Pergamon

Tetrahedron, Vol. 52, No. 8, pp. 2839-2846, 1996

0040-4020/96 $15.00 + 0.00

S0040-4020(96)00005-1

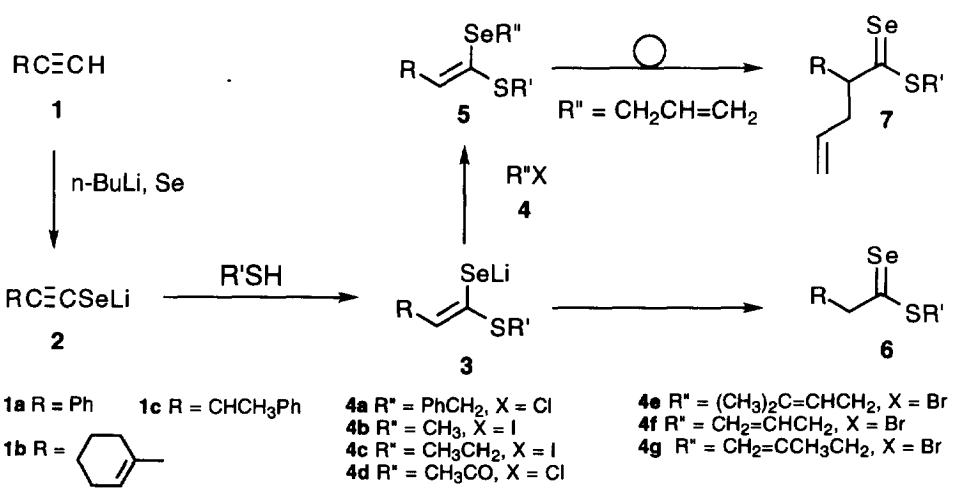
Stereoselective Generation and Trapping of Lithium Eneselenolates Leading to Ketene Selenothioacetals and Selenothioesters

Toshiaki Murai,* Kaori Kakami, Naoshi Itoh, Takahiro Kanda, and Shinzi Kato*

Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-11, Japan

Abstract: The reaction of lithium alkyneselenolates generated from terminal acetylenes with thiols gave rise to lithium eneselenolates with high stereoselectivity. The trapping with alkyl halides afforded ketene selenothioacetals, whereas the trapping with allylic bromides yielded γ,δ-unsaturated selenothioesters via seleno-Claisen rearrangement.

Organoselenium chemistry is of current interest from synthetic and structural point of view.[1] Nevertheless, synthetic methods of organoselenium compounds via lithium eneselenolates,[2] i.e., selenium counterparts of lithium enolates, have not been studied to any great extent, although the similar approach using lithium enethiolates has been extensively explored.[3] The ordinary route to lithium eneselenolates may be the proton abstraction from the corresponding selenocarbonyl compounds.[2] However, some of them such as enolizable selenoaldehydes and selenoketones[4] are not stable enough to treat under basic reaction conditions. Furthermore, only a limited number of selenocarbonyl compounds are easily accessible[5] except for selenoamides.[6] Very recently, we have found that selenothioesters **6** were synthesized by the reaction of lithium alkyneselenolates **2** with thiols (Scheme 1).[7]



Scheme 1

We report here the generation of lithium eneselenolates **3** from terminal acetylenes with high stereoselectivity and their trapping with alkyl halides or allylic bromides to lead to ketene selenothioacetals or selenothioesters, respectively (Scheme 1).

Lithium alkyneselenolate **2** (R = Ph) derived from phenylacetylene (**1a**) was slowly added to *iso*-butanethiol at -78 °C. Then, to the resulting mixture was added benzyl chloride (**4a**) at room temperature to give *Se*-benzyl ketene selenothioacetal **5a** (R = Ph, R' = *iso*-Bu, R" = $PhCH_2$) (*E* / *Z* = 8/92) as a major product in 47% yield.

The intermediacy of lithium eneselenolate **3** in the present reaction was confirmed by NMR spectra in d8-THF. The selected NMR data of **3a** generated from **1a** was shown in Figure 1.

The nucleus observed was denoted in parenthesis. ^1H NMR spectrum of the mixture of *iso*-butanethiol and lithium alkyneselenolate **2a** (R = Ph), showing the signals of the vinylic proton and $SC\underline{H}_2$ of **3a** (R = Ph, R' = *iso*-Bu) at 6.55 and 2.69 ppm was in good agreement with those of **3a** generated by the proton abstraction of the corresponding selenothioester **6** (R = Ph, R' = *iso*-Bu). The stereochemistry of *E* and *Z* isomers of **3a** was assigned through the differential NOE experiment. Irradiation of the signal at 2.69 ppm of **3a** enhanced the intensity of vinylic proton of **3a** by 3 %. The ratio of *E* and *Z* isomers of **3a** was determined to be 6 : 94.

