Heteroatom Chemistry
Volume 6, Number 3, 1995

Reactions of Diselenoic Acid Esters with Amines and X-ray Crystal Structure Analyses of Aromatic Selenoamides

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Received 16 September 1994

ABSTRACT

Aromatic diselenoic acid Se-methyl esters **1** *react with amines at 0°C in tetrahydrofuran (THF) to yield selenoamides in moderate to good yields. The reaction course is highly dependent on the steric requirements of both starting materials. In the reactions of the ester* **1a** *with 2-methylpiperidine and of the ester* **1b** *with piperidine, the starting materials disappear within 1 hour with the liberation of black selenium, but the corresponding selenoamides are not produced. These results may be ascribed to the steric congestion caused by the formation of the selenoamide group from the tetrahedral intermediate* **15**. *X-ray crystal structure analyses of the selenoamides* **3** *and* **9** *have been performed. The bond length of C(Se)–N is shorter than a carbon nitrogen single bond. On the other hand, the C=Se bond is longer than that of the ordinary carbon–selenium double bond. These results are indicative of the efficient delocalization of the electrons of nitrogen to the carbon–selenium double bond. The double bond character between the carbon attached to selenium and the nitrogen is also supported by the nitrogen atom showing sp^2 character. When a methyl group is introduced at the meta position of the aromatic ring, the deviation of the aromatic ring from the plane involving the carbon–selenium double bond and nitrogen atom becomes substantially large, perhaps due to the steric bulkiness of the selenium atom.*

INTRODUCTION

The synthesis of compounds having a carbon–selenium double bond and their reactions have received increasing attention in recent years [1]. However, these compounds are generally unstable unless the carbon–selenium double bond is attached to a sterically bulky group providing kinetic protection or stabilized by a mesomeric effect with oxygen- or nitrogen-containing groups. Accordingly, the reactivity of the carbon–selenium double bond has been studied only in a limited number of cases. Very recently, we have succeeded in the synthesis of diselenoic acid esters **1** by the reaction of aluminum methylselenolate with selenoic acid *O*-esters and have reported that the aromatic derivatives are green oils and can be handled in the air [2], unlike the instability previously reported [3]. The esters **1** undergo a Diels–Alder reaction with cyclopentadiene similar to that of selenoaldehydes and selenoketones, and the coupling reactions of the esters **1** take place in the presence of copper, in analogy to the behavior of selenoamides [2]. The reactivity of the esters **1** toward nucleophiles is also of interest. Herein we report that the reaction of the esters **1** with amines occurs easily to form selenoamides and the yields are highly dependent on the steric requirements of both starting materials. In order to elucidate the steric conditions around the carbon–selenium double bond, X-ray crystallographic analyses of the aromatic selenoamides have been carried out.

RESULTS AND DISCUSSION

Initially, the reaction of the ester **1a** with pyrrolidine was carried out in tetrahydrofuran (THF) (run

Dedicated to Prof. Shigeru Oae on the occasion of his seventy-fifth birthday.

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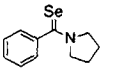
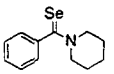
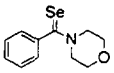
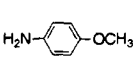
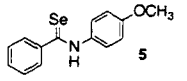
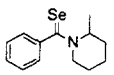
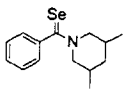
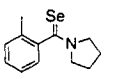
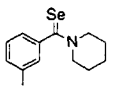
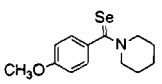
1042-7163/95/$5.00 + .25

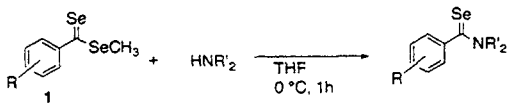
TABLE 1 Reaction of Diselenoic Acid Methyl Esters 1 with Amines[a]

