Synthesis and Properties of Selenoiminium Salts Derived from Secondary Selenoamides

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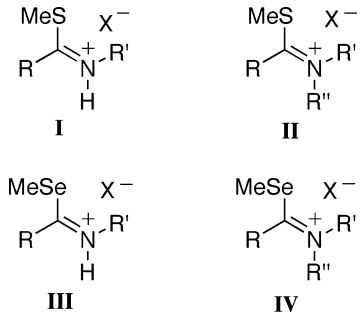
A variety of *N*-monosubstituted selenoiminium salts were obtained by reacting the corresponding secondary selenoamides with methyl triflate at room temperature for 30 s. All of the salts were stable under air below room temperature. The structures of the selenoiminium salts were determined by X-ray molecular analysis and compared with those of the starting selenoamide and its anionic derivative, i.e., an ammonium selenoimidate. Their benzene rings and selenoamide moieties were found to not be planar. ^{13}C and ^{77}Se NMR spectra of these compounds were also compared, and the results suggested that the electrons on the selenium atom of the salts are somewhat delocalized to the C═N double bond and the carbon−selenium bond of the salts shows a partial double-bond character. The degree of the delocalization of the electrons can be explained by considering the electron-donating ability of the selenium atom and the electron-accepting ability of the carbon−nitrogen bond. The reaction of the selenoiminium salt with several bases gave the corresponding methyl selenoimidate in high yield. Methylation of an ammonium selenoimidate also gave the methyl selenoimidate. The *Z*-isomer was predominantly formed in exactly the same ratio in these different reactions. The stereochemical outcome of the formation of a methyl thioimidate formed by two different reactions is also discussed.

Introduction

Thioiminium salts **I** and **II**, in which a sulfenyl group is attached to the carbon atom of an iminium salt, play important roles as key precursors in organic synthesis (Chart 1).[1] For example, in Eschenmoser coupling reactions, salts **II** are formed by the reaction of thioamides with α-halo acetic acid esters and ketones, and benzylic halides. Cyclization of *N*-monosubstituted salts **I** has led to 4*H*-indeno[2,1-*d*]thiazolium salts.[2b] These salts have also been applied to the synthesis of 1,2,4,3-triazophospholes.[2f] In ordinary experimental procedures, salts **I** and **II** have been generated in situ and are used without isolation. To the best of our knowledge, there has been no previous structural elucidation of salts **I**.

Chart 1



Meanwhile, increasing attention has been paid to the chemistry of selenocarbonyl compounds.[3] In particular, the development of new synthetic methods for selenoamides and their reactions have been extensively studied.[4] During the course of our studies on the chemistry

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(1) For example, see: (a) Shiosaki, K. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 2, p 865. (b) Mukaiyama, T.; Yamaguchi, T.; Nohira, H. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 2107. (c) Mukaiyama, T.; Yamaguchi, T. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2005. (d) Yamaguchi, T.; Inomata, K.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 673. (e) Mathew, S. I.; Stansfield, F. *J. Chem. Soc., Perkin Trans. 1* **1974**, 540. (f) Okecha, S. A.; Stansfield, F. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1811. (g) Shiosaki, K.; Fels, G.; Rapoport, H. *J. Org. Chem.* **1981**, *46*, 3230. (h) Sundberg, R. J.; Walters, C. P.; Bloom, J. D. *J. Org. Chem.* **1981**, *46*, 3730. (i) Singh, P.; Barata, M. S.; Singh, H. *J. Chem. Res. (S)* **1985**, 204. (j) Takahata, H.; Yamabe, K.; Yamazaki, T. *Synthesis* **1986**, 1063. (k) Sauve, G.; Mansour, T. S.; Lachance, P.; Belleau, B. *Tetrahedron Lett.* **1988**, *29*, 2295. (l) Sauve, G.; Le Berre, N.; Zacharie, B. *Tetrahedron Lett.* **1988**, *29*, 2299. (m) Tomimaga, Y.; Matsuoka, Y.; Hayashida, H.; Kohra, S.; Hosomi, A. *Tetrahedron Lett.* **1988**, *29*, 5771. (n) Takahata, H.; Takahashi, K.; Wang, E.-C.; Yamazaki, T. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1211. (o) Heathcock, C. H.; Davidsen, S. K.; Mills, S. G.; Sanner, M. A. *J. Org. Chem.* **1992**, *57*, 2531. (p) Devine, P. N.; Meyers, A. I. *J. Am. Chem. Soc.* **1994**, *116*, 2633. (q) Marchand, P.; Fargeau-Bellassoued, M.-C.; Bellec, C.; Lhommet, G. *Synthesis* **1994**, 1118. (r) Mook, R. A., Jr.; Lackey, K.; Bennett, C. *Tetrahedron Lett.* **1995**, *36*, 3969. (s) Munchhof, M. J.; Meyers, A. I. *J. Am. Chem. Soc.* **1995**, *117*, 5399. (t) Smith, D. C.; Fuchs, P. L. *J. Org. Chem.* **1995**, *60*, 2692. (u) Sosnicki, J. G.; Liebscher, J. *Synlett* **1996**, 1117. (v) May, P. J.; Bradley, M.; Harrowven, D. C.; Pallin, D. *Tetrahedron Lett.* **2000**, *40*, 1627. (w) Murai, T.; Mutoh, Y.; Ohta, Y.; Murakami, M. *J. Am. Chem. Soc.* **2004**, *126*, 5968.

(2) For example, see: (a) Chosho, H.; Ichimura, K.; Ohta, M. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1670. (b) Reid, D. H.; Salmond, W. G. *J. Chem. Soc. (C), Org.* **1966**, *7*, 686. (c) Hartke, K. *Chem. Ber.* **1966**, *99*, 3163. (d) Jensen, K. A.; Nielsen, P. H. *Acta Chem. Scand.* **1966**, *20*, 597. (e) Kjellin, G.; Sandström, J. *Acta Chem. Scand.* **1972**, *27*, 209. (f) Haddad, M.; Dahan, F.; Legros, J.-P.; Lopez, L.; Boisdon, M.-T. Barrans, J. *J. Chem. Soc., Perkin Trans. 2* **1992**, 671.

(3) For reviews, see: (a) Back, T. G., Ed. *Organoselenium Chemistry: A Practical Approach*; Oxford University Press: U.K., 1999. (b) Wu, R.; Hernández, G.; Dunlap, R. B.; Odom, J. D.; Martinez, R. A.; Silks, L. A. *Trends Org. Chem.* **1998**, *7*, 105. (c) Litvinov, V. P. *Russ. Chem. Rev.* **1999**, *68*, 737. (d) Murai, T.; Kato, S. In *Topics in Current Chemistry*; Wirth, T., Ed.; Springer-Verlag: Berlin, 2000; Vol. 208, p 177.

