JOC Article

Highly Efficient Peterson Olefination Leading to Unsaturated Selenoamides and Their Characterization[†]

Toshiaki Murai,* Akinori Fujishima, Chigusa Iwamoto, and Shinzi Kato

Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan

mtoshi@cc.gifu-u.ac.jp

Received May 15, 2003

The Peterson olefination of aromatic aldehydes with an α-silyl selenoacetamide proceeded smoothly with high stereoselectivity to give *E*-α,*β*-unsaturated selenoamides in good to high yields. The reaction with aldehydes bearing alkenyl and dienyl groups gave the corresponding selenoamides bearing dienyl and trienyl groups, but the stability of the products depended on the substituents on the aromatic ring. X-ray molecular analysis disclosed that the α,*β*,*γ*,*δ*-unsaturated selenoamides had a nearly planar structure. In the ^{77}Se NMR spectra, signals were observed in the region greater than 130 ppm depending on the substituents on the aromatic ring, whereas the ^1J coupling constant between the carbon atom and the selenium atom was almost independent of the substituents. A linear relationship was observed between the chemical shifts in the ^{77}Se NMR spectra and Hammet σ parameters, and this correlation was retained even when one or two alkenyl groups were introduced to α,*β*-unsaturated selenoamides, although it became less sensitive.

Introduction

The synthesis and reactions of α,*β*-unsaturated thioamides[1] have been extensively studied over the past few years. In contrast, much less attention has been paid to the chemistry of α,*β*-unsaturated selenoamides, despite recent advances in the rich chemistry of organoselenium compounds[2] and selenocarbonyl compounds.[3] This is mainly due to the lack of convenient methods for synthesizing α,*β*-unsaturated selenoamides. The direct conversion of α,*β*-unsaturated amides to α,*β*-unsaturated selenoamides with disilyl selenide has been reported, but has only been used for the synthesis of selenocinnamamide.[4] The synthesis of *β*-aminoselenoacrylamides has been achieved by reacting acetamides with Vilsmeier reagents and sodium selenide.[5] In these two methods, the preparation of disilyl selenide and sodium selenide, which are labile toward water, is cumbersome. Very recently, amides have been converted to selenoamides with reagents prepared in situ from elemental selenium and $LiAlH_4$,[6] but this reaction has not been applied to the synthesis of α,*β*-unsaturated selenoamides. Alternatively, metal complexes of selenoaldehydes and -ketones or trifluoromethyl selenoaldehyde can be reacted with alkynylamines followed by demetalation to give α,*β*-unsaturated selenoamides.[7] During the course of our studies on the chemistry of selenoamides,[8−10] we found

---

[†] Dedicated to Prof. N. Sonoda on the occasion of his 70th birthday.

(1) For recent examples, see: (a) Roy-Gourvennec, S. L.; Masson, S. *Synthesis* **1995**, 1393. (b) Sakamoto, M.; Takahashi, M.; Kamiya, K.; Yamaguchi, K.; Fujita, T.; Watanabe, S. *J. Am. Chem. Soc.* **1996**, *118*, 10664. (c) Kinbara, K.; Saigo, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 779. (d) Samet, A. V.; Shestopalov, A. M.; Nesterov, V. N.; Semenov V. V. *Russ. Chem. Bull.* **1998**, *47*, 127. (e) Sakamoto M.; Takahashi, M.; Kamiya, K.; Arai, W.; Yamaguchi, K.; Mino, T.; Watanabe, S.; Fujita, T. *J. Chem. Soc., Perkin Trans. 1* **1998**, 3731. (f) Lopez, P.; Oh, T. *Tetrahedron Lett.* **2000**, *41*, 2313. (g) Sakamoto, M.; Takahashi, M.; Arai, W.; Mino, T.; Yamaguchi, K.; Watanabe, S.; Fujita, T. *Tetrahedron* **2000**, *56*, 6795 (h) Sosnicki, J. G.; Jagodzinski, T. S.; Hansen, P. E. *Tetrahedron* **2001**, *57*, 8705. (i) Hosoya, T.; Ohhara, T.; Uekusa, H.; Ohashi, Y. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 2147.