Run	Ester	Amine	Selenoamide	Yield, %[b]
1	**1a**		 **2**	49
2	**1a**		 **3**	45
3	**1a**		 **4**	44
4	**1a**		 **5**	33
5	**1a**		 **6**	0
6	**1a**		 **7**	56
7	**1b**		 **8**	49
8	**1c**		 **9**	42
9	**1d**		 **10**	23

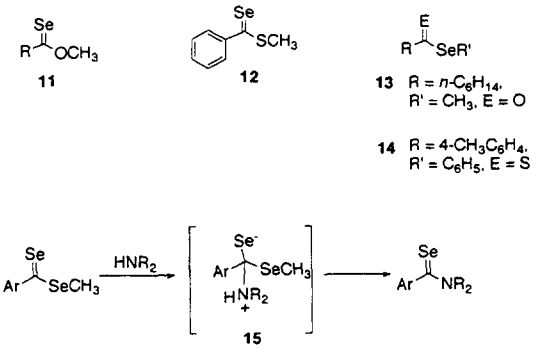
[a]The ester (1 mmol) was reacted with the amine (2 mmol) in THF at 0°C for 1 hour.
[b]Isolated yields.

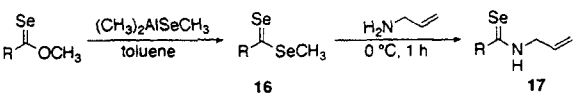
1, Table 1). The green reaction mixture turned yellow at 0°C within 1 hour, and the starting ester had been consumed, based on thin-layer chromatography (TLC) analysis. After column chromatography on silica gel using *n*-hexane as an eluent, selenoamide **2** was obtained in 49% yield. Similar reactions of esters **1** with a variety of amines were carried out. The results are summarized in Table 1. The reaction of the ester **1a** with a cyclic amines such as piperidine or morpholine was complete within 1 hour to give the corresponding selenoamides **3** and **4** in 45 and 44% yields (runs 2 and 3), respectively, as isolable products along with light yellow complex mixtures. When **1a** was treated with 4-methoxyaniline, the green color of **1a** disappeared within 1 hour to yield selenoamide **5** (run 4), whereas the reaction with acyclic secondary amines, such as *N*-methyl-4-methoxyaniline and diethylamine, proceeded only sluggishly and led to the recovery of the ester **1a**. The high reactivity of the ester **1a** toward primary amines and cyclic amines is in sharp contrast to the reactivity of esters **11**–**14**. As for the reactions of esters **11**, longer reaction times and higher reaction temperatures are necessary [4]. The attempted reaction of the ester **12** with piperidine at 0°C did not take place, and decomposition of **12** took place to a predominant degree at higher temperatures [5]. Although reactions of selenoesters **13** with cyclohexyamine have been reported to proceed at room temperature, $HgCl_2$ and $CaCO_3$ are necessary as additives [6]. The formation of thioamides from esters **14** requires the reaction to be carried out at 70°C [7,8].

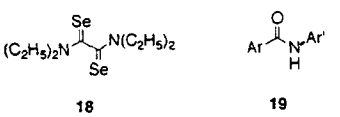
The comparison of the ^1H NMR spectra of **5** and benzanilide [9] supports the conclusion that **5** mainly exists in the *trans* form in analogy to benzanilide. However, 20% of the *cis* form of **5** was also observed.



1a R = H, **1b** R = 2-CH_3, **1c** R = 3-CH_3, **1d** R = 4-CH_3O







The reaction of **1a** with 2-methylpiperidine was complete within 1 hour with the liberation of black selenium, but the corresponding selenoamide **6** was not obtained (run 5), whereas the reaction of **1a** with 3,5-dimethylpiperidine afforded the selenoamide **7** in 56% yield (run 6). On the basis of the results of runs 1, 5, and 6, the nucleophilic attack of a cyclic amine at the carbon of the selenocarbonyl group takes place highly efficiently to form intermediate **15** (run 2), although the possibility that