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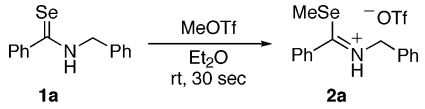
of thio- and selenoamides[5,6] we found that the methylation of selenoamides with methyl trifluoromethanesulfonate (methyl triflate) gave selenoiminium salts **IV** as stable compounds.[6] A molecular structure analysis of the salt **IV** (R = Ph, R′ = R″ = Me) was also performed. We further found that even *N*-monosubstituted selenoiminium salts **III** were isolated and could be stored under air. Although the first example of *N*,*N*-disubstituted salts **IV** was reported in 1966,[2d] no example of *N*-monosubstituted salts **III** has yet been reported. We report here the details of the synthesis, spectroscopic properties, and reaction of *N*-monosubstituted selenoiminium salts **III**. The molecular structures of a selenoamide, a selenoiminium salt, and a selenoimidate bearing identical carbon skeletons are also described.

Results and Discussion

Isolation of Selenoiminium Salts from Various Secondary Selenoamides. Initially, *N*-benzyl selenobenzamide **1a**[7] was reacted with methyl triflate (Scheme 1). Methyl triflate (1 equiv) was added to an

Scheme 1

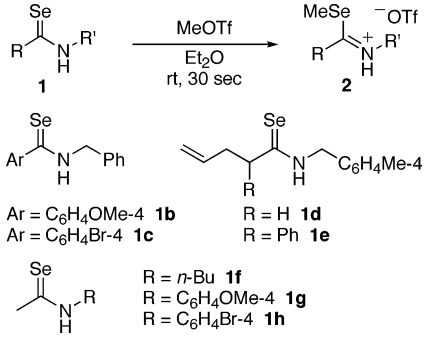


1a **2a**

Et_2O solution of selenoamide **1a** at room temperature. The homogeneous yellow solution immediately changed to a yellow suspension. After stirring for 30 s, a pale yellow solid was deposited. The solid was filtered through a glass filter (G4) and washed with Et_2O and hexane to give selenoiminium salt **2a** selectively as the *Z*-isomer with respect to the C=N double bond in 99% yield.[8]

The methylation of various secondary selenoamides **1** leading to selenoiminium salts **2** was then carried out

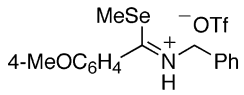
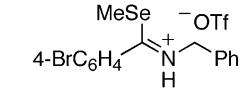
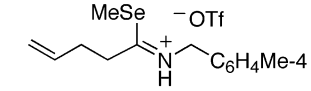
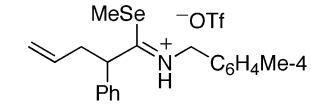
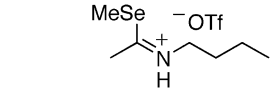
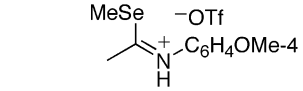
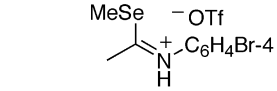
Scheme 2



1 **2**

(Scheme 2). The results are summarized in Table 1. The reaction of *N*-benzyl selenobenzamides with a methoxy group **1b**[7] and bromine **1c**[7] at the *para* position with methyl triflate was complete within 30 s to form the corresponding salts **2b** and **2c** in respective yields of 95 and 60% (entries 1 and 2). Although single stereoisomers of selenoamides **1b** and **1c** were used, stereoiso-

Table 1. Synthesis of Selenoiminium Salts 2[a]

entry	selenoamide **1** (*E* : *Z*)[b]	selenoiminium salt **2** yield[c] (*E* : *Z*)[b]
1	**1b** (0 : 100)	 **2b** 95% (2 : 98)
2	**1c** (0 : 100)	 **2c** 60% (8 : 92)
3	**1d** (0 : 100)	 **2d** 82% (3 : 97)
4	**1e** (0 : 100)	 **2e** 90% (4 : 96)
5	**1f** (5 : 95)	 **2f** 90% (1 : 99)
6	**1g** (64 : 36)	 **2g** 91% (4 : 96)
7[d]	**1h** (48: 52)	 **2h** 92% (6 : 94)

[a] The reaction was carried out as follows, unless otherwise noted. Selenoamide **1** was treated with methyl triflate (1 equiv) in Et_2O at room temperature for 30 s. [b]The ratio was determined by ^1H NMR in $CDCl_3$. [c]Isolated yield. [d]CH_2Cl_2 was used as a solvent.

(4) For recent examples: (a) Koketsu, M.; Kanoh, M.; Itoh, E.; Ishihara, H. *J. Org. Chem.* **2001**, *66*, 4099. (b) Koketsu, M.; Tanaka, Y.; Ishihara, H. *Synthesis* **2001**, 731. (c) Zhang, P.-F.; Chen, Z.-C. *J. Heterocycl. Chem.* **2001**, *38*, 503. (d) Koketsu, M.; Takenaka, Y.; Hiramatsu, S.; Ishihara, H. *Heterocycles* **2001**, *55*, 1181. (e) Bhattacharyya, P.; Woollins, J. D. *Tetrahedron Lett.* **2001**, *42*, 5949. (f) Ishihara, H.; Koketsu, M.; Fukuta, Y.; Nada, F. *J. Am. Chem. Soc.* **2001**, *123*, 8408. (g) Koketsu, M.; Okayama, Y.; Aoki, H.; Ishihara, H. *Heteroat. Chem.* **2002**, *13*, 195. (h) Zhao, H.-R.; Zhao, X.-J.; Huang, X. *Synth. Commun.* **2002**, *32*, 3383. (i) Huang, X.; Chen, J. *Synth. Commun.* **2003**, *33*, 2823. (j) Bethke, J.; Karaghiosoff, K.; Wessjohann, L. A.; *Tetrahedron Lett.* **2003**, *44*, 6911. (k) Saravanan, V.; Mukherjee, C.; Das, S.; Chandrasekaran, S. *Tetrahedron Lett.* **2004**, *45*, 681.

(5) (a) Murai, T.; Ezaka, T.; Niwa, N.; Kanda, T.; Kato, S. *Synlett* **1996**, 865. (b) Murai, T.; Ezaka, T.; Kanda, T.; Kato, S. *J. Chem. Soc., Chem. Commun.* **1996**, 1809. (c) Murai, T. Ezaka, T.; Ichimiya, T.; Kato, S. *Synlett* **1997**, 775. (d) Murai, T.; Mori, T.; Kato, S. *Synlett* **1998**, 619. (e) Murai, T.; Niwa, N.; Ezaka, T.; Kato, S. *J. Org. Chem.* **1998**, *63*, 374. (f) Murai, T.; Ezaka, T.; Kato, S. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1193. (g) Murai, T.; Ezaka, T.; Kato, S. *Tetrahedron Lett.* **1998**, *39*, 4329. (h) Murai, T.; Suzuki, A.; Ezaka, T.; Kato, S. *Org. Lett.* **2000**, *2*, 311. (i) Murai, T.; Mutoh, Y.; Kato, S. *Org. Lett.* **2001**, *3*, 1993. (j) Murai, T.; Suzuki, A.; Kato, S. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2711. (k) Murai, T.; Aso, H.; Kato, S. *Org. Lett.* **2002**, *4*, 1407. (l) Murai, T.; Ishizuka, M.; Suzuki, A.; Kato, S. *Tetrahedron Lett.* **2003**, *44*, 1343. (m) Murai, T.; Fujishima, A.; Iwamoto, C.; Kato, S. *J. Org. Chem.* **2003**, *68*, 7979. (n) Murai, T.; Aso, H.; Tatematsu, Y.; Itoh, Y.; Niwa, H.; Kato, S. *J. Org. Chem.* **2003**, *68*, 8514.

