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N-Carbonylation of Lithium Azaenolates of Amides, Formamides, Ureas, and Carbamates with Carbon Monoxide Mediated by Selenium

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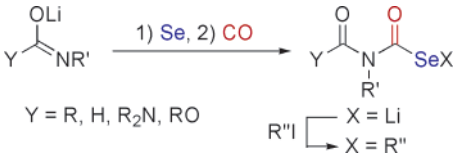
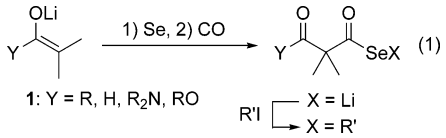
Received August 1, 2006



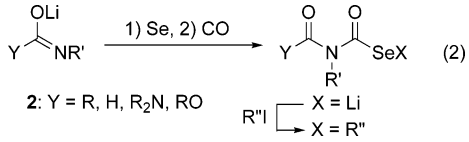
N-Carbonylation of less nucleophilic nitrogen compounds was achieved by the reaction of the lithium azaenolates with carbon monoxide and selenium. This reaction proceeds in the cases of amides, formamides, ureas, and carbamates, leading to the formation of the corresponding carbamoselenoates in good to high yields after trapping with BuI.

The use of carbon monoxide for the *N*-carbonylation of nitrogen nucleophiles is an important transformation in organic synthesis.[1] However, *N*-carbonylation of less nucleophilic nitrogen compounds such as amides,[2] ureas,[3] and carbamates[4] is not an easy process. We already disclosed that selenium exhibited extremely high activity in the carbonylation of amines with carbon monoxide (Scheme 1);[5−8] however, these processes cannot be applied to carbonylation of less nucleophilic nitrogen compounds.

Recently, we have found an effective method for carbonylation of ketones,[9] aldehydes,[9] amides,[10] and esters[10] by the reaction of the corresponding lithium enolates **1** with carbon monoxide and selenium (eq 1).



In addition, we have already succeeded in carbonylation of hydrocarbons, which have pK_a values ranging from 18 to 31.5.[11] These successful results prompted us to examine *N*-carbonylation of lithium azaenolates of less nucleophilic nitrogen compounds for the following reasons: (1) lithium azaenolates **2** of amides, formamides, ureas, and carbamates have structures similar to those of lithium enolates **1** of ketones, aldehydes, amides, and esters, respectively; and (2) pK_a values of these nitrogen compounds may be in the range from 18 to 31.5.[12,13] Here we describe the first examples of *N*-carbonylation of lithium azaenolates with carbon monoxide mediated by selenium (eq 2).



We first examined *N*-carbonylation of lithium azaenolates of amides. When a lithium azaenolate of *N*-methylacetamide **3a**, generated by deprotonation of **3a** with LDA in the presence of HMPA, was allowed to react with selenium at −78 °C and then with CO (1 atm) at 20 °C, a stoichiometric amount of CO was absorbed within 1 h. Addition of BuI and usual workup followed by purification by column chromatography on silica gel using Et_2O gave 62% yield of carbamoselenoate **4a** in pure

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(12) For example, pK_a values of acetamide ($CH_3C(O)NH_2$), formamide ($HC(O)NH_2$), urea ($H_2NC(O)NH_2$), and *O*-ethylcarbamate ($EtOC(O)NH_2$) in DMSO are 25.5 (ref 13a), 23.5 (ref 13a), 26.9 (ref 13b), and 24.2 (ref 13c), respectively.

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10.1021/jo0615908 CCC: $37.00
Published on Web 12/09/2006

SCHEME 1. Selenium-Assisted Carbonylation of Amines

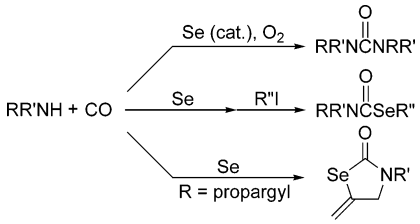
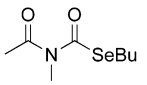
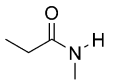
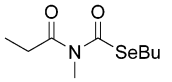
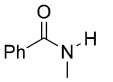
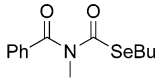
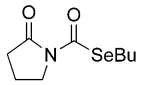
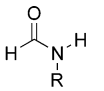
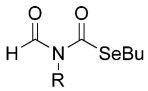


