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Reaction of an Ammonium Eneselenolate Derived from a Selenothioacetic Acid *S*-Ester with Electron-Deficient Alkenes and Alkynes

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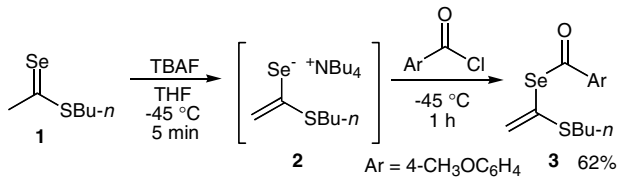
ABSTRACT: *Ammonium eneselenolate* **2** *derived from selenothioic acid* S*-ester* **1** *was reacted with electron-deficient alkenes* **4** *and alkynes* **9**. *Ammonium eneselenolate* **2** *underwent Michael addition with* **4** *to give two types of Michael adducts,* **5** *and* **6**. *Products* **6** *incorporated two molecules of* **4**. *In contrast, the reaction of* **2** *with* **9** *took place at the selenium atom to give* γ*-oxo divinyl selenides* **10** *with high Z-stereoselectivity. During the further elaboration of the reactivity of the products derived from* **2** *and carbonyl compounds, unexpected reaction was found in the addition of vinylmagnesium bromide to Se-vinyl ester* **3**. *The spectroscopic data supported the formation of the enol form* **12** *of* β*-oxo selenothioic acid S-ester* **13**. © 2004 Wiley Periodicals, Inc. Heteroatom Chem 15:187–192, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20003

INTRODUCTION

The chemistry of selenocarbonyl compounds has attracted much attention [1]. In particular, a wide variety of procedures for the synthesis of selenocarbonyl compounds substituted with heteroatom-containing substituents such as selenoamides [2] and selenothioic acid *S*-esters [3] have been developed. These achievements stimulated research to elucidate the chemistry of their enolates, i.e. eneselenolates. During the course of our studies on selenothioic acid *S*-esters [4,5], we found that ammonium fluorides were basic enough to abstract an α-hydrogen of the esters [5]. The eneselenolates derived from α-monosubstituted selenothioic acid *S*-esters can be spectroscopically characterized at room temperature, whereas those from selenothioacetic acid *S*-esters are reactive and rapidly decompose above 0°C. For example, ammonium eneselenolate **2** is generated from ester **1** and tetrabutylammonium fluoride (TBAF) at −45°C, and the subsequent addition of 4-methoxybenzoic acid chloride gives Se-vinyl selenoic acid ester **3** in good yield [Eq. (1)].



(1)

The acylation takes place selectively at the selenium atom of **2**. The reactivity of ammonium eneselenolate **2** toward a variety of oxygen-containing carbon electrophiles was explored further. We report here the reaction of ammonium eneselenolate **2** with electron-deficient alkenes and alkynes. The vinylation of **3** is also described.

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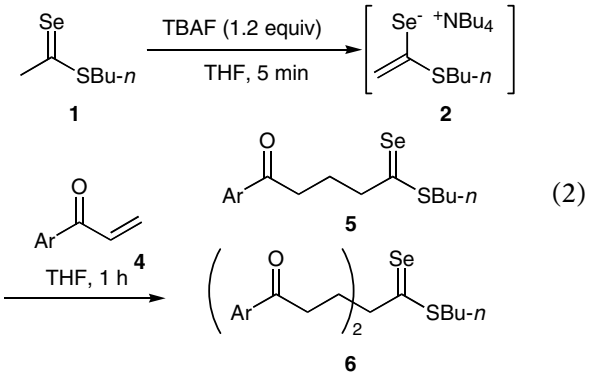
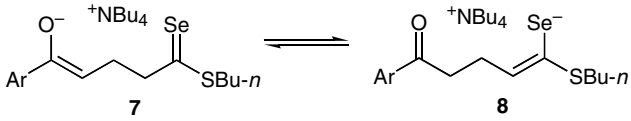
RESULTS AND DISCUSSION

Initially, the reaction of ammonium eneselenolate **2** with 1.1 equiv of α,β-unsaturated ketones **4** was carried out [Eq. (2), Table 1].



