Ammonium Eneselenolates: Stereochemistry and Electronic Properties

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Ammonium eneselenolates were generated with high efficiency by reacting selenothioic acid *S*-esters with a THF solution of TBAF. The methylation of ammonium eneselenolates gave ketene selenothioacetals as stereoisomeric mixtures. The ratio of the two stereoisomers depended on the duration of the reaction before the addition of MeI. Ammonium eneselenolates were characterized by examining their ^{1}H, ^{13}C, and ^{77}Se NMR spectra, which indicated that ammonium eneselenolates were present almost exclusively as *Z*-isomers. These results suggested that ammonium eneselenolates are kinetically generated as stereoisomeric mixtures, and isomerization of *E*-isomers to *Z*-isomers then takes place to result in the exclusive formation of *Z*-isomers. During the methylation of *Z*-isomers of ammonium eneselenolates, the isomerization of *Z*-isomers to *E*-isomers occurs to give stereoisomeric mixtures of ketene selenothioacetals. NMR spectra of ammonium eneselenolates implied that the electrons at the selenium atom are somewhat delocalized to the carbon−carbon double bond and the carbon−selenium bond shows partial double-bond character.

Introduction

Organoselenium compounds have been an interesting topic in chemistry for more than 30 years.[1] A variety of methods for the synthesis of new types of organoselenium compounds have been developed in recent years.[2] In particular, considerable attention has been paid to the synthesis and reactions of selenocarbonyl compounds.[3] In our studies on selenocarbonyl compounds, we developed a highly efficient synthesis of aliphatic selenothioic acid *S*-esters (RC(Se)SR′).[4] We further demonstrated an efficient generation of ammonium eneselenolates from selenothioic acid *S*-esters with tetrabutylammonium fluoride (TBAF).[5] Ammonium eneselenolates are selenium counterparts of ammonium enolates, which have been the subject of synthetic[6] and structural[7] analysis. Experimental studies on the properties of heavier congeners of enolates have been reported in recent years, but they have been limited to enolates substituted with third-row elements such as a silicon[8] and a sulfur.[9] Very recently, theoretical studies on the electronic structures of enolizable selenocarbonyl compounds and their enolates have been described.[10] Several types of metal eneselenolates have been generated by the reaction of vinylmetallic species with a selenium atom.[11] Alternatively, deprotonation of selenoamides,[12] selenoic acid *O*-esters,[13] and selenothioic acid *S*-esters[14] with metal amides has been shown to form the corresponeding metal eneselenolates, which can be used as key intermediates

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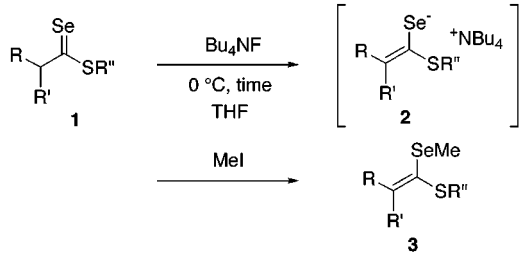
Scheme 1



for the synthesis of new types of organoselenium compounds. We report here our detailed results regarding the stereochemistry and electronic properties of ammonium eneselenolates.

Results and Discussion

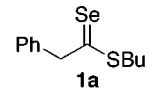
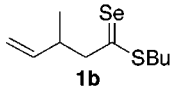
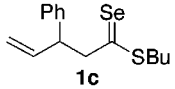
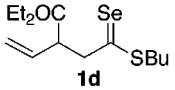
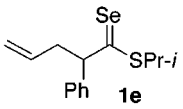
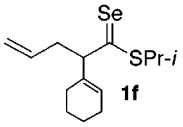
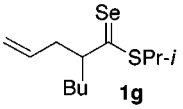
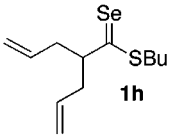
Selenothioic acid *S*-esters **1** were reacted with a THF solution of TBAF (Scheme 1). The reaction mixture gradually changed from deep violet blue to light yellow. To confirm the formation of ammonium eneselenolates **2**, methyl iodide was added to the reaction mixture.