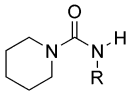
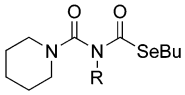
TABLE 1. *N*-Carbonylation of Amides and Formamides[a]

run	amide		carbamoselenoate		isolated yield (%)[b]
1		**3a**		**4a**	62(77)
2					(81)[c]
3					(72)[d]
4					(0)[e]
5		**3b**		**4b**	68
6		**3c**		**4c**	56
7		**3d**		**4d**	82
8					
	5a: R = Me			**6a**	66
9	**5b**: R = Bu			**6b**	88
10	**5c**: R = allyl			**6c**	73
11[f]	**5d**: R = *trans*-3-pentenyl			**6d**	72
12	**5e**: R = cyclohexyl			**6e**	76
13	**5f**: R = *t*-Bu			**6f**	19

[a] Conditions: **3** or **5** (2.0 mmol), Se (2.0 mmol), LDA (2.2 mmol), HMPA (6.0 mmol), THF (25 mL), −78 °C, 30 min, then 20 °C, 30 min; CO (1 atm), 20 °C, 1 h; BuI (4.0 mmol), 20 °C, 30 min. [b] Yields in parentheses are NMR yields. [c] At 0 °C. [d] At −23 °C. [e] At −78 °C. [f] At 13.5 mmol scale.

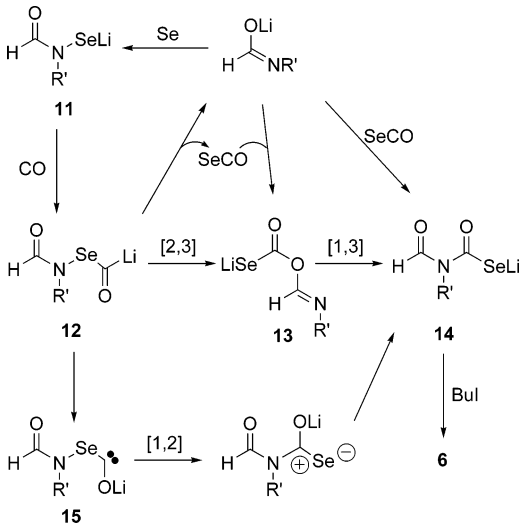
form (run 1 in Table 1). In the absence of HMPA, **4a** was not obtained. Carbonylation at 0 and −23 °C also afforded the product in high yields; however, carbonylation at −78 °C did not proceed (runs 2−4). *N*-Methylpropionamide (**3b**), *N*-methylbenzamide (**3c**), and pyrrolidone (**3d**) afforded the carbonylated products (runs 5−7). However, acetamide, an unprotected amide, gave the desired product **4e** only in 5% yield due probably to decomposition of the intermediary lithium carbamoselenoate. The effect of the substituent at the nitrogen atom was then examined by the use of a variety of formamides, and the results are also summarized in Table 1. Formamides having a primary or secondary alkyl group, **5a**−**e**, gave the products in good to high yields (runs 8−12). However, introduction of a tertiary alkyl group on the nitrogen reduced the rate of CO absorption (run 13). Carbonylation did not proceed when phenyl-substituted formamide was used, due probably to its low nucleophilicity.

TABLE 2. *N*-Carbonylation of Ureas[a]

run	substrate	R	time (h)	product	isolated yield (%)
					
1	**7a**	Bu	1.5	**8a**	86
2	**7b**	Me	1	**8b**	82
3	**7c**	allyl	2	**8c**	78
4	**7d**	cyclohexyl	2	**8d**	83
5	**7e**	*t*-Bu	2	**8e**	40(62[b])
6	**7f**	Ph	2	**8f**	48(56[b])

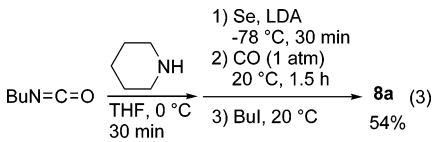
[a] Conditions: **7** (2.0 mmol), LDA (2.3 mmol), Se (2.1 mmol), THF (25 mL), −78 °C, 30 min; CO (1 atm), 0 °C, time; BuI (4.0 mmol), 0 °C to rt, 30 min. [b] In the presence of HMPA (6 mmol).