(2)

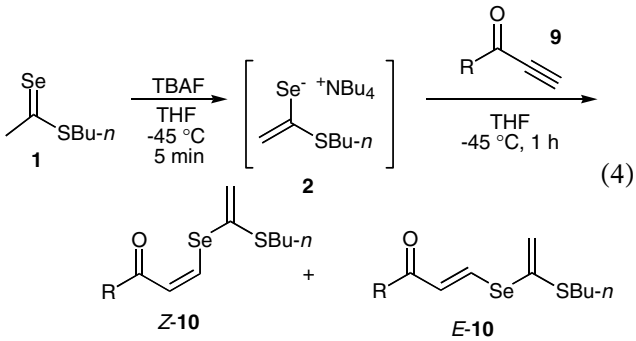
When phenyl vinyl ketone **4a** was added-to a THF solution of **2**, the reaction mixture gradually changed from light brown to deep purple. After chromatographic purification, two types of δ-oxo selenothioic acid *S*-esters [6], **5a** and **6a**, were obtained in respective yields of 34% and 13% (entry 1). Since the Michael addition of lithium enethiolates of dithioic acid esters to α,β-unsaturated ketones proceeds with high efficiency [7], a similar reaction using the lithium eneselenolate generated from ester **2** was attempted, but only a complex mixture was formed. In contrast, the reaction of **2** to **4a** proceeded at the carbon atom of eneselenolate **2** to give Michael adducts, **5a** and **6a**. Notably, two molecules of α,β-unsaturated ketone **4a** were introduced in ester **6a**. α,β-Unsaturated ketones **4b** and **4c** were also reacted with ammonium eneselenolate **2** (entries 2 and 3). For the reaction of **4b**, the yield of **6b** was higher than that of **5b**. Although several attempts to obtain **5** or **6** selectively failed, the use of a decreased amount of **4b** improved the yield of **5b** (entry 4). In the initial step of the reaction in Eq. (2), ammonium enolate **7** may be formed from **2** and **4** [Eq. (3)].



(3)

Proton transfer may then occur from the carbon atom α to the selenocarbonyl group to the enolate moiety of **7** to form ammonium eneselenolate **8**, which reacts with a second molecule of **4** to give ester **6**. This implies that a hydrogen atom α to the selenocarbonyl group is acidic enough to be deprotonated by the enolate moiety of **7**. Furthermore, eneselenolate **8** appears to be more nucleophilic than **2** toward **4** because esters **6** were formed even with the use of 0.1 equiv of **4**.

The reactivity of ammonium eneselenolate **2** toward alkynes bearing a carbonyl group **9** was also tested [Eq. (4), Table 2].



(4)

The reaction of **2** with 1-phenyl-2-propyn-1-one [8], **9a** proceeded smoothly at −45°C to give γ-oxo divinyl selenide**10a** in 69% yield with high *Z*-stereoselectivity (entry 1). A similar reaction using alkynes bearing electron-donating and -withdrawing substituents on an aromatic ring proceeded, and

TABLE 1 Reaction of Ammonium Eneselenolate **2** with α,β-Unsaturated Ketones **4**[a]

			Product, Yield (%)[b]	
Entry	**4**	*Ar*	**5**	**6**
1	**4a**	Ph	34	13
2	**4b**	4-$CH_3OC_6H_4$	12	22
3	**4c**	4-ClC_6H_4	34	6
4[c]	**4a**	4-$CH_3OC_6H_4$	26	12

[a]To a THF solution of ammonium eneselenolate **2** was added **4** (1.1 equiv) and stirred for 30∼60 min at −45°C unless otherwise noted.
[b]Isolated yields based on the amount of ester **1**.
[c]**4a** (0.1 equiv) was used.