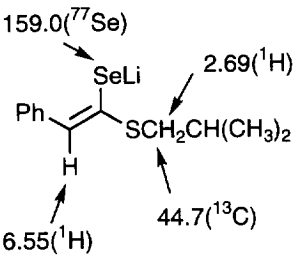
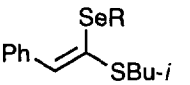
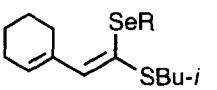
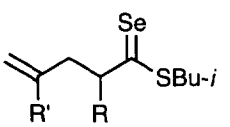
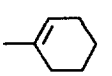
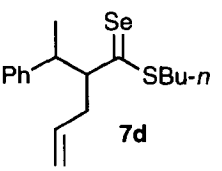


Figure 1

The signals of **3a** from **1a** in ^{13}C and ^{77}Se NMR spectra were also consistent with those of **3a** from **6a**.

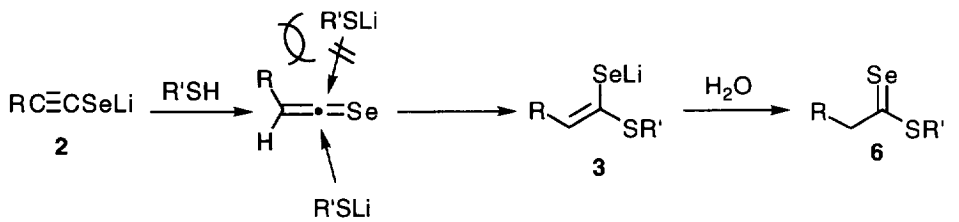
The reaction of a variety of lithium eneselenolates **3** and alkyl halides was carried out (Table 1). *iso*-Butane- or *n*-butanethiol gave the products in the yields higher than cyclopentane- and phenethylthiols. In the reaction with **4a–4e**, ketene selenothioacetals, whose synthesis and reactivity have rarely been studied[2d,8] compared with ketene dithio-[9] and diselenoacetals,[10] were obtained as a product. The efficiency of alkylation is highly dependent on electrophiles in analogy to the alkylation of lithium enethiolates generated from $RCH_2C(S)SeMe$.[9b] When methyl iodide (**4b**) was used as an electrophile, the corresponding *Se*-methyl ketene selenothioacetal **5b** was obtained only in 21% yield with *E* / *Z* selectivity of 6/94 at 25 °C. On raising the temperature, the yield of the product was slightly improved, and the *E* isomer of **5b** was predominantly formed (entry 1). In the alkylation with ethyl iodide (**4c**) under the conditions similar to entry 1, the stereochemistry of lithium eneselenolate **3a** was retained in the product **5c** (entry 2). As for the reaction with allylic bromide **4e**, the stereoselectivity of the product was lowered. This is probably due to the thermal isomerization of the starting lithium eneselenolate or the product, which is often observed for the push-pull alkenes, although the mechanistic detail has not been understood yet.[11] As an acetylene, eneyne **1b** also predominantly led to *Z*-isomers of **5f** and **5g** in good yields (entries 5 and 6), whereas the reaction using aliphatic acetylenes such as 1-hexyne gave a complex mixture. When allylic bromides **4f** and **4g** were employed as a trapping agent, the products **7a–7d** where the allylation took place at the olefinic carbon away from alkylthio group in **3** were obtained as a deep purple liquid or solid in good yields (entries 7-10). The reaction in entry 10 gave two stereoisomers of **7d** in a ratio of 86 : 14, although their stereochemistry has not been determined yet. The esters **7** may be formed via the seleno-Claisen rearrangement[2d,12] of the *Se*-allyl ketene selenothioacetals **5**. The formation of *Se*-prenyl ketene selenothioacetal in the reaction with **4e** (entry 4) may support that the allylation of **3** initially occurs at the selenium atom.

Table 1. Generation and Trapping of Lithium Eneselenolates [a]

entry	acetylene **1** electrophile **4**	temp./ °C time / h	product	yield/ % [b]
				
1	**1a, 4b**	rt, 0.5 h 66 °C, 3 h	**5b** R = CH_3	36% (*E* / *Z* = 62 / 38)
2	**1a, 4c**	rt, 1.5 h 66 °C, 3 h	**5c** R = CH_2CH_3	32% (*E* / *Z* = 8 / 92)
3	**1a, 4d**	rt, 1 h 66 °C, 0.5 h	**5d** R = 	37% (*E* / *Z* = 7 / 93)
4	**1a, 4e**	rt, 0.5 h 66 °C, 3 h	**5e** R = $CH_2CH{=}C(CH_3)_2$	41% (*E* /*Z* = 52 /48)
				
5	**1b, 4a**	rt, 0.5 h 66 °C, 3 h	**5f** R = CH_2Ph	57% (*E* / *Z* = 18 / 82)
6	**1b, 4d**	rt, 1.5 h	**5g** R = 	51% (*E* / *Z* = 14 / 86)
				
7	**1a, 4f**	rt, 0.5 h 66 °C, 3 h	**7a** R = Ph, R' = H	55%
8	**1a, 4g**	rt, 0.5 h 66 °C, 3 h	**7b** R = Ph, R' = CH_3	57%
9	**1b, 4f**	rt, 0.5 h 66 °C, 3 h	**7c** R =  , R' = H	58%
10	**1c, 4f**	rt, 0.5 h 66 °C, 3 h	 **7d**	49% [c]

[a] The reaction was carried out with terminal acetylene (1 mmol), butyllithium (1 mmol), selenium (79 mg, 1 mmol), *iso*-butanethiol (2 mmol), and alkyl halide (2 mmol) in THF (5 mL). [b] Isolated yield. [c] *n*-Butanethiol was used.