(2) (a) Krief A. In *Comprehensive Organometallic Chemistry*; Abel, W. W., Stone, F, G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 11, p 515. (b) *Organoselenium Chemistry: A Practical Approach*; Back, T. G., Ed.; Oxford U. P.: Oxford, U.K., 1999. (c) *Topics in Current Chemistry*; Wirth, T., Ed.; Springer-Verlag: Berlin, 2000; Vol. 208.

(3) (a) Guziec, F. S. Jr.; Guziec, L. J. In *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Pergamon: Oxford, 1995; Vol. 3, p 381. (b) Ogawa, A.; Sonoda, N. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 6, p 461. (c) Ogawa, A.; Sonoda, N. *Rev. Heteroatom Chem.* **1994**, *10*, 43. (d) Ishii A.; Nakayama, J. In *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Pergamon: Oxford, 1995; Vol. 5, p 505. (e) Dell, C. P. In *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Pergamon: Oxford, 1995; Vol. 5, p 565. (f) Murai, T.; Kato, S. *Sulfur Rep.* **1998**, *20*, 397.

(4) Takikawa, Y.; Watanabe, H.; Sasaki, R.; Shimada, K. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 876.

(5) Hartmann, H.; Heyde, C.; Zug, I. *Synthesis* **2000**, 805.

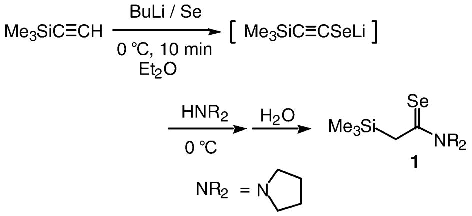
(6) (a) Ishihara, H.; Koketsu, M.; Fukuta, Y.; Nada, F. *J. Am. Chem. Soc.* **2001**, *123*, 8408. (b) Koketsu, M.; Okayama, Y.; Aoki, H.; Ishihara, H. *Heteroatom Chem.* **2002**, *13*, 195.

(7) (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) Fischer, H.; Hofmann, J.; Gerbing, U.; Tiriliomis, A. *J. Organomet. Chem.* **1988**, *358*, 229. (d) Fischer, H.; Treier, K.; Hofmann, J. *J. Organomet. Chem.* **1990**, *384*, 305. (e) Blau, H.; Grobe, J.; Van, D. L.; Krebs, B.; Läge, M. *Chem. Ber.* **1997**, *130*, 913.

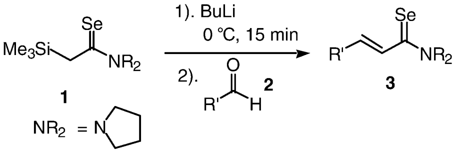
(8) (a) Murai, T.; Ezaka, T.; Niwa, N.; Kanda, T.; Kato, S. *Synlett* **1996**, 865. (b) Murai, T.; Ezaka, T.; Kanda, T.; Kato, S. *J. Chem. Soc., Chem. Commun.* **1996**, 1809. (c) Murai, T.; Ezaka, T.; Niwa, N.; Kato, S. *J. Org. Chem.* **1998**, *63*, 374. (d) Murai, T.; Ezaka, T.; Kato, S. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1193. (e) Murai, T.; Ezaka, T.; Kato, S. *Tetrahedron Lett.* **1998**, *39*, 4329. (f) Murai, T.; Suzuki, A.; Ezaka, T.; Kato, S. *Org. Lett.* **2000**, *2*, 311. (g) Murai, T.; Mutoh, Y.; Kato, S. *Org. Lett.* **2001**, *3*, 1993. (h) Murai, T.; Aso, H.; Kato, S. *Org. Lett.* **2002**, *4*, 1407. (i) Murai, T.; Ishizuka, M.; Suzuki, A.; Kato, S. *Tetrahedron Lett.* **2003**, *44*, 1343. (j) Mutoh, Y.; Murai, T. *Org. Lett.* **2003**, *5*, 1361.