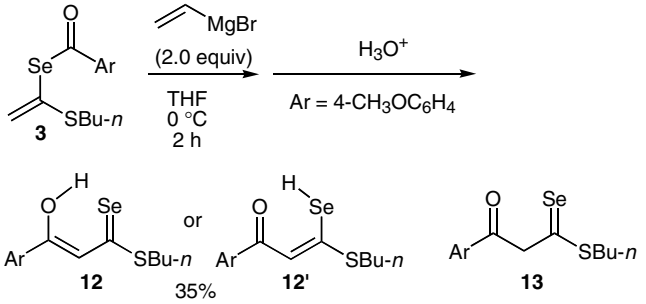
TABLE 2 Reaction of Ammonium Eneselenolate **2** with α,β-Unsaturated Carbonyl Compounds **9**[a]

			Product, Yield (%)[b]	
Entry	**9**	*R*	*Z*-**10**	*E*-**10**
1	**9a**	Ph	65	4
2	**9b**	4-$CH_3OC_6H_4$	71	5
3	**9c**	4-ClC_6H_4	63	3
4	**9d**	CH_3O	76	5
5[c]	**9e**	CH_3	60	3

[a]To a THF solution of ammonium eneselenolate **2** was added **9** (1.2 equiv) and stirred for 30∼60 min at −45°C unless otherwise noted.
[b]Isolated yields.
[c]**9e** (1.5 equiv) was used.

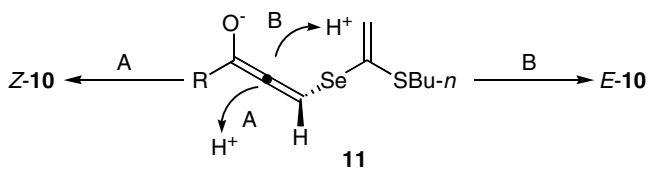
Z-isomers **10b** and **10c** were predominantly obtained in moderate yields (entries 2 and 3). The reaction of propiolic acid methyl ester (**9d**) and 3-butyn-2-one [9] (**9e**) also showed a similar efficiency and selectivity (entries 4 and 5). The *Z*-selectivity in the present reaction is in a marked contrast to the reaction of ester **1** with **9a** in the presence of Et_3N [10], where the selectivity depended on the substituents adjacent to the alkynyl group in **9**. In the initial stage of the present reaction, allenenolate **11** may be formed, and the protonation of **11** may occur during aqueous work-up. At that stage, protonation may take place exclusively from the face close to a hydrogen atom (route A) to result in the formation of *Z*-**10**, since in the reverse face (route B), a bulky vinylselenenyl group is present, as shown in Scheme 1. A similar *Z*-selective formation of vinylselenides has been reported in the reaction of electron-deficient alkynes with selenolate ions [11].

Finally, further tests of reactivities of a wide range of vinyl selenides derived from ester **1** and carbonyl compounds toward organometallic reagents were performed. The reaction of Se-vinyl ester **3** with vinylmagnesium bromide showed an unexpected result. The reaction of **3** and vinylmagnesium bromide in THF at 0°C for 2 h gave enol **12** or the eneselenol form **12′** of **13** [Eq. (5)].



(5)

Although the reaction pathway leading to **12** or **12′** is not yet clear, the formation of enol form **12** was supported by the following spectroscopic data. The signal due to the hydrogen atom of the hydroxyl group was observed at 15.2 ppm in ^1H NMR. The ^1J coupling constant between the hydrogen atom and the selenium atom was determined to be 18.0 Hz. The signal due to the selenocarbonyl group was observed at 213.2 ppm in ^{13}C NMR. The ^1J coupling constant between the carbon atom and the selenium atom was also detected to be 206.2 Hz, and this value was close to that of the carbon-selenium double bond [12]. The signal observed at 830.3 ppm in ^{77}Se NMR was also close to the value of the C=Se group. In addition, broad-absorption due to the hydroxyl group was observed at 3414 cm^{-1}, whereas the absorption due to the carbonyl group was not observed in the IR spectra. Interestingly, ester **13** is present as the enol form **12** which contains a carbon-selenium double bond rather than eneselenol form **12′** containing the carbon-selenium single bond. Although a few β-oxo selenocarbonyl compounds have been isolated as stable compounds [13], their tautomerization has not been reported. On the other hand, theoretical studies on β-oxo selenoaldehydes have suggested that their enol forms and eneselenol forms are energetically close [14].