As reported previously,[7] esters **6** were synthesized from **1a–1c** at most in 29% yields. At first, this was considered to be due to the low conversion of **2** to **3** via selenoketene intermediates (Scheme 2). However, the present results have suggested that **3** was generated with high efficiency. Accordingly, the moderate yields of **6** from **2** may be ascribed to the step in the hydrolysis of **3**. As a matter of fact, ester **6** was recovered only in 30% yield even in the hydrolysis of **3a** generated by the addition of **6** to THF solution of LDA. The higher yields of **7** may be partly because of the enhancement of the stability of esters **7** by introducing allylic group to the α-position of selenocarbonyl group.[13] The high stereoselectivity of the formation of Z-isomers of **3** may be understood by considering that the nucleophilic attack of R'SLi to selenoketene intermediates takes place from their sterically vacant site as shown in Scheme 2.



Scheme 2

In summary, we have demonstrated that the lithium eneselenolates were generated efficiently from terminal acetylenes. The trapping of lithium eneselenolates with alkyl halides gave ketene selenothioacetals, whereas trapping with allylic bromides resulted in the formation of γ,δ-unsaturated selenothioesters via seleno-Claisen rearrangement.

EXPERIMENTAL

Acetylenes **1a** and **1b**, *n*-butyllithium-hexane solution, selenium powder, butanethiols, and alkyl halides **4** were purchased and used without further purification. Acetylene **1c** was prepared by the procedure in the literature.[14] Column chromatography was run on Silica gel (70-230 mesh ASTM) of Cica Merck. High performance liquid chromatography was performed on a model LC-908 (Japan Analytical Industry Co., Ltd.). Melting point was determined on a Yanagimoto melting point apparatus without correction. The IR spectra were measured on a Perkin Elmer FT-IR 1640 instrument. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded on a JEOL A-400 MHz spectrometer using TMS as the internal standard for ^{1}H spectra and $CDCl_3$ for ^{13}C NMR. In ^{77}Se NMR (76.3 MHz) Me_2Se was used as an external standard.

General procedure for the preparation of ketene selenothioacetals ***5a-5g*** and selenothioesters ***7a-7d***

To THF (3 mL) were added terminal acetylene **1** (1.0 mmol) and *n*-butyllithium (1*N* *n*-hexane solution, 0.63 mL, 1.0 mmol) and stirred for 15 min at 0 °C. Then, to the mixture was added selenium powder (0.079g, 1.0 mmol) and stirred for 5 min. at that temperature. The resulting mixture was dropped to *iso*-butanethiol (0.22 mL, 2.0 mmol) over 15 min. and stirred for 1 h at -78°C~25°C. Alkyl halide (2.0 mmol) was added to the solution at -78°C, and the mixture was stirred for the period at the temperature described in Table 1. The reaction mixture was poured into water and extracted with ether and dried over $MgSO_4$. The solvent was removed in vacuo, and the residue was purified through silica gel column chromatography by

using *n*-hexane as an eluent to give **5** or **7** with the purity higher than 90%. Further purification was performed with high performance liquid chromatography when necessary.

*Z-2-(Benzylseleno)-2-((2-methyl)propylthio)ethenylbenzene (**5a**)* Obtained as an oil: IR (neat) 3060, 3026, 2957, 2868, 1944, 1600, 1560, 1494, 1453, 1383, 1365, 1320, 1242, 1170, 1074, 1030, 921, 888, 750, 695, 598, 552, 522 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (d, J = 6.6Hz, 6H, $CH(CH_3)_2$), 1.89 (qui, J = 6.7 Hz, 1H, $CH(CH_3)_2$), 2.72 (d, J = 6.8 Hz, 2H, SCH_2), 4.05 (s, 2H, $SeCH_2$), 7.09 (s, 1H, PhCH), 7.16-7.34 (m, 10H, Ph); ^{13}C NMR ($CDCl_3$) δ 22.2 ($CH(CH_3)_2$), 28.1 ($CH(CH_3)_2$), 31.9($SeCH_2$), 44.5 (SCH_2), 126.9, 127.2, 128.0, 128.4, 128.6, 128.9, 129.3, 134.5, 137.2, 138.9 (PhCH=C, Ph); ^{77}Se NMR ($CDCl_3$) δ 352.0; MS (*m/z*) 362 (M^+), 271 (M^+-$C_6H_5CH_2$), 91 ($C_6H_5CH_2$); Anal. Calcd for $C_{19}H_{22}SSe$: C, 63.15; H, 6.14. Found: C, 63.35: H, 6.24.