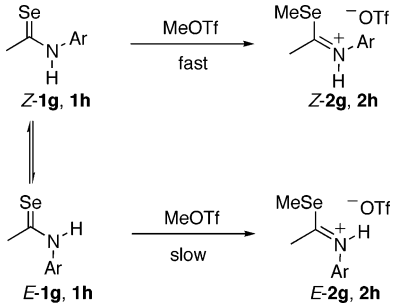
(6) Mutoh, Y.; Murai, T. *Org. Lett.* **2003**, *5*, 1361.

(7) Cohen, V. I. *J. Org. Chem.* **1977**, *42*, 2645.

(8) The stereochemistry was determined by phase-sensitive NOESY spectroscopy and X-ray molecular structure analysis.

mers **2b** and **2c** with respect to the C═N bond were also formed. The methylation of *N*-benzyl aliphatic selenoamides **1d**[5b,f] and **1e**[5b,f] also proceeded to give the corresponding salts **2d** and **2e** with *Z*-stereoselectivity in high yields (entries 3 and 4). *N*-Butyl selenoacetamide **1f**[5a] was converted to the corresponding salt **2f** in 90% yield (entry 5). The ratio of the *Z*-isomer of **2f** was greater than that of the starting selenoamide **1f**. Finally, methylation was applied to *N*-aryl selenoacetamides **1g**[5e] and **1h**,[5e] and the corresponding salts **2g** and **2h** were isolated in respective yields of greater than 90% (entries 6 and 7). Notably, regardless of the use of stereoisomeric mixtures of **1g** and **1h**, *Z*-isomers of the salts **2g** and **2h** were formed with high stereoselectivity.[9] Since interconversion of the two isomers of *N*-aryl selenoamides has been reported to occur at room temperature,[5e] methylation of the *Z*-isomers of **1g** and **1h** may proceed faster than that of the *E*-isomers (Scheme 3). All of the crude products **2** were washed

Scheme 3



with solvents such as hexane, Et_2O, and/or Et_2O/CH_2Cl_2 to give the salts **2** with purity higher than 95%. They were also stable and could be stored even under air at room temperature, but were thermally less stable.

The characteristic signals due to N−H protons of the *Z*-selenoiminium salts **2** were observed at around 12.6 ppm, which were shifted downfield by about 3.0 ppm compared to the corresponding signals of the starting selenoamides **1**. Furthermore, the signals of the *Z*-isomers of **2** (12.0−13.3 ppm) were observed downfield of those of the *E*-isomers (11.2−11.6 ppm). In the ^{77}Se NMR spectra, the signals of the *Z*-isomers of **2** (380−420 ppm) were observed upfield of those of the *E*-isomers (420−470 ppm).

X-ray Crystallography and Spectroscopic Properties. To elucidate the structural features of selenoiminium salts **2** in the solid state, an X-ray molecular structure analysis of **2a** was carried out. An ORTEP drawing of **2a** is shown in Figure 1. Typical bond lengths and angles and torsion angles are also shown in Table 2. The methyl group of the methylselenenyl (MeSe) group is located *cis* to the phenyl group with respect to

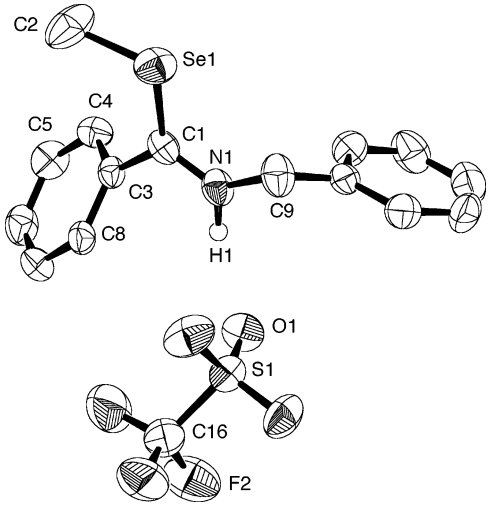


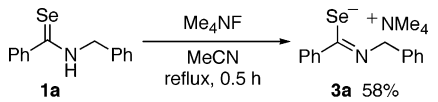
Figure 1. ORTEP drawing of selenoiminium salt **2a**. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) of Selenoiminium Salt 2a

Bond Lengths			
Se1−C1	1.857(4)	N1−C1	1.302(5)
Se1−C2	1.923(5)	N1−C9	1.467(5)
C1−C3	1.481(5)	N1···O1	2.920(4)
Bond Angles			
Se1−C1−N1	119.2(3)	N1−C1−C3	115.7(4)
Se1−C1−C3	125.0(3)	C1−N1−C9	127.8(4)
C1−Se1−C2	102.0(2)	N1−H1···O1	155.268.
Torsion Angles			
Se−C1−N1−C9	−4.5(5)	N1−C1−Se1−C2	179.0(3)
Se1−C1−C3−C8	−121.1(4)	C3−C1−N1−C9	178.2(3)

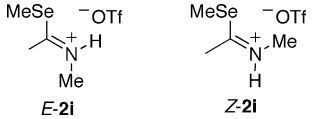
a C−Se single bond. A similar *cis* configuration was observed for the *N*,*N*-disubstituted selenoiminium salt derived from *N*,*N*-dimethyl selenobenzamide.[6] The intramolecular distance N1···O1 is 2.920(4) Å, which is shorter than the sum of the van der Waals radii[10] (3.70 Å) of both atoms, and the angle N1−H1···O1 is 155.3°. These results indicate that a hydrogen bond may be present between the hydrogen attached to the nitrogen atom and the oxygen atom of the triflate anion in **2a**. The torsion angle Se1−C1−N1−C9 in **2a** is −4.5(5)°, and these four atoms are located nearly in the same plane. In contrast, the torsion angle Se1−C1−C3−C8 in **2a** is −121.1(4)°, and the benzene ring deviates from the plane that is formed by the Se1, C1, and N1 atoms. X-ray molecular structure analyses of the starting selenoamide **1a**[5k−m,11] and ammonium selenoimidate **3a**[5k] derived from **1a** and tetramethylammonium fluoride (Scheme 4) were also carried out. The structures

Scheme 4



of **1a** and **3a** are illustrated in Figures 2 and 3, respectively. Typical bond lengths and angles and torsion angles of **1a** and **3a** are also shown in Tables 3 and 4. The *Z*-configurations of **1a** and **3a** with respect to a C−N single or C═N double bond were confirmed. The methylation of **1a** shown in Scheme 1 and deprotonation of **1a** shown in Scheme 4 were clearly shown

(9) To elucidate the predominant formation of *Z*-isomers of the salts **2**, molecular orbital calculations of two model compounds *E*-**2i** and *Z*-**2i** were carried out using the Gaussian 03 program at the B3LYP/LANL2DZ level. As a result, *Z*-**2i** was energetically more favorable than *E*-**2i** by about 2.2 kcal/mol: *E*-**2i**, −222.008082 au; *Z*-**2i**, −222.012381 au.