SCHEME 1

CONCLUSION

The ammonium eneselenolate **2** generated from selenoic acid *S*-ester **1** showed dual reaction patterns toward electron-deficient alkenes **4** and alkynes **9**. Michael addition of **2** to α,β-unsaturated ketones **4** gave two types of δ-oxo selenothioic acid *S*-esters. For the reaction with alkynes **9**, γ-oxo divinyl selenides **10** were obtained with high *Z*-stereoselectivity. Treatment of *Se*-vinyl selenoic acid ester **3** with vinylmagnesium bromide produced the enol form **12** of β-oxo α,β-unsaturated selenothioic acid *S*-ester **13**.

EXPERIMENTAL

General

Melting points were measured by a Yanagimoto micromelting point apparatus and are uncorrected. IR spectra were measured on a JASCO FT/IR-410 Fourier Transform Infrared Spectrometer. NMR spectra were measured with $CDCl_3$ or CD_2Cl_2on a JEOL α-400. Mass spectra were taken on SHIMADZU GCMS QP1000 (EI mode). High-resolution mass spectra were measured on a JEOL GCmate II. Elemental analyses were performed at the Elemental Analysis Center of Kyoto University.

*Reaction of S-butyl Ethaneselenothioate (**1**) with TBAF and 1-Phenyl-2-propene-1-one (**4a**)*

In a 20-ml two-necked flask, TBAF (1.2 ml, 1.2 mmol) was added to a THF solution (10 ml) of *S*-butyl

ethaneselenothioate (**1**) (0.197 g, 1.0 mmol) at −45°C, and the mixture was stirred at that temperature for 5 min. A THF solution (1 ml) of 1-phenyl-2-propen-1-one (**4a**) (0.145 g, 1.1 mmol) was then added to the reaction mixture at −45°C, and stirring was continued at this temperature for 30 min. The reaction mixture was poured into a saturated aqueous solution of $NaHCO_3$ and extracted with Et_2O (20 ml). The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel using hexane-Et_2O as an eluent to give *S*-butyl 5-oxo-5-phenyl-pentaneselenothioate (**5a**) (0.112 g, 34%) and *S*-butyl 5-oxo-5-phenyl-2-(3-oxo-3-phenylpropyl)-pentaneselenothioate (**6a**) (0.071 g, 16%) as a purple oil. **5a**: ^{1}H NMR ($CDCl_3$) δ 0.94 (t, J = 7.3 Hz, 3H), 1.45 (sex, J = 7.3 Hz, 2H), 1.72 (qui, J = 7.3 Hz, 2H), 2.36 (qui, J = 7.2 Hz, 2H), 3.03–3.10 (m, 4H), 3.25 (t, J = 7.3 Hz, 2H), 7.46 (t, J = 7.7 Hz, 2H), 7.56 (t, J = 7.7 Hz, 1H), 7.90 (d, J = 7.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.6, 22.2, 25.2, 28.8, 36.8, 40.7, 56.0, 128.0, 128.6, 133.0, 136.8, 199.3, 243.3;^{77}Se NMR ($CDCl_3$) δ 1498.5; EIMS (*m/z*) 328 (M^+); Anal. Calcd for $C_{15}H_{20}OSSe$: C, 55.04; H, 6.16. Found: C, 55.29; H, 6.06. **6a** : ^{1}H NMR ($CDCl_3$) δ 0.92 (t, J = 7.4 Hz, 3H), 1.41 (sex, J = 7.4 Hz, 2H), 1.69 (qui, J = 7.4 Hz, 2H), 2.14–2.23 (m, 2H), 2.33 (m, 2H), 2.98–3.02 (m, 4H), 3.28 (t, J = 7.5 Hz, 2H), 3.63 (tt, J = 9.5, 4.8 Hz, 1H), 7.44 (t, J = 7.8 Hz, 4H), 7.55 (t, J = 7.8 Hz, 2H), 7.91 (d, J = 7.8 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 13.7, 22.2, 28.8, 31.5, 35.7, 39.6, 63.2, 128.0, 128.6, 133.0, 136.9, 199.4, 248.7;^{77}Se NMR ($CDCl_3$) δ 1451.3; EIMS (*m/z*) 458 (M^+); Anal. Calcd for $C_{24}H_{28}O_2SSe$: C, 62.73; H, 6.14. Found: C, 62.75; H, 6.12.