SCHEME 2. Plausible Reaction Pathways



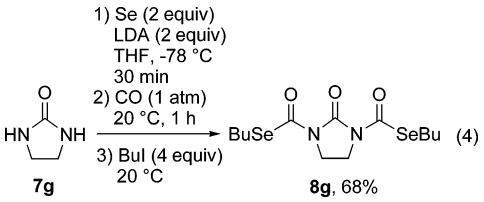
N-Carbonylation of ureas was then examined and was found to proceed well under similar conditions without HMPA. Representative results are shown in Table 2. Ureas **7a**−**d** having a butyl, methyl, allyl, or cyclohexyl group on the nitrogen atom afforded expected products **8a**−**d** in high yields. When R was a tertiary alkyl or an aryl group, the yields of carbonylation products dropped probably due to the same reasons described above. However, addition of 3 equiv of HMPA improved the yields (runs 5 and 6).

Since ureas employed in this study were prepared by the reaction of piperidine with the corresponding isocyanates, we then examined one-pot carbonylation starting from piperidine and butyl isocyanate, and the expected product **8a** was obtained in 54% yield (eq 3).

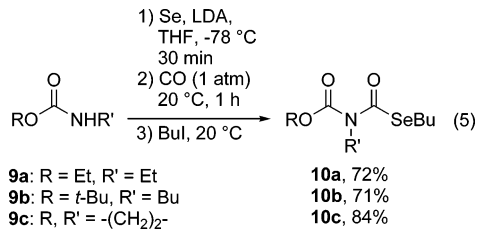


Interestingly, carbonylation of imidazolidine (**7g**) gave dicarbonylated product **8g** in 40% yield under similar conditions without the monocarbonylated product. Thus, by the use of 2

equiv of Se and LDA, the yield of **8g** was improved up to 68% (eq 4).



N-Carbonylation of carbamates also proceeded efficiently without HMPA. As shown in eq 5, *N*-ethyl *O*-ethylurethane (**9a**), *N*-butyl *O*-*tert*-butylurethane (**9b**), and oxazolidine-2-one (**9c**) were carbonylated to give the expected products **10a**−**c** in high yields.



N-Carbonylation of lithium azaenolates may proceed through a similar mechanism we already proposed for carbonylation of lithium enolates.[9] Plausible pathways exemplified by carbonylation of azaenolate of formamide are depicted in Scheme 2. Reaction of azaenolate with selenium affords selenolate **11**, which then reacts with carbon monoxide to give lithium selenocarbonate **13**, probably via formal rearrangement of **12**. HMPA may enhance the nucleophilicity of azaenolate to react with selenium and/or that of selenolate **11** to react with carbon monoxide. Unlike the case of lithium enolates of aldehydes, alkylation products of **13** were not obtained at all even when carbonylation and trapping were performed at lower temperatures. This result indicates that [1,3]-rearrangement of **13** to lithium carbamoselenoate **14** proceeds very fast or that the nitrogen atom of lithium azaenolate attacks the central carbon of carbonyl selenide to produce **14** directly. Finally, product **6** is obtained by trapping **14** with BuI. As for the formation of carbamoselenoate **14** from **12**, a path involving lithoxycarbene **15** as an intermediate may also be possible.

In conclusion, *N*-carbonylation of less nucleophilic nitrogen compounds such as amides, formamides, ureas, and carbamates was attained by the reaction of the corresponding lithium azaenolates with selenium and carbon monoxide.

Experimental Section

THF was distilled from sodium benzophenone ketyl. Diisopropylamine and BuI were distilled from CaH_2. BuLi and Se were used as purchased. HMPA was fractionally distilled and dried over CaH_2. Formamides **5a**−**f** were prepared from the corresponding amines and ethyl formate. Ureas **7a**−**f** were prepared from the corresponding isocyanates and piperidine.