(10) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

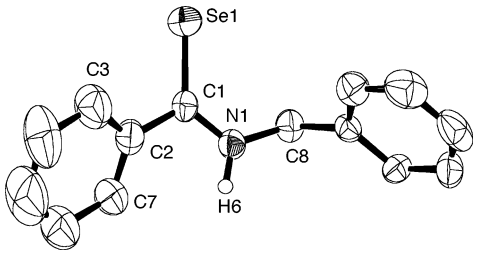


Figure 2. ORTEP drawing of selenoamide **1a**. Hydrogen atoms are omitted for clarity.

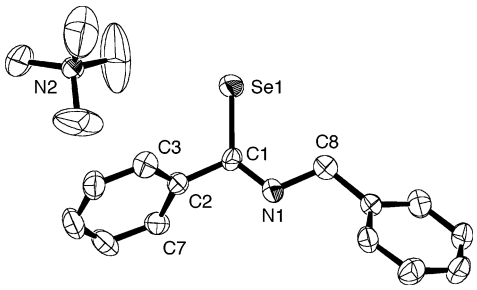


Figure 3. ORTEP drawing of ammonium selenoimidate **3a**. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) of Selenoamide 1a

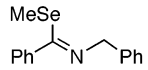
	Bond Lengths		
Se1−C1	1.815(5)	N1−C1	1.316(6)
C1−C2	1.473(8)	N1−C8	1.464(7)
	Bond Angles		
Se1−C1−C2	115.2(3)	N1−C1−C2	116.9(4)
Se1−C1−N1	127.9(4)	C1−N1−C8	117.0(4)
	Torsion Angles		
Se−C1−N1−C8	−4.0(8)	C2−C1−N1−C8	175.3(5)
Se1−C1−C2−C7	142.1(5)		

Table 4. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) of Ammonium Selenoimidate 3a

	Bond Lengths		
Se1−C1	1.893(5)	N1−C1	1.285(6)
C1−C2	1.492(6)	N1−C8	1.456(6)
	Bond Angles		
Se1−C1−C2	120.3(4)	N1−C1−C2	115.5(5)
Se1−C1−N1	124.2(4)	C1−N1−C8	125.7(5)
	Torsion Angles		
Se−C1−N1−C8	0.2(7)	C2−C1−N1−C8	178.8(4)
Se1−C1−C3−C7	112.8(4)		

to proceed with retention of configuration. It should be noted that the benzene rings in **1a** and **3a** also deviate from the plane formed by the Se1, C1, and N1 atoms, as in the case of **2a**. These results suggest that the benzene rings in **1a**, **2a**, and **3a** are almost not conjugated with a C=Se double bond or C=N double bond. The lengths of the Se1−C1 bond in **2a** (1.857(4) Å) and **3a** (1.893(5) Å) are longer than that in **1a** (1.815(5) Å),

Table 5. Typical Spectroscopic Data of Selected Selenoamides *Z*-1, Selenoiminium Salts *Z*-2, Ammonium Selenoimidate 3a, and Methyl Selenoimidate *Z*-6

compound	^{13}C NMR[a,b] [ppm]	^{77}Se NMR[a] [ppm]	$^{1}J_{C\text{-}Se}$[c] [Hz]
1a	204.0	618.6	210.1
1d	209.5	536.4	211.9
1e	211.6	567.0	214.5
1f	204.2	516.9	209.6
1g	207.8	622.0	206.7
2a	197.6	382.9	167.7
2d	200.7	383.9	166.7
2e	201.2	413.7	171.6
2f	196.6	390.7	162.3
2g	200.4	416.8	162.8
3a	180.5[d]	226.6[d]	179.9[d]
 **6**	164.2	262.9	138.9

[a] $CDCl_3$ was used as a solvent except for ammonium selenoimidate **3a**. [b]The signals of the carbon atom of selenocarbonyl or iminium groups are shown. [c]Coupling constants were determined by ^{13}C NMR. [d]CD_3CN was used as a solvent.

but still shorter than a typical C−Se single bond (1.94 Å[12]). This implies that the carbon−selenium bonds of **2a** and **3a** show a partial double-bond character.

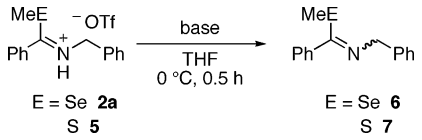
The spectroscopic properties of **2** in solutions were also compared with those of **1**, **3a**, and methyl selenoimidate **6**. The results are summarized in Table 5. In the ^{13}C NMR spectra, the signals of the carbon atom of the iminium group of **2** were shifted upfield by about 7 ppm compared to those of the carbon atom of the selenocarbonyl group of the corresponding selenoamides **1**. In the ^{77}Se NMR spectra, the signals of the selenium atoms of **2** were shifted upfield by about 130−235 ppm compared to those of the corresponding selenoamides **1**, but were still at a lower field than those of **6**. Furthermore, the coupling constants between the carbon and selenium atoms of **2** were greater than those of **6** and less than those of **1**. These NMR spectra suggest that the electrons on the selenium atom of **2** and **3a** are to some extent delocalized to the C=N double bond. On the basis of the coupling constants[13] between the carbon−selenium bonds of **1a**, **2a**, **3a**, and **6**, the degree of the delocalization of the electrons on the selenium atom was evaluated. To understand this tendency, the structures of **1a**, **2a**, **3a**, **6**, and their resonance forms are shown in Chart 2. The degree of delocalization appears to increase in the order **6** to **2a**, **3a**, and **1a′**. This tendency can be understood by considering the greater ability of the C=N groups of **1a′** and **2a** to accept electrons from the selenium atom compared with that of the C=N groups of **3a** and **6**. In addition, the electron-donating ability of the selenium atoms bearing the

(11) For the X-ray structure analysis of tertiary selenoamides, see: (a) Fischer, H.; Tiriliomis, A.; Gerbing, U.; Huber, B.; Müller, G. *J. Chem. Soc., Chem. Commun.* **1987**, 559. (b) Fischer, H.; Gerbing, U.; Tiriliomis, A.; Müller, G.; Huber, B.; Riede, J.; Hofmann, J.; Burger, P. *Chem. Ber.* **1988**, *121*, 2095. (c) Murai, T.; Mizutani, T.; Kanda, T.; Kato, S. *Heteroat. Chem.* **1995**, *6*, 241. (d) Otten, P. A.; Gorter, S.; Gen, A. *Chem. Ber. Recl.* **1997**, *130*, 49. (e) Li, G. M.; Zingaro, R. A.; Segi, M.; Reibenspies, J. H.; Nakajima, T. *Organometallics* **1997**, *16*, 756. (f) Blau, H.; Grobe, J.; Van, D. L.; Krebs, B.; Läge, M. *Chem. Ber. Recl.* **1997**, *130*, 913. (g) Niu, S.; Li, G. M.; Zingaro, R. A.; Reibenspies, J. H.; Ichiye, T. *Heteroat. Chem.* **2002**, *13*, 380.