The results are shown in Table 1. The reaction of α-monosubstituted esters **1a**−**c** with TBAF was complete within 1 s, and the subsequent reaction with MeI gave ketene selenothioacetals, which are of synthetic interest but are not easily prepared,[15] in high yields (entries 1, 5, and 8). On the other hand, a longer reaction time was necessary for the deprotonation of α-disubstituted esters **1e**−**h** (entries 12−15). In the reaction of **1a**, the ratio of the *Z*-isomer of **3a** improved by changing the duration of the reaction between **1a** and TBAF (entries 1−4). In contrast, for esters **1b**−**d** the ratio of the two isomers was nearly equal even when the esters and TBAF were stirred for prolonged reaction times before the addition of MeI (entries 5−10).

Ammonium eneselenolates **2a**−**c** and **2e** were then characterized by their NMR spectra. The reaction mixture of esters **1** and TBAF was concentrated in vacuo for 2 h to give ammonium eneselenolates along with an excess amount of TBAF. Further purification of **2** was not carried out because of the high sensitivity of **2** toward moisture. To the residue was added THF-d_8, and the spectra were measured. The *Z*-isomers of **2a**−**c** and the *E*-isomer of **2e** were selectively formed on the basis of phase-sensitive NOESY spectroscopy. Representative ^{1}H, ^{13}C, and ^{77}Se spectra of **2** are listed in Table 2 along with those of **1** and **3**.

For example, in the series of ester **1a**, ammonium salt **2a**, and ketene selenothioacetal **3a**, the selenium atom of ketene selenothioacetal *Z*-**3a** was observed at δ 202.2 in the ^{77}Se NMR spectrum. The signal of ammonium salt

Table 1. Reaction of Selenothioic Acid *S*-Esters 1 with TBAF and Methyl Iodide[a]

entry	ester **1**	time	product **3**	yield (%)[b]	*E*/*Z*[c]
1	 **1a**	1 s	**3a**	87	54/46
2		10 min		-[d]	50/50
3		20		-[d]	18/82
4		30		82	12/88
5	 **1b**	1 s	**3b**	-[d]	45/55
6		30 min		89	43/57
7		2 h		68	32/68
8	 **1c**	1 s	**3c**	85	54/46
9		30 min		84	54/46
10		2 h		91	23/77
11	 **1d**	30 min	**3d**	90	54/46
12	 **1e**	1.5 h	**3e**	77	97/3
13	 **1f**	1.5 h	**3f**	51	99/1
14	 **1g**	1.5 h	**3g**	80	62/38[e]
15	 **1h**	1.5 h	**3h**	83	–

[a] Selenothioic acid *S*-butyl esters **1** (0.5 mmol) was treated with a THF solution of TBAF (0.75 mmol) at 0 °C; then to the reaction mixture was added methyl iodide (0.5 mmol). [b] Isolated yield. [c] The ratio of the stereoisomers was determined by ^{1}H NMR spectra. [d] Not determined. [e] The stereochemistry of the major isomer was not determined.

2a was shifted to a lower field by about 50 ppm. The selenium atom with a negative charge is generally observed at a field higher than 0 ppm.[15] In contrast, the selenium of ammonium salt **2a** is strongly deshielded even if **2a** has an anionic character. This can be explained by noting that the electrons on the selenium atom efficiently delocalize on the carbon−carbon double bond. The carbon atom bound to the selenium atom in ammonium salt **2a** was shifted to a lower field by about 20 ppm, and the olefinic carbon atom remote from the selenium atom was shifted to a higher field by about 15 ppm, in comparison with those of **3a**. Furthermore, the olefinic proton in **2a** was shifted to a field higher than that of **3a**. Delocalization of the electrons in ammonium eneselenolate **2a** is further supported by the coupling constant between the carbon atom and the selenium atom of the ammonium salt **2a** (^1J = 187.5 Hz). It is close to the normal value for a carbon−selenium double bond (ca. 200 Hz), which is consistent with a partial double-bond character of the carbon−selenium bond in **2a**. In