*Z-2-(Methylseleno)-2-((2-methyl)propylthio)ethenylbenzene (**5b**).* Obtained as an oil: IR (neat) 2957, 2927, 2868, 1719, 1686, 1655, 1638, 1598, 1560, 1508, 1490, 1464, 1444, 1382, 1365, 1267, 1243, 1168, 1076, 1030, 921, 884, 749, 693, 597, 557, 518 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (d, J = 6.6 Hz, 6H, $CH(CH_3)_2$), 1.92 (qui, J = 6.7 Hz, 1H, $CH(CH_3)_2$), 2.20 (s, 3H, $SeCH_3$), 2.71 (d, J = 6.8 Hz, 2H, SCH_2), 7.10 (s, 1H, PhCH), 7.19-7.24 (m, 1H, *p*-CH), 7.31 (dd, J = 8.1, 7.3 Hz, 2H, *m*-CH), 7.54 (d, J = 7.3Hz, 2H, *o*-CH); ^{13}C NMR ($CDCl_3$) δ 8.4 ($SeCH_3$), 21.8 ($CH(CH_3)_2$), 28.2 ($CH(CH_3)_2$), 43.5 (SCH_2), 127.1, 128.0, 128.9, 133.4, 135.4, 137.3 (C_6H_5, C=CH); ^{77}Se NMR ($CDCl_3$) δ 201.9; MS (*m/z*) 286 (M^+); Anal. Calcd for $C_{13}H_{18}SSe$: C, 54.73; H, 6.36. Found: C, 54.97; H, 6.52.

*Z-2-(Ethylseleno)-2-((2-methyl)propylthio)ethenylbenzene (**5c**).* Obtained as an oil: IR (neat) 3056, 3022, 2957, 2923, 2867, 1655, 1600, 1579, 1560, 1490, 1464, 1444, 1385, 1382, 1321, 1231, 1168, 1076, 1047, 1030, 961, 921, 887, 800, 746, 693, 596, 556, 504 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (d, J = 6.6Hz, 6H, $CH(CH_3)_2$), 1.36 (t, J = 7.4 Hz, 3H, CH_2CH_3), 1.92 (qui, J = 6.7 Hz, 1H, $CH(CH_3)_2$), 2.74 (d, J = 6.8 Hz, 2H, SCH_2), 2.83 (q, J = 7.5 Hz, 2H, $SeCH_2$), 7.11 (s, 1H, PhCH), 7.21-7.24 (m, 1H, *p*-CH), 7.30-7.34 (m, 2H, *m*-CH), 7.46-7.48 (m, 2H, *o*-CH); ^{13}C NMR ($CDCl_3$) δ 15.5 ($SeCH_2$), 21.9 (CH_2CH_3), 22.1 ($CH(CH_3)_2$), 28.1 ($CH(CH_3)_2$), 43.5 (SCH_2), 127.1, 128.0, 128.0, 129.0, 133.9, 137.4 (C_6H_5, C=CH); MS (*m/z*) 300 (M^+); Anal. Calcd for $C_{14}H_{20}SSe$: C, 56.18; H, 6.73. Found: C, 56.29: H, 6.70.

*Z-2-(Acetylseleno)-2-((2-methyl)propylthio)ethenylbenzene (**5d**).* Obtained as an oil: IR (neat) 3056, 3023, 2958, 2869, 1732 (C=O), 1582, 1565, 1490, 1464, 1444, 1412, 1384, 1366, 1348, 1241, 1168, 1095, 1030, 1000, 925, 888, 746, 695, 595, 570, 499 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (d, J = 6.6 Hz, 6H, $CH(CH_3)_2$), 1.94 (qui, J = 6.7 Hz, 1H, $CH(CH_3)_2$), 2.38 (s, 3H, CCH_3), 2.75 (d, J = 6.8 Hz, 2H, SCH_2), 7.20-7.38 (m, 6H, C_6H_5CH); ^{13}C NMR ($CDCl_3$) δ 22.2 ($CH(CH_3)_2$), 27.9 ($CH(CH_3)_2$), 33.7 (CCH_3), 43.5 (SCH_2), 125.0 (CSe), 127.7, 128.0, 128.8, 129.6 (CH), 136.9 (*ipso*-C), 195.1 (C=O); MS (*m/z*) 314 (M^+); Anal. Calcd for $C_{14}H_{18}OSSe$: C, 53.67 H, 5.79. Found: C, 53.46; H, 5.67.

