Aldol-Type Condensation Reactions of Selenothioacetic Acid *S*-Butyl Ester Leading to *β*-Hydroxy Selenothioic Acid *S*-Esters and Ketene Selenothioacetals

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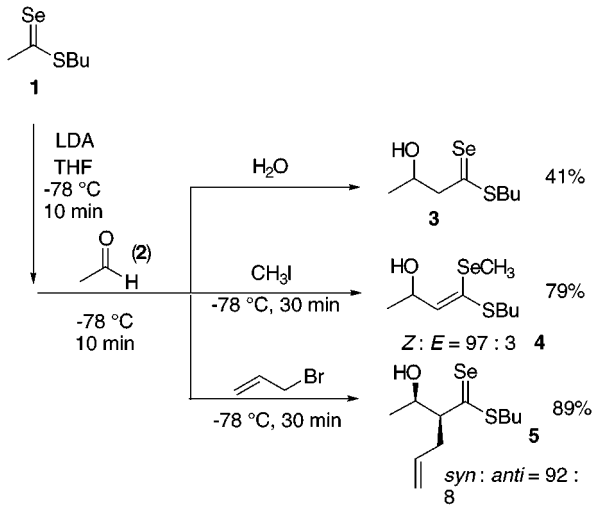
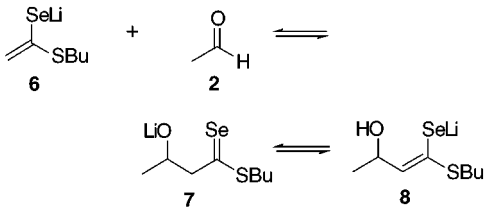
Organoselenium compounds have provided fruitful chemistry in recent years.[1] A number of synthetic methods of organoselenium compounds have been developed over the last 20 years. However, most of them are still limited to derivatives having simple alkyl and aryl groups, and the more convenient synthetic procedures of derivatives having functional groups are necessary, as in the syntheses of organosulfur compounds. For example, the aldol-type condensation reactions of thiocarbonyl compounds such as dithioic acid esters and thioamides have been well documented,[2] and some of the reactions have been utilized in the synthesis of biologically active compounds.[3] However, the reactivity of selenium isologues of enolates, i.e., eneselenolates, toward carbonyl compounds has been elucidated to a much lesser extent. The best known method for the generation of selenium counterparts of metal eneselenolates is the insertion reaction of a selenium atom into a vinylmetallic species.[4] In contrast, only a few examples of the deprotonation of enolizable selenocarbonyl compounds have been studied,[5] although this type of reaction is general for normal carbonyl compounds. This is partly because of the instability of selenocarbonyl compounds and the lack of convenient synthetic methods.[6] During the course of our studies on selenocarbonyl compounds, we have found that lithium eneselenolates are generated efficiently by treating selenothioic acid *S*-esters (RC(Se)SR′)[7] and selenoacetamides ($CH_3C(Se)NR'_2$)[8] with LDA. Furthermore, the aldol-type condensation reaction of selenoacetamide with aldehydes was found to give not *β*-hydroxy selenoamides but α,*β*-unsaturated selenoamides selectively in moderate to good yields.[8] We report herein the aldol-type condensation reactions of selenothioacetic acid *S*-butyl ester and subsequent treatment with carbon electrophiles leading to *β*-hydroxy selenothioic acid *S*-esters and ketene selenothioacetals.

