Syntheses, Structures, and Thermolyses of Tetracoordinate 1,2-Oxaselenetanes

Takayuki Kawashima,* Fumihiko Ohno, and Renji Okazaki*

*Department of Chemistry
Graduate School of Science
The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan*

Received July 19, 1993

Oxetanes bearing highly coordinate main-group elements at the neighboring position have been well-known as intermediates or transition states of very important reactions in organic synthesis such as the Wittig and Peterson reactions. There are many reports on their synthetic utility,[1] but investigation on isolation and spectroscopic observation of such species has been limited to 1,2-oxaphosphetanes.[1c,d,2,3]

Very recently, we succeeded in the syntheses of pentacoordinate 1,2-oxaphosphetanes, 1,2-oxasiletanides, and 1,2-oxastannetanides, i.e., intermediates of the Wittig, Peterson, and tin-Peterson reactions, respectively.[4] From our interest in the effect on the stability and reactivity of such a species on changing a center atom from groups 14 and 15 elements to group 16 elements, we have studied the syntheses of tetracoordinate 1,2-oxaselenetanes as a novel type of selenuranes.[5] We now report their first syntheses, crystal structures, and thermal reactivities.

Sequential treatment of dilithio derivative **1**[6] with 1.1 equiv of elemental selenium (THF, 0 °C, 5 h), with 1.1 equiv of tributyl-(iodomethyl)stannane (THF, 0 °C → 25 °C), and then with aqueous NH₄Cl gave stannylmethyl selenide **2** (87%). Tin–lithium transmetallation of selenide **2** with 2.4 equiv of *n*-BuLi

(THF, –78 °C, 30 min), followed by reaction with 2.4 equiv of carbonyl compounds **3a** and **3b** (THF, 25 °C, overnight), gave the corresponding β-hydroxyalkyl selenides **4a** (77%) and **4b** (56%), respectively (Scheme I). Reactions of **4a** and **4b** with 1 equiv of bromine in the presence of 2 equiv of triethylamine (CCl₄, 25 °C, 3 h) afforded quantitatively 1,2-oxaselenetanes **5a** and **5b**, respectively.[7]

Recrystallization of **5a** from ether gave colorless plates, which melted at 161–163 °C with decomposition. In the ¹H NMR spectrum of **5a**, a downfield shift for the ortho proton of the Martin ligand was observed as one of the features of compounds with a trigonal bipyramidal (TBP) structure.[4a,b,d,5b,8] In the ¹⁹F and ⁷⁷Se NMR spectra of **5a** were observed two quartets due to the chirality on Se atom with centers of δ_F –76.1 and –77.0 ($^4J_{FF}$ = 8 Hz) and a broad singlet (δ_{Se} 727.9) due to the long-range coupling with ¹⁹F nuclei, respectively. The large downfield shift[5e,9a] in δ_{Se} from **4a** (δ_{Se} 229.2) to **5a** and the chemical shift close to that of compound **6** (δ_{Se} 799)[9] strongly support the selenurane structure.[10]

6   **7**   **8**
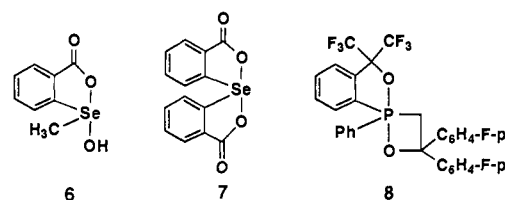
The X-ray crystallographic analysis of **5a** indicated that it has a distorted TBP structure (Figure 1).[11] This is the first example for a selenurane containing a four-membered ring. As expected, two oxygen atoms occupy apical positions, while two carbon atoms and a lone pair occupy equatorial positions. The bond angle O(1)–Se(1)–O(2) between two apical bonds deviates by 16.6-(2)° from 180°. The bond Se(1)–O(1) (1.977(4) Å) is close to the Se–O (1.968(7) Å) bond of selenurane **7**,[12] but Se(1)–O(2) (1.902(4) Å) is significantly shorter. This unusual phenomenon that the Se–O bond of a more strained four-membered ring is shorter than that of a five-membered ring was also shown in the 1,2-oxaphosphetane **8**,[4a] presumably because of electronic effect. The dihedral angles O(2)–Se(1)–C(1)–C(2) and Se(1)–C(1)–C(2)–O(2) are –3.7(4)° and 4.7(4)°, respectively, indicating that the four-membered ring is slightly puckered, which is a common structural feature of such oxetanes.[4]