*Z-2-(3-Methyl-2-butenylseleno)-2-((2-methyl)propylthio)ethenylbenzene (**5e**).* Obtained as an oil: IR (neat) 2958, 2828, 1664, 1655, 1578, 1560, 1508, 1491, 1459, 1444, 1382, 1241, 1170, 1075, 1130, 921, 888, 842, 747, 693, 596, 503 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (d, J = 6.8 Hz, 6H, $CH(CH_3)_2$), 1.63 (s, 3H, CCH_3), 1.68 (s, 3H, CCH_3), 1.93 (qui, J = 6.7 Hz, 1H, $CH(CH_3)_2$), 2.75 (d, J = 6.8 Hz, 2H, SCH_2), 3.54 (d, J = 9.0 Hz, 2H, $SeCH_2$), 5.27-5.32 (m, 1H, $SeCH_2CH$), 7.06 (s, 1H, PhCH), 7.20-7.25 (m, 1H, *p*-CH), 7.30-7.35 (m, 2H, *m*-CH), 7.48-7.50 (m, 2H, *o*-CH); ^{13}C NMR ($CDCl_3$) δ 17.7 ($SeCH_2$), 22.2 ($CH(CH_3)_2$), 25.8, 26.4 (CCH_3), 28.2 ($CH(CH_3)_2$), 43.6 (SCH_2), 119.9, 127.1, 128.0, 129.0, 129.3,

133.4, 136.4, 138.3 (C_6H_5CH=C, C=CH); MS (*m/z*) 340 (M^+); Anal. Calcd for $C_{17}H_{24}SSe$: C, 60.16; H, 7.13. Found: C, 60.00; H, 7.07.

*Z-2-(Benzylseleno)-2-((2-methyl)propylthio)ethenylcyclohexene (**5f**).* Obtained as an oil: IR (neat) 3061, 3027, 2930, 2868, 2831, 1601, 1560, 1494, 1452, 1432, 1382, 1364, 1320, 1241, 1169, 1134, 1066, 1030, 918, 898, 758, 696, 602, 554, 526 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.01 (d, J = 6.8 Hz, 6H, CH_3), 1.50-1.58 (m, 4H, CH_2 (cyclohexene)), 1.85 (qui, J = 6.7 Hz, 1H, C*H*(CH_3)$_2$), 2.04-2.14 (m, 4H, CH_2 (cyclohexene)), 2.64 (d, J = 6.8 Hz, 2H, SCH_2), 4.09 (s, 2H, $SeCH_2$), 5.62 (br, 1H, CH (cyclohexene)), 6.58 (s, 1H, C=CH), 7.15-7.30 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 22.0 ($SeCH_2$), 22.1 (CH_3), 22.7, 25.7 (CH_2 (cyclohexene)), 28.1 (*C*H(CH_3)$_2$), 28.6, 31.5 (CH_2 (cyclohexene)), 43.6 (SCH_2), 123.9 (CSe), 126.6 (CH (cyclohexene)), 128.4, 129.0, 130.6 (CH), 135.7 (*ipso*-C (cyclohexene)), 139.1 (*ipso*-C (Ph)), 139.7 (C=*C*H); MS (*m/z*) 275 (M^+-$C_6H_5CH_2$); Anal. Calcd for $C_{19}H_{26}SSe$: C, 62.45; H, 7.17. Found: C, 62.40; H, 7.34.

*Z-2-(Acetylseleno)-2-((2-methyl)propylthio)ethenylcyclohexene (**5g**).* Obtained as an oil: IR (neat) 2931, 2868, 2831, 1731 (C=O), 1612, 1560, 1464, 1431, 1383, 1365, 1348, 1321, 1270, 1241, 1169, 1134, 1097, 933, 902, 849, 798, 670, 572, 524, 464 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (d, J = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.52-1.63 (m, 4H, CH_2 (cyclohexene)), 1.85 (qui, J = 6.7 Hz, 1H, C*H*(CH_3)$_2$), 2.12-2.19 (m, 4H, CH_2 (cyclohexene)), 2.45 (s, 3H, CCH_3), 2.65 (d, J = 6.8 Hz, 2H, SCH_2), 5.79 (br, 1H, CH (cyclohexene)), 6.77 (s, 1H, CCH); ^{13}C NMR ($CDCl_3$) δ 21.8 (CH_2 (cyclohexene)), 22.1 (CH(*C*H$_3$)$_2$), 22.6, 25.9, 27.9 (CH_2 (cyclohexene)), 28.1 (*C*H(CH_3)$_2$), 33.6 (*C*CH_3), 43.7 (SCH_2), 119.1 (CSe), 132.5 (CH (cyclohexene)), 135.7 (*ipso*-C (cyclohexene)), 143.0 (*C*CH), 196.7 (C=O); MS (*m/z*) 275 (M^+-acyl); Anal. Calcd for $C_{14}H_{22}OSSe$: C, 52.99; H, 6.99. Found: C, 52.93; H, 7.03.