Scheme 1



Scheme 2



Selenothioacetic acid *S*-butyl ester (**1**) was treated with LDA at −78 °C for 10 min. The deep violet-blue reaction mixture turned light brown almost instantly when reacted with LDA. Then, acetaldehyde (**2**) was added to the reaction mixture, followed by the aqueous workup, to give *β*-hydroxy selenothioic acid *S*-butyl ester **3** (41%) as a violet-blue oil (Scheme 1). The *β*-hydroxy ester **3** was highly labile and could not be purified completely. It gradually decomposed even at low temperatures with the liberation of red selenium. The inefficiency of the condensation reaction was considered to be partly due to the instability of *β*-hydroxy ester **3**, but more importantly, it was because of the equilibrium between the starting lithium eneselenolate **6** and acetaldehyde (**2**), *β*-lithioxy ester **7**, and *β*-hydroxy eneselenolate **8** (Scheme 2). A similar type of the equilibrium has already been postulated in the reaction of dithioic acid esters.[9] The selective methylation at the sulfur atom was attained by adding

(1) Krief A. In *Comprehensive Organometallic Chemistry*; Abel, W. W., Stone, F, G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 11, p 515.

(2) Reviews: (a) Metzner, P. *Synthesis* **1992**, 1185. (b) Murai, T.; Kato, S. In *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 5, p 565. (c) Metzner, P.; Thuillier, A. *Sulfur Reagents in Organic Synthesis*; Academic Press: New York, 1994.

(3) (a) Meyers, A. I.; Roland, D. M.; Comins, D. L.; Henning, R.; Fleming, M. P.; Shimizu, K. *J. Am. Chem. Soc.* **1979**, *101*, 4732. (b) Meyers, A. I.; Comins, D. L.; Roland, D. M.; Henning, R.; Shimizu, K. *J. Am. Chem. Soc.* **1979**, *101*, 7104. (c) Meyers, A. I.; Babiak, K. A.; Campbell, A. L.; Comins, D. L.; Fleming, M. P.; Henning, R.; Heuschmass, M.; Hudspeth, J. P.; Kane, J. M.; Reider, P. J.; Roland, D. M.; Shimizu, K.; Tomioka, K.; Walkup, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 5015.

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(5) (a) Barton, D. H. R.; Hansen, P.-E.; Picker, K. *J. Chem. Soc., Perkin* Trans 1 **1977**, 1723. (b) Sukhai, R. S.;. Brandsma, L. *Synthesis* **1979**, 455. (c) Sekiguchi, M.; Ogawa, A.; Fujiwara, S.; Ryu, I.; Kambe, N.; Sonoda, N. *Chem. Lett.* **1990**, 2053. (d) Kanda, T.; Ezaka, T.; Murai, T.; Kato, S. *Tetrahderon Lett.* **1995**, *36*, 2807.

(6) 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, U.K., 1995; Vol. 3, p 381.

(7) (a) Kato, S.; Komuro, T.; Kanda, T.; Ishihara, H.; Murai, T. *J. Am. Chem. Soc.* **1993**, *115*, 3000. (b) Murai, T.; Fujii, M.; Kato, S. *Chem. Lett.* **1997**, 545.

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

(9) Tchertchian, S.; Vallée, Y. *Tetrahedron Lett.* **1995**, *36*, 6225.

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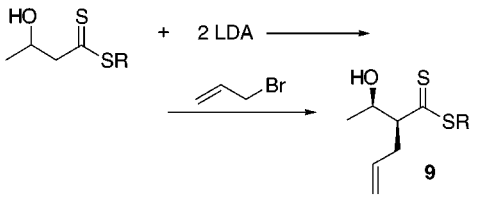
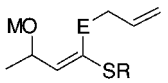
Scheme 3



methyl iodide in the case of sulfur derivatives of type **8**.[9] This procedure was applied to the present reaction. The β-hydroxy ketene selenothioacetal **4** was obtained (79%) by the addition of methyl iodide to the reaction mixture of lithium eneselenolate **6** and acetaldehyde (**2**) with high stereoselectivity. The stereochemistry of the product **4** was determined by phase-sensitive NOESY spectroscopy. The product derived from methylation at the oxygen atom of **7** was not observed. The use of allyl bromide as a second electrophile gave β-hydroxy α-allyl selenothioic acid ester **5** (89%). In the present reaction, a three-component coupling reaction of the ester, aldehyde, and allyl bromide was attained with high selectivity in one operation. The relative stereochemistry of the α- and β-carbon atoms of the selenocarbonyl group of the major isomer was estimated on the basis of the similarity of the chemical shifts and coupling constants of the corresponding dithioic acid esters.[10] Similar derivatives having the dithiocarboxyl group were synthesized by the reaction of β-hydroxy dithioic acid esters with 2 equiv of LDA (Scheme 3).[11] Three days were necessary to obtain the product **9** from the reaction in Scheme 3. This is in sharp contrast to the present reaction in which the conversion was complete within 30 min. These reactions leading to esters **5** and **9** may proceed via the seleno- or thio-Claisen rearrangement of the vinyl allyl selenide or sulfide **10**.

