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LETTERS

Novel formation of 1,2,4-triselenolanes by the reaction of *tert*-butylarylmethylenetriphenylphosphoranes with elemental selenium

Kentaro Okuma[a,b,]* and Tomoaki Kubota[a]

[a]*Department of Chemistry, Fukuoka University, Jonan-ku, Fukuoka 814-0180, Japan*
[b]*Advanced Materials Institute, Fukuoka University, Jonan-ku, Fukuoka 814-0180, Japan*

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Abstract—Reaction of *tert*-butylarylmethylenetriphenylphosphoranes with elemental selenium afforded the corresponding 1,2,4-triselenolanes (**1**), 1,3-diselenetanes (**4**), and triphenylphosphine selenide. Triselenolanes **1** were formed from selenation of **4**, which may suggest a stepwise selenation of selenoketones. © 2001 Elsevier Science Ltd. All rights reserved.

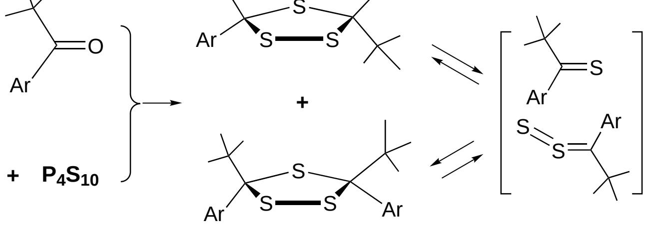
1,2,4-Triselenolanes (**1**) are one of the cyclic polyselenides. The rich literature on 1,2,4-trithiolanes (**2**)[1] oddly contrasts with the few reports on the formation of 1,2,4-triselenolanes (**1**).[2,3] In our and Erker's previous reports, the formation of selones (**3**) by the reaction of phosphorus ylides with elemental selenium was described.[4,5] In some cases, 1,3-diselenetanes (**4**) were isolated by dimerization of selenoketones.[6] Only the reported example of 1,2-diselenolanes was observed in the reaction of selenobenzophenone (**3a**) with cyclopentadiene.[7] Recently, we have reported the synthesis of *cis*- and *trans*-1,2,4-trithiolanes (**2**) by the reaction of pivalophenones with tetraphosphorus decasulfide and the thermal isomerization between the isolated stereoisomers of trithiolanes **2** (Scheme 1).[8]

These results prompted us to investigate the reaction of phosphorus ylides with elemental selenium as a practical method for the formation of cyclic polyselenides. This report offers the first practical synthesis of **1**.

A refluxing suspension of elemental selenium (3 atom equiv.) and the ylide, prepared from *tert*-butyl(*p*-methoxyphenyl)methyltriphenylphosphonium tetrafluoroborate and butyllithium in toluene, turned into a bright green suspension of *tert*-butyl(*p*-methoxyphenyl)selenoketone.[9] After 30 min, the reaction mixture was cooled to room temperature. After standing for 15 h, the suspension changed to pale green. The resulting mixture was chromatographed over silica gel to afford pale yellow crystals (**1a**) along with 2,4-di-*tert*-butyl-2,4-bis(*p*-methoxyphenyl)-1,3-diselenetane **4a** (24%), and triphenylphosphine selenide (75%).

Mass spectroscopy of **1a** has shown that we are dealing with [**4a**+Se], which is formally a [3+2] cycloaddition product. Its ^{1}H NMR spectrum suggests two *tert*-butyl, and two methoxy protons along with aromatic protons. Careful investigation of the above result suggested that the structure of **1a** was 3,5-di-*tert*-butyl-3,5-bis(*p*-methoxyphenyl)-1,2,4-triselenolane **1a** (36%).[10] Reaction of the ylide derived from *tert*-butyl(*p*-phenoxyphenyl)methyltriphenylphosphonium fluoroborate with elemental selenium was carried out in a similar manner to give the corresponding **1b** (42%) and **4b** (26%) (Scheme 2).

In the case of 1,2,4-trithiolane both *cis* and *trans* isomers were obtained, whereas in the case of selenium analogs only one isomer was isolated.[11]



Scheme 1.

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* Corresponding author.