(12) Pauling, L. *The Chemical Bond*; Cornell University Press: Ithaca, NY, 1976; p 135.

(13) (a) Duddeck, H. *Prog. Nucl. Magn. Reson. Spectrosc.* **1995**, *27*, 1. (b) Klapotke, T. M.; Broschag, M. *Compilation of Reported ^{77}Se NMR Chemical Shifts*; John Wiley & Sons: New York, 1996.

Table 6. Deprotonation of Seleno- 2a and Thio- 5 Iminium Salts[a]



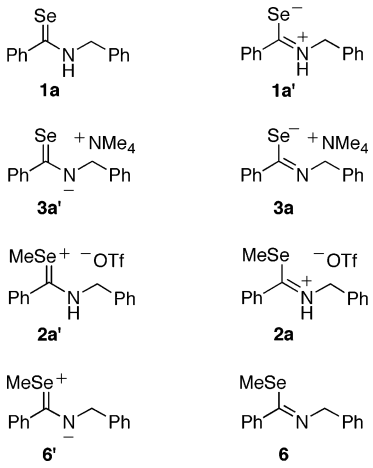
E = Se **2a** S **5** E = Se **6** S **7**

entry	E	base (equiv)	yield[b]	*E*:*Z*[c]
1	Se **2a**	*n*-Bu_4NF (1.5)	87%	15:85
2	Se	BuLi (1.2)	89%	15:85
3	Se	BuLi (1.0)	83%	15:85
4	Se	DIBALH (1.0)	88%	13:87
5	S **5**	*n*-Bu_4NF (1.5)	96%[d]	47:53

[a] The reaction was carried out as follows, unless otherwise noted. Selenoiminium salt **2a** was treated with an appropriate base (1 equiv) in Et_2O at room temperature for 0.5 h. [b]Isolated yield. [c]The ratio was determined by ^1H NMR in $CDCl_3$. [d]Crude yield.

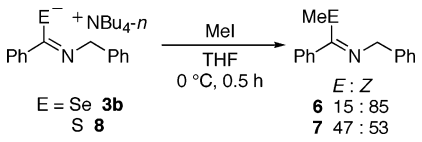
negative charge in **1a′** and **3a** is higher than that of the selenium atoms in **2a** and **6**.

Chart 2



Reactions. Finally, the deprotonation of *Z*-selenoiminium salt **2a** was examined with various bases. The results are shown in Table 6. Although the exclusive formation of the *Z*-isomer of **6** was expected, the *E*-isomer of **6** was also formed accompanied by the predominant formation of the *Z*-isomer of **6**. The ratio of these two isomers was not dependent on the bases used (entries 1−4). A similar reaction using a sulfur isologue of **2a**, i.e., thioiminium salt **5**, was carried out. Remarkably, the *Z*-isomer of **5** was converted to a stereoisomeric mixture of methyl thioimidate **7**[14] with a nearly equal ratio of stereoisomers (entry 5). As an alternative synthetic procedure, the methylation of *Z*-thio- **8** and *Z*-seleno- **3b** imidates was tested (Scheme

Scheme 5



E = Se **3b** S **8**

5). Methylation of the *Z*-isomers of **3b** and **8** resulted in the formation of two isomers of **6** and **7** in exactly the same ratio as that observed in Table 6. Thermodynamic factors may be more predominant than kinetic factors in the formation of **6** and **7**.

Conclusion

We have isolated a variety of selenoiminium salts with a hydrogen atom at the nitrogen atom. These selenoiminium salts were selectively obtained as *Z*-isomers. X-ray molecular structure analysis and ^{13}C and ^{77}Se NMR spectroscopy of these selenoiminium salts suggested that the electrons on the selenium atom of the salts are somewhat delocalized to the C═N double bond. The benzene rings in the selenobenzamide, the corresponding iminium salt, and imidate do not necessarily conjugate with their selenocarbonyl group and iminium group. In the deprotonation of the *Z*-selenoiminium salt with bases, the *Z*-isomer of the methyl selenoimidate was obtained as a major product, along with a small amount of *E*-isomer, whereas no stereoselectivity was observed for deprotonation of the *Z*-thioiminium salt.

Experimental Section

General Considerations. IR spectra were obtained on a JASCO FT/IR 410 spectrophotometer. ^1H (399.7 MHz), ^{13}C (100.4 MHz), ^{19}F (376.0 MHz), and ^{77}Se (76.2 MHz) NMR spectra were measured on a JEOL α-400 spectrometer. The ^1H and ^{13}C chemical shifts are reported in δ values with reference to Me_4Si or CD_3CN and $CDCl_3$ or CD_3CN as internal standards, respectively. The ^{19}F and ^{77}Se chemical shifts are expressed in δ values deshielded with respect to CF_3COOH and Me_2Se as external standards, respectively. All spectra were acquired in the proton-decoupled mode. Phase-sensitive NOESY spectra were measured with a Varian Inova 500 NMR spectrometer. Mass spectra (MS) were taken on a Shimadzu GCMS QP1000 (EI mode). Fast atom bombardment (FAB) mass spectra were measured on JEOL GC-mate II mass spectrometers. High-resolution mass spectra (HRMS) were measured on a JEOL JMS-700 spectrometer. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled from sodium/benzophenone ketyl prior to use. Acetonitrile (CH_3CN) and dichloromethane (CH_2Cl_2) were distilled over diphosphorus pentaoxide after refluxing for 5 h. Hexane was distilled from sodium metal. Anhydrous tetramethylammonium fluoride (Me_4NF) was obtained from the tetramethylammonium fluoride tetrahydrate by the removal of water under reduced pressure (150 °C/1.0 mmHg) with stirring for about 1 h.[15] Methyl trifluoromethanesulfonate (methyl triflate) was purchased from Aldrich Chemical Co., Inc., and used without further purification. Selenoamides **1** were prepared as described in the literature.[5,7]

General Procedure for the Synthesis of Selenoiminium Salts 2. A Representative Procedure for the Synthesis of [C(*Z*)]-*N*-(Phenylmethyl)benzenecarboximidoselenoic Acid Methyl Ester Trifluoromethanesulfonate (2a). To an Et_2O (7 mL) solution of selenoamide **1a** (0.274 g, 1.0 mmol) was added methyl triflate (0.115 mL, 1.0 mmol) at room temperature. After the mixture was stirred at this temperature for 30 s, the solvent was removed under reduced pressure and then washed with Et_2O and hexane to give selenoiminium salt **2a** (0.438 g, 99%) as a yellow solid: mp 109.0−112.0 °C; IR (KBr) 3192, 3066, 2967, 1717, 1700, 1685,

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1595, 1281, 1242, 1225, 1029, 638 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.27 (s, 3H, $SeCH_3$), 5.07 (s, 2H CH_2), 7.39−7.69 (m, 10H, Ar), 12.8 (br, s, 1H, NH); ^{13}C NMR ($CDCl_3$) δ 13.4 ($SeCH_3$), 54.9 (CH_2), 120.3 (q, $^1J_{C-F}$ = 318.9 Hz, CF_3), 128.5, 128.8, 129.2, 129.4, 129.9, 131.6, 132.0, 134.5 (Ar), 197.6 (CSe, $^1J_{C-SeMe}$ = 167.7 Hz); ^{19}F NMR ($CDCl_3$) δ −78.9; ^{77}Se NMR ($CDCl_3$) δ 382.9; MS (FAB+) *m*/*z* 290 (M^+ − OTf). Anal. Calcd for $C_{16}H_{16}F_3NO_3SSe$: C, 43.84; H, 3.68. Found: C, 43.85; H, 3.53.

