JOC*Note*

Stereoselective Synthesis of New Selenium-Containing Heterocycles by Cyclocarbonylation of Aminoalkynes with Carbon Monoxide and Selenium

Shin-ichi Fujiwara,[*,†] Yasukazu Shikano,[‡]
Tsutomu Shin-ike,[†] Nobuaki Kambe,[*,‡] and
Noboru Sonoda[*,§]

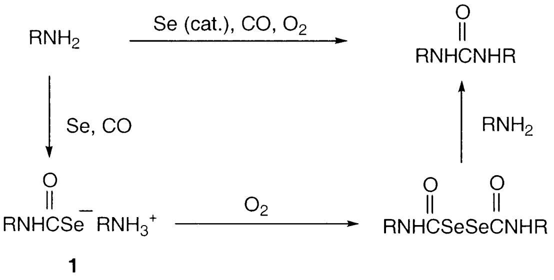
Department of Chemistry, Osaka Dental University, Hirakata, Osaka 573-1121, Japan, Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan, and Department of Applied Chemistry, Faculty of Engineering, Kansai University, Suita, Osaka 564-8680, Japan

fujiwara@cc.osaka-dent.ac.jp

Received March 12, 2002

Abstract: The reaction of 3-aminoalkynes **2** with carbon monoxide and selenium yielded 5-alkylideneselenazolin-2-ones **3** stereoselectively via cycloaddition of in situ generated carbamoselenoates to the carbon−carbon triple bond. 4-Aminoalkyne **7** also afforded the corresponding six-membered selenium-containing heterocycle with the aid of CuI.

Organoselenium compounds are important intermediates or materials not only in synthetic chemistry[1] but also in biological and medicinal chemistry.[2] We already reported that selenium exhibited extremely high catalytic activity in the carbonylation of a variety of amines producing urea derivatives,[3] where carbamoselenoates **1** were readily formed as the key intermediates from amines, CO, and selenium (eq 1).[4]



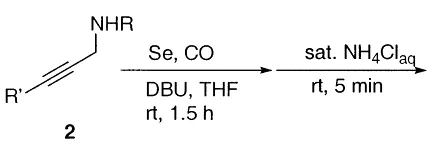
(1)

Since the carbamoselenoate group ($NCOSe^-$) has a highly nucleophilic site at selenium,[5] carbamoselenoates are expected to add to various unsaturated bonds to form new carbon−selenium bonds.[6−8] This reaction has been applied successfully to carbonylation of *o*-cyanoaniline and *o*-aminoacetophenone with CO and selenium where selenoxoquinazolinones and benzoselenazinones were formed via intramolecular cycloaddition of in situ generated carbamoselenoates toward cyano and carbonyl groups, respectively.[9] Here we disclose a novel synthetic method for 5-alkylideneselenazolin-2-ones **3** by the reaction of 3-aminoalkynes **2** with CO and elemental selenium under mild conditions (eq 2).

TABLE 1. Synthesis of 5-Alklideneselenazolin-2-ones[a]

run	aminoalkyne	R	R′	product	yield, %
1	**2a**	Bu	H	**3a**	95
2	**2b**	Me	H	**3b**	78
3	**2c**	*i*-Pr	H	**3c**	58
4	**2d**	*cyclo*-Hex	H	**3d**	76
5	**2e**	*t*-Bu	H	**3e**	10
6	**2f**	Ph	H	**3f**	0
7	**2g**	H	H	**3g**	26[b]
8	**2h**	Bu	Ph	**3h**	81
9	**2i**	Bu	Et	**3i**	11 (66)[c]
10	**2j**	Bu	Me_3Si	**3j**	22[c]

[a] Conditions: 3-aminoalkyne (2.4 mmol), Se (2 mmol), CO (1 atm), DBU (2 mmol), THF (20 mL), rt, 1.5 h, then saturated NH_4Cl_{aq} (2 mL), 5 min. [b] Propargylamine **2g** (12 mmol) without DBU. [c] Saturated NH_4Cl_{aq} (2 mL), 4 h.



(2)

Butyl(prop-2-ynyl)amine (**2a**: R = Bu, R′ = H; 2.4 mmol) was allowed to react with CO (1 atm) and selenium (2 mmol) in THF (20 mL) at room temperature in the presence of DBU (2 mmol). Within 1.5 h, a stoichiometric amount of CO was absorbed. Aqueous saturated NH_4Cl solution (2 mL) was then added, and the mixture was stirred for 5 min. Usual workup followed by purification by HPLC afforded the corresponding 5-methylideneselenazolin-2-one **3a** in 95% yield (based on Se, run 1 in Table 1).[10]

[†] Osaka Dental University.