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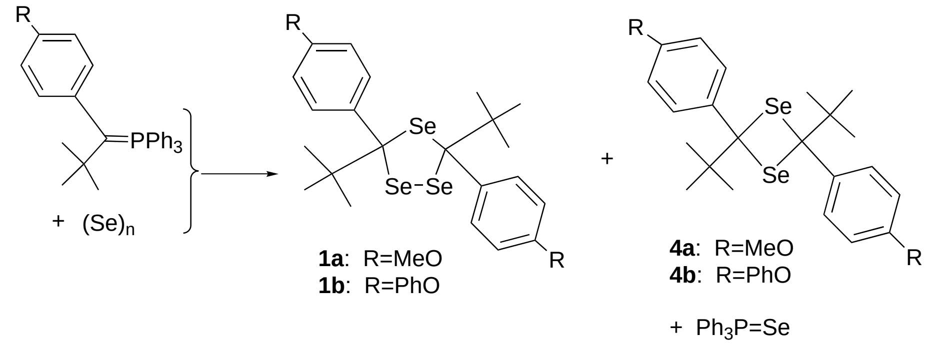
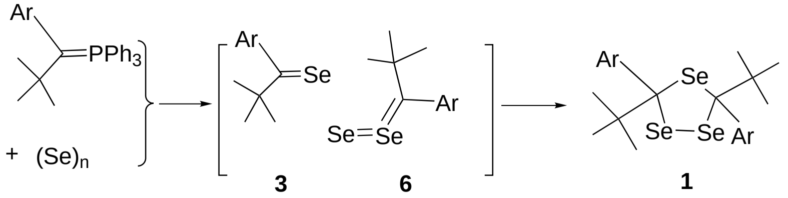
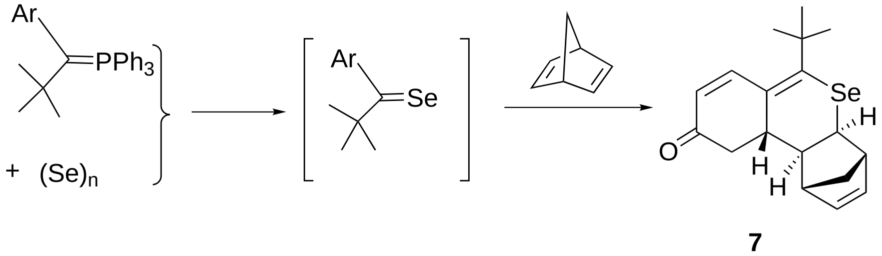


Scheme 2.



Scheme 3.



Scheme 4.

We first proposed that triselenolanes **1** were formed by the cycloaddition of selenocarbonyl Se–selenides (**6**) and selenoketones by analogy of their sulfur analogs (Scheme 3).

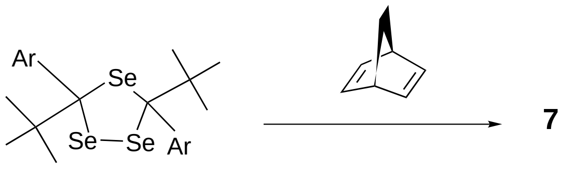
However, a trapping reaction of this intermediate **6** by using norbornadiene resulted in the formation of selenopivalophenone–norbornadiene cycloadduct **7** (Scheme 4). Attempted reaction of the ylide with elemental selenium and dimethyl acetylenedicarboxylate led to a similar product. These results suggested that the intermediate of these reactions was only the corresponding selone **3**. At present, we have no evidence for the formation of **6**.

Actually, when 1,3-diselenetane **4a** was treated with elemental selenium in the presence of a catalytic amount of triphenylphosphine or triphenylphosphine selenide in refluxing toluene, 1,2,4-triselenolane **1a** was obtained in 37% yield (Scheme 5). The reaction of **1a** with norbornadiene in refluxing toluene also afforded the adduct **7** (38%), which is identical with the cycloadduct obtained in the reaction of the ylide and elemental selenium in the presence of norbornadiene.

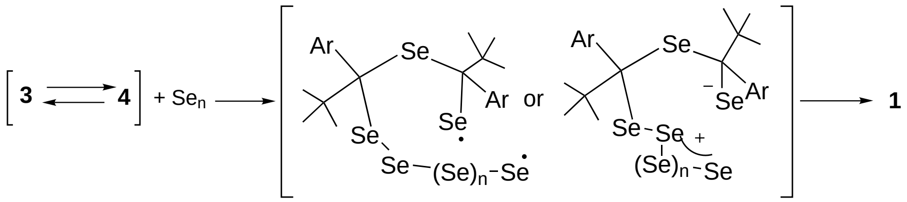
Thus, the reaction might proceed through a stepwise selenation of selenopivalophenones (Scheme 6).