***Se*-Butyl Acetylmethylcarbamoselenoate (4a): Typical Procedure for Carbonylation of Amides and Formamides.** To a THF (20 mL) solution of LDA, prepared from BuLi (1.60 M in hexane, 1.4 mL, 2.2 mmol) and diisopropylamine (2.2 mmol) at −78 °C, were added elemental selenium (2.0 mmol) and HMPA (6 mmol) at −78 °C under argon. A black suspension was obtained within 30 min at the same temperature. To the suspension was added dropwise *N*-methylacetamide (**2a**, 2.0 mmol) in THF (5 mL) over 10 min, and stirring was continued for an additional 20 min. The mixture temperature was then increased to 20 °C, and argon was replaced with carbon monoxide. A clear black solution was obtained within 1 h, and BuI (4.0 mmol) was added and stirring was continued for an additional 30 min. Aqueous saturated NH_4Cl solution (100 mL) was added, and the product was extracted with Et_2O (50 mL). After the organic layer was dried over $MgSO_4$, evaporation of the solvent gave a brown residue. Purification by column chromatography on silica gel using Et_2O yielded 62% of **4a** as a brown oil: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 3 H), 1.42 (sext, J = 7.3 Hz, 2 H), 1.69 (quint, J = 7.3 Hz, 2 H), 2.40 (s, 3 H), 2.86 (t, J = 7.3 Hz, 2 H), 3.29 (s, 3 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.6, 23.2, 25.8, 26.8, 31.8, 32.2, 169.6, 172.2. Anal. Calcd for $C_8H_{15}NO_2Se$: C, 40.68; H, 6.41; N, 5.93. Found: C, 40.86; H, 6.54; N, 5.82.

***Se*-Butyl Methylpropionylcarbamoselenoate (4b):** ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 3 H), 1.18 (t, J = 7.3 Hz, 3 H), 1.42 (sext, J = 7.3 Hz, 2 H), 1.68 (quint, J = 7.3 Hz, 2 H), 2.66 (q, J = 7.3 Hz, 2 H), 2.84 (t, J = 7.3 Hz, 2 H), 3.29 (s, 3 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 8.53, 13.6, 23.2, 26.6, 30.7, 31.8, 31.9, 169.5, 175.9. Anal. Calcd for $C_9H_{17}NO_2Se$: C, 43.20; H, 6.86; N, 5.60. Found: C, 43.13; H, 6.93; N, 5.59.

***Se*-Butyl Benzoylmethylcarbamoselenoate (4c):** mp 62.5−64.0 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 3 H), 1.43 (sext, J = 7.3 Hz, 2 H), 1.70 (quint, J = 7.3 Hz, 2 H), 2.88 (t, J = 7.3 Hz, 2 H), 3.29 (s, 3 H), 7.43−7.56 (m, 5 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.6, 23.2, 26.4, 31.9, 35.7, 127.8, 128.6, 131.7, 134.7, 169.7, 173.1. Anal. Calcd for $C_{13}H_{17}NO_2Se$: C, 52.34; H, 5.76; N, 4.70. Found: C, 52.29; H, 5.84; N, 4.56.

***Se*-Butyl 2-Oxopyrrolidine-1-carboselenoate (4d):** ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.92 (t, J = 7.3 Hz, 3 H), 1.42 (sext, J = 7.3 Hz, 2 H), 1.68 (quint, J = 7.3 Hz, 2 H), 2.10 (quint, J = 7.3 Hz, 2 H), 2.61 (t, J = 7.3 Hz, 2 H), 2.87 (t, J = 7.3 Hz, 2 H), 3.89 (t, J = 7.3 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.6, 17.6, 23.2, 24.5, 32.0, 33.0, 46.4, 166.4, 175.6. Anal. Calcd for $C_9H_{15}NO_2Se$: C, 43.55; H, 6.10; N, 5.64. Found: C, 43.52; H, 6.22; N, 5.55.

***Se*-Butyl Acetylcarbamoselenoate (4e):** mp 106.0−108.0 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 3 H), 1.42 (sext, J = 7.3 Hz, 2 H), 1.70 (quint, J = 7.3 Hz, 2 H), 2.24 (s, 3 H), 2.68 (t, J = 7.3 Hz, 2 H), 9.64 (s, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.6, 23.1, 24.2, 25.4, 32.0, 169.5, 170.4. Anal. Calcd for $C_9H_{13}NO_2Se$: C, 37.85; H, 5.90; N, 6.31. Found: C, 37.84; H, 6.04; N, 6.38.

***Se*-Butyl Formylmethylcarbamoselenoate (6a):** ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.95 (t, J = 7.3 Hz, 3 H), 1.44 (sext, J = 7.3 Hz, 2 H), 1.74 (quint, J = 7.3 Hz, 2 H), 3.06 (t, J = 7.3 Hz, 2 H), 3.18 (s, 3 H), 9.20 (s, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.5, 23.0, 27.4, 28.3, 32.2, 161.4, 170.1. Anal. Calcd for $C_7H_{13}NO_2Se$: C, 37.84; H, 5.91; N, 6.31. Found: C, 37.98; H, 6.05; N, 6.46.