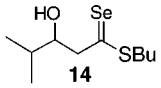
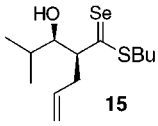
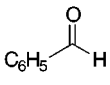
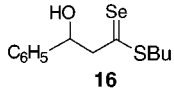
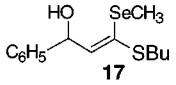
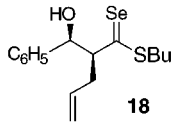
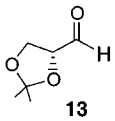
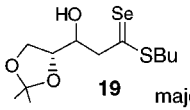
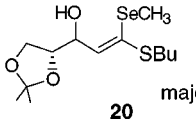
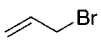
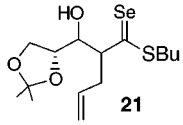


10 E = S, Se

These results have indicated that the seleno-Claisen rearrangement[12] takes place much faster than the thio-Claisen rearrangement. It should also be noted that the stability of the ester **3** was dramatically enhanced by introducing an allyl group to the α-carbon atom of the selenocarbonyl group. The ester **5** could be stored in the refrigerator for a long period, unlike the ester **3**.

The successful results of the reaction of aldehydes and water, methyl iodide, or allyl bromide with lithium eneselenolate **6** are summarized in Table 1. In the reaction of benzaldehyde (**12**) and 2,3-isopropylidene-D-glyceraldehyde (**13**), the corresponding products were obtained in good yields (entries 3−8). However, the reaction of isobutyraldehyde (**11**) gave products **14** and **15** in only moderate yields (entries 1 and 2), although their stability was greater than that of ester **3**. The formation of ketene selenothioacetals **17** and **20** was highly stereoselective (entries 4 and 7), similar to the reaction of acetaldehyde (**2**). The regulation of stereochemistry at the carbon atoms α and β to the selenocarbonyl group was also high (entries 2 and 5). The reaction of the aldehyde **13** gave diastereomers in a ratio of 77 to 23 (entries 6 and 7).

Table 1. Aldol-type Condensation Reaction of Selenothioacetic Acid *S*-Butyl Ester with Aldehydes and Electrophiles[a]

entry	aldehyde	electrophile	product	yield, %[b]
1	 **11**	H_2O	 **14**	15%
2			 **15**	37% *syn* : *anti*.> 99 : 1[c]
3	 **12**	H_2O	 **16**	57%
4		CH_3I	 **17**	65% *Z* : *E* = 88 : 12[d]
5			 **18**	68% *syn* : *anti* = 99 : 1[e]
6	 **13**	H_2O	 **19**	65% major : minor = 77 : 23[e]
7		CH_3I	 **20**	53% major : minor = 77 : 23 *Z* : *E* = 93 : 7[f]
8			 **21**	65%[g]

[a] The ester **1** (1.0 mmol) was reacted with LDA (1.2 mmol) at −78 °C for 10 min. To the reaction mixture was then added aldehyde (1 mmol) at −78 °C with stirring for 10−60 min. In entries 2, 4, 5, 7, and 8, carbon electrophile (1 mmol) was added to the reaction mixture at −78 °C with stirring for 10−60 min. [b] Isolated yield. [c] The ratio of two diastereoisomers was determined by ^{1}H NMR spectra. [d] The stereochemistry of the product **17** was assigned on the basis of phase-sensitive NOESY spectroscopy. The ratio of *Z* and *E* isomers was determined by the integral ratio of the olefinic protons of **17**. [e] The relative stereochemistry of the major isomer was not determined, and the ratio of two isomers was determined by the integral ratio of the protons attached to the β-carbon atoms of selenocarbonyl group in ^{1}H NMR spectra. [f] The ratio of *Z* and *E* isomers of the major diastereomers are shown. [g] Four stereoisomers were obtained, but the ratio of the products was not determined.