[‡] Osaka University.

[§] Kansai University.

(1) (a) Liotta, D., Ed. *Organoselenium Chemistry*; John Wiley & Sons: New York, 1987. (b) Back, T. G., Ed. *Organoselenium Chemistry: A Practical Approach*; Oxford University Press: Oxford, 1999. (c) Wirth, T., Ed. *Topics in Current Chemistry 208: Organoselenium Chemistry*; Springer: Berlin, Germany, 2000.

(2) (a) Nicolaou, K. C.; Petasis, N. A. *Selenium in Natural Products Synthesis*; CIS Inc.: Philadelphia, PA, 1984. (b) Wendel, A., Ed. *Selenium in Biology and Medicine*; Springer-Verlag: Berlin, Germany, 1989. (c) Nève, J.; Favier, A., Eds. *Selenium in Medicine and Biology*; Walter de Gruyter: Berlin, Germany, 1989.

(3) (a) Sonoda, N.; Yasuhara, T.; Kondo, K.; Ikeda, T.; Tsutsumi, S. *J. Am. Chem. Soc.* **1971**, *93*, 6344. (b) Sonoda N. *Pure Appl. Chem.* **1993**, *65*, 699−706 and references therein.

(4) Fujiwara, S.; Miyoshi, N.; Ogawa, A.; Kambe, N.; Sonoda, N. *J. Phys. Org. Chem.* **1989**, *2*, 359−362.

(5) Kondo, K.; Takarada, M.; Murai, S.; Sonoda, N. *Synthesis* **1979**, 597−598.

(6) Under basic conditions selenols are known to add onto carbon−carbon triple bonds exclusively or highly selectively in anti fashion, for example, see: (a) Luxen, A.; Christiaens, L.; Renson, M. *J. Org. Chem.* **1980**, *45*, 3535−3537. (b) Wadsworth, D. H.; Detty, M. R. *J. Org. Chem.* **1980**, *45*, 4611−4615.

(7) Selenols also add to alkynes via radical mechanism (a) or in the presence of transition-metal catalysis (b) to form alkenyl selenides:[8] (a) Ogawa, A.; Obayashi, R.; Sekiguchi, M.; Masawaki, T.; Kambe, N.; Sonoda, N. *Tetrahedron Lett.* **1992**, *33*, 1329−1332. (b) Kuniyasu, H.; Ogawa, A.; Sato, K.; Ryu, I.; Sonoda, N. *Tetrahedron Lett.* **1992**, *33*, 5525−5528.

(8) For reviews on alkenyl selenides: (a) Comasseto, J. V. *J. Organomet. Chem.* **1983**, *253*, 131−181. (b) Comasseto, J. V.; Ling, L. W.; Petragnani, N.; Stefani, H. A. *Synthesis* **1997**, 373−403.

(9) Yoshida, T.; Kambe, N.; Murai, S.; Sonoda, N. *J. Org. Chem.* **1987**, *52*, 1611−1613.

(10) The use of triethylamine or *N*-methylpyrrolidine as a base in place of DBU or sulfur in place of selenium hardly afforded the products.

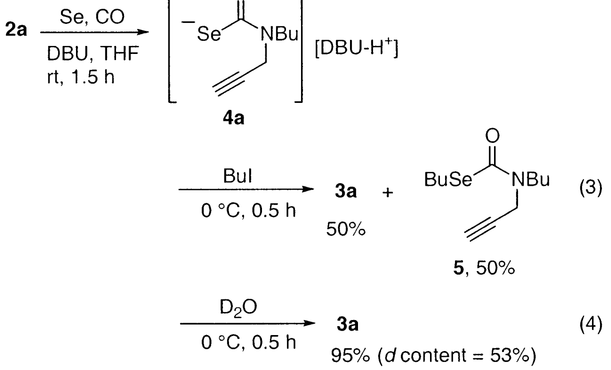
10.1021/jo025707d CCC: $22.00

There are several methods available for the synthesis of 5-alkylideneoxazolidin-2-ones[11] and only one example for the synthesis of sulfur analogues.[12] Described herein is the first example of the synthesis of 5-alkylideneselenazolin-2-ones **3**.[13−16]