*S-Butyl 5-(4-methoxyphenyl)-5-oxopentaneselenothioate (***5b***).* Purple oil; ^{1}H NMR ($CDCl_3$) δ 0.94 (t, J = 7.3 Hz, 3H), 1.45 (sex, J = 7.3 Hz, 2H), 1.72 (qui, J = 7.3 Hz, 2H), 2.34 (qui, J = 7.2 Hz, 2H), 3.01–3.06 (m, 4H), 3.24 (t, J = 7.3 Hz, 2H), 3.87 (s, 3H), 6.93 (d, J = 8.8 Hz, 2H), 7.94 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.7, 22.2, 25.5, 28.8, 36.5, 40.7, 55.5, 63.0, 113.7, 129.9, 130.7, 163.4, 197.9, 243.5;^{77}Se NMR ($CDCl_3$) δ 1493.0; EIMS (*m/z*) 358 (M^+); Anal. Calcd for $C_{16}H_{22}O_2SSe$: C, 53.77; H, 6.20. Found: C, 53.79; H, 6.00.

*S-Butyl 5-(4-methoxyphenyl)-2-(3-(4-methoxyphenyl)-3-oxopropyl)-5-oxo-pentaneselenothioate (***6b***).* Purple oil; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7.4 Hz, 3H), 1.42 (sex, J = 7.4 Hz, 2H), 1.68 (qui, J = 7.4 Hz, 2H), 2.11–2.20 (m, 2H), 2.29–2.38 (m, 2H), 2.87–3.01 (m, 4H), 3.29 (t, J = 7.4 Hz, 2H), 3.61 (tt, J = 9.3, 4.8 Hz, 1H), 3.85 (s, 6H), 6.90 (d, J = 9.1 Hz, 4H), 7.90 (d, J = 9.1 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 13.6, 22.2, 28.8, 31.7, 35.4, 39.5, 55.4, 63.4, 113.6, 129.9, 130.2, 163.4, 198.0, 248.9; ^{77}Se NMR ($CDCl_3$) δ 1444.8; EIMS (*m/z*) 519 (M^+); HRMS Calcd for $C_{26}H_{32}O_4SSe$: 520.1187. Found: 520.11763.

*S-Butyl 5-(4-chlorophenyl)-5-oxopentaneselenothioate (***5c***).* Purple oil; ^{1}H NMR ($CDCl_3$) δ 0.94 (t, J = 7.2 Hz, 3H), 1.45 (sex, J = 7.2 Hz, 2H), 1.72 (qui, J = 7.2 Hz, 2H), 2.34 (qui, J = 7.2 Hz, 2H), 3.01–3.07 (m, 4H), 3.24 (t, J = 7.2 Hz, 2H), 7.43 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.7, 22.3, 25.0, 28.8, 36.8, 40.7, 55.9, 128.9, 129.5, 135.2, 139.5, 198.1, 243.1; ^{77}Se NMR ($CDCl_3$) δ 1500.7; EIMS (*m/z*) 361 (M^+); HRMS Calcd for $C_{15}H_{19}ClOSSe$: 362.00104. Found: 362.00321.

*S-Butyl 2-(3-(4-chlorophenyl)-3-oxopropyl)-5-oxo-5-phenylpentaneselenothioate (***6c***).* Purple solid; mp. (dec.) 116–118 °C; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, J = 7.4 Hz, 3H), 1.41 (sex, J = 7.4 Hz, 2H), 1.68 (qui, J = 7.4 Hz, 2H), 2.11–2.20 (m, 2H), 2.29–2.39 (m, 2H), 2.94–2.98 (m, 4H), 3.28 (t, J = 7.4 Hz, 2H), 3.60 (tt, J = 9.5, 4.7 Hz, 1H), 7.41 (d, J = 8.8 Hz, 4H), 7.85 (d, J = 8.8 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 13.7, 22.2, 28.8, 31.4, 35.7, 39.6, 63.0, 128.9, 129.5, 135.2, 139.5, 198.2, 248.4;^{77}Se NMR ($CDCl_3$) δ 1455.5; EIMS (*m/z*) 528 (M^+); HRMS Calcd for $C_{24}H_{26}Cl_2O_2SSe$: 528.01958. Found: 528.01797.