In summary, the aldol-type condensation reactions of selenothioacetic acid *S*-butyl ester have been demonstrated. The successive addition of water, methyl iodide, or allyl bromide as a second electrophile has provided

(10) Beslin, P.; Perrio, S. *Tetrahedron* **1991**, *47*, 6275.
(11) Beslin, P.; Perrio, S. *J. Chem. Soc., Chem. Commun.* **1989**, 414.
(12) The seleno-Claisen rearrangement has been known to proceed even at −78 °C: Murai, T.; Takada, H.; Kakami, K.; Fujii, M.; Maeda, M.; Kato, S. *Tetrahedron* **1997**, *53*, 12237.

new synthetic methods to β-hydroxy selenothioic acid *S*-esters and ketene selenothioacetals that are potentially useful but are not easily accessible by other methods.[13]

Experimental Section

General. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded in $CDCl_3$ with TMS as the internal standard. The ^{77}Se NMR (76 MHz) spectra were obtained in $CDCl_3$ with Me_2Se as the external standard. All spectra were acquired in the proton-decoupled mode; generally, 0.05−0.3 mmol solutions in $CDCl_3$ (0.4 mL) were used. Elemental analyses were carried out by Elemental Analysis Center of Kyoto University. Selenothioacetic acid *S*-butyl ester (**1**)[14] and 2,3-*O*-isopropylidene-D-glyceraldehyde (**13**)[15] were prepared according to the literature.

General Procedure for the Aldol-Type Condensation Reaction of Selenothioacetic Acid *S*-Butyl Ester (1) with Aldehydes and Carbon Electrophiles. To a THF solution (5 mL) of LDA (1.2 mmol), prepared by the reaction of *n*-butyllithium (1.6 M in hexane, 0.65 mL, 1.2 mmol) and diisopropylamine (0.156 mL, 1.2 mmol), was added selenothioacetic acid *S*-ester (**1**) (0.195 g, 1 mmol) at −78 °C, with stirring for 10 min. To the reaction mixture was then added the aldehyde (1 mmol) with stirring for 10−60 min at −78 °C. Then, methyl iodide or allyl bromide (1 mmol) was added to the reaction mixture, which was stirred for 10−60 min at −78 °C. The reaction mixture was poured onto an ice/water mixture, extracted with ether, and washed with water. The organic layer was dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by column chromatography on silica gel using hexane:ether (5:1) as the eluent to give the pure product.

3-Hydroxybutaneselenothioic Acid *S*-Butyl Ester (3): violet-blue oil; IR (neat) 3374, 2959, 2928, 1458, 1110 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.83 (t, *J* = 7.5 Hz, 3 H) 1.17 (d, *J* = 6.3 Hz, 3 H), 1.35 (m, 2 H), 1.62 (m, 2 H), 2.86−2.95 (m, 3 H), 3.13 (t, *J* = 7.6 Hz, 2 H), 4.25 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.6, 22.0, 22.4, 28.6, 40.5, 64.6, 67.5, 240.8; ^{77}Se NMR ($CDCl_3$) δ 1471.3; MS(EI) *m*/*z* 240 (M^+).