10.1021/jo034653k CCC: $25.00

SCHEME 1. Synthesis of α-Silyl Selenoacetamide 1



SCHEME 2. Peterson Olefination of Aromatic Aldehydes with α-Silyl Selenoacetamide 1



that the treatment of selenoacetamides ($CH_3C(Se)NR'_2$) with LDA followed by reaction with aldehydes gave α,β-unsaturated selenoamides in moderate to good yields.[9] We further observed that a chiral α,β-unsaturated selenoamide underwent Michael addition of alkyllithiums with high stereoselectivity.[10] To establish more facile synthetic methods for α,β-unsaturated selenoamides, we envisioned the use of α-silyl selenoacetamides, which are readily prepared from commercially available starting materials. We report here the Peterson olefination of a variety of aromatic aldehydes with α-silyl selenoacetamide leading to unsaturated selenoamides and their characterization.

Results and Discussion

Initially, α-trimethylsilyl selenoacetamide **1** was synthesized in high yields by the successive reaction of (trimethylsilyl)acetylene, BuLi, selenium, amine, and water within 20 min (Scheme 1).[8a]

Selenoamide **1** was purified by recrystallization with hexane. Although the obtained mixture of **1** generally contained less than 10% of the protodesilylated selenoamide, it was used without further purification for the Peterson olefination (Scheme 2).

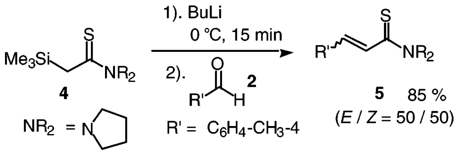
The results of the synthesis of α,β-unsaturated selenoamides from aromatic aldehydes **2** are shown in Table 1. For example, α-silyl selenoacetamide **1** was reacted with BuLi in THF at 0 °C for 15 min. 4-Methylbenzaldehyde was then added to the reaction mixture. The reaction mixture instantly turned reddish orange, and stirring was continued for 1 h. The solution was poured onto water and extracted with dichloromethane. Purification of the product via column chromatography on silica gel gave β-4-methylphenyl-α,β-unsaturated selenoamide **3h** in 97% yield (entry 8). In all cases, *E*-isomers of **3** were selectively formed, and *Z*-isomers were not observed. This is in sharp contrast to the ordinary Peterson olefination using α-trimethylsilyl acetamides, which generally gives stereoisomeric mixtures.[11]

TABLE 1. Reaction of α-Silyl Selenoamide 1 with BuLi and Aldehydes 2[a]

entry	**2**, R′	product **3**	yield[b] (%)
1	2-MeC_6H_4	**3a**	93
2	2-$MeOC_6H_4$	**3b**	91
3	4-$NO_2C_6H_4$	**3c**	44
4	4-NCC_6H_4	**3d**	76
5	4-ClC_6H_4	**3e**	79
6	4-FC_6H_4	**3f**	83
7	C_6H_5	**3g**	98
8	4-MeC_6H_4	**3h**	97
9	4-$MeOC_6H_4$	**3i**	99
10	4-*t*-BuC_6H_4	**3j**	94
11	4-$Me_2NC_6H_4$	**3k**	93

[a] α-Silyl selenoacetamide **1** (1.0 mmol) was reacted with BuLi (1.2 mmol) at 0 °C for 15 min in THF. To the reaction mixture was then added an aldehyde (1 mmol) at 0 °C, and it was stirred at room temperature for 60 min. [b] Isolated yield.

SCHEME 3. Peterson Olefination of *p*-Tolualdehyde with α-Silyl Thioacetamide 4



Furthermore, a similar reaction of α-silyl thioacetamide **4** also gave two isomers of α,β-unsaturated thioamide **5** in a nearly equal ratio (Scheme 3). The high stereoselectivity of the reaction of **1** may be due to the larger ionic radius of the selenium atom. In a *Z*-isomer, the steric and/or electronic repulsion may be present between the selenium atom and substituents at the β position.