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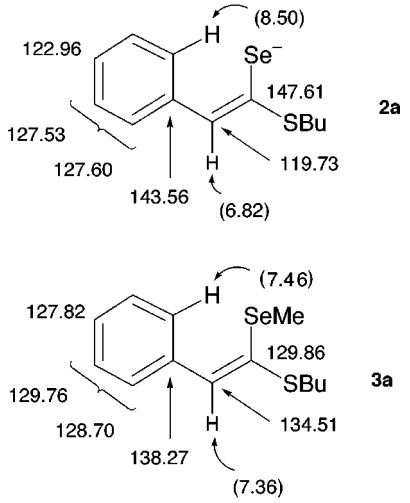
Table 2. Spectroscopic Data of Selenothioic Acid *S*-Esters 1, Ammonium Eneselenolates 2, and Ketene Selenothioacetals 3

	^{1}H NMR	^{13}C NMR		^{77}Se NMR	
compound	**H**-C-C-Se	**C**-Se	**C**-C-Se	C-**Se**	$^1J_{C-Se}$
1a[a]	4.50	241.0	64.1	1570.7	224.3
2a[a]	6.60	147.6	119.7	253.5	187.5
3a[a]	7.13	129.9	134.5	202.2	125.6
1b[a]	2.91	242.1	64.4	1518.4	223.9
2b[a]	5.12	136.4	109.1	282.2	175.7
3b[a]	5.88	125.6	141.2	232.8	122.6
1c[b]	3.33	240.4	62.2	1491.91	*d*
2c[a]	5.66	138.7	120.0	143.9	172.1
3c[b]	6.11	127.5	142.6	168.6	*d*
1e[b]	4.44	244.2	69.5	1483.2	*d*
2e[c]		148.1	138.7	166.2	172.6
3e[b]		126.1	148.1	190.5	*d*

[a] NMR spectra were recorded in THF-d_8. [b] NMR spectra were recorded in $CDCl_3$. [c] NMR spectra were recorded in $(CD_3)_2CO$. [d] The coupling between the carbon and selenium atoms were not observed.

Table 3. ^{1}H and ^{13}C NMR Chemical Shifts with Structures of 2a and 3a[a]



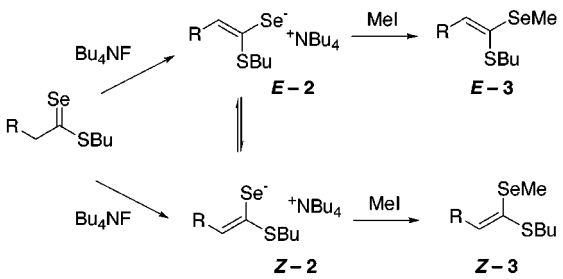
[a] The spectra were measured in THF-d_8. The chemical shifts of ^{1}H NMR spectra are in parentheses.

ammonium eneselenolates **2b**, **2c**, and **2e**, the signals due to the selenium atoms were also observed at fields lower than δ 140, and the coupling constants between the carbon and selenium atoms were greater than 170 Hz. Table 3 shows the ^{13}C NMR chemical shifts of **2a** and **3a**. A downfield shift was observed for the ipso carbon atom of ammonium salt **2a** compared with that of **3a**, whereas the signal due to that at the para-position was observed at a higher field. The deshielding of the proton at the ortho-position in **2a** is also characteristic. These results indicate the delocalization of the electrons at the selenium atom to the aromatic ring.

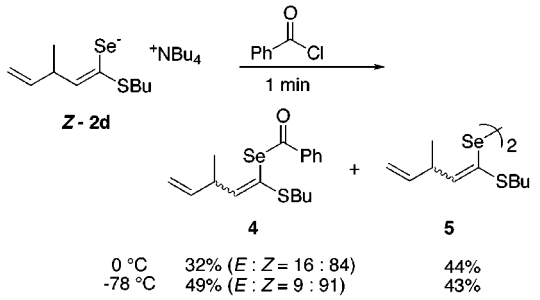
On the basis of the results in Tables 1 and 2, the stereochemical course of the formation and isomerization of ammonium eneselenolates **2** derived from α-monosubstituted esters may be understood as follows (Scheme 2).