***Z*-2-Hydroxy-4-methylseleno-5-thia-3-nonene (4)**: light yellow oil; IR (neat) 3340, 2959, 2927, 1456, 1137, 1058 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, *J* = 7.3 Hz, 3 H) 1.29 (d, *J* = 6.3 Hz, 2 H), 1.43 (sex, *J* = 7.4 Hz, 2 H), 1.59 (qui, *J* = 7.3 Hz, 2 H), 1.92 (s, 1 H), 2.24 (s, 3 H), 2.71 (m, 2 H), 4.85 (qui, *J* = 6.7 Hz, 1 H), 5.97 (d, *J* = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 8.0, 13.6, 21.9, 23.1, 30.4, 33.4, 67.9, 128.1, 137.7; ^{77}Se NMR ($CDCl_3$) δ 177.3; MS(EI) *m*/*z* 254 (M^+); HRMS calcd for $C_9H_{18}OSSe$ 254.02427, found 254.02453.

***syn*-2-(1-Hydroxy)ethyl-4-penteneselenothioic Acid *S*-Butyl Ester (5)**: violet-blue oil; IR (neat) 3393, 2961, 2929, 1458, 1118, 915, 801 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.94 (t *J* = 7.4 Hz, 3 H), 1.23 (d, *J* = 6.3 Hz, 3 H), 1.45 (m, 2 H), 1.71 (m, 2 H), 2.60 (m, 1 H), 2.75 (m, 1 H), 2.78 (d, *J* = 3.2 Hz, 1 H), 3.25 (dt, *J* = 10.2, 4.2 Hz, 1 H), 3.35 (t, *J* = 7.3 Hz, 2 H), 4.11 (m, 1 H), 4.97 (d, *J* = 10.0 Hz, 1 H), 5.03 (d, *J* = 17.1 Hz, 1 H), 5.69 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.6, 21.0, 22.1, 28.6, 36.0, 39.4, 70.0, 70.5, 116.7, 135.4, 246.9; ^{77}Se NMR ($CDCl_3$) δ 1405.9; MS(EI) *m*/*z* 280 (M^+). Anal. Calcd for $C_{11}H_{20}OSSe$: C, 47.30; H, 7.22. Found: C, 47.41; H, 7.28.

3-Hydroxy-4-methylpentaneselenothioic Acid *S*-Butyl Ester (14): violet-blue oil: IR (neat) 3424, 2959, 1465, 1051 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.93 (m, 3 H), 0.97 (d, *J* = 4.0 Hz, 6 H), 1.46 (m, 2 H), 1.72 (m, 2 H), 1.79 (m, 1 H), 2.81 (d, *J* = 3.7 Hz, 1 H), 2.98 (dd, *J* = 14.2, 8.8 Hz, 1 H), 3.06 (dd, *J* = 14.2, 2.7 Hz, 1 H), 3.26 (t, *J* = 7.6 Hz, 2 H), 3.94 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.6, 17.4, 18.6, 22.2, 28.6, 33.3, 40.6, 60.6, 76.0, 242.2;^{77}Se NMR ($CDCl_3$) δ 1463.3; MS(EI) *m*/*z*: 268 (M^+). Anal. Calcd for $C_{10}H_{20}OSSe$: C, 44.94; H, 7.54. Found: C, 44.65; H, 7.35.

***syn*-2-(2-Propenyl)-3-hydroxy-4-methylpentaneselenothioic Acid *S*-Butyl Ester (15)**: violet-blue oil: IR (neat) 3428, 2959, 1465, 991, 915 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.95 (m, 3 H), 0.99 (d, *J* = 6.5 Hz, 6 H), 1.45 (m, 2 H), 1.71 (m, 2 H), 1.83 (m, 1 H), 2.61 (m, 1 H), 2.71 (br, 1 H), 2.73 (m, 1 H), 3.24 (m, 2 H), 3.59 (dt, *J* = 15.3, 3.0 Hz, 1 H), 3.61 (m, 1 H), 4.94 (dd, *J* = 10.1, 1.0 Hz, 1 H), 4.99 (dq, *J* = 16.8, 1.7 Hz, 1 H), 5.69 (m, 1 H). Double irradiation at δ 1.82 and δ 2.71 showed doublet−doublet at δ 3.60 (*J* = 4.7, 7.3 Hz) and doublet at δ 3.65 (*J* = 4.7 Hz); ^{13}C NMR ($CDCl_3$) δ 13.6, 17.1, 19.9, 22.2, 28.6, 30.4, 36.3, 39.4, 66.4, 79.0, 116.6, 135.5, 247.4; ^{77}Se NMR ($CDCl_3$) δ 1411.1; MS(EI) *m*/*z*: 307(M^+); HRMS calcd for $C_{13}H_{24}OSSe$ 308.0712, found 308.0710.