(1) For the Wittig reactions, see: (a) Smith, D. J. H. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon: Oxford, 1979; Vol. 2, pp 1316–1329. (b) Gosney, I.; Rowley, A. G. In *Organophosphorus Reagents in Organic Synthesis*; Cadogan, J. I. G.; Ed.; Academic Press: New York, 1979; pp 17–153. (c) Maryanoff, B. E.; Reitz, A. B. *Phosphorus Sulfur* **1986**, *27*, 167–189. (d) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863–927. For the Peterson reactions, see: (e) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981; pp 141–152. (f) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: New York, 1983; pp 58–73. (g) Ager, D. J. *Synthesis* **1984**, 384–398. (h) Ager, D. J. *Org. React. (N.Y.)* **1990**, *38*, 1–223. For the Peterson-type reactions, see: (i) Kauffmann, T. *Top. Curr. Chem.* **1980**, *92*, 109–147. (j) Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 410–429. (k) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987; pp 176–177.
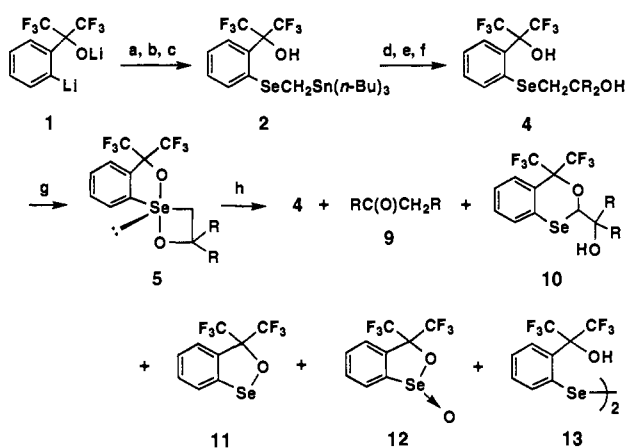
(2) For isolable 1,2-oxaphosphetanes, see: Birum, G. H.; Matthews, C. N. *J. Chem. Soc., Chem. Commun.* **1967**, 137–138. Ramirez, F.; Smith, C. P.; Pilot, J. F. *J. Am. Chem. Soc.* **1968**, *90*, 6726–6732. Aly, H. A. E.; Barlow, J. H.; Russell, D. R.; Smith, D. J. H.; Swindles, M.; Trippett, S. *J. Chem. Soc., Chem. Commun.* **1976**, 449–450. Bestmann, H. J.; Roth, K.; Wilheim, E.; Böhme, R.; Burzlaff, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 876–877. Saalfrank, R. W.; Paul, W.; Liebenow, H. *Ibid.* **1980**, *19*, 713–714. Trishin, J. G.; Konovalova, I. V.; Burangulova, R. N.; Burnaeva, L. A.; Chistokletov, V. N.; Pudovik, A. N. *Tetrahedron Lett.* **1989**, *30*, 577–580. Huang, Y.; Arif, A. M.; Bentrude, W. G. *J. Am. Chem. Soc.* **1991**, *113*, 7800–7802. Huang, Y.; Sopchik, A. E.; Arif, A. M.; Bentrude, W. G. *Ibid.* **1993**, *115*, 4031–4039.

(3) For spectral observations, see: Reitz, A. B.; Nortey, S. O.; Jordan, A. D., Jr.; Mutter, M. S.; Maryanoff, B. E. *J. Org. Chem.* **1986**, *51*, 3302–3308. Maryanoff, B. E.; Reitz, A. B.; Mutter, M. S.; Inners, R. R.; Almond, H. R., Jr.; Whittle, R. R.; Olofson, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 7664–7678. Vedejs, E.; Marth, C. F.; Ruggeri, R. *Ibid.* **1988**, *110*, 3940–3948.

(4) (a) Kawashima, T.; Kato, K.; Okazaki, R. *J. Am. Chem. Soc.* **1992**, *114*, 4008–4010. (b) Kawashima, T.; Iwama, N.; Okazaki, R. *Ibid.* **1992**, *114*, 7598–7599. (c) Kawashima, T.; Iwama, N.; Okazaki, R. *Ibid.* **1993**, *115*, 2507–2508. (d) Kawashima, T.; Kato, K.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 869–870.

(5) For a recent review, see: (a) Bergman, J.; Engman, L.; Siden, J. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1986; Vol. 1, Chapter 14. For some examples, see: (b) Reich, H. J. *J. Am. Chem. Soc.* **1973**, *95*, 964–966. (c) Fujihara, H.; Mima, H.; Ikemori, M.; Furukawa, N. *Ibid.* **1991**, *113*, 6337–6338. (d) Ogawa, S.; Sato, S.; Erata, T.; Furukawa, N. *Tetrahedron Lett.* **1992**, *33*, 1915–1918. (e) Fujihara, H.; Mima, H.; Erata, T.; Furukawa, N. *J. Am. Chem. Soc.* **1992**, *114*, 3117–3118.