*α-2-Propenylbenzeneethaneselenothioic acid S-2-methylpropyl ester (**7a**).* Obtained as an oil: IR (neat) 3062, 3027, 2959, 2870, 1640, 1599, 1493, 1452, 1413, 1385, 1367, 1321, 1246, 1168, 1123, 1067, 1032, 991, 916, 831, 801, 762, 697, 657, 629, 612, 588, 533 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (d, J = 6.6 Hz, 6H, CH_3), 2.02 (qui, J = 6.7 Hz, 1H, C*H*(CH_3)$_2$), 2.89-2.96 (m, 1H, CH_2), 3.06 (dd, J = 6.8, 13.2 Hz, 1H, SCH_2), 3.14 (dd, J = 7.1, 13.2 Hz, 1H, SCH_2), 3.14-3.21 (m, 1H, CH_2), 4.55 (t, J = 7.6, 1H, PhCH), 4.97 (d, J = 10.3 Hz, 1H, C*H*$_2$=CH), 5.07 (dd, J = 1.5, 7.1 Hz, 1H, C*H*$_2$=CH), 5.71 (ddt, J = 6.9, 13.9, 17.1 Hz, 1H, CH_2=C*H*), 7.22-7.31 (m, 3H, *m,p*-CH), 7.45-7.48 (m, 2H, *o*-CH); ^{13}C NMR ($CDCl_3$) δ 22.3 (CH_3), 27.1 (*C*H(CH_3)$_2$), 41.4 (CH_2), 48.6 (SCH_2), 69.6 (PhCH), 117.1 (*C*H$_2$=CH), 127.3, 128.1, 128.4 (CH), 135.4 (*C*H=CH_2), 139.5 (*ipso*-C), 245.5 (C=Se); MS (*m/z*) 312 (M^+); Anal. Calcd for $C_{15}H_{20}SSe$: C, 57.87; H, 6.47. Found: C, 57.87; H, 6.65.

*α-2-Methyl-2-propenylbenzeneethaneselenothioic acid S-2-methylpropyl ester (**7b**).* Obtained as a solid (mp: 51.9~52.2 °C): IR (neat) 2951, 1654, 1490, 1459, 1450, 1409, 1379, 1366, 1263, 1232, 1166, 1087, 1001, 938, 910, 899, 824, 900, 780, 751, 713, 696, 649, 537, 515 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (d, J = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.72 (s, 3H, CCH_3), 2.02 (qui, J = 6.8 Hz, 1H, C*H*(CH_3)$_2$), 2.87 (dd, J = 4.4, 7.1 Hz, 1H, CCH_2), 3.05 (dd, J = 3.2, 6.8 Hz, 1H, SCH_2), 3.13 (dd, J = 3.2, 6.8 Hz, 1H, SCH_2), 3.19 (dd, J = 8.1 Hz, 14.6 Hz, 1H, CCH_2), 4.69 (s, 1H, C*H*$_2$=C), 4.73 (s, 1H, C*H*$_2$=C), 4.77 (t, J = 7.4 Hz, 1H, PhCH), 7.22-7.30 (m, 3H, *m,p*-CH), 7.47-7.49 (m, 2H, *o*-CH); ^{13}C NMR ($CDCl_3$) δ 22.2, 22.3, 22.6 (CH_3), 27.1 (*C*H(CH_3)$_2$), 45.0 (*C*CH_2), 48.7 (SCH_2), 67.9 (PhCH), 113.1 (*C*H_2=C), 127.2, 128.1, 128.4 (CH), 139.8 (*ipso*-C), 142.4(*C*=CH_2), 245.8 (C=Se); ^{77}Se NMR ($CDCl_3$) δ 1484.1; MS (*m/z*) 326 (M^+); Anal. Calcd for $C_{16}H_{22}SSe$: C, 59.06; H, 6.82. Found: C, 58.97; H, 6.79.

α-2-Propenylcyclohexeneethaneselenothioic acid S-2-methylpropyl ester (7c). Obtained as an oil: IR (neat) 3076, 2958, 2928, 2835, 1639, 1460, 1437, 1384, 1366, 1320, 1247, 1168, 1139, 1064, 1020, 990, 915, 885, 801, 684, 617, 540 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (d, J = 7.6 Hz, 6H, CH_3), 1.50-1.58 (m, 4H, CH_2 (cyclohexene)), 2.10-2.11 (m, 5H, $CH(CH_3)_2$, CH_2 (cyclohexene)), 2.62-2.69 (m, 1H, $CHCH_2$), 2.76-2.83 (m, 1H, $CHCH_2$), 3.14 (dd, J = 2.1, 6.7 Hz, 2H, SCH_2), 3.84 (t, J = 7.6 Hz, 1H, CCH), 4.97 (dd, J = 2.0, 10.3 Hz, 1H, $CH=CH_2$), 5.04 (dd, J = 2.0, 17.1 Hz, 1H, CH_2=CH), 5.68-5.79 (m, 2H, C=CH, $CH=CH_2$); ^{13}C NMR ($CDCl_3$) δ 22.3 (CH_3), 22.3, 23.1, 25.5, 26.6 (CH_2 (cyclohexene)), 27.1 ($CH(CH_3)_2$), 38.8 ($CHCH_2$), 48.7 (SCH_2), 71.6 (CCH), 116.3 ($CH=CH_2$), 125.0 (C=CH), 135.9 (C=CH), 136.0 ($CH=CH_2$), 246.7 (C=Se); MS (*m/z*) 316 (M^+), 275 (M^+-allyl); Anal. Calcd for $C_{15}H_{24}SSe$: C, 57.13; H, 7.67. Found: C, 56.84; H, 7.61.