[C(*Z*)]-*N*-(Phenylmethyl)-4-methoxybenzenecaboximidoselenoic Acid Methyl Ester Trifluoromethanesulfonate (2b). The crude product was washed with Et_2O/CH_2Cl_2 (80:1) to give **2b** as a yellow oil: IR (neat) 3159, 3068, 2938, 2847, 1601, 1508, 1264, 1224, 1175, 638 cm^{-1}; *Z*-isomer ^1H NMR ($CDCl_3$) δ 2.32 (s, 3H, $SeCH_3$), 3.89 (s, 3H, OCH_3), 5.08 (s, 1H, CH_2), 7.04 (d, *J* = 8.8 Hz, 2H, Ar), 7.31−7.44 (m, 5H, Ar), 7.55 (d, *J* = 8.8 Hz, 2H, Ar), 12.6 (br, 1H, NH); ^{13}C NMR ($CDCl_3$) δ 13.4 ($SeCH_3$), 54.6 (OCH_3), 55.8 (CH_2), 120.3 (q, $^1J_{C-F}$ = 319.5 Hz, CF_3), 115.4, 123.7, 128.6, 129.0, 129.3, 131.7, 132.7, 165.2 (Ar), 195.8 (CSe, $^1J_{C-SeMe}$ = 163.3 Hz); ^{19}F NMR ($CDCl_3$) δ −78.9; ^{77}Se NMR ($CDCl_3$) δ 355.4; *E*-isomer ^1H NMR ($CDCl_3$) δ 11.7 (br, 1H, NH); MS (FAB+) *m*/*z* 321 (M^+ + 1 − OTf); HRMS (FAB+) calcd for $C_{16}H_{18}NOSe$ 320.0554 (M^+ − OTf), found 320.0569.

[C(*Z*)]-*N*-(Phenylmethyl)-4-bromobenzenecaboximidoselenoic Acid Methyl Ester Trifluoromethanesulfonate (2c). The crude product was washed with Et_2O/CH_2Cl_2 (80:1) to give **2c** as an orange oil: IR (neat) 3151, 3088, 2920, 1583, 1278, 1240, 1163, 1029, 638 cm^{-1}; *Z*-isomer ^1H NMR ($CDCl_3$) δ 2.72 (s, 3H, $SeCH_3$), 5.03 (br, 2H CH_2), 7.63−7.45 (m, 7H, Ar), 7.70 (d, *J* = 8.4 Hz, 2H, Ar), 12.8 (br, 1H, NH); ^{13}C NMR ($CDCl_3$) δ 13.1 ($SeCH_3$), 55.1 (CH_2), 120.2 (q, $^1J_{C-F}$ = 319.0 Hz, CF_3), 128.8, 129.1, 129.4, 129.8, 130.0, 130.4, 131.8, 133.2 (Ar), 196.6 (CSe, $^1J_{C-SeMe}$ = 167.7 Hz); ^{19}F NMR ($CDCl_3$) δ −78.9; ^{77}Se NMR ($CDCl_3$) δ 381.7; *E*-isomer ^1H NMR ($CDCl_3$) δ 12.04 (br, 1H, NH); ^{77}Se NMR ($CDCl_3$) δ 451.0; MS (FAB+) *m*/*z* 368 (M^+ − OTf). Anal. Calcd for $C_{16}H_{15}BrF_3NO_3SSe\cdot 0.25Et_2O$: C, 38.11; H, 3.29; N, 2.61. Found: C, 38.39; H, 3.16; N, 2.81.

(1*Z*)-*N*-[(4-Methylphenyl)methyl]-4-pentenimidoselenoic Acid Methyl Ester Trifluoromethanesulfonate (2d). The crude product was washed with Et_2O/CH_2Cl_2 (80:1) to give **2d** as a pale yellow oil: IR (neat) 3215, 3124, 3010, 1606, 1517, 1439, 1281, 1240, 1162, 1030, 638 cm^{-1}; *Z*-isomer ^1H NMR ($CDCl_3$) δ 2.33 (s, 3H, $ArCH_3$), 2.42 (q, *J* = 7.3 Hz, 2H, CH_2), 2.63 (s, 3H, $SeCH_3$), 3.13(t, *J* = 7.2 Hz, 2H, CH_2), 4.72 (d, *J* = 4.4 Hz, 2H, NCH_2), 5.03 (s, 1H, C*H*$_2$=CH), 5.07 (dd, *J* = 1.6, 6.4 Hz 1H, C*H*$_2$=CH), 5.79 (ddt, *J* = 6.8, 10.0, 17.6 Hz, 1H, CH_2=C*H*) 7.16 (d, *J* = 7.6 Hz, 2H, Ar), 7.25 (d, *J* = 7.6 Hz, 2H, Ar), 12.5 (br, 1H, NH); ^{13}C NMR ($CDCl_3$) δ 9.7 ($SeCH_3$), 21.1 ($ArCH_3$), 32.2, 37.5 8 (CH_2), 53.7 (NCH_2), 118.5 (*C*H_2=CH), 120.3 (q, $^1J_{C-F}$ = 318.9 Hz, CF_3), 128.1, 128.7, 129.7 (Ar), 133.2 (CH_2=*C*H), 239.1 (Ar), 200.7 (CSe, $^1J_{C-SeMe}$ = 166.7 Hz); ^{19}F NMR ($CDCl_3$) δ −79.0; ^{77}Se NMR ($CDCl_3$) 383.9; *E*-isomer ^1H NMR ($CDCl_3$) δ 11.4 (br 1H, NH); MS (FAB+) *m*/*z* 283 (M^+ − OTf); HRMS (FAB+) calcd for $C_{14}H_{20}NSe$ 282.0756 (M^+ − OTf), found 282.0733.