Initially, two stereoisomers of **2** are formed in a nearly equal ratio from esters **1**, since two stereoisomers are formed. The *E*-isomers then gradually isomerize to *Z*-isomers, and the equilibrium shifts toward the *Z*-isomers of **2** as observed in the NMR spectra of **2**. However,

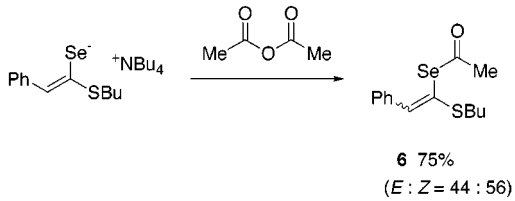
Scheme 2



Scheme 3



Scheme 4



methylation of *E*-isomers may be faster than that of *Z*-isomers in some cases, and isomerization of *Z*-isomers to *E*-isomers takes place during the reaction of **2** with methyl iodide to give two isomers, as in entries 6, 7, 9, and 10 in Table 1. Thus, the reaction of *Z*-isomers is expected to predominately take place with more reactive electrophiles. In fact, the use of benzoyl chloride mainly gave *Z*-**4** along with the oxidized product **5** (Scheme 3). On the other hand, with acetic acid anhydride in the reaction of *Z*-**2a**, a stereoisomeric mixture of **6** was formed (Scheme 4).

Ammonium enethiolates were also generated and reacted in ways similar to those in Scheme 1.[17] Generation of ammonium enethiolate **8** was carried out by the deprotonation of selenothioic acid *Se*-ester **7** with TBAF (Scheme 5). The reaction proceeded smoothly to form **8** followed by methylation to give ketene selenothioacetal **9** as a stereoisomeric mixture in a ratio of 55:45 in 84% yield. On the other hand, in the reaction of dithioic acid ester **10** with a THF solution of TBAF, ammonium enethiolate **11** was generated, but the starting ester **10** was also recovered even after a prolonged reaction time between **10** and TBAF or with excess TBAF. Nevertheless, the enethiolate **11** was obtained with high purity.

The spectroscopic properties of ammonium enethiolates **8** and **11** and eneselenolate **2a** are listed in Table 4.

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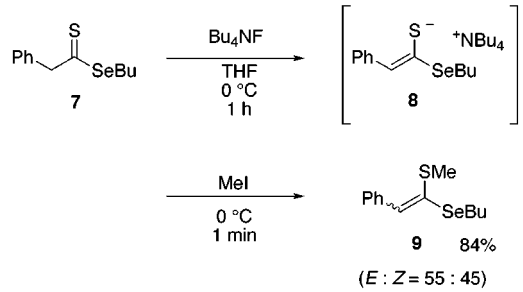
(17) Lithium enethiolates derived from thioaldehydes has been reported to be present as a stereoisomeric mixture: Schwan, A. L.; Refvik, M. D. *Synlett* **1998**, 96.

Scheme 5



Scheme 6

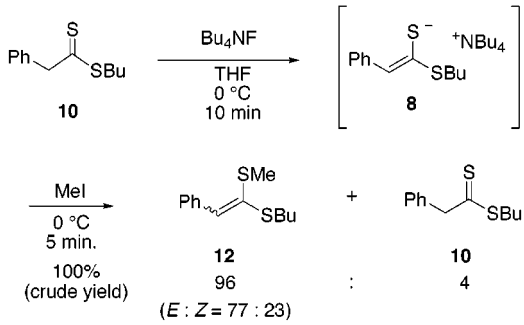
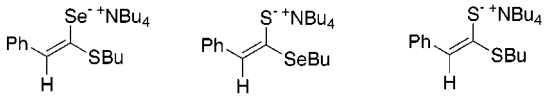


Table 4. Spectroscopic Data of Ammonium Eneselenolate 2a, Ammonium Enethiolate 8, Ammonium Enethiolate 11a



	^{1}H NMR	^{13}C NMR		^{77}Se NMR	
compound	**H**-C-C-E[b]	**C**-E[b]	**C**-C-E[b]	C-**Se**	$^1J_{C-Se}$
2a	6.82	147.6	119.7	253.5	187.5
8	6.16	156.4	117.9	447.1	104.5
11	6.55	159.9	115.6		

[a] NMR spectra were recorded in THF-d_8. [b] E represents sulfur or selenium atom.

