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Synthesis, Crystal Structure, and Thermolysis of the First Tetracoordinate $1\lambda^4$,2-Selenazetidines: Aziridine Formation Reaction from a Four-Membered Heterocycle Bearing Highly Coordinate Selenium

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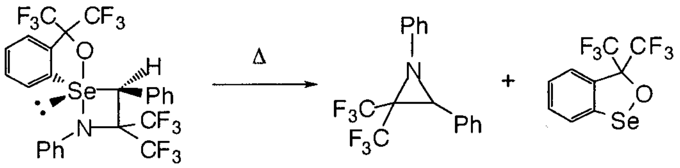
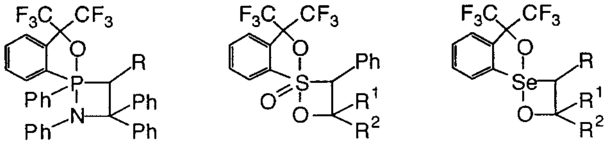
ABSTRACT



The first tetracoordinate $1\lambda^4$,2-selenazetidines were synthesized by taking advantage of the Martin ligand and characterized by X-ray crystallographic analysis. The selenazetidines gave the corresponding aziridine and the cyclic selenenate on their thermolysis, which indicates the possibility that a highly coordinate 1,2-heterachalcogenetane may provide the corresponding heterocyclopropane regardless of the heteroatoms.

Oxetanes bearing highly coordinate heavier main-group elements at the neighboring position of oxygen have been known as intermediates or transition states of very important reactions in organic synthesis such as the Wittig reaction and Peterson-type reactions.[1] In the course of our study on the heterocyclobutanes, we previously reported the olefin formation reactions of such oxetanes bearing highly coordinate group 13, 14, and 15 elements.[2,3] Furthermore, we also reported the synthesis of 1,2-azaphosphetidines **1**,[4] nitrogen versions of oxaphosphetanes,[3] which undergo the olefin extrusion on their thermolysis (Figure 1). Contrary to such heterocyclobutanes, we found that pentacoordinate 1,2-



1 **2** **3a**: R = H
3b: R = Ph

Figure 1.

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[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. *Chem. Rev.* **1989**, *89*, 863−927. (d) Vedejs, E.; Peterson, M. J. *Top. Stereochem.* **1994**, *20*, 1−157. For the Peterson reactions, see: (e) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworth: London, 1981; pp 141−152. (f) Ager, D. J. *Synthesis* **1984**, 384−398. (g) Ager, D. J. *Org. React. (N.Y.)* **1990**, *38*, 1−223. For the Peterson-type reactions, see: (h) Kauffmann, T. *Top. Curr. Chem.* **1980**, *92*, 109−147. (i) Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 410−429. (j) Pereyre, M.; Quitard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworth: London, 1987; pp 176−177.

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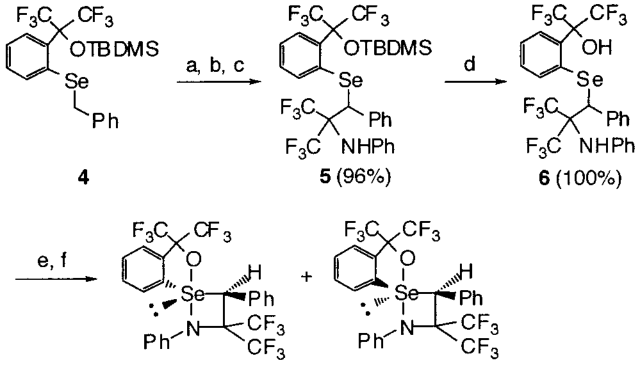
oxathietanes **2** and tetracoordinate 1,2-oxaselenetanes **3** do not give the corresponding olefins.[5,6] Moreover, oxachalcogenetanes **2** and **3b**, which bear phenyl groups at the 3-positions, extruded the corresponding oxiranes.[5b,6b] These reactions giving the corresponding three-membered ring compounds on their thermolysis are expected to proceed for other heteracyclobutanes, e.g., a 1,2-selenazetidine with highly coordinate chalcogen atoms. However, there has been no report on the compounds with such a ring system. We herein describe the synthesis of tetracoordinate 1,2-selenazetidines by taking advantage of the Martin ligand,[7] together with the crystal structure and thermolysis.