α-2-Propenyl-β-methylbenzenepropaneselenothioic acid S-butyl ester (7d). Obtained as an oil: IR (neat) 3061, 3027, 2959, 1716, 1640, 1602, 1455, 1395, 1249, 1087, 995, 916, 1764, 700, 650, 576 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.96 (t, J = 7.3 Hz, 3H, CH_2CH_3), 1.21 (d, J = 6.6 Hz, 3H, $CHCH_3$), 1.47 (qui, J = 7.3 Hz, 2H, CH_2CH_3), 1.74 (qui, J = 7.3 Hz, 2H, $CH_2CH_2CH_3$), 1.96 (m, 1H, $CHCH_2$), 2.51 (m, 1H, $CHCH_2$), 3.25 (t, J = 7.0 Hz, 1H, $CHCH_3$), 3.32 (t, J = 7.3 Hz, 2H, SCH_2), 3.50(dt, J = 3.4, 10.5 Hz, 1H, CHC=Se), 4.77 (d, J = 6.2 Hz, 1H, $CH=CH_2$), 4.82 (s, 1H, $CH=CH_2$), 5.50 (m, 1H, $CH=CH_2$), 7.20-7.35 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 13.7 (CH_2CH_3), 20.7 ($CHCH_3$), 22.3 (CH_2CH_3), 28.9 ($CH_2CH_2CH_3$), 39.5 (SCH_2), 40.4 (PhCH), 46.6 ($CHCH_2$), 71.5 ($CHCH_2$), 116.2 ($CH=CH_2$), 126.6, 127.8, 128.7 (CH), 135.4 ($CH=CH_2$), 144.9 (*ipso*-C), 247.8 (C=Se); MS (*m/z*) 340 (M^+); Anal. Calcd for $C_{17}H_{24}SSe$: C, 60.16; H, 7.13. Found: C, 60.38; H, 7.38.

Acknowledgment. This work was supported by the Grant-in-Aid for Scientific Research on Priority Area of Reactive Organometallics No. 05236102 and partially by the Grant-in-Aid for Scientific Research provided from the Ministry of the Education, Science, Sports and Culture, Japan.

References and Notes

1. For reviews: (a) Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis*; Baldwin, J. E., Ed.; Pergamon Press: 1986. (b) *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Ed.; John Wiley & Sons: New York, 1987; Vol. 1 and 2. (c) *Organoselenium Chemistry*, Liotta, D. Ed., Wiley-Interscience, New York, 1987, p 277. (d) Deryagina, E. N.; Voronkov, M. G.; Korchevin, N. A. *Russ. Chem. Rev.* **1993**, *62*, 1107.
2. (a) Barton, D. H. R.; Hanse, P.-E.; Picker, K. *J. Chem. Soc., Perkin I* **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) Kato, S.; Komuro, T.; Kanda, T.; Ishihara, H., Murai, T. *J. Am. Chem. Soc.* **1993**, *115*, 3000. (e) Ogawa, A.; Sonoda, N. *Rev. Heteroatom Chem.* **1994**, *10*, 43. (f) Kanda, T.; Ezaka, T.; Murai, T.; Kato, S. *Tetrahedron Lett.* 1995, **36**, 2807.
3. (a) Kato, S.; Ishida, M. *Sulfur Report* **1988**, *8*, 155. (b) Metzner, P. *Synthesis* **1992**, 1185. (c) Murai, T.; Kato, S. *Comprehensive Organic Functional Group Transformations*, Katritzky, A. R.; Meth-Cohn, O.; Rees, C. W., Eds. Pergamon, 1995, Vol. 5, Chapter 5.13 and references cited therein.

4. (a) Krafft, G. R.; Meinke, P. T. *J. Am. Chem. Soc.* **1986**, *108*, 1314. (b) Meinke, G. A.; Krafft, G. A. *Tetrahedron Lett.* **1987**, *28*, 5121. (c) Meinke, P. T.; Krafft, G. A. *J. Am. Chem. Soc.* **1988**, 110, 8671. (d) Segi, M.; Nakajima, T.; Suga, S.; Murai, S.; Ryu, I.; Ogawa, A.; Sonoda, N. *J. Am. Chem. Soc.* **1988**, *110*, 1976. (e) Segi, M.; Koyama, T.; Nakajima, T.; Suga, S.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1989**, *30*, 2095. (f) Takikawa, Y.; Uwano, A.; Watanabe, H.; Asanuma, M. *Tetrahedron Lett.* **1989**, *30*, 6047. (g) Shimada, K.; Jin, N.; Fujimura, M.; Nagano, Y.; Kudoh, E.; Takikawa, Y. *Tetrahedron Lett.* **1992**, 1843.