The reaction of aromatic aldehydes bearing various functional groups, such as cyano, nitro, methoxy, and dimethylamino groups, chlorine, and fluorine, also proceeded smoothly to give the corresponding α,β-unsaturated selenoamides in moderate to good yields (entries 2−6, 9, 11). The substituents at the ortho position of aromatic aldehydes did not affect the yields of the products **3** (entries 1 and 2). Peterson olefination was further carried out with unsaturated aldehydes **6** to synthesize selenoamides possessing longer unsaturated alkyl chains.[12] The results are shown in Table 2. The reaction with α,β-unsaturated aldehydes **6**[13] ($n = 0$) proceeded similarly to the reaction with aldehydes **2**. *E*,*E*-Isomers of the corresponding α,β,γ,δ-unsaturated selenoamides **7** ($n = 0$) were obtained with high stereoselectivity in 63−95% yields (entries 1−7). No isomerization of the alkenyl groups of the starting aldehydes occurred. The substituents on the aromatic ring did not affect the yields of the products **7**. On the other hand, in the reaction of α,β,γ,δ-unsaturated aldehydes **6** ($n = 1$) bearing electron-donating groups, such as methoxy and dimethylamino groups, the yields of the products were decreased (entries 11 and 12) compared to those of products bearing bromine and nitro group (entries 8 and 9).

---

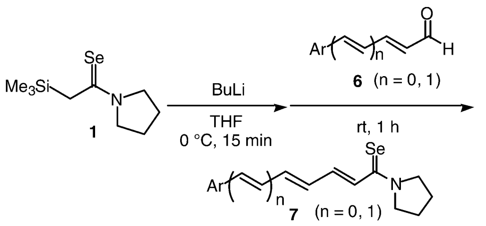
(9) Murai, T.; Ezaka, T.; Ichimiya, T.; Kato, S. *Synlett* **1997**, 775.

(10) Murai, T.; Mori, T.; Kato, S. *Synlett.* **1998**, 619.

(11) (a) Ager, D. J. *Org. React.* **1990**, *38*, 1. (b) Kojima, S.; Inai, H.; Hidaka, T.; Ohkata, K. *Chem. Commun.* **2000**, 1795. (c) Kojima, S.; Inai, H.; Hidaka, T.; Fukuzaki, T.; Ohkata, K. *J. Org. Chem.* **2002**, *67*, 4093.

(12) The reaction of alkynyl propargyl selenides with secondary amines has been reported to give α,β,γ,δ-unsaturated selenoamides as stereoisomeric mixtures: (a) Shimada, K.; Akimoto, S.; Itoh, H.; Nakamura, H.; Takikawa, Y. *Chem. Lett.* **1994**, 1743. (b) Koketsu, M.; Kanoh, M.; Itoh, E.; Ishihara, H. *J. Org. Chem.* **2001**. *66*, 4099.

TABLE 2. Reaction of α-Silyl Selenoamide 1 with BuLi and Aldehydes 6[a]



entry	Ar, **6**	n	product **3**	yield[b] (%)
1	4-$NO_2C_6H_4$	0	**7a**	63
2	4-BrC_6H_4	0	**7b**	85
3	4-FC_6H_4	0	**7c**	66
4	C_6H_5	0	**7d**	82
5	4-MeC_6H_4	0	**7e**	64
6	4-$MeOC_6H_4$	0	**7f**	95
7	4-$Me_2NC_6H_4$	0	**7g**	64
8	4-$NO_2C_6H_4$	1	**7h**	95
9	4-BrC_6H_4	1	**7i**	62
10	C_6H_5	1	**7j**	89
11	4-$MeOC_6H_4$	1	**7k**	51
12	4-$Me_2NC_6H_4$	1	**7l**	36[c]

[a] α-Silyl selenoacetamide **1** (1.0 mmol) was reacted with BuLi (1.2 mmol) at 0 °C for 15 min in THF. To the reaction mixture was then added an aldehyde (1 mmol) at 0 °C, and it was stirred at room temperature for 60 min. [b] Isolated yield. [c] Crude yield.

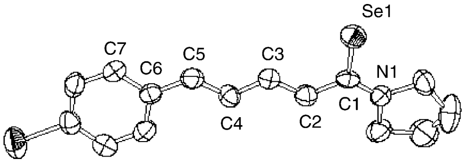


FIGURE 1. ORTEP representation of **7b**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Se1–C1, 1.848(6); N1–C1, 1.313(7); C1–C2, 1.464(8); C2–C3, 1.324(8); C3–C4, 1.427(8); C4–C5, 1.326(8); C5–C6, 1.457(8). Selected bond angles (deg): Se1–C1–N1, 121.7(5); Se1–C1–C2, 120.2(5); N1–C1–C2, 118.1(5). Selected torsion angles (deg): Se1–C1–C2–C3, 0.9(9); N1–C1–C2–C3, 166.5(7); C1–C2–C3–C4, 178.6(6); C2–C3–C4–C5, 177.0(7); C3–C4–C5–C6, 178.8(6)

In particular, during the purification of **7l** by column chromatography, it gradually decomposed and could not be isolated in pure form.