(1*Z*)-*N*-[(4-Methylphenyl)methyl]-2-phenyl-4-pentenimidoselenoic Acid Methyl Ester Trifluoromethanesulfonate (2e). The crude product was washed with Et_2O/CH_2Cl_2 (80:1) to give **2e** as a slightly yellow oil: IR (neat) 3196, 3086, 3030, 29.83, 2925, 1643, 1593, 1284, 1217, 1164, 1029, 703, 638 cm^{-1}; *Z*-isomer ^1H NMR ($CDCl_3$) δ 2.31 (s, 3H, CH_3), 2.51 (s, 3H, $SeCH_3$), 2.82 (dt, *J* = 6.4, 14.8 Hz, 1H, CH_2=CHC*H*$_2$), 3.00 (dt, *J* = 7.8, 14.8 Hz, 1H, CH_2=CHC*H*$_2$), 4.45 (t, *J* = 7.6 Hz, 1H, PhCH), 4.93 (d, *J* = 5.6 Hz 2H, NCH_2), 5.03 (d, *J* = 10.4 Hz 1H, C*H*$_2$=CH), 5.13 (d, *J* = 17.2 Hz 1H, C*H*$_2$=CH), 5.67 (ddt, *J* = 6.6, 10.4, 17.2 Hz, 1H, CH_2=C*H*) 7.13 (d, *J* = 8.4 Hz, 2H, Ar), 7.23−7.37 (m, 7H, Ar), 12.1 (br, 1H, NH); ^{13}C NMR ($CDCl_3$) δ 10.3 ($SeCH_3$), 21.1 (CH_3), 37.4 (CH_2), 53.9 (NCH_2), 53.9 (PhCH), 115.7 (*C*H_2=CH), 120.6 (q, $^1J_{C-F}$ = 319.8 Hz, CF_3), 127.9, 128.2, 128.9, 129.7, 129.8, 132.6 (Ar), 135.0 (CH_2=*C*H), 139.2 (Ar), 201.2 (CSe, $^1J_{C-SeMe}$ = 171.6 Hz); ^{19}F NMR ($CDCl_3$) δ −78.7; ^{77}Se NMR ($CDCl_3$) δ 413.7; *E*-isomer ^1H NMR ($CDCl_3$) δ 11.3 (br, 1H, NH); ^{77}Se NMR ($CDCl_3$) δ 415.5; MS (FAB+) *m*/*z* 359 (M^+ + 1 − OTf). Anal. Calcd for $C_{21}H_{25}F_3NO_3SSe\cdot 0.5H_2O$: C, 48.93; H, 4.89; N, 2.72. Found: C, 49.10; H, 4.81; N, 2.74.

(1*Z*)-*N*-Butyl-4-ethanimidoselenoic Acid Methyl Ester Trifluoromethanesulfonate (2f). The crude product was washed with Et_2O/CH_2Cl_2 (80:1) to give **2f** as a black green oil: IR (neat) 3496, 3231, 3145, 3050, 2965, 2878, 1617, 1467, 1440, 1415, 1379, 1243, 1163, 1030, 639, 575, 518 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.97 (t, *J* = 7.2 Hz, 3H, C*H*$_3$CH$_2$CH$_2$CH$_2$), 1.44 (sext, *J* = 7.2 Hz, CH$_3$C*H*$_2$CH$_2$CH$_2$), 1.84 (quint, *J* = 7.2 Hz, CH$_3$CH$_2$C*H*$_2$CH$_2$), 2.71 (s, 3H, $SeCH_3$), 2.81 (s, 3H, CH_3), 3.51 (dd, *J* = 7.2, 13.6 Hz, CH$_3$CH$_2$CH$_2$C*H*$_2$), 11.94 (br, 1H, NH); ^{13}C NMR ($CDCl_3$) δ 9.4 ($SeCH_3$), 13.2 (CH_3), 19.9 (CH_2), 26.0 (CH_3), 28.4, 50.7 (CH_2), 120.3 (q, $^1J_{C-F}$ = 318.9 Hz, CF_3), 196.6 (CSe, $^1J_{C-SeMe}$ = 162.3 Hz); ^{19}F NMR ($CDCl_3$) δ −79.2; ^{77}Se NMR ($CDCl_3$) δ 390.7; MS (FAB+) *m*/*z* 193 (M^+ − OTf); HRMS (FAB+) calcd for $C_7H_{16}NSe$ 194.0443 (M^+ − OTf), found 194.0453.

(1*Z*)-*N*-(4-Methoxylphenyl)ethanimidoselenoic Acid Methyl Ester Trifluoromethanesulfonate (2g). CH_2Cl_2 was used as a solvent for the synthesis of **2g**. The crude product was washed with Et_2O/hexane/CH_2Cl_2 (50:50:1) to give **2g** as a red-yellow oil: IR (neat) 2939, 2845, 1737, 1725, 1610, 1580, 1512, 1256, 1170, 1030, 639 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.59 (s, 3H, $SeCH_3$), 2.95 (s, 3H CH_3), 3.83 (s, 3H, OCH_3), 6.97 (d, *J* = 8.8 Hz, 2H, Ar), 7.34 (d, *J* = 8.8 Hz, 2H, Ar), 13.1 (br, s, 1H NH); ^{13}C NMR ($CDCl_3$) δ 9.7 ($SeCH_3$), 26.3 (CH_3), 55.6 (OCH_3), 115.2 (Ar), 120.2 (q, $^1J_{C-F}$ = 319.5 Hz, CF_3), 125.4, 129.1, 160.9 (Ar), 200.4 (CSe, $^1J_{C-SeMe}$ = 162.8 Hz); ^{19}F NMR ($CDCl_3$) δ −79.1; ^{77}Se NMR ($CDCl_3$) δ 416.8; MS (FAB+) *m*/*z* 244 (M^+ − OTf). Anal. Calcd for $C_{11}H_{14}F_3NO_4SSe\cdot 0.05$hexane: C, 34.22; H, 3.74. Found: C, 34.36; H, 3.72.

(1*Z*)-*N*-(4-Bromolphenyl)ethanimidoselenoic Acid Methyl Ester Trifluoromethanesulfonate (2h). CH_2Cl_2 was used as a solvent for the synthesis of **2h**. The crude product was washed with Et_2O/CH_2Cl_2 (50:1) to give **2h**: white solid; mp 92.5−95.0 °C (dec); IR (KBr) 3421, 2999, 1625, 1491, 1240, 1223, 1179, 1165, 1033, 819, 636 cm^{-1}; *Z*-isomer ^1H NMR ($CDCl_3$) δ 2.63 (s, 3H, $SeCH_3$), 2.98 (s, 3H, CH_3), 7.33 (d, *J* = 8.8 Hz, 2H, Ar), 7.63 (d, *J* = 8.8 Hz, 2H, Ar), 13.3 (1H, br, NH); ^{13}C NMR ($CDCl_3$) δ 10.1 ($SeCH_3$), 26.8 (CH_3), 120.2 (q, $^1J_{C-F}$ = 318.9 Hz, CF_3), 125.1, 125.9, 133.6, 135.3 (Ar), 202.2 (CSe, $^1J_{C-SeMe}$ = 164.8 Hz); ^{19}F NMR ($CDCl_3$) δ −79.0; ^{77}Se NMR ($CDCl_3$) δ 424.0; *E*-isomer ^1H NMR ($CDCl_3$) δ 9.27 (1H, br, NH); ^{77}Se NMR ($CDCl_3$) δ 474.8; MS (FAB+) *m*/*z* 277 (M^+ − OTf − CH_3); HRMS (FAB+) calcd for $C_9H_{11}BrNSe$ 291.9234 (M^+ − OTf), found 291.0210.