Phase-sensitive NOESY spectroscopy of **8** and **11** showed that *E*-isomers of **8** and **11** were formed as thermodynamic enethiolates; i.e., the phenyl group and the sulfur atom with a negative charge in **8** and **11** are located in a cis orientation. This trend is identical to that with ammonium eneselenolates **2**, where the substituents at the β-position to the carbon atom attached to the selenium atom are cis to the negatively charged selenium atom. This is also consistent with the case of ammonium enolates derived from α-phenylacetic acid esters.[7b] The ^{1}H and ^{13}C NMR shifts for ammonium salts **2a**, **8**, and **11** showed tendencies similar to those of the corresponding ketene selenothio or dithioacetals. For example, vinylic carbon atoms are shifted to higher fields, and carbon atoms attached to the sulfur atom are shifted to lower fields in the ^{13}C NMR spectra. Accordingly, the electronic properties of these three salts may also be similar.

In summary, the stereochemical and electronic properties of ammonium eneselenolates and thiolates have been demonstrated. Ammonium eneselenolates were formed as stereoisomeric mixtures, but the *E*-isomers gradually isomerized to give the exclusive formation of *Z*-isomers. The thermodynamic stability of *Z*-isomers is consistent with the case of ammonium enethiolates where the sulfur atom has a negative charge and the substituents have a cis orientation. During the alkylation of ammonium eneselenolates, the isomerization of *Z*-isomers to *E*-isomers took place to form ketene selenothioacetals as stereoisomeric mixtures. The spectroscopic data of ammonium eneselenolates suggested that the electrons at the selenium atom of eneselenolates are somewhat delocalized to the carbon−carbon double bond, and the carbon−selenium bond possesses partial double-bond character.

Experimental Section

Materials, THF was distilled from sodium/benzophenone ketyl immediately prior to use. All of the starting esters were prepared as reported in a literature method.[4] A THF solution of TBAF was purchased from Aldrich Chemcal Company, Inc. Silica gel used in column chromatography was silica gel 60 from Kanto Chemical Co., Inc.

General Procedure for the Synthesis of Ketene Selenothioacetals 3 via Ammonium Eneselenolates 2. A representative procedure for the synthesis of 3-methyl-5-methylseleno-6-thia-1,4-decadiene (**3b**). In a 20-mL two-necked flask, a THF solution of TBAF (0.75 mL, 0.75 mmol) was added to a THF solution (3 mL) of selenothioic acid *S*-butyl ester **1b** (0.126 g, 0.5 mmol) at 0 °C, and the mixture was stirred at that temperature for 30 min. Methyl iodide (0.038 mL, 0.5 mmol) was then added to the reaction mixture, and stirring was continued at this temperature for 1 min. The reaction mixture was poured onto water and extracted with Et_2O (15 mL). The organic layer was dried over Mg_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel using hexane as an eluent to give 0.117 g (89%) of **3b** as a yellow oil: R_f 0.32 (hexane); *Z*-isomer ^{1}H NMR ($CDCl_3$) δ (ppm) 0.89 (t, J = 7.3 Hz, 3 H), 1.06 (d, J = 6.8 Hz, 3 H), 1.40 (sex, J = 7.6 Hz, 2 H), 1.52 (m, 2 H), 2.17 (s, 3 H), 2.65 (t, J = 7.3 Hz, 2 H), 3.46 (m, 1 H), 4.96 (m, 2 H), 5.74 (m, 1 H), 5.88 (d, J = 8.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ (ppm) 7.6, 14.1, 20.0, 21.9, 30.8, 33.6, 40.9, 113.1, 125.6, 141.2, 141.6; ^{77}Se NMR ($CDCl_3$) δ (ppm) 232.8; *E*-isomer ^{1}H NMR ($CDCl_3$) δ (ppm) 0.89 (t, J = 7.3 Hz, 3 H), 1.08 (d, J = 6.8 Hz, 3 H), 1.40 (sex, J = 7.6 Hz, 2 H), 1.52 (m, 2 H), 2.15 (s, 3 H), 2.70 (t, J = 7.3 Hz, 2 H), 3.62 (m, 1 H), 4.96 (m, 2 H), 5.74 (m, 1 H), 5.95 (d, J = 9.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ (ppm) 7.8, 13.7, 19.9, 21.8, 31.8, 34.1, 39.4, 113.1, 124.9, 141.6, 143.5; ^{77}Se NMR ($CDCl_3$) δ (ppm) 166.3; IR (neat) 3079, 2959, 2928, 1639, 1560, 1508, 1540, 1414, 1378, 1272, 1132, 915 cm^{-1}; MS (EI) m/z 249 ($M^+ - CH_3$). Anal. Calcd for $C_{11}H_{20}SSe$: C, 50.18; H, 7.66. Found: C, 50.26; H, 7.43.