The stereochemistry of α,β,γ,δ-unsaturated selenoamides **7** was confirmed by NMR spectra[14] and X-ray structure analysis.[15] The ORTEP drawing of **7b** is shown in Figure 1 along with selected bond lengths, angles, and torsion angles.

TABLE 3. Representative UV–Vis Spectroscopic Data of 3 and 7[a]

R′ or Ar	unsaturated selenoamide	UV–vis (nm) λ_{max} (log ϵ)
4-$NO_2C_6H_4$	**3c**	310 (4.43), 409 (3.75)
	7a	355 (4.42), 420 (3.85)
	7h	385 (4.84), 415 (4.70)
4-$NO_2C_6H_4$	**3e**	302 (4.26), 384 (3.74)
C_6H_5	**3g**	304 (4.17), 387 (3.60)
	7d	339 (4.46), 400 (3.81)
	7j	369 (5.13), 430 (4.48)
4-$MeOC_6H_4$	**7f**	356 (4.43), 450 (3.70)
	7k	383 (4.96), 450 (4.57)
4-$Me_2NC_6H_4$	**3k**	390 (4.21), 423 (4.19)

[a] $CHCl_3$ was used as a solvent.

The results indicate that two alkenyl groups of **7b** adopt an *E* configuration, and **7b** is nearly planar. This is in sharp contrast to the structure of the reported α-methyl α,β-unsaturated selenoamides, where alkenyl and selenocarbonyl groups are almost perpendicular and not in the same plane.[7a,b,e] Due to the nearly planar structure of **7**, the efficient delocalization of the electrons on the substituents on the aromatic rings attached to the position δ to the selenocarbonyl group was expected.

Representative UV–vis spectroscopic data for selenoamides **3** and **7** are shown in Table 3.

Absorptions that could be ascribed to $\pi-\pi^*$ transitions were observed at ~310–390 nm. They were shifted to a longer wavelength when the number of alkenyl groups increased or when electron-donating groups were introduced. On the other hand, the absorptions due to n–π^* transitions at 384–450 nm did not show any correlation with the number of alkenyl groups or substituents on the aromatic ring.

NMR studies were carried out for the unsaturated selenoamides. The chemical shifts in ^{77}Se NMR spectra and the coupling constants between the carbon atom and the selenium atom of the selenoamides **3** and **7** are shown in Table 4.

As for α,β-unsaturated selenoamides **3**, signals were observed in the region greater than 130 ppm starting from δ 470.2. When electron-withdrawing groups were introduced to the aromatic ring, the signals were shifted to lower fields, whereas the introduction of electron-donating groups shifted the signals to higher fields.

This indicates that the ^{77}Se NMR signals are highly sensitive to the electronic properties of the aromatic ring attached to the carbon atom β to the selenocarbonyl group. This sensitivity was retained even when one or two alkenyl groups were introduced to α,β-unsaturated selenoamides, although the substituent effects gradually decreased. The signals of the selenoamides **7** ($n = 0$) were at 540 ± 41 ppm, and those of the selenoamides **8** ($n = 0$) were at 540 ± 26 ppm.[16,18] In contrast, the coupling constants between the selenium and carbon atoms were nearly independent of the substituents on the aromatic ring and changed by at most 4 Hz between selenoamides **3c** and **3k**.

---

(13) Bellassoued, M.; Majidi, A. *J. Org. Chem.* **1993**, *58*, 2517.

(14) The interpretation of the signals of the olefinic carbon atoms of **7** was based on C–H COSY and phase-sensitive NOESY spectroscopy.