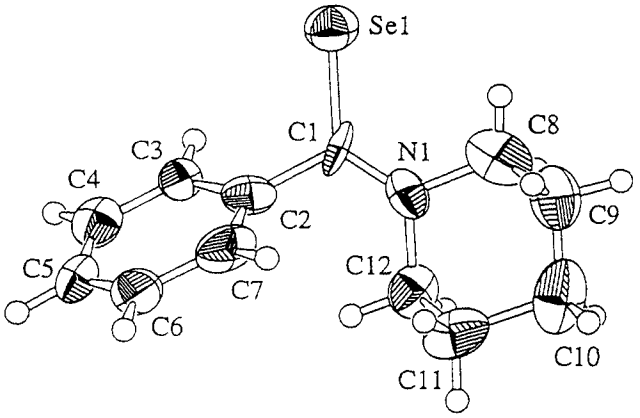


FIGURE 1 Molecular structure of 1-(phenylselenoxomethyl)piperidine (**3**).

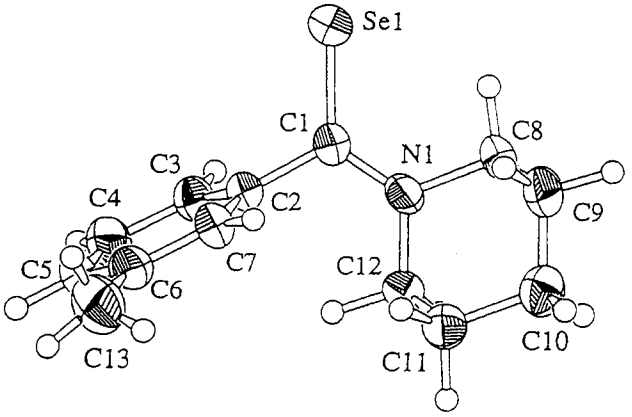


FIGURE 2 Molecular structure of 1-(3-methylphenylselenoxomethyl)piperidine (**9**).

selenophilic attack of the amines partly occurs cannot be excluded. In the second step leading to selenoamides, the formation of a carbon–selenium double bond and of a carbon–nitrogen single bond having double bond character from **15** may give rise to steric congestion around the selenoamide group. Accordingly, in the case of attack by 2-methylpiperidine, other processes to deposit selenium may become predominant to give only a complex mixture. The influence of the steric factor on the formation of selenoamides was further observed for the reactions of the ester **1b** with cyclic amines. Although the ester **1b** was completely consumed within 1 hour in reaction with 2-methylpiperidine, piperidine, and pyrrolidine, only the reaction with pyrrolidine was successful in affording the selenoamide **8** (run 7).

Diselenoesters having the substituent on a *meta* or *para* position were also reacted with amines. These substituents did not affect the reaction course (unlike the situation when the substituent is present on the *ortho* position) to yield selenoamides **9** and **10** (runs 8 and 9).

In contrast to the stability of aromatic diselenoesters, the aliphatic derivatives are easily susceptible to self-oligomerization. Thus, the reaction with amines was carried out with ester **16** formed in situ (run 3). The deep violet reaction mixture involving the ester **16** turned to light yellow when treated with allylamine and gave *N*-allyl selenoamide **17** in 30% yield.

The X-ray crystal structure analyses of selenoamides **3** and **9** were performed in order to evaluate the steric features around the selenoamide group. ORTEP drawings depicted in Figures 1 and 2 show molecular structures of the selenoamides **3** and **9**. The selected bond lengths, angles, and torsion angles are listed in Table 2. Similar to the structure of diselenoamide **18** [10], the bond lengths of C1–N1 in **3** and **9** are shorter than that of the normal carbon–nitrogen single bond, whereas the bond lengths of C1–Se1 are longer than that of the normal carbon–selenium double bond. These features have already been studied with benzanilides **19** [11] and have been explained by the partial double bond character in the C–N bond, owing to delocalization of the lone pair electrons on nitrogen to the C=O group [10,12]. This notion is applicable to the present cases. The facts that the sums of the three bond angles around the nitrogen atom are almost 360° and that Se, C1, N1, C2, and C8 atoms lie almost in the same plane further support the double bond character of the C–N bond.