Preparation of Tetramethylammonium *N*-(Phenylmethyl)benzenecarboximidoselenoate (3a). To a CH_3CN suspension (2 mL) of tetramethylammonium fluoride (0.094 g, 1.0 mmol) was added selenoamide **1a** (0.183 g, 0.67 mmol) at room temperature, and the mixture was heated at 95 °C. After the mixture was stirred for 0.5 h at this temperature, the solvent was removed under reduced pressure. To the resulting mixture was added THF (4 mL) at room temperature, and this was stirred for 5 min. To this mixture was added CH_3CN (2 mL), and the mixture was stirred for 2 min. This was filtered through a glass filter (G4) to separate the insoluble parts, and the solvent was removed under reduced pressure. To this was added THF (3 mL) at room temperature, and the mixture was stirred for 5 min. Filtration of the resulting deposits through a glass filter (G4) gave ammonium selenoimidate **3a** (0.134 g, 58%) as a slightly green solid: mp 128.0−133.5 °C (dec); IR (KBr) 3013, 2943, 2861, 1644, 1534, 1486, 1026, 949 cm^{-1}; ^1H NMR (CD_3CN) δ 3.02 (s, 12H, NMe_4), 4.75 (s, 2H, CH_2), 7.15−7.23 (m, 4H, Ar), 7.28 (t, *J* = 7.2 Hz, 2H, Ar), 7.45 (d, *J* = 7.2 Hz, 2H, Ar), 8.04−8.07 (m, 2H, Ar); ^{13}C NMR (CD_3CN) δ 56.5, 56.5, 56.6 (NMe_4), 65.0 (CH_2), 127.0,

Table 7. Crystallographic Data for 1a, 2a, and 3a

	1a	2a	3a
empirical formula	$C_{14}H_{13}NSe$	$C_{16}H_{16}F_3NO_3SSe$	$C_{18}H_{24}N_2Se$
fw	274.22	438.32	347.36
cryst size (mm)	0.11 × 0.14 × 0.26	0.09 × 0.09 × 0.26	0.04 × 0.11 × 0.26
temperature (°C)	23.0	23.0	23.0
cryst color, habit	orange, prism	colorless, prism	colorless, prism
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/a$ (#14)	$P2_1/c$ (#14)	$P2_1/c$ (#14)
a (Å)	9.487(1)	10.600(7)	8.947(5)
b (Å)	10.136(2)	15.960(9)	10.979(6)
c (Å)	13.331(3)	11.100(6)	17.759(10)
β (deg)	97.759(10)	107.930(8)	98.240(8)
volume of unit cell (Å^3)	1270.0(4)	1786(1)	1726(1)
Z value	4	4	4
D_{calc} (g/cm^3)	1.434	1.629	1.336
no. of reflns (all, $2\theta < 54.99°$)	2899	4108	3945
no. of variables	149	226	190
residuals: R, R_w	0.103, 0.151	0.092, 0.090	0.107, 0.144
residuals: R1 ($I > 2.0\sigma(I)$)	0.073	0.043	0.070
goodness of fit	1.08	0.79	0.99

128.1, 128.4, 129.4, 129.6, 130.0, 145.4, 151.2 (Ar), 180.5 (CSe, $^1J_{C-Se}$ = 179.9 Hz); ^{77}Se NMR (CD_3CN) δ 226.6.; MS (FAB+) m/z 274 ($M^+ - NMe_4$).

Reaction of Selenoiminium Salt 2a with Tetrabutylammonium Fluoride. *N*-(Phenylmethyl)benzenecarboximidoselenoic Acid Methyl Ester (6). To a THF solution (2 mL) of selenoiminium salt **2a** (0.200 g, 0.46 mmol) was added tetra-*n*-butylammonium fluoride (0.69 mL, 0.69 mmol) at 0 °C, and this was stirred for 0.5 h at this temperature. The resulting mixture was poured into water and extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (Al_2O_3, hexane) to give selenoimidate **6** (0.115 g, 87%) as a pale yellow oil: IR (neat) 3060, 3028, 2962, 2930, 1702, 1616, 1494, 1452, 1418, 1261, 1075, 1028, 799, 765, 697 cm^{-1}; *Z*-isomer ^{1}H NMR ($CDCl_3$) δ 1.95 (s, 3H, $SeCH_3$), 4.80 (s, 2H, CH_2), 7.22−7.51 (m, 8H, Ar), 7.52 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$) δ 7.8 ($SeCH_3$), 60.6 (CH_2), 126.8, 127.9, 128.3, 128.3, 128.4, 129.4, 139.0, 139.3, (Ar), 164.2 (CSe, $^1J_{C-SeMe}$ = 138.9 Hz); ^{77}Se NMR ($CDCl_3$) δ 262.9; *E*-isomer ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3H, $SeCH_3$), 4.59 (s, 2H, CH_2), 7.22−7.51 (m, 8H, Ar), 7.52 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$) δ 6.6 ($SeCH_3$), 57.3 (CH_2), 126.4, 126.6, 127.3, 128.3, 128.5, 129.3, 137.6, 140.3 (Ar), 165.2 (CSe); ^{77}Se NMR ($CDCl_3$) δ 339.1; MS (EI) m/z 288 ($M^+ - 1$). Anal. Calcd for $C_{15}H_{15}NSe \cdot 0.25H_2O$: C, 61.54; H, 5.34; N, 4.78. Found: C, 61.21; H, 5.47; N, 4.86.

X-ray Structure Analysis of 1a, 2a, and 3a. The measurement of selenoamide **1a**, selenoiminium salt **2a**, and ammonium selenoimidate **3a** was carried out on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The structure was solved and refined using the teXsan crystallographic software package from Molecular Structure Corporation. The X-ray quality crystals were obtained as follows: for **1a**, slow diffusion of hexane into a hexane/CH_2Cl_2 (1:1) solution of **1a** (0.020 g); for **2a**, slow diffusion of Et_2O (0.8 mL) into a CH_2Cl_2 solution (0.4 mL) of **2a** (0.020 g); for **3a**, slow evaporation of a saturated CD_3CN solution of **3a**. The crystal was cut from the grown crystals and mounted on a glass fiber. The structures were solved by the direct method using SHELXS86[16] and expanded using DIRDIF94.[17] Scattering factors for neutral atoms were from Cromer and Waber,[18] and anomalous dispersion effects[19] were used. The function minimized was $\sum w(F_o^2 - F_c^2)^2$, and the weighting scheme used was $w = [\sigma^2_c(F_o^2) + (p(\max(F_o^2,0) + 2F_c^2/3)^2)^{-1}$. A full-matrix least-squares refinement was executed with non-hydrogen atoms considered to be anisotropic. The final least-squares cycle included fixed hydrogen atoms at calculated positions for which each isotropic thermal parameter was set to 1.2 times that of the connecting atom. Crystal data and a description of the measurement are summarized in Table 7.

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Supporting Information Available: Characterization of new compounds **1b**−**e** and crystallographic data including atomic positional and thermal parameters for **1a**, **2a**, and **3a** (PDF, CIF). This material is available free of charge via the Internet at http://pubs/acs/org.

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