Sequential treatment of benzyl selenide **4**[6b] with lithium diisopropylamide (LDA), (hexafluoroisopropylidene)aniline (HFIA), and an aqueous solution of NH_4Cl gave β-aminoalkyl selenide **5** (Scheme 1). The oxidation of β-aminoalkyl selenide **6**, which was quantitatively obtained by the desilylation of **5** with n-Bu_4NF, with mCPBA gave a mixture of two diastereomers of tetracoordinate 1,2-selenazetidines **7a** and **7b**. The chromatography of the mixture afforded **7a** (40%) and **7b** (8%) separately as stable colorless crystals.

Scheme 1[a]



4 **5** (96%) **6** (100%) **7a** (40%) **7b** (8%)

[a] LDA, THF, −78 °C, 2 h; (b) PhN═C(CF_3)$_2$, THF, −78 °C, 10 h; (c) aqueous NH_4Cl; (d) n-Bu_4NF, THF, 0 °C, 30 min; (e) mCPBA, $CHCl_3$, 0 °C, 30 min; (f) chromatography (SiO_2, hexane/benzene 3/1).

In the ^{19}F NMR spectra of **7a** and **7b** (xylene-d_{10}), four sets of quartets for the trifluoromethyl groups derived from the HFIA unit and the Martin ligand unit were observed due to their nonequivalence consistent with the ring formation. Downfield shifts of the ^{77}Se resonance ($CDCl_3$) in going from **6** (δ 435.1) to **7a** (δ 713.0) and **7b** (δ 759.5), respectively, are consistent with tetracoordinate selenurane structures.[8,9] In the ^1H NMR spectra ($CDCl_3$) of **7a** and **7b**, the ortho proton of the “Martin ligand” resonated at low field (δ 7.96 and 8.08, respectively), which is a typical feature of compounds with a trigonal-bipyramidal (TBP) or a pseudo-TBP structure bearing a polar apical bond.[10] These spectroscopic features support their structures as tetracoordinate 1,2-selenazetidines.

The X-ray crystallographic analysis of **7a** revealed its distorted pseudo-TBP structure at a selenium atom (Figure 2).[11,12] Oxygen and nitrogen atoms occupied two apical positions, whereas two carbon atoms as well as the lone pair occupied three equatorial positions. This is the first example of the synthesis and structural analysis of a 1,2-selenazetidine.

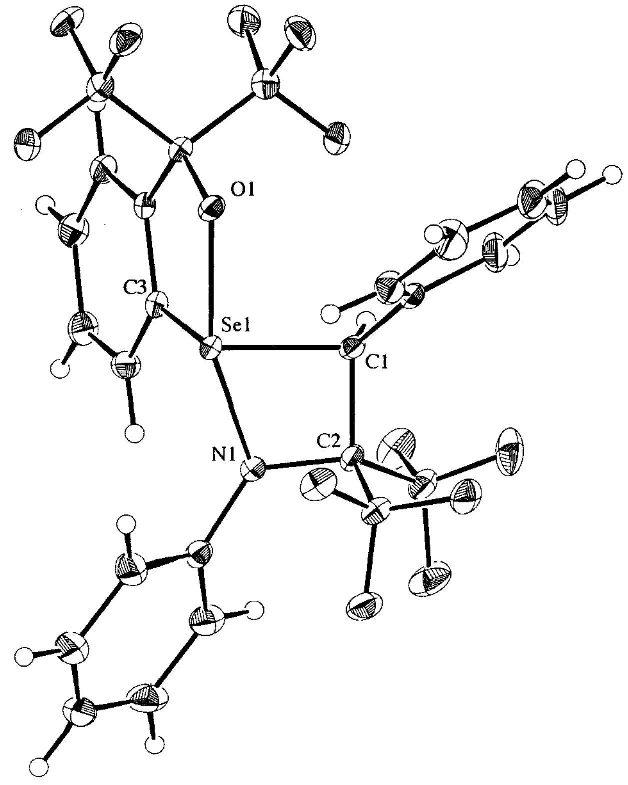


Figure 2. ORTEP drawing of **7a** with thermal ellipsoid plot (30% probability). Selected bond lengths [Å], angles [deg], and torsion angles [deg] for **7a**: Se1−N1, 1.974(2); Se1−C1, 1.991(2); Se1−O1, 2.008(1); Se1−C3, 1.924(2); C1−C2, 1.566(3); C2−N1, 1.450(3); O1−Se1−N1, 158.70(7); C1−Se1−C3, 107.64(9); C1−Se1−N1, 69.72(8); Se1−C1−C2, 91.0(1); C1−C2−N1, 97.4(2); C2−N1−Se1, 95.2(1); Se1−N1−C2−C1, 21.9(1); Se1−C1−C2−N1, 21.6(1).