*Reaction of S-butyl Ethaneselenothioate (***1***) with TBAF and 1-Phenyl-2-propyn-1-one (***9a***)*

In a 20-ml two-necked flask, TBAF (1.2 ml, 1.2 mmol) was added to a THF solution (10 ml) of *S*-butyl ethaneselenothioate (**1**) (0.195 g, 1.0 mmol) at −45°C, and the mixture was stirred at that temperature for 10 min. A THF solution (2 ml) of 1-phenyl-2-propyn-1-one (**9a**) (0.156 g, 1.2 mmol) was then added to the reaction mixture at −45°C, and stirring was continued at this temperature for 1 h. The reaction mixture was poured onto a saturated aqueous solution of $NaHCO_3$ and extracted with Et_2O (20 ml). The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel using hexane-Et_2O as an eluent to give (*Z*)-2-(1-butylthioethenylseleno)-1-ethenyl phenyl ketone (**10a**) (0.211 g, 65%) as a yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 3H), 1.44 (sex, J = 7.3 Hz, 2H), 1.58 (qui, J = 7.3 Hz, 2H), 2.76 (t, J = 7.3 Hz, 2H), 5.73 (s, 1H), 5.77 (s, 1H), 7.47 (t, J = 7.3 Hz, 2H), 7.55 (t, J = 7.3 Hz, 1H), 7.64 (d, J = 9.0 Hz, 1H), 7.99 (d, J = 7.3 Hz, 2H), 8.45 (d, J = 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.7, 22.0, 30.4, 33.7, 118.9, 119.3, 128.1, 128.7, 132.8, 137.4, 137.9,

151.9, 189.7; ^{77}Se NMR ($CDCl_3$) δ 581.8; EIMS (*m/z*) 325 (M^+); Anal. Calcd for $C_{15}H_{18}OSSe$: C, 55.38; H, 5.58. Found: C, 55.67; H, 5.63.

*(Z)-2-(1-Butylthioethenylseleno)-1-ethenyl 4-methoxyphenyl Ketone (***10b***).* Yellow solid; mp. (dec.) 66–68°C; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 3H), 1.43 (sex, J = 7.3 Hz, 2H), 1.64 (quint, J = 7.3 Hz, 2H), 2.76 (t, J = 7.3 Hz, 2H), 3.87 (s, 3H), 5.72 (s, 1H), 5.76 (s, 1H), 6.96 (d, J = 8.8 Hz, 2H), 7.60 (d, J = 9.0 Hz, 1H), 7.99 (d, J = 8.8 Hz, 2H), 8.36 (d, J = 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.7, 22.0, 30.5, 33.7, 55.5, 113.9, 118.8, 119.2, 130.4, 138.1, 150.6, 163.3, 188.3; ^{77}Se NMR ($CDCl_3$) δ 574.8; EIMS (*m/z*) 355 (M^+); Anal. Calcd for $C_{16}H_{20}O_2SSe$: C, 54.08; H, 5.67. Found: C, 53.98; H, 5.55.

*(Z)-2-(1-Butylthioethenylseleno)-1-ethenyl 4-chlorophenyl Ketone (***10c***).* Yellow solid; mp. (dec.) 33–34°C; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 3H), 1.44 (sex, J = 7.3 Hz, 2H), 1.64 (qui, J = 7.3 Hz, 2H), 2.76 (t, J = 7.3 Hz, 2H), 5.73 (s, 1H), 5.77 (s, 1H), 7.45 (d, J = 8.6 Hz, 2H), 7.58 (d, J = 9.1 Hz, 1H), 7.92 (d, J = 8.6 Hz, 2H), 8.48 (d, J = 9.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.7, 22.0, 30.5, 33.7, 118.9, 119.1, 129.0, 129.5, 135.8, 137.7, 139.1, 152.8, 188.3; ^{77}Se NMR ($CDCl_3$) δ 585.7; EIMS (*m/z*) 359 (M^+); Anal. Calcd for $C_{15}H_{17}ClOSSe$: C, 50.08; H, 4.76. Found: C, 49.87; H, 4.71.