1-(Butylthio)-1-(methylseleno)-3-phenyl-1,4-pentadiene (3c). R_f 0.32 (hexane); *Z*-isomer ^{1}H NMR ($CDCl_3$) δ (ppm) 0.81 (t, J = 7.1 Hz, 3 H), 1.33 (m, 2 H), 1.45 (qui, J = 7.4 Hz, 2 H), 2.13 (s, 3 H), 2.62 (dt, J = 2.4 Hz, J = 7.3 Hz, 2 H), 4.69 (t, J = 7.8 Hz, 1 H), 5.12 (m, 2 H), 5.92 (m, 1 H), 6.11 (d, J = 9.8 Hz, 1 H), 7.11−7.24 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ (ppm) 7.8, 13.7, 21.8, 30.8, 33.7, 50.1, 115.3, 126.5, 127.5, 127.8 (Ar), 128.6, 137.9, 139.5, 142.6; *E*-isomer ^{1}H NMR ($CDCl_3$) δ (ppm) 0.82 (t, J = 7.1 Hz, 3 H), 1.33 (m, 2 H), 1.45 (qui, J = 7.4 Hz, 2 H), 2.10 (s, 3 H), 2.68 (t, J = 7.3 Hz, 2 H), 4.81 (t, J = 7.8 Hz, 1 H), 5.01−5.07 (m, 2 H), 5.87−5.96 (m, 1 H), 6.19 (d, J = 9.3 Hz, 1 H), 7.11−7.24 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ (ppm) 7.9, 13.7, 21.8, 31.9, 34.2, 50.1, 115.3, 126.5, 126.7, 127.7, 128.6, 139.4, 140.2, 142; IR (neat) 3081, 3028, 2958, 2872, 2366, 1686, 1038, 1601, 1638, 1601, 1493, 1453, 1416, 1296, 1205, 1133, 1074, 916 cm^{-1}; MS (EI) m/z 326 (M^+). Anal. Calcd for $C_{16}H_{22}OSSe$: C, 59.06; H, 6.81. Found: C, 58.97; H, 6.68.

1-(Butylthio)-1-(methylseleno)-3-ethoxycarbonyl-1,4-pentadiene (3d). R_f 0.32 (hexane); *Z*-isomer ^{1}H NMR ($CDCl_3$) δ (ppm) 0.88 (t, J = 7.3 Hz, 3 H), 1.24 (t, J = 7.1 Hz, 3 H), 1.39 (sex, J = 8.6 Hz, 2 H), 1.54 (m, 2 H), 2.18 (s, 3 H), 2.68 (t, J = 7.3 Hz, 2 H), 4.11 (q, J = 7.2 Hz, 2 H), 4.51−4.56 (m, 1 H), 5.09−5.14 (m, 2 H), 5.85−5.91 (m, 1 H) 6.15 (d, J = 9.3

Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ (ppm) 8.0, 13.7, 14.2, 21.7, 31.8, 34.3, 51.4, 61.1, 117.1, 130.5, 133.4, 134.1, 171.6; ^{77}Se NMR ($CDCl_3$) δ (ppm) 241.9; IR (neat) 3449, 3084, 2959, 2930, 2873, 1732, 1634, 1465, 1367, 1245, 1175, 1031 cm^{-1}: MS (EI) *m*/*z* 348 (M^+). Anal. Calcd for $C_{13}H_{22}O_2SSe$: C, 48.59; H, 6.90. Found: C, 48.29; H, 6.89.