***Se*-Butyl Butylformylcarbamoselenoate (6b):** ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.94 (t, J = 7.3 Hz, 3 H), 0.95 (t, J = 7.3 Hz, 3 H), 1.34 (sext, J = 7.3 Hz, 2 H), 1.43 (sext, J = 7.3 Hz, 2 H), 1.59 (quint, J = 7.3 Hz, 2 H), 1.73 (quint, J = 7.3 Hz, 2 H), 3.06 (t, J = 7.3 Hz, 2 H), 3.68 (t, J = 7.3 Hz, 2 H), 9.15 (s, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.5, 13.7, 20.1, 23.0, 27.2, 30.6, 32.2, 42.5, 161.7, 169.3. Anal. Calcd for $C_{10}H_{19}NO_2Se$: C, 45.45; H, 7.26; N, 5.30. Found: C, 45.31; H, 7.46; N, 5.42.

***Se*-Butyl Allylformylcarbamoselenoate (6c):** ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.94 (t, J = 7.3 Hz, 3 H), 1.43 (sext, J = 7.3 Hz, 2 H), 1.73 (quint, J = 7.3 Hz, 2 H), 3.07 (t, J = 7.3 Hz, 2 H), 4.32 (d, J = 5.6 Hz, 2 H), 5.21 (dd, J = 10.3, 2.7 Hz, 1 H), 5.23 (dd, J = 17.1, 2.7 Hz, 1 H), 5.80 (ddt, J = 17.1, 10.3, 5.6 Hz, 1 H), 9.19 (s, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.5, 23.0, 27.3, 32.3, 44.5, 118.2, 131.3, 161.3, 169.2. Anal. Calcd for $C_9H_{15}NO_2Se$: C, 43.55; H, 6.10; N, 5.64. Found: C, 43.67; H, 6.23; N, 5.79.

***Se*-Butyl Formyl-*trans*-3-pentenylcarbamoselenoate (6d):** ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.94 (t, J = 7.3 Hz, 3 H), 1.43 (sext,

J = 7.3 Hz, 2 H), 1.64 (d, J = 6.2 Hz, 3 H), 1.73 (quint, J = 7.3 Hz, 2 H), 2.27 (dt, J = 7.3, 6.8 Hz, 2 H), 3.36 (t, J = 7.3 Hz, 2 H), 3.70 (t, J = 7.3 Hz, 2 H), 5.33 (dt, J = 15.3, 6.8 Hz, 1 H), 5.48 (dq, J = 15.3, 6.2 Hz, 1 H), 9.13 (s, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.5, 17.9, 23.0, 27.2, 31.6, 32.3, 42.4, 126.5, 128.4, 161.6, 169.1. Anal. Calcd for $C_{11}H_{19}NO_2Se$: C, 47.82; H, 6.95; N, 5.07. Found: C, 47.83; H, 7.01; N, 4.91.

***Se*-Butyl Cyclohexylformylcarbamoselenoate (6e):** ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.94 (t, J = 7.3 Hz, 3 H), 1.15−2.11 (m, 14 H), 3.00 (t, J = 7.3 Hz, 2 H), 4.13−4.22 (m, 1 H), 9.04 (s, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.6, 23.1, 25.1, 26.3, 27.2, 30.1, 32.1, 56.4, 162.8, 168.5. Anal. Calcd for $C_{12}H_{21}NO_2Se$: C, 49.65; H, 7.31; N, 4.83. Found: C, 49.37; H, 7.22; N, 4.72.

***Se*-Butyl *tert*-Butylformylcarbamoselenoate (6f):** ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 3 H), 1.42 (sext, J = 7.3 Hz, 2 H), 1.57 (s, 9 H), 1.68 (quint, J = 7.3 Hz, 2 H), 2.86 (t, J = 7.3 Hz, 2 H), 8.98 (s, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.6, 23.2, 26.6, 29.5, 31.7, 61.0, 163.7, 169.4. Anal. Calcd for $C_{10}H_{19}NO_2Se$: C, 45.45; H, 7.26; N, 5.30. Found: C, 45.51; H, 7.35; N, 5.45.