5. (a) Kato, S.; Murai, T.; Ishida, M. *Org. Prep. Proceds. Int.*, **1986**, *18*, 369. (b) Guziec, F. S. Jr. in *Organoselenium Chemistry*, Ed. Liotta, D. Wiley-Interscience, New York, 1987; Vol. 2, p 277. (c) Gunziec, F. S. Jr. in *The Chemistry of Organic Selenium and Tellurium Compounds*, Ed. Patai, S. Jon Wiley & Sons Ltd., London, 1987, Vol. 1, p 215. (d) Okazaki, R. *J. Synth. Org. Chem.. Jpn.* **1988**, *46*, 1149. (e) Ogawa, A.; Sonoda, N. in *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds. Pergamon Press: Oxford, 1991; Vol. 6, Chapter 2.6. (d) Segi, M.; Nakajima, T. *J. Synth. Org. Chem. Japan* **1995**, *53*, 678.

6. For recent examples of the synthesis of enolizable selenoamides: (a) Malek-Yazdi, F.; Yalpani, M. *Synthesis*, **1977**, 328. (b) Sukhai, R. S.; Jong, R.; Brandsma, L. *Synthesis*, **1977**, 888. (c) Cohen, V. I. *J. Org. Chem.* **1977**, *42*, 2645. (d) Ogawa, A.; Miyake, J.; Karasaki, Y.; Murai, S.; Sonoda, N. *J. Org. Chem.* **1985**, *50*, 384. (e) Ogawa, A.; Miyake, J.; Kambe, N.; Murai, S.; Sonoda, N. *Bull. Chem. Soc. Jpn.*, **1985**, *58*, 1448. (f) Shimada, K.; Hikage, S.; Takeishi, Y.; Takiakawa, Y. *Chem. Lett.* **1990**, 1403. (g) Takikawa, Y.; Watanabe, H.; Sasaki, R.; Shimada, K. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 876. (h) An, D.-L.; Toyota, K.; Yasunami, M.; Yoshifuji, M. *Chem. Lett.* **1995**, 199.

7. Murai, T.; Hayashi, A.; Kanda, T.; Kato, S. *Chem. Lett.* **1993,** 1469.

8. (a) Harirchian, B.; Magnus, P. *J. Chem. Soc., Chem. Commun.*, **1977**, 522. (b) Lemarié, M.; Vallée, Y.; Worrell, M. *Tetrahedron Lett.* **1992**, *33*, 6131. (c) Murai, T.; Takada, H.; Kanda, T.; Kato, S. *Tetrahedron Lett.* **1994**, *35*, 8817.

9. For reviews, see: (a) Luh, L.-Y.; Ni, Z.-J. *Synthesis*, **1990**, 89. (b) Kolb, M. *Synthesis*, **1990**, 171.

10. (a) Jensen, K.; Henriksen, L. *Acta Chem. Scand.* **1970**, *24*, 3213. (b) Gronowitz, S.; Frejd, T. *Acta Chem. Scand.* **1973**, *27*, 2242. (c) Gröbel, B. -T.; Seeback, D. *Chem. Ber.* **1977**, *110*, 852. (d) Denis, J. N.; Krief, A. *Tetrahedron Lett.* **1982**, *23*, 3407. (e) Denis, J. N.; Krief, A. *Tetrahedron Lett.* **1982**, *23*, 3411. (f) Stang, P. J.; Roberts, K. A.; Lynch, L. E. *J. Org. Chem.* **1984**, *49*, 1653.

11. Eliel, E. L.; Wilen, S. H.; Mander, L. N. in *Stereochemistry of Organic Compounds*, John Wiley & Sons Inc.: New York. 1994 p 539.

12. (a) Vallée, Y.; Worrell, M. *J. Chem. Soc., Chem. Commun.* **1992**, 1680. (b) Shimada, K.; Oikawa, S.; Nakamura, H.; Takikawa, Y. *Chem. Lett.* **1995**, 135. (c) Murai, T.; Takada, H.; Kanda, T.; Kato, S. *Chem. Lett.* **1995**, 1057.

13. The instability of α-monosubstituted selenothioesters **6** was in sharp contrast to that of α-disubstituted esters **7**. For example, during the purification of **6** (R = cyclohexenyl, R' = *n*-Bu) through silica gel column, the deep purple color of **6** gradually turned yellow to give a complex mixture, whereas ester **7c** could be stored in the refrigerator at least for one month.

14. Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769.

(*Received in Japan* 24 *November* 1995; *accepted* 25 *December* 1995)