(6) Perrozzi, E. F.; Michalak, R. S.; Figuly, G. D.; Stevenson, W. H., III; Dess, D. B.; Ross, M. R.; Martin, J. C. *J. Org. Chem.* **1981**, *46*, 1049–1053.

(7) **5a**: colorless plates, mp 161–163 °C dec; HRMS (70 eV) *m/z* calcd for C₂₃H₁₆F₆O₂⁸⁰Se 518.0220, found 518.0219; ¹H NMR (CDCl₃, 500.1 MHz) δ 5.36 (d, 1H, ²J = 11 Hz), 5.40 (d, 1H, ²J = 11 Hz), 7.16–7.20 (m, 1H), 7.23–7.31 (m, 5H), 7.37–7.41 (m, 2H), 7.55–7.58 (m, 2H), 7.59–7.64 (m, 2H), 7.72–7.75 (m, 1H), 8.31–8.35 (m, 1H); ¹³C{¹H} NMR (CDCl₃, 125.8 MHz) δ 72.92 (s, ¹J_CSe = 26 Hz), 80.03 (s), 85.39 (sept, ²J_CF = 31 Hz), 122.84 (q, ¹J_CF = 288 Hz), 123.02 (q, ¹J_CF = 288 Hz), 125.17 (s), 125.40 (s), 127.18 (s), 127.24 (s), 127.48 (s), 128.24 (s), 128.52 (s), 129.84 (s), 131.53 (s), 132.25 (s), 133.52 (s), 135.74 (s), 147.25 (s), 147.39 (s); ¹⁹F NMR (CDCl₃, 84.3 MHz) δ –76.1 (q, ⁴J_FF = 8 Hz), –77.0 (q, ⁴J_FF = 8 Hz); ⁷⁷Se NMR (CDCl₃, 51.48 MHz) δ 727.9 (br s). Anal. Calcd for C₂₃H₁₆F₆O₂Se: C, 53.49; H, 3.12; Se, 15.26. Found: C, 53.19; H, 3.27; Se, 15.55. The coupling constant J_CSe was obtained from the satellite peak.

(8) Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 4618–4622.

(9) (a) Nakanishi, W.; Ikeda, Y.; Iwamura, H. *Chem. Lett.* **1981**, 1353–1356. (b) Nakanishi, W.; Ikeda, Y.; Iwamura, H. *Org. Magn. Reson.* **1982**, *20*, 117–122.

(10) For reviews on the ⁷⁷Se NMR, see: Luthra, N. P.; Odom, J. D. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1986; Vol. 1, Chapter 6. Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon: Oxford, 1986; pp 17–21.

(11) C₂₃H₁₆F₆O₂Se, FW = 517.33, crystal dimensions (mm) 0.500 × 0.500 × 0.200, monoclinic, space group *P*2₁/*c*, *a* = 11.130(4) Å, *b* = 16.862(9) Å, *c* = 11.633(5) Å, β = 106.48(3)°, *V* = 2093(3) Å³, *Z* = 4, *D*calcd = 1.641 g/cm³, *R* = 0.047 (*R*w = 0.046). Full details of the crystallographic structure analysis are described in the supplementary material.

(12) Dahlén, B.; Lindgren, B. *Acta Chem. Scand.* **1973**, *27*, 2218–2220. Dahlén, B. *Acta Crystallogr.* **1974**, *B30*, 647–651.

Communications to the Editor

J. Am. Chem. Soc., Vol. 115, No. 22, 1993 10435

Scheme I[a]

a: R= Ph; b: R= CH$_2$Ph

[a] (a) Se, THF, 0 °C, 5 h; (b) ICH$_2$Sn(n-Bu)$_3$, 0 °C → 25 °C; (c) aqueous NH$_4$Cl; (d) 2.4 equiv of n-BuLi, THF, -78 °C, 30 min; (e) R$_2$C=O (3), THF, 25 °C, overnight; (f) aqueous NH$_4$Cl; (g) Br$_2$, 2 equiv of Et$_3$N, CCl$_4$, 25 °C, 3 h; (h) toluene-d_8, 150 °C, 2 days (for 5a) or 180 °C, 2 days (for 5b).
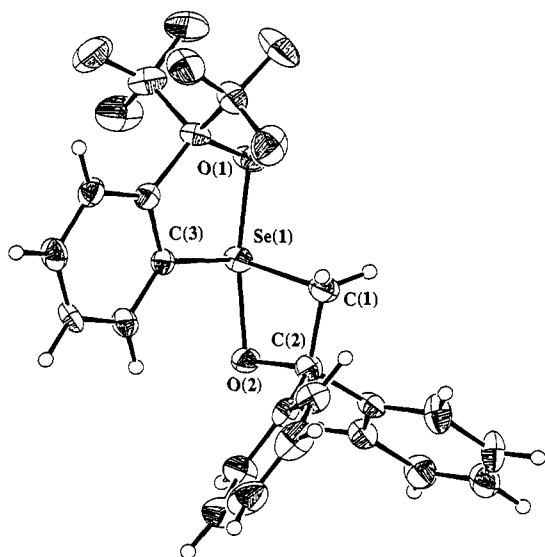