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(2) (a) Kawashima, T.; Okazaki, R. *Synlett* **1996**, 600−608. (b) Kawashima, T.; Okazaki, R. In *Advances in Strained and Interesting Organic Molecules*; Halton, B., Ed.; JAI Press Inc.: Stamford, 1999; Vol. 7, pp 1−41. (c) Kawashima, T. *J. Organomet. Chem.* **2000**, *611*, 256−263.

(3) (a) Kawashima, T.; Kato, K.; Okazaki, R. *J. Am. Chem. Soc.* **1992**, *114*, 4008−4010. (b) Kawashima, T.; Kato, K.; Okazaki, R. *J. Am. Chem. Soc.* **1998**, *120*, 6848−6848. (c) Kawashima, T.; Kato, K.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 869−870. (d) Kawashima, T.; Watanabe, K.; Okazaki, R. *Tetrahedron Lett.* **1997**, *38*, 551−554. (e) Kawashima, T.; Okazaki, R.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2500−2502.

(4) Kawashima, T.; Soda, T.; Okazaki, R.; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1096−1098.

(5) (a) Ohno, F.; Kawashima, T.; Okazaki, R. *J. Am. Chem. Soc.* **1996**, *118*, 697−698. (b) Kawashima, T.; Ohno, F.; Okazaki, R.; Ikeda, H.; Inagaki, S. *J. Am. Chem. Soc.* **1996**, *118*, 12455−12456.

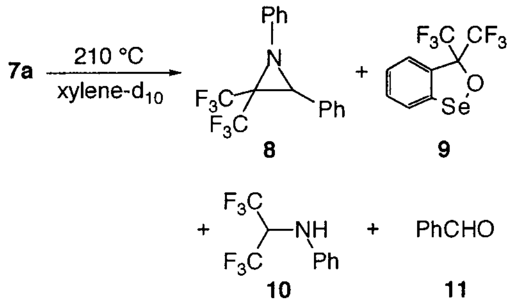
(6) (a) Kawashima, T.; Ohno, F.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 10434−10435. (b) Ohno, F.; Kawashima, T.; Okazaki, R. *Chem. Commun.* **1997**, 1671−1672.

(7) A bidentate ligand, -$C_6H_4C(CF_3)_2O$-, developed by Martin for stabilizing hypervalent species, see: (a) Martin, J. C.; Perozzi, E. F. *Science* **1976**, *191*, 154−159. (b) Perozzi, 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. (c) Martin, J. C. *Science* **1983**, *221*, 509−514.

Interestingly, the nitrogen atom of **7a** is not trigonal planar in marked contrast to that of **1**, which is isoelectronic to **7a**, though other structural features of **7a** are almost the same as those of **1** and **3a**.[4,6a] Pyramidal configuration for the nitrogen atom of **7a** would emerge from the steric repulsion between the Martin ligand and the phenyl group on the nitrogen atom.

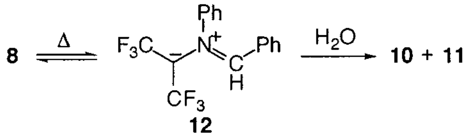
Consequently, the four-membered ring significantly deviates from planarity as indicated by the torsion angle [Se1−N1−C2−C1] of **7a** [21.9(1)°]. The Se1−C1 bond length [1.991(2) Å] is slightly longer than that of previously reported oxaselenetanes **3a** [1.923(7) Å].[6a] Taking into account the standard deviations, other common bond lengths of the four-membered ring are almost same as those of **1** and **3a**.[4,6a] The Se1−O1 and Se1−C3 bond lengths are also almost same as those of **3a**. The bond angle between two apical bonds deviates by 21.30(7)° from 180°, probably due to its ring strain. Such deviation was also observed for **1** and **3a**.[4,6a] Since the spectral features of both **7a** and **7b** are very similar, **7b** should be another diastereomer of 1,2-selenazetidine in regard to the configuration at the selenium, that is, the phenyl group at 4-position in **7b** is *trans* to that of the lone pair but *cis* in **7a**.

Scheme 2



Thermolysis of **7a** at 210 °C in xylene-d_{10} was monitored by ^{1}H and ^{19}F NMR spectroscopy (Scheme 2). The signals due to the corresponding aziridine **8** and cyclic selenenate **9** increased with the decrease in those of **7a**. Finally, **8** (78%), **9** (100%), **10** (16%), and **11** (16%) were obtained after complete consumption of **7a**.[13] No formation of the corresponding olefin was observed, in sharp contrast to the phosphorus analogue **1**. This is the first finding for aziridine formation pathways from heteracyclobutanes with highly coordinate main-group elements. Compounds **10** and **11** are most likely formed by the ring-opening reaction of aziridine **8**, giving azomethine ylide **12**, followed by the hydrolysis of **12** with water in the reaction mixture, indicating that **10** and **11** are the secondary products of **8** (Scheme 3).