Representative results of this reaction are listed in Table 1. Amines having a primary or secondary alkyl group (**2a**−**d**) gave the products in good yields as shown in runs 1−4. However, introduction of a tertiary alkyl group on the nitrogen reduced the rate of CO absorption (run 5). Carbonylation did not proceed when phenyl-substituted amine **2f** was used, due probably to its low nucleophilicity (run 6). Propargylamine **2g** did not give the desired product under similar conditions; however, use of large excess amounts of the amine without DBU increased the yield of **3g** up to 26% although CO absorption was slow (run 7). The use of *N*-butylallylamine instead of 3-aminoalkynes did not afford the desired product, and an attempt for intermolecular carbonylative addition by the combined use of dipropylamine and phenylacetylene failed. Since in both reactions CO was absorbed almost quantitatively, carbamoselenoates might be formed in situ but they could not add to the carbon−carbon double bond intramolecularly nor to the carbon−carbon triple bond intermolecularly.

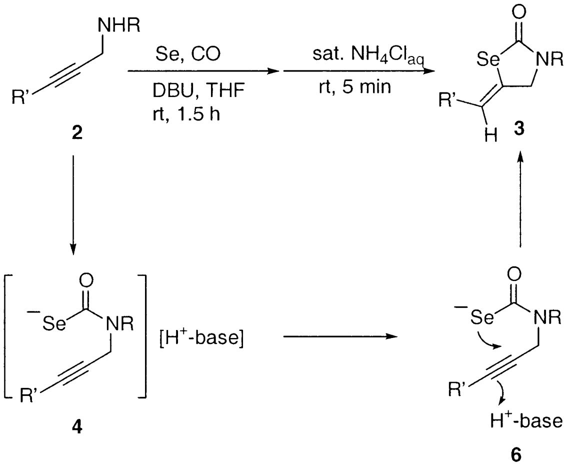
Next, the effect of substituents at the acetylenic terminus was examined, and the results are also summarized in Table 1. 3-Phenylprop-2-ynylamine **2h** afforded the corresponding (*Z*)-5-benzylidene-3-butylselenazolidin-2-one (**3h**) stereoselectively in 81% yield (run 8). Pent-2-ynylamine **2i** gave **3i** in 11% yield under similar conditions; moreover, prolonging the reaction after the addition of aqueous saturated NH_4Cl solution increased the yield up to 66% (run 9). These results indicate that the α-anion stabilizing substituents may facilitate the present reaction. However, introduction of a Me_3Si group at the alkynyl carbon did not improve the yield of **3j** probably due to steric hindrance (run 10). All 5-alkylideneselenazolidin-2-ones **3h**−**j** have the *Z*-configuration, which was determined by NOE experiments, and the structure of **3h** was confirmed also by X-ray analysis.

To examine the reaction mechanism, we added BuI to the reaction mixture of **2a** at 0 °C after the reaction with CO for 1.5 h and stirred the solution for 30 min. The resulting mixture contained **3a** in 50% yield along with 50% yield of **5**, which was formed by trapping of carbamoselenoate **4a** (eq 3). Similar quenching by D_2O instead of BuI yielded **3a** in 95% yield having a deuterium at the terminal vinylic carbon (eq 4). The *d* content (53%) of the vinylic hydrogen indicates that almost half of **4a** undergoes cyclization before quenching. This is consistent with the result of eq 3.



When the mixture was quenched with D_2O after being stirred for 6 h, the yield of **3a** was also excellent (97%) and the *d* content of **3a** was reduced to 10%. These controlled experiments indicate that **4a** does undergo intramolecular cycloaddition, but this process is not fast and is accelerated by an additional proton source. The effect of an additional proton source and the stereoselectivity of the products can be explained by the trans addition mechanism (**4** → **6** → **3**) shown in Scheme 1, where a proton assists the nucleophilic addition of

SCHEME 1



---

[11] (a) Badische Anilin & Soda-Fabrik A.-G. German Patent, 1,098,953; *Chem. Abstr.* **1962**, *56*, 2453. (b) Badische Anilin & Soda-Fabrik A.-G. German Patent, 1,164,411; *Chem. Abstr.* **1964**, *60*, 14510d. (c) Mitsudo, T.; Hori, Y.; Yamakawa, Y.; Watanabe, Y. *Tetrahedron Lett.* **1987**, *28*, 4417−4418. (d) Shimizu, M.; Yoshioka, H. *J. Chem. Soc., Chem. Commun.* **1987**, 689−690. (e) Costa, M.; Chiusoli, G. C.; Rizzardi, M *Chem. Commun.* **1996**, 1699−1700. (f) Costa, M.; Chiusoli, G. C.; Taffurelli, D.; Dalmonego, G. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1541−1546. (g) Shi, M.; Shen, Y.-M. *J. Org. Chem.* **2002**, *67*, 16−21.