The X-ray study of the selenoamide **3** indicated the torsion angle for N–C(=Se)–C–C to be 57°, which was substantially larger than that found for benzanilides **19**. This may be due to the steric repulsion between the bulky selenium atom and hydrogen at the *ortho* position of the aromatic ring. Furthermore, the large deviation (79°) of the aromatic ring from the plane involving the C=Se group was observed for the ester **9**. Steric congestion may exist between the methyl group at the *meta* position of aromatic ring and the methylene group adjacent to nitrogen. These results may be in accord with the difficulty of the formation of selenoamide from ester **1b** and piperidine, as described previously, and with the lack of examples of sterically crowded aromatic selenoamides [13].

In summary, the reaction of diselenoic acid methyl esters with primary amines and secondary cyclic amines was found to be complete within 1 hour to afford the corresponding selenoamides in moderate to good yields. The present reaction can serve as a new preparative method of selenoamides [14]. The high reactivity of the esters **1** is in sharp contrast to the inertness of their oxygen and sulfur counterparts toward amines under similar conditions. Nucleophilic attack of amines appears to take place predominantly at the carbon atom of the C=Se group, although the yields of selenoamides are affected by the steric requirements of both

TABLE 2 Selected Bond Distances (Å), Bond Angles (°), and Torsion Angles (°) of **3** and **9**

	Bond Distances		*Bond Angles*		*Torsion Angles*			
	3	**9**	**3**	**9**	**3**	**9**		
Se1–C1	1.83 (1)	1.811 (3)	Se1–Cl–N1	126 (1)	126.3 (2)	Se1–C1–N1–C8	2 (2)	5.1 (4)
C1–N1	1.22 (1)	1.318 (3)	Se1–C1–C2	115.0 (9)	117.5 (2)	Se1–C1–C2–C3	57 (1)	78.6 (3)
C1–C2	1.49 (2)	1.507 (4)	C1–N1–C8	123 (1)	122.5 (2)	N1–C1–C2–C3	−126 (1)	−102.6 (3)
N1–C8	1.45 (2)	1.496 (3)	C8–N1–C12	109 (1)	111.8 (2)	Se1–C1–N–C12	−174 (1)	−178.5 (2)
N1–C12	1.48 (2)	1.477 (3)	C1–N1–C12	125.6 (2)	126 (1)	Se1–C1–C2–C7	−115 (1)	−100.1 (3)
C2–C7	1.41 (2)	1.392 (4)	C1–C2–C7	120 (1)	119.5 (3)	N1–C1–C2–C7	60 (1)	78.7 (4)
C2–C3	1.40 (2)	1.386 (4)	C1–C2–C3	121 (1)	120.3 (3)			

esters **1** and amines. X-ray crystal structure analyses also disclosed the steric congestion around the selenoamide group.

EXPERIMENTAL

General

Melting points were measured by a Yanagimoto micromelting point apparatus and are uncorrected. The IR spectra were measured on a PERKIN-ELMER FT-IR 1640 instrument. The ^{1}H-NMR spectra were recorded on a JEOL JNM-GX-270 (270 MHz) instrument with tetramethylsilane as an internal standard, and the following abbreviations are used; s, singlet; t, triplet; q, quartet; and m, multiplet. The ^{13}C NMR spectra were obtained by use of a JEOL JNM-GX-270 (67.9 MHz) instrument. The mass spectra were recorded on a Shimadzu GCMS QP1000 (A) (EI/CI, model) mass spectrometer. The high resolution mass spectroscopy (HRMS) was taken on a Shimadzu GCMS 9020DF high resolution mass spectrometer.

The intensity data of X-ray crystal analyses were collected on a Rigaku AFC7R diffractometer, and the structures were solved by direct methods. All the nonhydrogen atoms were refined with anisotropic thermal parameters. Crystal and intensity data are summarized in Table 3. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $25.08° < 2\theta < 28.53°$ for **3**, $29.31 < 2\theta < 29.95°$ for **9**. The final coordinates are complied in Tables 4 (**3**) and 5 (**9**).

