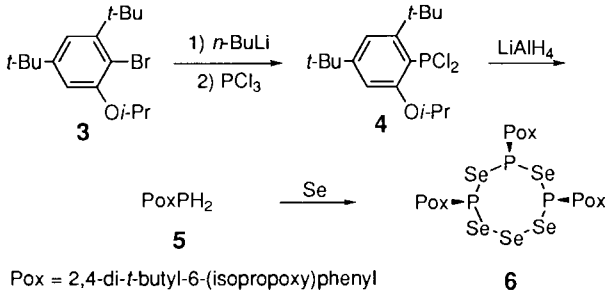
Recently, we have reported on the preparation of phosphorus-selenium five-membered heterocyclic compound, 3,4,5 -tris (2,4- di -*t*-butyl-6-methoxyphenyl)-3,4,5 -triselenoxo-1,2-diselena-3,4,5-triphospholane ("**1**")[1] bearing the 2,4-di-*t*-butyl-6-methoxyphenyl group (abbreviated to Mox) and the selenation reaction of amides to selenoamides by utilizing this new heterocycle. In an attempt to prepare a similar heterocycle carrying the 2,4-di-*t*-butyl-6-isopropoxyphenyl group (abbreviated to Pox), we have found that the previously-assigned structure "**1**" was erroneous and that it should be corrected to 1,2,3,5,7-pentaselena-4,6,8-triphosphocane of a novel eight-membered heterocycle **2**,[2] according to the X-ray analysis of the corresponding Pox derivative.




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

1,5-Di-*t*-butyl-2-bromo-3-isopropoxybenzene (**3**) was prepared from the corresponding *o*-bromophenol[3] and isopropyl iodide in the presence of sodium hydroxide and benzyltriethylammonium chloride in aqueous THF in 94% yield. **3**: $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ = 1.30 (9H, s, $^t$Bu), 1.38 (6H, d, $J$ = 6.1 Hz, CH$\underline{Me}_2$), 1.53 (9H, s, $^t$Bu), 4.50 (1H, sept, $J$ = 6.1 Hz, C$\underline{H}$Me$_2$), 6.84 (1H, d, $J$ = 2.3 Hz, arom.), and 7.10 (1H, d, $J$ = 2.3 Hz, arom.). The bromide **3** was converted to the corresponding phenyllithium with 1.1 equiv. of butyllithium at –78 °C in THF and was allowed to react with 3 equiv. of $PCl_3$ at that temperature to give the corresponding phosphonous dichloride **4**. **4**: $^{31}$P NMR (81 MHz, $CDCl_3$) $\delta_P$ = 160.3. 2,4-Di-*t*-butyl-6-isopropoxyphenylphosphine (**5**) was prepared by the reaction of **4** with $LiAlH_4$ in ether. **5**: $^{31}$P NMR $\delta_P$ = –152.6 (t, $^1J_{PH}$ = 208.7 Hz). A solution of 7.12 mmol of **5** 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, **6** was obtained in 11% yield based on **3** as a stable compound among other products.[4]

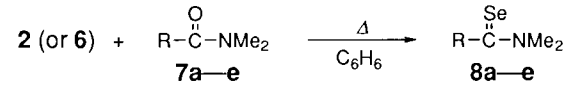
The $^{31}$P NMR spectrum of **6** gave signals of $AB_2$ pattern which is completely identical with that obtained by the computer-




Pox = 2,4-di-*t*-butyl-6-(isopropoxy)phenyl

simulation with parameters, $\delta_{PA}$ 70.7 and $\delta_{PB}$ 77.9, and $^2J_{PP}$ = 294.3 Hz, except for some satellite peaks caused by $^{31}$P-$^{77}$Se couplings. The chemical shifts and the $AB_2$ pattern were very similar to those observed for the Mox derivative "**1**" (or **2**) with parameters described before.[1]