3-Hydroxy-3-phenylpropaneselenothioic Acid *S*-Butyl Ester (16): violet-blue oil: IR (neat) 3414, 2957, 2928, 1453, 1055, 699, cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.94 (t, *J* = 7.3 Hz, 3 H), 1.44 (m, 2 H), 1.71 (m, 2 H), 3.17 (d, *J* = 3.2 Hz, 1 H), 3.22 (m, 2 H), 3.27 (d, *J* = 3.4 Hz, 1 H), 3.31 (m, 1 H), 5.31 (dd, *J* = 5.4, 3.3 Hz, 1 H), 7.33 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 13.6, 22.1, 28.6, 40.6, 65.0, 73.5, 125.9, 127.7, 128.4, 142.2, 239.9; ^{77}Se NMR ($CDCl_3$) δ 1473.3; MS(EI) *m*/*z*: 301(M^+). Anal. Calcd for $C_{13}H_{18}$-OSSe: C, 51.82; H, 6.02. Found: C, 51.70; H, 6.09.

(*Z*)-1-Hydroxy-1-phenyl-3-methylseleno-4-thia-2-octene (17): light yellow oil: IR (neat) 3359, 2957, 2928, 1452, 1270, 1019, 761, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0. 89 (t, *J* = 7.3 Hz, 3 H), 1.41 (sex, *J* = 7.3 Hz, 2 H), 1.55 (qui, *J* = 7.5 Hz, 2 H), 2.26 (s, 3 H), 2.72 (m, 2 H), 5.83 (d, *J* = 8.3 Hz, 1 H), 6.11 (d, *J* = 8.3 Hz, 1 H), 7.33 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 8.1, 13.6, 21.7, 30.4, 33.5, 73.7, 126.0, 127.5, 128.2, 128.5, 129.6, 129.7, 135.4, 142.8; ^{77}Se NMR ($CDCl_3$) δ 182.8; MS(EI) *m*/*z*: 316 (M^+); HRMS calcd for $C_{14}H_{20}OSSe$ 316.03991, found 316.04185.

2-(Hydroxybenzyl)-methyl-4-penteneselenothioic Acid *S*-Butyl Ester (18): violet-blue oil: IR (neat) 3419, 2958, 2928, 1455, 1024, 915, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, *J* = 7.3 Hz, 3 H), 1.35 (m, 2 H), 1.58 (m, 2 H), 2.55 (m, 1 H), 2.90 (m, 1 H), 3.17 (m, 2 H), 3.31 (d, *J* = 1.95 Hz, 1 H), 3.68 (dt, *J* = 7.8, 3.9 Hz, 1 H), 4.91 (d, *J* = 10.0 Hz, 1 H), 4.96 (d, *J* = 16.8 Hz, 1 H), 5.06 (d, *J* = 2.7 Hz, 1 H), 5.59 (m, 1 H), 7.32 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 13.5, 22.0, 28.5, 35.2, 39.3, 70.7, 75.7, 116.8, 126.5, 127.5, 128.1, 135.1, 141.3, 246.0; ^{77}Se NMR ($CDCl_3$) δ 1407.3; MS(EI) *m*/*z*: 342 (M^+). Anal. Calcd for $C_{16}H_{22}OSSe$: C, 56.30; H, 6.50. Found: C, 56.56; H, 6.64.