(15) Crystal data of **7b**: Rigaku/MSC Mercury CCD, Mo–Kα radiation, graphite monochromator, reflections recorded at 296 K from a brown prism crystal with dimensions of $0.30 \times 0.20 \times 0.20$ mm^3 to $2\theta_{max}$ 54.9°, structure solved by direct methods (SHELXL86) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Formula: $C_{15}H_{16}BrNSe$ mol wt 369.16, monoclinic, space group *P*21/*c* (#14), $Z = 8$, $a = 6.550(1)$ Å, $b = 29.510(5)$ Å, $c = 15.509(3)$ Å, $V = 2960.6(9)$ Å^3, $D_{calcd} = 1.656$ g cm^{-3}, $\mu = 52.27$ cm^{-1}; 6767 reflections measured, 2924 reflections calculated R1 ($I > 2\sigma(I)$) = 0.054), *R*, Rw = 0.097, 0.15, GOF = 0.87. All other details are reported in the Supporting Information.

(16) The ^{77}Se chemical shifts of selenocarbonyl compounds have been reported to linearly correlate with the energy of their n–π^* transition.[17] However, no linear relationship was observed in this case.

(17) Cullen, E. R.; Guziec Jr., F. S.; Murphy, C. J.; Wong, T. C.; Andersen, K. K. *J. Am. Chem. Soc.* **1981**, *103*, 7055.

TABLE 4. ^{77}Se NMR Spectroscopic Data of 3 and 7[a]

R′ or Ar	δ (para)	3	^{77}Se δ (ppm) (Δδ(^{77}Se))	$^{1}J_{C=Se}$ (Hz) (Δδ$^{1}J_{C=Se}$)	7	^{77}S δ (ppm) (Δδ(^{77}Se))	$^{1}J_{C=Se}$ (Hz) (Δδ$^{1}J_{C=Se}$)	7	^{77}Se δ (ppm) (Δδ(^{77}Se))
4-$NO_2C_6H_4$	0.778	**3c**	608.4 (64.6)	206.7 (1.9)	**7a**	580.1 (40.8)	204.8	**7h**	560.6 (25.6)
4-NCC_6H_4	0.660	**3d**	598.0 (54.2)	206.7 (1.9)					
4-ClC_6H_4	0.227	**3e**	556.0 (12.2)	205.1 (0.3)					
4-BrC_6H_4	0.227				**7b**	549.0 (9.7)	204.3	**7i**	541.3 (6.3)
4-FC_6H_4	0.062	**3f**	543.9 (0.1)	204.8 (0)	**7c**	540.7 (1.4)			
C_6H_5	0	**3g**	543.8 (0)	204.8 (0)	**7d**	539.3 (0)	204.3	**7j**	535.0 (0)
4-MeC_6H_4	−0.170	**3h**	530.5 (−13.3)	204.8 (0)	**7e**	531.9 (−8.4)	203.8		
4-$MeOC_6H_4$	−0.268	**3i**	512.7 (−31.1)	203.4 (−1.4)	**7f**	523.1 (−16.2)		**7k**	525.4 (−9.6)
4-$Me_2NC_6H_4$	−0.83	**3k**	470.2 (−73.6)	202.8 (−2.0)	**7g**	499.6 (−39.7)	202.3		

[a] $CDCl_3$ was used as a solvent.

The linear correlation between ^{13}C NMR chemical shifts of side-chain carbons in α,β-unsaturated and α,β,γ,δ-unsaturated acids and esters and Hammet σ parameters is well documented.[19] In a series of selenoamides **3** and **7**, a similar correlation was observed for the signals due to alkenyl carbon atoms.[20] More interestingly, although no linear correlation was observed for ^{13}C NMR chemical shifts of C=Se groups, the ^{77}Se NMR signals of **3** were linearly correlated with Hammet σ parameters by the expression Δδ (^{77}Se of **3**) = −2.65 + 85.14σ (R^2 = 0.992). A linear correlation of the selenium signals was also observed for unsaturated selenoamides and selenoamides bearing dienyl and trienyl groups **7**. These correlations could be expressed as follows: Δδ (^{77}Se of **7**, n = 0) = −0.33 + 50.12σ (R^2 = 0.995), Δδ (^{77}Se of **7**, n = 1) = 0.58 + 33.42σ (R^2 = 0.999). The slope of these three equations decreased on going from **3** to **7** (n = 0) to **7** (n = 1) as shown in Figure 2.