[12] Sato, A.; Ikeda, T.; Sueyoshi, T.; Nakamura, Y.; Shimada, T. German Offen. 2,520,834; *Chem. Abstr.* **1976**, *84*, 97812m.

[13] The related benzoselenazolinones,[14] 5-alkylideneselenazolidine-2,4-diones,[15] and selenazolidin-2-one[16] possessing an N−C(O)-Se unit have already been prepared. Some of the benzoselenazolinones exhibited antiinflammatory activities.

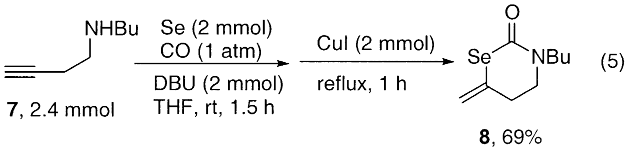
[14] (a) Galet, V.; Vaccher, M. P.; Bernier, J. L.; Henichart, J. P.; Lesieur, D. *Synth. Commun.* **1993**, *23*, 621−629. (b) Galet, V.; Vaccher, M. P.; Bernier, J. L.; Henichart, J. P.; Lesieur, D.; Abadie, C.; Rochette, L.; Lindenbaum, A.; Chaclas, J.; de la Faverie, J. F. R.; Pfeiffer, B.; Renard, P. *J. Med. Chem.* **1994**, *37*, 2903−2911. (c) Miyata, T.; Mizuno, T.; Nishiguchi, I.; Kambe, N.; Sonoda, N. *Kagaku to Kogyo (Osaka)* **1996**, *70*, 374−377; *Chem. Abstr.* **1996**, *125*, 247984.

[15] (a) Comrie, A. M.; Dingwall, D.; Steinlake, J. B. *J. Chem. Soc.* **1963**, 5713−5717. (b) Comrie, A. M.; Dingwall, D.; Steinlake, J. B. *J. Pharm. Pharmacol.* **1964**, *16*, 268−272. (c) Levshin, I. E.; Tsurkan, A. A.; V'yunov, K. A. *J. Org. Chem. USSR* **1981**, *17*, 760−763. (d) Levshin, I. B.; V'yunov, K. A.; Tsurkan, A. A.; Ginak. A. I.; Isaeva, N. L. *Khim. Geterotsikl. Soedin.* **1983**, 338−340; *Chem. Abstr.* **1983**, *99*, 212461v. (e) Levshin, I. B.; Tsurkan, A. A.; V'yunov, K. A.; Ginak. A. I. *J. Appl. Chem. USSR* **1983**, *56*, 1361−1362. (f) Levshin, I. B.; V'yunov, K. A.; Tsurkan, A. A.; Knizhnik, A. Z.; Ginak. A. I. *J. Org. Chem. USSR* **1983**, *19*, 574−577. (g) Levshin, I. B.; V'yunov, K. A.; Tsurkan, A. A.; Ginak. A. I. *Khim. Geterotsikl. Soedin.* **1984**, 266; *Chem. Abstr.* **1984**, *100*, 209704k. (h) Levshin, I. B.; V'yunov, K. A.; Ginak. A. I.; Tsurkan, A. A. *J. Org. Chem. USSR* **1985**, *21*, 580−583.

[16] Xie, Y.; Short, M. D.; Cassidy, P. B.; Roberts, J. C. *Bioorg. Med. Chem. Lett.* **2001**, *11*, 2911−2915.

selenium to a carbon−carbon triple bond by coordinating from the opposite site. An alternative mechanism via intramolecular addition of a carbamoselenoic acid moiety (NC(O)SeH) to the alkyne part is not likely because (i) this process will not account for the complete trans selectivity and (ii) carbamoselenoic acids are acidic groups and would ionize completely in the presence of a strong base such as DBU.