Major Isomer of 3-Hydroxy-4,5-*O*-isopropylidenepentaneselenothioic Acid *S*-Butyl Ester (19): violet-blue oil: IR (neat) 3455, 2958, 1371, 1215, 1155, 1065, 845 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.96 (t, *J* = 7.3 Hz, 3 H), 1.36 (s, 3 H), 1.44 (s, 3 H), 1.47 (sex, *J* = 5.6 Hz, 2 H), 1.75 (qui, *J* = 7.5 Hz, 2 H), 2.93 (dd, *J* = 8.8, 14.9 Hz, 1 H), 3.19 (d, *J* = 3.2 Hz, 1 H), 3.26 (t, *J* = 7.4 Hz, 2 H), 3.8−4.3 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 13.6, 22.2, 25.2, 26.7, 28.6, 40.6, 59.0, 66.5, 72.1, 77.4, 109.5, 240.5; ^{77}Se NMR ($CDCl_3$) δ 1471.0; MS(EI) *m*/*z*: 326 (M^+). Anal. Calcd for $C_{12}H_{22}O_3SSe$: C, 44.30; H, 6.82. Found: C, 44.35; H, 7.10.

3-Hydroxy-1,2-*O*-isopropylidene-5-methylseleno-8-thianon-4-ene (20): light yellow oil: IR (neat) 3443, 2930, 1371, 1214, 1066 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, *J* = 7.3 Hz, 3 H), 1.34 (s, 3 H), 1.39 (sex, *J* = 8.2 Hz, 2 H), 1.42 (s, 3 H), 1.56 (qui, *J* = 7.4 Hz, 2 H), 2.22 (s, 3 H), 2.23 (s, 1 H), 2.70 (m, 2 H), 3.89 (dd, *J* = 6.8, 8.1 Hz, 1 H), 4.00 (dd, *J* = 6.7, 8.2 Hz, 1 H), 4.15 (dt, *J* = 4.5, 6.6 Hz, 1 H), 4.67 (m, 1 H), 4.81 (qui, *J* = 3.8 Hz, 1 H), 4.89 (qui, *J* = 3.8 Hz, 1 H), 5.85 (d, *J* = 8.1 Hz, 1 H), 6.00 (d, *J* = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 8.2, 13.6, 21.9, 25.1, 26.3, 30.4, 33.6, 65.1, 71.4, 77.8, 109.4, 130.5; ^{77}Se NMR ($CDCl_3$) δ.188.5; MS(EI) *m*/*z*: 340 (M^+); HRMS calcd for $C_{13}H_{24}O_3SSe$ 340.06103, found 340.06375.

3-Hydroxy-4,5-*O*-isopropylidene-2-(2-propenyl)-pentaneselenothioic Acid *S*-Butyl Ester (21): violet blue oil: IR (neat) 3450, 2959, 2930, 1371, 1250, 1217, 1067 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.95 (t, *J* = 7.5 Hz, 3 H), 1.35 (s, 3 H), 1.44 (s, 3 H), 1.46 (sex, *J* = 6.6 Hz, 2 H), 1.57 (s, 1 H), 1.72 (qui, *J* = 7.4 Hz, 2 H), 2.63 (m, 1 H), 2.78 (m, 1 H), 3.2−3.3 (m, 3 H), 3.73 (td, *J* = 3.9, 10.5 Hz, 1 H), 4.00 (m, 1 H), 4.09 (m, 2 H), 4.97 (d, *J* = 10.3 Hz, 1 H), 5.03 (d, *J* = 17.1 Hz, 1 H), 5.70 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ

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13.6, 22.2, 25.3, 26.8, 28.5, 35.4, 39.5, 64.3, 66.2, 74.0, 75.3, 109.3, 116.9, 134.9, 246.7; ^{77}Se NMR ($CDCl_3$) δ 1411.9; MS(EI) *m*/*z*: 368 (M^+). Anal. Calcd for $C_{15}H_{26}O_3SSe$: C, 49.31; H, 7.17. Found: C, 49.52; H, 7.39.

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Supporting Information Available: ^{1}H NMR spectra of **3**, **4**, **17**, and **20**. This material is available free of charge via the Internet at http://pubs.acs.org.

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