1-(Methylethylthio)-1-(methylseleno)-2-phenyl-1,4-pentadiene (3e). R_f 0.28 (hexane); ^{1}H NMR ($CDCl_3$) δ (ppm) 1.06 (d, J = 6.8 Hz, 6 H), 2.20 (s, 3 H), 3.05 (m, J = 6.7 Hz, 1 H), 3.43 (dt, J = 6.8, 1.7 Hz, 2 H), 4.96 (m, 2 H), 5.67 (m, 1 H), 7.10 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ (ppm) 8.4, 22.5, 38.8, 44.5, 116.2, 126.1, 126.7, 127.8, 128.5, 134.7, 143.0, 148.7; ^{77}Se NMR ($CDCl_3$) δ (ppm) 190.5; IR (neat) 3850, 3078, 2960, 2926, 2351, 1635, 1488, 1441, 1239, 1154, 913 cm^{-1}; MS (EI) *m*/*z* 312 (M^+); Anal. Calcd for $C_{15}H_{20}SSe$: C, 57.87; H, 6.47, Found: C, 57.73; H, 6.35.

1-(Methylethylthio)-1-(methylseleno)-2-(1-cyclohexenyl)-1,4-pentadiene (3f). R_f 0.26 (hexane); ^{1}H NMR ($CDCl_3$) δ (ppm) 1.19 (d, J = 6.8 Hz, 6 H), 1.56 (m, 4 H), 2.00 (m, 4 H), 2.16 (s, 3 H), 3.20 (m, 1 H), 3.21 (m, 2 H), 5.03 (m, 2 H), 5.30 (m, 1 H), 5.71 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ (ppm) 8.1, 22.1, 21.7, 22.9, 25.0, 28.5, 38.0, 42.4, 115.6, 123.0, 125.0, 135.5, 139.3, 151.8; ^{77}Se NMR ($CDCl_3$) δ (ppm) 172.8; IR (neat) 3850, 2925, 1682, 1641, 1446, 1365, 1238, 1156, 1048 cm^{-1}; MS (EI) *m*/*z* 316 (M^+); exact mass M^+ 316.0746 (calcd for $C_{15}H_{24}SSe$ 316.0763).

1-(Methylethylthio)-1-(methylseleno)-2-(2-propenyl)-1-hexene (3g). R_f 0.47 (hexane); major isomer ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 7.1 Hz, 3 H), 1.22 (d, J = 6.4 Hz, 6 H), 1.32 (m, 4 H), 2.14 (S, 3H), 2.45 (t, J = 7.6 Hz, 2 H), 3.19 (m, 1 H), 3.20 (m, 2 H), 4.99 (m, 2 H), 5.69 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 8.1, 14.1, 22.6, 22.8, 30.1, 35.3, 38.4, 41.6, 115.7, 122.3, 135.6, 151.0; ^{77}Se NMR ($CDCl_3$) δ 177.5; minor isomer ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J = 7.1 Hz, 3 H), 1.21 (d, J = 6.4 Hz, 6 H), 1.32 (m, 4 H), 2.15 (S, 3H), 2.39 (t, J = 7.8 Hz, 2 H), 3.25 (m, 1 H), 3.26 (m, 2 H), 4.99 (m, 2 H), 5.69 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 8.1, 14.1, 22.5, 22.7, 31.6, 36.6, 38.3, 40.0, 115.7, 122.0), 135.8, 151.1; ^{77}Se NMR ($CDCl_3$) δ 178.4; IR (neat) 3849, 2958, 2860, 1637, 1454, 1380, 1364, 1238, 1155, 1052 cm^{-1}; MS (EI) *m*/*z* 249 ($M^+ - C_3H_7$). Anal. Calcd for $C_{13}H_{24}SSe$: C, 53.59; H, 8.30. Found: C, 53.35; H, 8.05.