The reaction of homopropargylamine **7** under similar conditions did not afford the expected 6-methyleneselenazinan-2-one **8**. However, addition of MeI to the reaction mixture prior to proton quenching gave a methylated product of the corresponding carbamoselenoate in 100% yield. This result indicates that the carbonylation process proceeded quantitatively. Since it is known that CuI promotes the cyclization of *O*-propargyl thiocarbonic acid,[17] we added 1 equiv of CuI after carbonylation and refluxed the reaction mixture for 1 h. This procedure brought about successful formation of **8** in 69% yield (eq 5).[18]



In summary, aminoalkynes were carbonylated with CO and selenium under mild conditions to give carbamoselenoates which underwent intramolecular cycloaddition affording new selenium-containing heterocycles.

Experimental Section

THF and DBU were distilled from sodium benzophenone ketyl and CaH_2, respectively. Propargylamine **2g** was purchased from a commercial source, and aminoalkynes **2a**−**f** were synthesized by the reactions of the corresponding propargyl chlorides or tosylates with primary amines according to the reported procedure.[19,20] Aminoalkynes **2h**−**j** and **7** were also prepared similarly. For characterization data of aminoalkynes **2h**−**j** and **7**, see the Supporting Information.

3-Butyl-5-methyleneselenazolidin-2-one (3a): Typical Experimental Procedure. Into a 20-mL flask were placed butyl(prop-2-yl)amine (**2a**, 2.5 mmol, 277 mg), selenium (2.0 mmol, 157 mg), DBU (2.0 mmol, 311 mg), and THF (20 mL) under N_2. The flask was charged with CO (1 atm) and the mixture was vigorously stirred for 1.5 h. After removing CO, saturated aqueous NH_4Cl solution (2 mL) was added and the mixture was stirred for an additional 5 min. The product was poured into saturated aqueous NH_4Cl solution (50 mL) and extracted with Et_2O (50 mL × 2). The combined organic layer was dried over $MgSO_4$ and concentrated. Purification by preparative HPLC eluted with $CHCl_3$ afforded 411 mg (95% based on Se used) of 3-butyl-5-methyleneselenazolidin-2-one (**3a**) as a yellow liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, J = 7.3 Hz, 3 H), 1.29−1.40 (m, 2 H), 1.51−1.61 (m, 2 H), 3.38 (t, J = 7.3 Hz, 2 H), 4.27 (t, J = 2.2 Hz, 2 H), 5.26 (q, J = 2.2 Hz, 1 H), 5.63 (q, J = 2.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 19.8, 29.3, 44.6, 56.3, 110.4 ($^2J_{Se-C}$ = 6.9 Hz), 134.8 ($^1J_{Se-C}$ = 98.7 Hz), 166.1 ($^1J_{Se-C}$ = 109.3 Hz); IR (neat) 1686 (C=O) cm^{-1}; MS (EI) *m/e* (relative intensity) 219 (M$^+$, 100). Anal. Calcd for $C_8H_{13}NOSe$: C, 44.04; H, 6.01; N, 6.42. Found: C, 43.91; H, 6.00; N, 6.51.

3-Methyl-5-methyleneselenazolidin-2-one (3b). Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.95 (s, 3 H), 4.25 (t, J = 2.3 Hz, 2 H), 5.27 (q, J = 2.3 Hz, 1 H), 5.63 (q, J = 2.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.4, 58.1, 110.5 ($^2J_{Se-C}$ = 12.0 Hz), 134.4 ($^1J_{Se-C}$ = 59.0 Hz), 166.2; IR (neat) 1682 (C=O) cm^{-1}; MS (EI) *m/e* (relative intensity) 177 (M$^+$, 82). Anal. Calcd for C_5H_7NOSe: C, 34.11; H, 4.01; N, 7.95. Found: C, 34.32; H, 4.07; N, 8.00.

3-Isopropyl-5-methyleneselenazolidin-2-one (3c). Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (d, J = 6.8 Hz, 6 H), 4.23 (t, J = 2.2 Hz, 2 H), 4.47 (heptet, J = 6.8 Hz, 1 H), 5.26 (q, J = 2.2 Hz, 1 H), 5.65 (q, J = 2.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9, 45.9, 51.4, 110.5 ($^2J_{Se-C}$ = 12.0 Hz), 135.0 ($^1J_{Se-C}$ = 98.2 Hz), 165.9 ($^1J_{Se-C}$ = 107.9 Hz); IR (neat) 1682 (C=O) cm^{-1}; MS (EI) *m/e* (relative intensity) 205 (M$^+$, 76). Anal. Calcd for $C_7H_{11}NOSe$: C, 41.19; H, 5.43; N, 6.86. Found: C, 41.45; H, 5.37; N, 6.90.