The structure of **6** was unambiguously determined by the X-ray analysis.[5] Some selected bond lengths (Å) and angles (°) are as follows: Se1–Se2, 2.319(2); Se1–P1, 2.289(4); Se3–P1, 2.272(4); Se3–P2, 2.280(3); P1–C1, 1.86(1); P1–Se1–Se2, 98.8(1); Se1–Se2–Se1*, 103.6(1); P1–Se3–P2, 92.9(2); Se1–P1–Se3, 103.0(2); Se3–P2–Se3*, 102.5(2). Figure 1 shows an ORTEP drawing of molecular structure from top and side, indicating that the compound consists of eight-membered heterocycle of the crown type with a mirror plane. The three phosphorus atoms and the middle selenium atom (Se2) form upper rim (or P-rim) while the other four selenium atoms (Se1, Se3, Se1*, Se3*) form lower rim (or Se-rim) of the crown. The three Pox groups are of *syn* configuration and located almost perpendicular to the mean plane of the crown. Furthermore, the three isopropoxy groups are directing in the same direction of the Se-rim of the crown. It should be noted here that the lone-pair electrons of the phosphorus on the P-rim are directing at the same point. This might be an explanation for a considerably large coupling constant observed for $^2J_{PP}$, previously mis-assigned to $^1J_{PP}$ for the compound "**1**." Therefore, we correct the structure "**1**" of five-membered ring to **2** of eight-membered ring.[2]




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

In order to compare the efficiency of the Pox derivative **6** to the Mox derivative **2** as a selenation reagent, very similar reactions of compound **6** with various amides **7a**—**e** have been carried out at 90 °C in benzene.[1] The reactions gave the corresponding selenoamides **8a**—**e**, but the results from **2** were better than those from **6** in terms of the yields of **8**,[6] probably due to steric hindrance of the isopropoxy group than the methoxy group during the addition of the amide oxygen to one of the

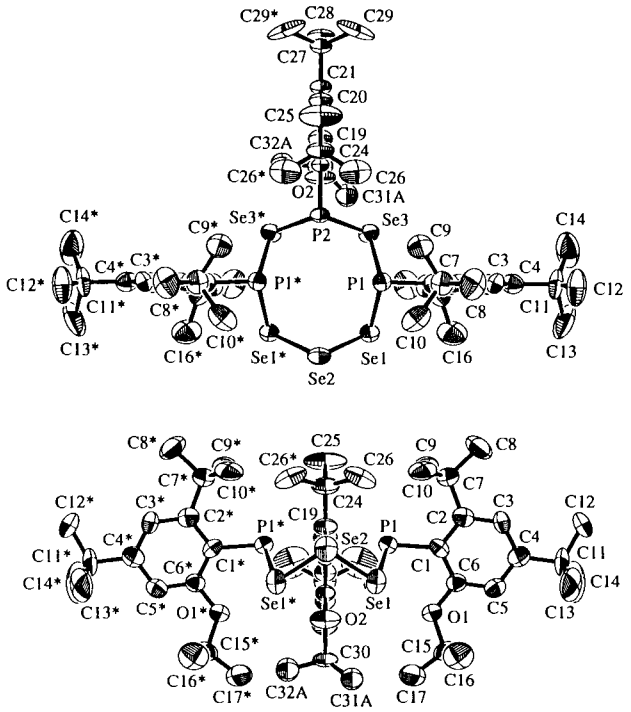



**Figure 1**. Molecular structure of **6** by X-ray analysis (top view and side view). One of the isopropoxy groups is disordered but only one set is displayed. Hydrogen atoms and the solvent molecule were omitted for clarity.

phosphorus atoms of the eight-membered ring. Then the reaction might involve the elimination of [RP(=Se)(=O)], [RP(=Se)$_2$], [RP=Se], and/or [RP=O] to give selenoamides.

Although there have been reported several methods of converting the carbonyl group into the selenocarbonyl group using $(Me_3Si)_2Se$,[7] $(Me_2Al)_2Se$,[8] NaHSe,[9] and $Se_2Br_2$,[10] we have accomplished an additional direct and straightforward selenation reaction of amides using a phosphorus-selenium heterocycles **2** or **6**.