Further details of the crystal structure determination can be obtained from Crystallographic Data Centre, University Chemical Laboratory, Cambridge CB2 1EW, United Kingdom.

Typical Procedure for the Reaction of Diselenobenzoic Acid Methyl Ester (**1a**) *with an Amine.* In a 20 mL two-necked flask, diselenobenzoic acid methyl ester (**1a**) (0.26 g, 1.0 mmol) and THF (10 mL) were placed under an argon atmosphere. To this was added dropwise the amine (2.0 mmol) at 0°C. After having been stirred at 0°C for 1 hour, the reaction mixture was poured into water and extracted with ether (10 mL). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was chromatographed on a silica gel column using dichloromethane/hexane (1:1) as eluent to give the corresponding selenoamide as a yellow solid.

Spectral Properties of New Selenoamides

1-(Phenylselenoxomethyl)-4-methoxybenzeneamine (**5**). Mp 128–130°C; IR (KBr) 3143, 2989, 1654, 1610, 1508, 1464, 1446, 1361, 1303, 1249, 1214, 1179, 1110, 1039, 963, 945, 913, 823, 798, 776, 748, 689, 644, 600, 537, 510 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.82 (s, 3H, CH_3), 6.99 (d, J = 9.2 Hz, 2H, CH), 7.40 (t, J = 7.5 Hz, 2H, CH), 7.50 (t, J = 7.5 Hz, 2H, CH), 7.65 (d, J = 9.2 Hz, 2H, CH), 7.82 (d, J = 7.5 Hz, 2H, CH), 9.51 (br, 1H, NH); ^{13}C NMR ($CDCl_3$) δ 55.5, 114.3, 125.8, 126.6, 128.6, 131.1, 133.3, 146.2, 158.6, 203.9; CIMS (*m/e*) 212 [(M^+ + 1)–Se]; anal. calcd for $C_{14}H_{13}NOSe$: C, 57.92; H, 4.52. Found: C, 58.19; H, 4.51.

1-(Phenylselenoxomethyl)-3,5-dimethylpiperidine (**7**). Mp 152–154°C; IR (KBr) 2954, 1506, 1480, 1436, 1273, 1231, 1174, 1147, 1103, 1072, 1030, 973, 950, 933, 919, 894, 856, 763, 703, 684, 582, 486 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.76 (d, J = 6.6 Hz, 3H, CH_3), 0.95 (m, 1H, CH_2), 1.04 (d, J = 6.6 Hz, 3H, CH_3), 1.67–1.71 (m, 1H, CH_2), 1.90–2.01 (m, 2H, CH), 2.51 (t, J = 12.5 Hz, 1H, CH_2), 2.63 (t, J = 12.1 Hz, 1H, CH_2), 3.86–3.93 (m, 1H, CH_2), 5.79–5.84 (m, 1H, CH_2), 7.19–7.37 (m, 5H, Ar); ^{13}C NMR ($CDCl_3$) δ 18.3, 18.7, 30.8, 32.7, 41.7, 59.6, 59.8, 124.3, 128.1, 128.2, 146.0, 603.2; CIMS (*m/e*) 282 (M^+ + 1); anal. calcd for $C_{14}H_{19}NSe$: C, 59.98; H, 6.84. Found: C, 59.72; H, 4.93.