3-Cyclohexyl-5-methyleneselenazolidin-2-one (3d). White solid, mp 57−58 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98−1.17 (m, 1 H), 1.09−1.51 (m, 4 H), 1.64−1.72 (m, 1 H), 1.76−1.86 (m, 4 H), 4.00−4.10 (m, 1 H), 4.20−4.28 (m, 2 H), 5.21−5.27 (m, 1 H), 5.61−5.66 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.2, 25.6, 30.4, 52.5, 54.0, 110.3 ($^2J_{Se-C}$ = 8.3 Hz), 135.3 ($^1J_{Se-C}$ = 98.2 Hz), 165.9 ($^1J_{Se-C}$ = 107.9 Hz); IR (neat) 1663 (C=O) cm^{-1}; MS (EI) *m/e* (relative intensity) 245 (M$^+$, 78). Anal. Calcd for $C_{10}H_{15}NOSe$: C, 49.19; H, 6.19; N, 5.74. Found: C, 49.37; H, 6.22; N, 5.76.

3-*tert*-Butyl-5-methyleneselenazolidin-2-one (3e). Yellow solid, mp 31−34 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (s, 9 H), 4.37 (t, J = 2.1 Hz, 2 H), 5.19 (q, J = 2.1 Hz, 1 H), 5.60 (q, J = 2.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.1, 55.5, 57.8, 109.9 ($^2J_{Se-C}$ = 11.5 Hz), 135.2 ($^1J_{Se-C}$ = 97.7 Hz), 166.1; IR (neat) 1682 (C=O) cm^{-1}; MS (EI) *m/e* (relative intensity) 219 (M$^+$, 21); HRMS (EI) calcd for $C_8H_{13}NOSe$ 219.0162, found 219.0153.

5-Methyleneselenazolidin-2-one (3g). White solid, mp 105−107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23−4.29 (m, 2 H), 5.25−5.31 (m, 1 H), 5.63 (q, J = 2.1 Hz, 1 H), 6.77 (br, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.8, 110.9, 138.2 ($^1J_{Se-C}$ = 100.0 Hz), 171.4; IR (KBr) 1676 (C=O) cm^{-1}; MS (EI) *m/e* (relative intensity) 163 (M$^+$, 100); HRMS (EI) calcd for C_4H_5NOSe 162.9536, found 162.9534.

(*Z*)-5-Benzylidene-3-butylselenazolidin-2-one (3h). Colorless crystals, mp 82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, J = 7.3 Hz, 3 H), 1.31−1.41 (m, 2 H), 1.55−1.63 (m, 2 H), 3.42 (t, J = 7.4 Hz, 2 H), 4.36 (d, J = 2.2 Hz, 2 H), 6.87 (t, J = 2.1 Hz, 1 H), 7.22−7.28 (m, 3H), 7.36 (t, J = 7.7 Hz, 2 H); NOE experiment, irradiation of the allyl methylene doublet at δ 4.36 resulted in 15% enhancement of the signal at δ 6.87 (vinyl triplet); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 19.9, 29.4, 44.6, 57.3, 124.1, 127.0, 127.1, 127.4, 128.3, 136.0, 166.0 ($^1J_{Se-C}$ = 109.2 Hz); IR (KBr) 1693 cm^{-1}; MS (EI) *m/e* (relative intensity) 295 (M$^+$, 87). Anal. Calcd for $C_{14}H_{17}NOSe$: C, 57.15; H, 5.82; N, 4.76. Found: C, 57.09; H, 5.79; N, 4.79.

(*Z*)-Butyl-5-propylideneselenazolidin-2-one (3i). Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, J = 7.3 Hz, 3 H), 1.02 (t, J = 7.4 Hz, 3 H), 1.34 (sextet, J = 7.4 Hz, 2 H), 1.55 (quint, J = 7.4 Hz, 2 H), 1.99 (tquint, J = 1.6, 7.4 Hz, 2 H), 3.36 (t, J = 7.4 Hz, 2 H), 4.22 (q, J = 1.9 Hz, 2 H), 5.79 (tt, J = 6.8, 2.2 Hz, 1 H). NOE experiment, irradiation of the allyl methylene quartet at δ 4.22 resulted in 8% enhancement of the signal at δ 5.79 (vinyl triplet−triplet); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.1, 13.7, 19.9, 26.5, 29.4, 44.7, 55.7, 125.7, 126.20, 166.0; IR (neat) 1690 (C=O) cm^{-1}; MS (EI) *m/e* (relative intensity) 247 (M$^+$, 65); HRMS (EI) calcd for $C_{10}H_{17}NOSe$ 247.0475, found 247.0490.