General Procedure for the Formation of Ammonium Eneselenolates 2. A representative experimental procedure for the formation of **2a**. In a two-necked flask, a THF solution of TBAF (0.6 mL, 0.6 mmol) was added to a THF solution of ester **1a** (0.136 g, 0.5 mmol) at 0 °C. After 2 h of stirring at 0 °C, removal of the solvent under reduced pressure gave **2a** as a brown oil.

Benzenecarboselenoic Acid *Se*-(1-(butylthio)-3-methyl-1,4-pentadienyl) Ester (4). R_f 0.26 (hexane); ^{1}H NMR ($CDCl_3$) δ (ppm) 0.89 (t, J = 8.1 Hz, 3 H), 1.12 (d, J = 6.8 Hz, 3 H), 1.40 (sex, J = 7.4 Hz, 2 H), 1.59 (qui, J = 7.4 Hz, 2 H), 2.76 (t, J = 7.3 Hz, 2 H), 3.30 (m, 1 H), 5.77 (m, 2 H), 5.82 (m, 1 H), 6.21 (d, J = 9.8 Hz, 1 H), 7.45 (t, J = 7.1 Hz, 2 H), 7.58 (t, J = 7.3 Hz, 1 H), 7.88 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ (ppm) 13.6, 19.4, 22.0, 30.7, 34.6, 41.9, 113.6, 121.1, 127.5, 128.9, 133.9, 138.5, 141.0, 147.2, 191.4; ^{77}Se NMR (CDCl3) δ (ppm) 603.6; IR (neat) 3082, 2959, 2928, 1694, 1637, 1581, 1540, 1447, 1198, 1174, 1000, 915, 868 cm^{-1}; MS (EI) *m*/*z* 354 (M^+). Anal. Calcd for $C_{17}H_{22}OSSe$: C, 50.18; H, 7.66. Found: C, 50.26; H, 7.43.

Ethaneselenoic Acid *Se*-(1-(butylthio)-2-phenyl-1-ethenyl) Ester (6). R_f 0.19 (hexane); ^{1}H NMR ($CDCl_3$) δ (ppm) 0.85 (m, 3 H, CH_3), 1.36 (m, 2 H), 1.51 (m, 2 H), 2.51 (s, 3 H), 2.83 (m, 2 H), 7.46 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ (ppm) 13.6, 21.9, 31.7, 34.5, 35.8, 124.6, 128.0, 128.8, 129.6, 137.0, 146.0, 197.2; MS (EI) *m*/*z* 282 (M^+). Anal. Calcd for $C_{14}H_{18}OSSe$: C, 53.67; H, 5.79. Found: C, 53.55; H, 5.83.

1-(Butylseleno)-1-(methylthio)-2-phenylethene (9). R_f 0.29 (hexane); *E*-isomer ^{1}H NMR ($CDCl_3$) δ (ppm) 0.85 (m, 3H), 1.35 (sex, J = 7.3 Hz, 2H), 1.64 (qui, J = 7.3 Hz, 2H), 2.34 (s, 3H), 2.84 (m, 2H), 6.78 (s, 1H), 7.23−7.50 (m, 5H); ^{77}Se NMR ($CDCl_3$) δ 306.1; *Z*-isomer ^{1}H NMR ($CDCl_3$) δ (ppm) 0.78 (t, J = 7.3 Hz, 3H), 1.25 (sex, J = 7.3 Hz, 2H), 1.66 (qui, J = 7.3 Hz, 2H), 2.26 (s, 3H), 2.80 (m, 2H), 7.09 (s, 1H), 7.23−7.50 (m, 5H); ^{77}Se NMR ($CDCl_3$) δ (ppm) 282.7; IR (neat) 3055, 2958 2971, 2871, 1580, 1562, 1490, 1443, 1257, 1075, 1030 cm^{-1}; MS (EI) *m*/*z* 286 ($M^+ + 1$); exact mass M^+ 286.0294 (calcd for $C_{13}H_{18}SSe$ 286.0294).

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