Previously, 1,2,4-triselenolanes were prepared by deselenation of bis[tris(trimethylsilyl)methyl triselenide[2] or by the reaction of diketone dihydrazone with Se_2Cl_2.[3] However, to our knowledge, there is no report on the formation of 1,2,4-triselenolanes from phosphorus ylides. The present method is very simple and only requires commercially available butyllithium, elemental selenium, and phosphonium salts prepared by a two-step reaction from commercially available 4-phenoxypivalophenone.

$$\mathbf{4a} + Se_n \xrightarrow[\text{toluene, reflux}]{\text{cat. } Ph_3P \text{ or } Ph_3P{=}Se} \mathbf{1a}$$



Scheme 5.



Scheme 6.

Tokitoh and co-workers reported the deselenation of cyclic polyselenides by triphenylphosphine to afford the 1,3-diselenetane at room temperature.[12] In our case, deselenation of triselenolanes **1** was also successful by using triphenylphosphine in refluxing benzene to give the corresponding diselenetane. Diselenetane was also obtained in refluxing toluene.

$$\mathbf{1a} + Ph_3P \xrightarrow[\text{benzene, reflux}]{} \mathbf{4a} + Ph_3P{=}Se$$

In summary, we have found that phosphonium ylides react with elemental selenium to afford 1,2,4-triselenolanes **1**, which are also formed by the reaction of 1,3-diselenetanes **4** with elemental selenium and a catalytic amount of triphenylphosphine.

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9. The formation of selenoketone was confirmed by its ^{13}C NMR signal of C=Se (275.3 ppm).
10. All new compounds gave satisfactory analytical data. Selected spectral data: Compound **1a**: yellow crystals, mp 128–129°C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.30 (s, 9 H, *tert*-Bu), 3.70 (s, 3 H, OMe), 6.52 (d, 2H, $J=8.8$ Hz, *p*-MeOC$_6$H$_4$), 7.53 (d, 2H, $J=8.8$ Hz, *p*-MeOC$_6$H$_4$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 29.60 (*tert*-Bu), 43.68 (C-Me$_3$), 54.95 (MeO), 94.71 (Se-C-Se), 110.79, 132.33, 134.54, 157.25 (Ar); ^{77}Se NMR (CDCl$_3$): δ 690.84, 729.15. Compound **1b**: yellow crystals, mp 116–117°C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.33 (s, 9 H, *tert*-Bu), 6.65 (d, 2H, $J=8.8$ Hz, PhOC$_6$H$_4$-), 6.86 (d, 2H, $J=8.0$ Hz, PhO), 7.05 (t, 1H, $J=8.0$ Hz, PhO), 7.28 (t, 2H, $J=8.0$ Hz, PhO), 7.59 (d, 2H, $J=8.8$ Hz, PhOC$_6$H$_4$). Compound **4a**: yellowish green crystals, mp 203–204°C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.00 (s, 9 H, *tert*-Bu), 3.71 (s, 3 H, OMe), 6.52 (d, 2H, $J=8.8$ Hz, *p*-MeOC$_6$H$_4$), 7.45 (d, 2H, $J=8.8$ Hz, *p*-MeOC$_6$H$_4$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 26.75 (q, *tert*-Bu), 39.03 (s, Se-C, with ^{77}Se Satellite), 39.78 (s, C-Me$_3$), 54.95 (q, MeO), 94.71 (s, Se-C-Se), 110.79 (d), 132.33 (d), 134.54 (s), 157.25 (s); ^{77}Se NMR (CDCl$_3$): δ 780.40. Compound **7**: colorless crystals, mp 112–114°C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.37 (s, 9 H, *t*-Bu), 1.56, (d, 1H, $J=11$ Hz, CH$\underline{H}$), 1.75 (dd, $J=6$ and 11 Hz, CH), 2.26 (d, 1H, $J=11$ Hz, C$\underline{H}$H), 2.73 (d, 1H, $J=16$ Hz, C$\underline{H}$H), 2.78–2.85 (m, 2H, CH and CH), 2.90 (dd, 1H, $J=16$ and 8 Hz, CH$\underline{H}$), 2.98 (br s, 1H, CH), 3.17 (1H, dd, 2 and 8 Hz, CH), 5.79 (1H, d, $J=11$ Hz, =CH), 6.05 (dd, 1H, $J=3$ and 7 Hz, =CH), 6.19 (dd, 1H, $J=3$ and 7 Hz, =CH), 7.48 (1H, d, $J=11$ Hz, =CH); ^{13}C NMR (100 MHz, CDCl$_3$): δ 31.26 (q), 39.49 (s), 40.30 (t), 42.77 (d), 45.29 (t), 47.04 (d), 48.23 (d), 48.97 (d), 50.37 (d), 120.57 (d), 133.99 (s), 136.41 (d), 138.79 (d), 138.89 (d), 165.13 (s), 198.98 (s, C=O).
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