---

(17) Mizuno, T.; Nakamura, F.; Ishino, Y.; Nishiguchi, I.; Hirashima, T.; Ogawa, A.; Kambe, N.; Sonoda, N. *Synthesis* **1989**, 770−771.

(18) For synthesis of the related benzo[1,3]selenazine-2,3-diones: (a) Mbuyi, M.; Christiaens, L.; Renson, M. *Bull. Soc. Chim. Belg.* **1989**, *98*, 395−403; *Chem. Abstr.* **1990**, *112*, 77121d. (b) Fong, M. C.; Laws, M. J.; Schiesser, C. H. *Aust. J. Chem.* **1995**, *48*, 1221−1226.

(19) Arya, V. P.; Grewal, R. S.; Kaul, C. L.; David, J.; Honkan, V. *Ind. J. Chem.* **1977**, *15B*, 133−140.

(20) NMR spectra of 3-aminoalkynes **2a**−**f**, see: (a) **2a**: Barluenga, J.; Canteli, R.-M.; Flórez, J. *J. Org. Chem.* **1996**, *61*, 3646−3649. (b) **2b**: Masse, G.; Sturtz, G. *Synthesis* **1988**, 907−910. (c) **2c**−**d**: Barluenga, J.; Foubelo, F.; Fananas, F. J.; Yus, M. *J. Chem. Soc., Perkin Trans. 1* **1989**, 553−557. (d) **2e**: Ben-Efraim, D. A. *Tetrahedron* **1973**, *29*, 4111−4125. (e) **2f**: Capella, L.; Montevecchi, P. C.; Nanni, D. *J. Org. Chem.* **1994**, *59*, 3368−3374.

(*Z*)-3-Butyl-5-trimethylsilanylmethyleneselenazolidin-2-one (3j). Brown liquid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.14 (s, 9 H), 0.94 (t, J = 7.3 Hz, 3 H), 1.29−1.40 (m, 2 H), 1.51−1.60 (m, 2 H), 3.38 (t, J = 7.3 Hz, 2 H), 4.27 (d, J = 2.2 Hz, 2 H), 5.98 (t, J = 2.2 Hz, 1 H); NOE experiment, irradiation of the allyl methylene doublet at δ 4.27 resulted in 16% enhancement of the signal at δ 5.98 (vinyl triplet); ^{13}C NMR (100 MHz, CDCl$_3$) δ −1.43, 13.7, 19.9, 29.4, 44.3, 59.3, 123.2, 143.0 ($^1J_{\mathrm{Se-C}} = 100.0$ Hz), 166.6; IR (neat) 1694 (C═O) cm^{-1}; MS (EI) *m/e* (relative intensity) 291 (M$^+$, 26). Anal. Calcd for $C_{11}H_{21}NOSeSi$: C, 45.51; H, 7.29; N, 4.82. Found: C, 45.91; H, 7.30; N, 4.85.

3-Butyl-6-methylene[1,3]selenazinan-2-one (8). Into a 20-mL flask were placed butyl(but-3-ynyl)amine (**7**, 2.4 mmol, 307 mg), selenium (2.0 mmol, 156 mg), DBU (2.1 mmol, 319 mg), and THF (20 mL) under N$_2$. The flask was charged with CO (1 atm) and the mixture was vigorously stirred for 1.5 h. After removing CO, CuI (2.0 mmol, 387 mg) was added and the mixture was refluxed for 1 h. After cooling to room temperature, the product was poured into saturated aqueous NaCl solution (50 mL) and extracted with Et$_2$O (50 mL × 2). The combined organic layer was dried over MgSO$_4$ and concentrated. Purification by preparative HPLC eluted with CHCl$_3$ followed by preparative TLC (silica gel) eluted with *n*-hexanes−Et$_2$O (4:1) afforded 317 mg (69% based on Se used) of 3-butyl-6-methylene-[1,3]selenazinan-2-one (**8**) as yellow liquid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.94 (t, J = 7.4 Hz, 3 H), 1.33 (sextet, J = 7.4 Hz, 2 H), 1.55 (quintet, J = 7.4 Hz, 2 H), 2.76 (t, J = 5.4 Hz, 2 H), 3.41 (t, J = 5.4 Hz, 2 H), 3.48 (t, J = 7.4 Hz, 2 H), 5.09 (s, 1 H), 5.39 (s, 1 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 13.8, 20.0, 29.8, 35.3, 49.0, 49.6, 111.0 ($^2J_{\mathrm{Se-C}} = 20.8$ Hz), 138.9 ($^1J_{\mathrm{Se-C}} = 102.6$ Hz), 161.4 ($^1J_{\mathrm{Se-C}} = 122.6$ Hz); IR (neat) 1652 (C═O) cm^{-1}; MS (EI) *m/e* (relative intensity) 233 (M$^+$, 100). Anal. Calcd for $C_9H_{15}NOSe$: C, 46.56; H, 6.51; N, 6.03. Found: C, 46.86; H, 6.56; N, 6.07.