Scheme 3



The above experimental result shows that a 1,2-selenazetidine has a reactivity similar to that of 1,2-oxaselenetanes **3b** at the point of giving the corresponding three-membered ring compound on the thermolysis. Such ligand coupling reactions on selenium would be favorable compared with the olefin formation, because the energy gain obtained by the formation of the double-bond between selenium and oxygen or nitrogen is too small to be the driving force of the latter reaction. We previously reported the possibility that the 1,2-oxachalcogenetanes are intermediates of the Corey−Chaykovsky reaction of chalcogenonium ylides with carbonyl compounds.[5,6b] In addition, such an aziridine formation of a sulfonium ylide with a cyclic imine was previously reported as a nitrogen version of the Corey−Chaykovsky reaction.[14] The result of thermolysis of **7a** giving **8** indicates that a 1,2-selenazetidine might be the intermediate of the selenium version of this reaction.

Similarly, thermolysis of **7b** (xylene-d_{10}, at 210 °C) also gave **8** (79%), **9** (100%), **10** (15%), and **11** (16%) as final products, but **7a** was also observed during the reaction. The thermal reaction of **7b** at 150 °C gave predominantly **7a** (78%) with a small amount of **8** (13%) and **9** (13%) in 91% conversion of the reaction (10 h), resulting in the formation of **8**, **9**, **10**, and **11** as the final products (225 h). These results indicate that **7b** isomerized to **7a** before its thermolysis.

In summary, we have revealed an interesting difference in reactivity between azetidines with group 15 elements and those with group 16 elements. Hence, the above experimental

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(8) For reviews on the ^{77}Se NMR, see: (a) 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, pp 189−241. (b) Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon: Oxford, 1986; pp 17−21.

(9) For selenuranes with Se−N bond(s), see: (a) Roesky, H. W.; Ambrosius, K. *Z. Naturforsch.* **1978**, *33B*, 759−762. (b) Fujihara, H.; Mima, H.; Erata, T.; Furukawa, N. *J. Chem. Soc., Chem. Commun.* **1991**, 98−99. (c) Fujihara, H.; Mima, H.; Ikemori, M.; Furukawa, N. *J. Am. Chem. Soc.* **1991**, *113*, 6337−6338. (d) Fujihara, H.; Ueno, Y.; Chiu, J.-J.; Furukawa, N. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2247−2248. (e) Fujihara, H.; Mima, H.; Erata, T.; Furukawa, N. *J. Am. Chem. Soc.* **1993**, *115*, 9826−9827. (f) Fujihara, H.; Mima, H.; Furukawa, N. *Tetrahedron* **1996**, *52*, 13951−13960. (g) Mima, H.; Fujihara, H.; Furukawa, N. *Tetrahedron* **1998**, *54*, 743−752.

(10) Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 4618−4621.

(11) A crystal data of **7a**. $C_{25}H_{15}F_{12}NOSe$, FW = 652.34, colorless crystals, monoclinic, space group $P2_1/n$, a = 9.7010(2), b = 15.3350(5), and c = 16.8410(5) Å, β = 101.446(2)°, V = 2455.5(1) Å^3, Z = 4, ρ_{calcd} = 1.764 g cm^{-3}, T = 150 K. Of the 4474 reflections which were collected, 4340 were unique. The structure was solved by direct methods and expanded by using Fourier techniques. The final cycle of full-matrix least-squares refinement on F^2 was based on all 4340 observed reflections and 361 variable parameters and converged with unweighted and weighted agreement factors of R1 = 0.039 and wR2 = 0.118.

(12) Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-149505. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax (+44)1223−336−033; e-mail deposit@ccdc.cam.ac.uk).

(13) The yields of these products were determined on the basis of the integral of ^{1}H and ^{19}F NMR spectra of the reaction solution.

(14) Hortmann, A. G.; Robertson, D. A. *J. Am. Chem. Soc.* **1967**, *89*, 5974−5975.

results suggest that thermolysis of a highly coordinate 1,2-heterachalcogenetane provides the corresponding heteracyclopropane regardless of the heteroatom in contrast to the group 15 analogues. The investigation on the stereochemistry of the aziridine formation and its kinetic study are in progress.

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Supporting Information Available: Experimental procedure for the preparation of **5**−**7**, spectral data for **5**, **6**, **7a**, **7b**, and **8**, and crystal details of **7a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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