1-(2-Methylphenylselenoxomethyl)pyrrolidine (**8**). IR (neat) 2972, 2873, 1660, 1446, 1380, 1327, 1256, 1218, 1174, 1150, 1112, 1039, 983, 932, 918, 874, 830, 754, 724, 690, 642, 625 cm^{-1}; ^{1}H NMR

TABLE 3 Crystallographic Parameters of **3** and **9**

Selenoamide	**3**	**9**
Formula	$C_{12}H_{15}NSe$	$C_{13}H_{17}NSe$
Molecular weight	252.22	266.24
α (°)	90	101.78 (3)
β (°)	90	106.65 (3)
γ (°)	90	74.23 (3)
a (Å)	14.948 (2)	7.920 (3)
b (Å)	6.936 (4)	13.197 (4)
c (Å)	10.964 (1)	6.600 (2)
V (Å^3)	1136.7 (5)	630.1 (4)
Z	4	2
Space group	$P2_12_12_1$ (no. 19)	$P\bar{1}$ (no. 2)
F (000)	512.00	272.00
d_{calcd} (g/cm^3)	1.474	1.403
Crystal system	orthorombic	triclinic
Temperature (K)	296	296
Radiation	Mo K_α (λ = 0.71069)	Mo K_α (λ = 0.71069)
Crystal size (mm)	0.33 × 0.10 × 0.23	0.40 × 0.30 × 0.30
μ, (Mo K_α) (cm^{-1})	32.65	29.49
Scan mode	$\omega - 2\theta$	$\theta - 2\theta$
$2\theta_{max}$ (°)	55.0	55.0
No. of unique reflections	1546	2903
No. of observations ($I > 3.0\sigma(I)$)	741	2342
No. of variables	128	204
Largest residuals (e/Å^3)	0.58/−0.52	0.43/−0.62
R	0.056	0.032
R_w	0.060	0.024

TABLE 4 Final Fractional Atomic Coordinates for Non-H Atoms for Selenoamide **3**

Atom	*X*	*Y*	*Z*
Se1	−0.68596 (8)	−0.00149 (3)	−0.0131 (1)
N1	−0.8040 (6)	−0.307 (2)	0.036 (1)
C1	−0.7920 (8)	−0.145 (2)	−0.006 (1)
C2	−0.8716 (8)	−0.034 (2)	−0.048 (1)
C3	−0.8760 (8)	0.044 (2)	−0.166 (1)
C4	−0.9497 (10)	0.147 (2)	−0.204 (1)
C5	−1.0193 (10)	0.182 (2)	−0.126 (1)
C6	−1.0163 (9)	0.124 (2)	−0.008 (2)
C7	−0.9405 (9)	0.012 (3)	0.034 (1)
C8	−0.734 (1)	−0.422 (3)	0.092 (1)
C9	−0.760 (1)	−0.490 (4)	0.222 (1)
C10	−0.846 (1)	−0.597 (3)	0.225 (2)
C11	−0.9197 (10)	−0.471 (2)	0.156 (1)
C12	−0.8884 (10)	−0.418 (2)	0.034 (1)

TABLE 5 Final Fractional Atomic Coordinates for Non-H Atoms for Selenoamide **9**

Atom	*X*	*Y*	*Z*
Se1	0.84498 (5)	0.36304 (3)	0.39491 (6)
N1	0.4872 (3)	0.3492 (2)	0.3366 (4)
C1	0.6610	0.3128 (2)	0.4181 (4)
C2	0.7096 (4)	0.2190 (2)	0.5375 (5)
C3	0.7563 (4)	0.2331 (3)	0.7589 (5)
C4	0.8028 (5)	0.1441 (3)	0.8667 (5)
C5	0.8033 (5)	0.0446 (3)	0.7520 (6)
C6	0.7583 (4)	0.0288 (3)	0.5306 (6)
C7	0.7108 (4)	0.1176 (2)	0.4242 (5)
C8	0.4188 (4)	0.4343 (2)	0.1950 (5)
C9	0.3211 (5)	0.3885 (3)	−0.0236 (5)
C10	0.1682 (4)	0.3428 (3)	−0.0098 (5)
C11	0.2401 (4)	0.2605 (3)	0.1457 (5)
C12	0.3384 (4)	0.3090 (2)	0.3611 (5)
C13	0.7589 (5)	−0.0799 (3)	0.4045 (6)