*Methyl (Z)-3-((1-(butylthio)ethenyl)seleno)-2-propenoate (***10d***).* Yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 3H), 1.43 (sex, J = 7.3 Hz, 2H), 1.62 (qui, J = 7.3 Hz, 2H), 2.74 (t, J = 7.3 Hz, 2H), 3.72 (s, 3H), 5.73 (s, 1H), 5.74 (s, 1H), 6.37 (d, J = 9.3 Hz, 1H), 8.00 (d, J = 9.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.7, 22.0, 30.4, 33.7, 51.6, 116.1, 119.3, 136.2, 148.3, 167.8; ^{77}Se NMR ($CDCl_3$) δ 525.1; EIMS (*m/z*) 279 (M^+); Anal. Calcd for $C_{10}H_{16}O_2SSe$: C, 43.01; H, 5.77. Found: C, 42.74; H, 5.55.

*(Z)-4-((1-(Butylthio)ethenyl)seleno)-3-butene-2-one (***10e***).* Yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 3H), 1.43 (sex, J = 7.3 Hz, 2H), 1.62 (qui, J = 7.3 Hz, 2H), 2.27 (s, 3H), 2.73 (t, J = 7.3 Hz, 2H), 5.68 (s, 1H), 5.72 (s, 1H), 6.87 (d, J = 9.3 Hz, 1H), 8.12 (d, J = 9.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.7, 22.0, 30.4, 29.9, 33.7, 118.8, 123.1, 137.5, 148.8, 197.5; ^{77}Se NMR ($CDCl_3$) δ 574.4; EIMS (*m/z*) 263 (M^+); Anal. Calcd for $C_{10}H_{16}OSSe$: C, 45.62; H, 6.13. Found: C, 45.92; H, 6.24.

*Reaction of Se-(1-butylthioethenyl)-4-methoxybenzenecarboselenoate (***3***) with Vinylmagnesium Bromide*

In a 50-ml two-necked flask, vinylmagnesium bromide (1.0 ml, 1.0 mmol) was added to a THF solution (10 ml) of *Se*-(1-butylthioethenyl)-4-methoxybenzenecarboselenoate (**3**) (0.165 g, 0.5 mmol) at 0°C, and the mixture was stirred at that temperature for 1 h. Methyl triflate (57 μL, 0.5 mmol) was then added to the reaction mixture at 0°C, and stirring was continued at that temperature for 1 h. The reaction mixture was poured into a saturated aqueous solution of NH_4Cl and extracted with Et_2O (20 ml). The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel using hexane-Et_2O as an eluent to give **12** (0.058 g, 35%) as a red oil; IR (neat) 3414, 2957, 2927, 1602, 1580, 1556, 1502, 1233, 1175, 1049, 1028, 931, 839, 764, 611, 528 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 0.97 (t, J = 7.3 Hz, 3H), 1.49 (sex, J = 7.3 Hz, 2H), 1.75 (qui, J = 7.3 Hz, 2H), 3.30 (t, J = 7.3 Hz, 2H), 3.86 (s, 3H), 6.97 (d, J = 9.2 Hz, 2H), 7.26 (s, 1H), 7.95 (d, J = 9.2 Hz, 2H), 15.2 (s, $^1J_{H\text{-}Se}$ = 18.0 Hz, 1H); ^{13}C NMR (CD_2Cl_2) δ 13.2, 21.9, 29.5, 36.0, 55.2, 110.7, 114.0, 126.4, 128.3, 162.8, 169.6, 213.2 ($^1J_{C\text{-}Se}$ = 206.2 Hz); ^{77}Se NMR (CD_2Cl_2) δ 830.3 ($^1J_{H\text{-}Se}$ = 18.0 Hz); EIMS (*m/z*) 331 (M^+); HRMS Calcd for $C_{14}H_{18}O_2SSe$: 330.01927. Found: 330.02081.

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