***Se*-Butyl Butyl(piperidine-1-carbonyl)selenocarbamate (8a): Typical Procedure for Carbonylation of Ureas and Carbamates.** To a THF (20 mL) solution of LDA, prepared from BuLi (1.60 M in hexane, 1.4 mL, 2.2 mmol) and diisopropylamine (2.2 mmol) at −78 °C, was added elemental selenium (2.0 mmol) at −78 °C under argon. A black suspension was obtained within 30 min at the same temperature. To the suspension was added dropwise *N*-butylpiperidylformamide (**7a**, 2.0 mmol) in THF (5 mL) over 10 min, and stirring was continued for an additional 20 min. The mixture was then warmed to 0 °C, and argon was replaced with carbon monoxide. A clear pale brown solution was obtained within 1.5 h, and BuI (4.0 mmol) was added and stirring was continued for an additional 30 min. Aqueous saturated NH_4Cl solution (100 mL) was added, and the product was extracted with Et_2O (2 × 50 mL). After the combined organic layer was dried over $MgSO_4$, evaporation of the solvent gave a brown residue. Purification by column chromatography on silica gel using *n*-hexane/Et_2O (4:1) yielded 86% of **8a** as a brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90−0.94 (m, 6 H), 1.32−1.43 (m, 4 H), 1.56−1.70 (m, 10 H), 2.92 (t, J = 7.2 Hz, 2 H), 3.45 (br s, 4 H), 3.57 (br s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 13.7, 20.1, 23.0, 24.2, 25.7, 26.7 ($^1J_{Se}$−C = 58.5 Hz), 30.9, 32.6, 46.5, 47.0, 154.5, 164.3 ($^1J_{Se}$−C = 136.5 Hz); HRMS (EI) calcd for $C_{15}H_{28}N_2O_2Se$ 348.1316, found 348.1324.

***Se*-Butyl Methyl(piperidine-1-carbonyl)selenocarbamate (8b):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, J = 7.3 Hz, 3 H), 1.40 (sext, J = 7.4 Hz, 2 H), 1.64−1.72 (m, 8 H), 2.92 (t, J = 7.3 Hz, 2 H), 3.12 (s, 3 H), 3.44 (br s, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 23.0, 24.2, 25.7, 26.7 ($^1J_{Se}$−C = 59.0 Hz), 32.6, 33.8, 46.6, 155.2, 165.3. Anal. Calcd for $C_{12}H_{22}N_2O_2Se$: C, 47.21; H, 7.26; N, 9.18. Found: C, 47.48; H, 7.20; N, 9.19.

***Se*-Butyl Allyl(piperidine-1-carbonyl)selenocarbamate (8c):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, J = 7.3 Hz, 3 H), 1.40 (sext, J = 7.1 Hz, 2 H), 1.63−1.72 (m, 8 H), 2.93 (t, J = 7.3 Hz, 2 H), 3.47 (br s, 4 H), 4.20 (d, J = 6.3 Hz, 2 H), 5.21 (d, J = 10.3 Hz, 1 H), 5.29 (d, J = 17.1 Hz, 1 H), 5.80−5.90 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 13.6, 13.7, 23.0, 24.2, 25.7, 26.8 ($^1J_{Se}$−C = 58.5 Hz), 32.6, 46.6, 49.4, 118.9, 131.96, 131.99, 154.2, 164.4. Anal. Calcd for $C_{14}H_{24}N_2O_2Se$: C, 50.75; H, 7.30; N, 8.46. Found: C, 50.74; H, 7.28; N, 8.56.

***Se*-Butyl Cyclohexyl(piperidine-1-carbonyl)selenocarbamate (8d):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, J = 7.3 Hz, 3 H), 1.12−1.92 (m, 22 H), 2.93 (t, J = 7.3 Hz, 2 H), 3.33 (br s, 2 H), 3.65 (br s, 0.5 H), 3.87 (br s, 0.5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 22.9, 24.1, 25.1, 25.5, 25.9, 26.5 ($^1J_{Se}$−C = 59.0 Hz), 30.8, 32.7, 46.2, 57.7, 152.9, 163.0. Anal. Calcd for $C_{17}H_{30}N_2O_2Se$: C, 54.68; H, 8.10; N, 7.50. Found: C, 55.06; H, 7.96; N, 7.62.