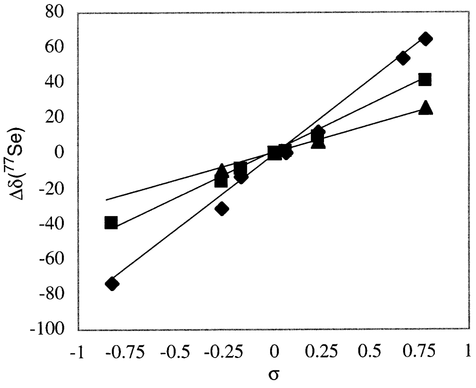


FIGURE 2. Plot of Δδ(^{77}Se) against Hammett σ parameters: relative chemical shift of **3** (◆), **7a**−**7g** (■), and **7h**−**k** (▲).

In summary, we have demonstrated that Peterson olefination of a variety of aldehydes with α-trimethylsilyl selenoacetamide **1** led to unsaturated selenoamides in moderate to high yields. The planarity of unsaturated selenoamides was disclosed by X-ray structure analysis. Since the selenocarbonyl group of selenoamides is known to be converted to an ordinary carbonyl group by reaction with m-CPBA[12a] and oxiranes,[8i,21] the present methods have provided a new synthetic route to stereochemically defined unsaturated amides.[11c,22] Furthermore, a linear correlation was noted between ^{77}Se NMR chemical shifts of the C=Se group of unsaturated selenoamides **3** and **7** and Hammet σ parameters.

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

Supporting Information Available: Experimental procedures and spectroscopic and analytical data for **3**, **4**, **5**, and **7** and tables of crystallographic data including atomic positional and thermal parameters for **7b**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO034653K

---

(18) The electronic effects of aromatic substituents on the ^{77}Se NMR chemical shifts in aryl selenides have recently been studied. Their signals changed within the range of 50 ppm, although the selenium atom was directly attached to the aromatic ring: (a) Nakanishi, W.; Hayashi, S. *Chem. Lett.* **1998**, 523. (b) Poleschner, H.; Heydenreich, M.; Radeglia, R. *Magn. Reson. Chem.* **1999**, *37*, 333. (c) Nakanishi, W.; Hayashi, S. *J. Phys. Chem. A* **1999**, *103*, 6074.

(19) (a) Christoforou, D.; Happer, D. A. R. *Aust. J. Chem.* **1982**, *35*, 729. (b) Banerji, A.; Ghosal, T.; Acharyya, A. K. *Ind. J. Chem.* **1984**, *23B*, 546. (c) Happer, D. A. R.; Steenson, B. E. *J. Chem. Soc., Perkin Trans. 2* **1988**, 19. (d) Jovanovic, B.; Misic-Vukovic, M.; Drmanic, S.; Csanadi, J. *Heterocycles* **1994**, *37*, 1495. (e) Banerji, A.; Banerjee, T.; Sengupta, R.; Sengupta, P.; Maiti, S.; Banerji, K. K.; Gupta, S. *J. Indian Chem. Soc.* **2001**, *78*, 739.

(20) The signals of the carbon atoms α and γ to C=Se groups of **7** (n = 0) were observed at 123.1−133.3 ppm and shifted to higher fields on going from **7a** to **7g**. On the other hand, those of the carbon atoms β and δ to C=Se groups of **7**, which were at 145−150 ppm and 136−142 ppm, respectively, showed the reverse tendency. These signals were linearly correlated with Hammett σ parameters as follows: δ(C**7**α) = 3.4σ + 130.6 (R^2 = 0.991), δ(C**7**β) = −2.7σ + 147.2 (R^2 = 0.996), δ(C**7**γ) = 5.1σ + 127.1 (R^2 = 0.983), and δ(C**7**δ) = −3.1σ + 139.4 (R^2 = 0.922).

(21) Ogawa, A.; Miyake, J.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1985**, *26*, 669.

(22) Petrova, J.; Momchilova, S.; Vassilev, N. G. *Phosphorus, Sulfur Silicon* **2000**, *164*, 87.