Figure 1. ORTEP drawing of **5a**. Selected bond lengths (Å), bond angles (deg), and dihedral angles (deg): Se(1)-O(1), 1.977(4); Se(1)-O(2), 1.902(4); Se(1)-C(1), 1.923(7); Se(1)-C(3), 1.915(6); C(1)-C(2), 1.537(9); C(2)-O(2), 1.447(7); O(1)-Se(1)-O(2), 163.4(2); O(1)-Se(1)-C(3), 83.3(2); C(1)-Se(1)-O(2), 72.5(2); Se(1)-C(1)-C(2), 92.5(4); C(1)-C(2)-O(2), 98.5(5); Se(1)-O(2)-C(2), 96.3(3); O(2)-Se(1)-C(1)-C(2), -3.7(4); Se(1)-C(1)-C(2)-O(2), 4.7(4).

In sharp contrast to the oxetanes containing groups 14 and 15 elements previously prepared,[4] the oxaselenetane **5a** did not undergo an olefin-forming reaction on thermolysis. The reaction (toluene-d_8, 150 °C, 2 days) became somewhat complicated to give **4a** (12%), R-migrated ketone **9a**[13] (55%), ring expansion

(13) For similar rearrangement reactions via a selenonium oxide, see: Krief, A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 1, pp 714–720.

Scheme II
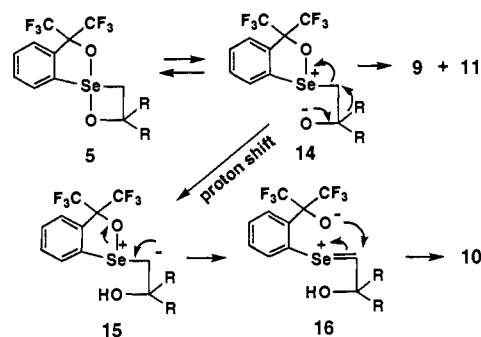
product **10a** (10%), and cyclic selenenate **11** (16%) along with a mixture (35%) of cyclic seleninate **12** and diselenide **13**.[14] On the other hand, thermolysis of **5b** (toluene-d_8, 180 °C, 2 days) gave **4b** (13%) and **10b** (47%) as identifiable products (Scheme I).[15] The absence of R-migrated product **9b** in the reaction of **5b** seems to be due to the difference in the migrating ability between the phenyl and benzyl groups.

The present results have revealed an interesting difference in reactivity between oxetanes with group 15 elements and those with group 16 elements. Thus, in the case of the oxaselenetane **5**, an energy gain enough to undergo the Wittig-type reaction cannot be acquired because of the lower bond energy of Se=O compared with that of P=O, and hence a heterolysis of the Se—O bond becomes favorable to afford *syn*-betaine **14**, which undergoes competitively either R-group migration leading to **9** and **11** or a proton shift followed by a Pummerer-type rearrangement giving **10** via **15** and **16** (Scheme II).

Supplementary Material Available: Physical and spectral data for **2, 4a, 4b, 5b, 10a, 10b, 11, 12, 13**, an experimental procedure for the synthesis of **5a**, and X-ray crystallographic data with tables of thermal and positional parameters, bond lengths, and bond angles for **5a** (15 pages). Ordering information is given on any current masthead page.

(14) The ^{19}F NMR spectrum of the reaction mixture showed that the product ratio of **4a**:**10a**:**11**:**12** was 21:14:56:11. The cyclic selenenate **11** was susceptible to hydrolysis and partially decomposed to give selenenic acid ArSeOH [Ar = o-C$_6$H$_4$C(CF$_3$)$_2$OH], which underwent a mutual redox reaction to afford diselenide **13** and seleninic acid ArSe(O)OH, the latter giving cyclic seleninate **12** by cyclodehydration. Product **4a** is considered to be formed along with **12** by reduction of **5a** with **11** followed by hydrolysis with adventitious water. For the mutual redox reaction of selenenic acids, see: Sonoda, N.; Ogawa, A. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1986; Vol. 1, pp 624–628.

(15) Sulfur analogues of **5** were similarly synthesized, but they could not be isolated because of their high sensitivity to moisture. The reactions of sulfonium ylides with carbonyl compounds are well-known as the Corey-Chaykovsky reaction to give the corresponding epoxides. However, neither the sulfur analogues nor **5a,b** gave any epoxide on thermolysis.