This work was supported in part by the Grants-in-Aid for Scientific Research (Nos. 08454193 and 09239101) from the Ministry of Education, Science, Sports and Culture.

## References and Notes

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2 **2**: Yellow crystals, mp 166 °C (decomp); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, $AB_2$) $\delta$ = 72.9 ($P^A$) and 81.2 ($P^B$), $^2J_{PP}$ = 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 M. Yoshifuji, D.-L. An, K. Toyota, and M. Yasunami, *Chem. Lett.*, **1993**, 2069.

4 **6**: Yellow crystals, mp 146—147 °C (decomp); $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ = 1.21 (9H, s, *p*-$^t$Bu-6), 1.26 (18H, s, *p*-$^t$Bu-4,8), 1.42 (9H, s, *o*-$^t$Bu-6), 1.49 (6H, d, $^3J_{HH}$ = 6.0 Hz, CHMe$_2$-4,8), 1.50 (6H, d, $^3J_{HH}$ = 6.0 Hz, CHMe$_2$-4,8), 1.57 (6H, d, $^3J_{HH}$ = 6.0 Hz, CHMe$_2$-6), 1.68 (18H, s, *o*-$^t$Bu-4,8), 4.69 (2H, sept, $^3J_{HH}$ = 6.0 Hz, CHMe$_2$-4,8), 4.72 (1H, sept, $^3J_{HH}$ = 6.0 Hz, CHMe$_2$-6), 6.64 (1H, d, $^4J_{HH}$ = 0.4 Hz, 6-arom.), 6.65 (2H, d, $^4J_{HH}$ = 0.2 Hz, 4,8-arom.), 6.84 (1H, dd, $^4J_{PH}$ = 1.4 Hz, $^4J_{HH}$ = 0.4 Hz, 6-arom.), and 6.95 (2H, dd, $^4J_{PH}$ = 0.8 Hz, $^4J_{HH}$ = 0.2 Hz, 4,8-arom.); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, $AB_2$) $\delta$ = 70.7 ($P^A$) and 77.9 ($P^B$), $^2J_{PP}$ = 294.3 Hz; UV-Vis (hexane) 214 (log $\varepsilon$ 4.9), 253 (4.7), and 301 nm (4.4); FAB-MS *m/z* (rel intensity) 1231 ($M^+$–3; 6), 1151 ($M^+$–Se–3; 4), 1072 ($M^+$–2Se–2; 4), 794 ($Pox_2P_2Se_3^+$–2; 89), 714 ($Pox_2P_2Se_2^+$–2; 54), and 395 ($PoxPSe_2^+$–*i*Pr; 100). Found: C, 49.91; H, 6.75%. Calcd for $C_{51}H_{81}O_3P_3Se_5$: C, 49.81; H, 6.64%.

5 Crystal Data for **6**: Recrystallized from benzene-chloroform. $C_{51}H_{81}O_3P_3Se_5 \cdot 2CHCl_3$, *Mr* = 1468.68, monoclinic, *a* = 11.323(8) Å, *b* = 27.04(2) Å, *c* = 11.767(9) Å, $\beta$ = 107.24(5)°, *V* = 3441(3) Å$^3$, $P2_1/m$, *Z* = 2, *T* = 296 K, *R* = 0.069, *Rw* = 0.075; 6215 unique reflections with $2\theta \leq 50.0°$. Of these, 3101 $I > 3\sigma(I)$. The structure was solved with teXsan crystallographic software package of Molecular Structure Corporation (1985 and 1992). Further details of the crystal structure investigation for **6** are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ (UK).

6 The yields of selenoamides **8** from the reaction of **6** with amides **7a**—**e** in benzene at 90 °C were as follows. **8a**, 10% (188 h); **8b**, 15% (288 h); **8c**, 7% (187 h); **8d**, 12% (160 h); **8e**, 7% (408 h). The yields are based on **7** and the numbers in parentheses are the reaction time.

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