***Se*-Butyl *tert*-Butyl(piperidine-1-carbonyl)selenocarbamate (8e):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, J = 7.3 Hz, 3 H), 1.34−1.83 (m, 19 H), 2.88 (t, J = 7.4 Hz, 2 H), 3.49 (br s, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 23.1, 24.0, 24.9, 25.5, 26.8 (t, J = 59.5 Hz), 28.0, 32.6, 44.4, 48.1, 59.7, 153.5, 161.7 ($^1J_{Se}$−C = 59.5 Hz). Anal. Calcd for $C_{15}H_{28}N_2O_2Se$: C, 51.87; H, 8.12; N, 8.06. Found: C, 51.80; H, 8.08; N, 8.04.

***Se*-Butyl Phenyl(piperidine-1-carbonyl)selenocarbamate (8f):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J = 7.4 Hz, 3 H), 1.36 (sext, J = 7.4 Hz, 2 H), 1.59−1.70 (m, 8 H), 2.88 (t, J = 7.3 Hz, 2 H), 3.56 (br s, 4 H), 7.39−7.46 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 23.0, 24.2, 25.6, 27.4 ($^1J_{Se}$−C = 59.0 Hz), 32.4, 46.6, 128.8, 128.9, 128.9, 136.7, 152.7, 165.7. Anal. Calcd for $C_{17}H_{24}N_2O_2Se$: C, 55.58; H, 6.58; N, 7.63. Found: C, 55.82; H, 6.60; N, 7.63.

Di-*Se*-butyl 2-Oxoimidazolidine-1,3-dicarboselenoate (8g): Two equivalents of Se and LDA and 4 equiv of BuI were used; mp 102.0−104.0 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 6 H), 1.42 (sext, J = 7.3 Hz, 4 H), 1.70 (quint, J = 7.3 Hz, 4 H), 2.72 (t, J = 7.3 Hz, 4 H), 4.00 (s, 4 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.6, 23.1, 25.2, 31.9, 40.4, 152.3, 166.1; HRMS (EI) calcd for $C_{13}H_{22}N_2O_3Se_2$ 413.9977, found 413.9969.

Ethoxy-*N*-ethyl-*N*-(butylselenocarbonyl)formamide (10a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 3 H), 1.17 (t, J = 7.0 Hz, 3 H), 1.31−1.47 (m, 5 H), 1.68 (quint, J = 7.5 Hz, 2 H), 2.81 (t, J = 7.4 Hz, 2 H), 3.83 (q, J = 6.9 Hz, 2 H), 4.31 (q, J = 7.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 13.8, 14.3, 23.2, 26.1 ($^1J_{Se}$−C = 60.9 Hz), 31.8, 40.5, 62.9, 154.3, 167.8 ($^1J_{Se}$−C = 166.4 Hz). Anal. Calcd for $C_{10}H_{19}NO_3Se$: C, 42.86; H, 6.83; N, 5.00. Found: C, 43.14; H, 6.81; N, 5.13.

***tert*-Butoxy-*N*-butyl-*N*-(butylselenocarbonyl)formamide (10b):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, J = 7.2 Hz, 6 H), 1.29−1.68 (m, 17 H), 2.79 (t, J = 7.6 Hz, 2 H), 3.72 (t, J = 7.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 13.8, 20.0, 23.3, 26.0 ($^1J_{Se}$−C = 61.3 Hz), 28.1, 30.7, 31.8, 45.3, 83.5, 153.1, 167.8 ($^1J_{Se}$−C = 163.7 Hz); HRMS (EI) calcd for $C_{14}H_{27}NO_3Se$ 337.1156, found 337.1151.

***Se*-Butyl 2-Oxooxazolidine-3-carboselenoate (10c):** mp 62.5−64.0 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 3 H), 1.42 (sext, J = 7.3 Hz, 2 H), 1.69 (quint, J = 7.3 Hz, 2 H), 2.91 (t, J = 7.3 Hz, 2 H), 4.09 (t, J = 7.8 Hz, 2 H), 4.47 (t, J = 7.8 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.6, 23.1, 25.2, 32.0, 43.3, 62.8, 153.8, 162.2. Anal. Calcd for $C_8H_{13}NO_3Se$: C, 38.40; H, 5.25; N, 5.60. Found: C, 38.39; H, 5.32; N, 5.43.

Acknowledgment. This work was supported in part by a Grant-in-Aid from the Ministry of Education, Science, Sports and Culture, Japan.

Supporting Information Available: Characterization data of all new compounds (^{1}H and ^{13}C NMR, IR, MS, HRMS, or elemental analysis). This material is available free of charge via the Internet at http://pubs.acs.org.

JO0615908