($CDCl_3$) δ 1.97–2.16 (m, 4H, CH_2), 2.24 (s, 3H, CH_3), 2.96–3.20 (m, 2H, CH_2), 3.89–4.03 (m, 2H, CH_2), 7.09–7.22 (m, 4H, Ar); ^{13}C NMR ($CDCl_3$) δ 18.9, 24.5, 26.2, 53.4, 55.9, 123.7, 125.9, 128.0, 130.0, 146.3, 200.1; CIMS (*m/e*) 254 (M^+ + 1), 174 [(M^+ + 1)-Se]; anal. calcd for $C_{12}H_{15}NSe$: C, 57.15; H, 5.99. Found: C, 57.10; H, 6.01.

1-(3-Methylphenylselenoxomethyl)piperidine (**9**). Mp 88–89°C; IR (KBr) 2921, 1598, 1505, 1450, 1290, 1243, 1171, 1133, 1104, 1084, 1020, 1004, 907, 856, 826, 784, 700, 664, 586, 472 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.56–1.61 (m, 2H, CH_2), 1.76–1.79 (m, 2H, CH_2), 1.86–1.99 (m, 2H, CH_2), 2.34 (s, 3H, CH_3), 3.50 (brs, 2H, CH_2), 4.49 (brs, 2H, CH_2), 6.99–7.28 (m, 4H, Ar); ^{13}C NMR ($CDCl_3$) δ 21.3, 23.9, 25.5, 26.7, 53.8, 54.9, 121.2, 125.0, 128.0, 129.0, 138.0, 146.0, 203.5; CIMS (*m/e*) 268 (M^+ + 1). Crystallization of selenoamide **9**: the small amount of the solid **9** was

dissolved in ether (1 mL), and poured into a test tube. Then hexane (3 mL) was added slowly to this tube and the solution was kept in the refrigerator for 7 days.

Reaction of Pentanediselenoic Acid Methyl Ester (**16**) *with Allylamine*

In a 10 mL two-necked flask, selenium powder (0.24 g, 3.0 mmol) was placed. It was then heated in vacuo and subsequently cooled. To the resulting selenium was added Me_3Al (1.50 mL, 3.0 mmol, 2.0 M in toluene, Aldrich). After the mixture had been stirred at 110°C for 2 hours, selenopentanoic acid *O*-methyl ester (0.36 g, 2.0 mmol) was added, and the mixture was stirred at 0°C for 1.5 hours. To this was added allylamine (0.53 mL, 7.0 mmol) at 0°C. After having been stirred at 0°C for 1 hour, the reaction mixture was poured into water. The organic layer was extracted with ether (10 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed on a silica gel column using dichloromethane/hexane (1:1) as eluent to give 0.120 (30%) of **17** as a pale yellow oil: IR (neat) 3190, 3042, 2958, 2872, 1645, 1538, 1402, 1317, 1274, 1204, 1160, 1078, 990, 928, 868, 732, 617, 564 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 3H, CH_3), 1.38 (sextet, J = 7.3 Hz, 2H, CH_2), 1.79 (quintet, J = 7.3 Hz, 2H, CH_2), 2.78 (t, J = 7.3 Hz, 2H, CH_2), 4.36 (m, 2H, CH_2), 5.27–5.36 (m, 2H, CH_2), 5.89–6.03 (m, 1H, CH), 8.21 (br, 1H, NH); ^{13}C NMR ($CDCl_3$) δ 13.7, 21.9, 31.7, 50.7, 51.8, 119.7, 131.1, 221.3; CIMS (*m/e*) 206 ($M^+ + 1$), 126 [($M^+ + 1$)-Se]; anal. calcd for $C_8H_{15}NSe$: C, 47.06; H, 7.40. Found: C, 47.08; H, 7.43.

ACKNOWLEDGMENT

This work was supported by Grant-in-Aid for Scientific Research on Priority Area of Reactive Organometallics No. 05236102 and partially by Grant-in-Aid for Scientific Research provided from the Ministry of Education, Science and Culture, Japan.

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