***Se*-Butyl Butyl(prop-2-ynyl)carbamoselenoate (5).** Obtained as an *s-cis*/*trans* mixture; brown liquid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.89−1.02 [overlapping m, 6 H (major, minor)], 1.28−1.49 [overlapping m, 4 H (major, minor)], 1.52−1.75 [overlapping m, 4 H (major, minor)], 2.25 [br s, 1 H (major)], 2.31 [br s, 1 H (minor)], 2.96 [t, J = 7.3 Hz, 2 H (major, minor)], 3.38 [br s, 2 H (major)], 3.50 [br s, 2 H (minor)], 4.08 [br s, 2 H (minor)], 4.23 [br s, 2 H (major)]; ^{13}C NMR (100 MHz, CDCl$_3$) δ 13.6 (major, minor), 13.7 (major, minor), 20.0 (major, minor), 23.1 (major, minor), 26.8 (major), 27.1 (minor), 29.6 (minor), 30.1 (major), 32.8 (major, minor), 35.6 (major), 38.0 (minor), 47.4 (minor), 48.0 (major), 71.9 (major), 72.6 (minor), 77.9 (minor), 78.3 (major), 164.6 (minor), 164.8 (major); IR (neat) 1656 (C═O) cm^{-1}; MS(EI) *m/e* (relative intensity) 275 (M$^+$, 0.5). Anal. Calcd for $C_{12}H_{21}NOSe$: C, 52.55; H, 7.72; N, 5.11. Found: C, 52.64; H, 7.77; N, 5.23.

***Se*-Methyl Butyl(but-3-ynyl)selenocarbamate.** Obtained as an *s-cis*/*trans* mixture; pale yellow liquid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.88−1.00 [overlapping m, 3 H (major, minor)], 1.25−1.40 [overlapping m, 2 H (major, minor)], 1.49−1.67 [overlapping m, 2 H (major, minor)], 2.00 [s, 1 H (major)], 2.06 [s, 1 H (minor)], 2.23 [s, 3 H, (major, minor)], 2.43−2.58 [overlapping m, 2 H (major, minor)], 3.32 [t, J = 7.6 Hz, 2 H (major)], 3.38−3.50 [overlapping m, 4H (minor)], 3.53 [t, J = 7.0 Hz, 2 H, (major)]; ^{13}C NMR (100 MHz, CDCl$_3$) δ 6.2 (major), 6.3 (minor), 13.8 (major, minor), 17.8 (major), 18.9 (minor), 20.0 (major, minor), 29.9 (minor), 30.7 (major), 46.5 (major), 47.4 (minor), 47.9 (minor), 49.5 (major), 69.7 (major), 70.5 (minor), 80.3 (minor), 81.2 (major), 164.0 (minor), 164.3 (major); IR (neat) 1658 (C═O) cm^{-1}; MS(EI) *m/e* (relative intensity) 247 (M$^+$, 7). Anal. Calcd for $C_{10}H_{17}NOSe$: C, 48.78; H, 6.96; N, 5.69. Found: C, 48.86; H, 6.90; N, 5.86.

Acknowledgment. This research was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas (A) “Exploitation of Multi-Element Cyclic Molecules” from the Ministry of Education, Culture, Sports, Science and Technology, Japan. Thanks are due to the Instrumental Analysis Center, Faculty of Engineering, Osaka University.

Supporting Information Available: Characterization data of all new compounds and an ORTEP diagram and X-ray structure data for **3h**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO025707D