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Reaction of Selenoic Acid *O*-Methyl Esters with Aluminum Thiolates Leading to Aromatic Selenothioic Acid *S*-Alkyl Esters and Their Characterization

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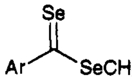
Much attention has been paid to the chemistry of selenocarbonyl compounds such as selenoaldehydes and selenoketones for the past 15 years.[1-3] In contrast, chalcogenoesters where the oxygen atom is replaced by selenium (RC(Se)ER, E = S, Se, or Te) have been studied to a lesser extent,[4] although the first synthesis of selenoesters (RC(Se)OR) was reported more than 30 years ago.[5] Nevertheless, these compounds are of great interest from the standpoint of synthetic utility and fundamental interest since sulfur counterparts such as dithioesters have provided fruitful chemistry.[6,7] In 1973, Jensen described that selenothioic acid *S*-alkyl esters and diselenoesters were prepared by the reaction of the corresponding iminonium salts with selenium and were beautifully colored compounds,[4a] although no detail was available. Very recently, we have demonstrated the synthesis of diselenoesters **1** from the corresponding selenoesters **2** and aluminum selenolate and disclosed that the aromatic derivatives are a relatively stable green oil, whereas the aliphatic ones easily undergo self-oligomerization.[8] Aliphatic selenothioic acid *S*-alkyl esters **3** were also found to be distillable blue-violet liquid.[9] Accordingly, the aromatic esters **4** were expected to be isolated as a stable compound. In this paper, we report on the reaction of selenoesters **2** with aluminum thiolates leading to the esters **4** and their stability compared with that of the esters **1**, **2**, and **3**.



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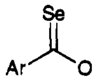

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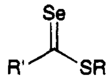

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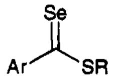

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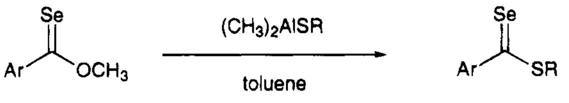
Initially, the reaction of the selenoester **2a** with dimethylaluminum methanethiolate[10] prepared from trimethylaluminum in hexane and sulfur in toluene was carried out at 0–20 °C for 1.5 h (eq 1).



2 **4** (1)

2a Ar = Ph, **2b** Ar = 4-$CH_3C_6H_4$,
2c Ar = 4-$CH_3OC_6H_4$, **2d** Ar = 2-$CH_3C_6H_4$

The reaction mixture gradually turned deep blue. The reaction was complete within 2 h on the basis of TLC analysis of the reaction mixture. After the aqueous workup of the reaction mixture, it was dried over $MgSO_4$, followed by the chromatographic purification to give the selenothiobenzoic acid *S*-methyl ester (**4a**) in 82% yield as a blue-green liquid. The formation of the ester **4a** was confirmed by the ^1H NMR, ^{13}C NMR, and UV spectra. In the ^{13}C NMR spectrum, the signal due to selenocarbonyl carbon was observed at 233.7 ppm. The UV spectrum of the ester **4a** displayed the maximum absorptions at 227 (ϵ 4.51), 305 (ϵ 4.57), 358 (ϵ 4.36), and 607 (ϵ 2.72) nm. The selenocarbonyl group in the ester **2a** was not formally cleaved during the reaction in a manner analo-

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Table 1. Reaction of Selenoic Acid *O*-Methyl Esters 2 with Aluminum Thiolates[a]

run	ester **2**	$(CH_3)_2AlSR$ R	time (h)	isolated yield (%)[b] of **4**	^{13}C NMR[c] of C=S (ppm)	UV−vis spectra[d] λ_{max} (nm) (log ϵ)
1	**2a**	C_4H_9-*n*	2	**4b** (75)	233.0	264 (4.63), 363 (4.02), 623 (2.91)
2	**2a**[e]	C_4H_9-*s*	3.5	**4c** (42)	232.4	228 (3.87), 305 (3.99), 366 (3.77), 614 (2.53)
3	**2a**	C_2H_5	2	**4d** (40)	232.8	235 (5.03), 267 (4.81), 362 (4.34), 601 (3.48)
4	**2a**	C_6H_5	3	**4e** (0)		
5	**2b**	C_4H_9-*t*	7	**4f** (81)	232.3	215 (4.17), 319 (4.15), 365 (3.93), 629 (2.01)
6	**2c**	CH_3[f]	5	**4g** (54)	231.5	233 (4.10), 340 (4.36), 604 (2.33)
7	**2d**[g]	CH_3[f]	4	**4h** (92)	237.9	228 (5.18), 277 (4.84), 340 (5.28), 499 (3.00)
8	**2d**[h]	C_4H_9-*n*	2	**4i** (80)	237.0	230 (3.81), 273 (3.50), 344 (3.94), 597 (2.07)

[a] The reaction was carried out as follows unless otherwise noted: Aluminum thiolate was prepared from trimethylaluminum in hexane (2.0 mL, 2.0 mmol) and thiol (3 mmol) for 30 min at −78 °C. Then, to this solution was added ester **2** (1 mmol) in toluene (15 mL) at 0 °C, and the mixture was stirred for the hours shown above. [b] The purity of the ester **4** was confirmed to be more than 90% by its ^1H NMR spectra. [c] In $CDCl_3$. [d] In cyclohexane. [e] **2a** (0.4 mmol) was used. [f] Aluminum methanethiolate was prepared from trimethylaluminum in hexane and sulfur at 69 °C for 2 h. [g] **2d** (0.5 mmol) was used. [h] **2d** (0.6 mmol) was used.

gous to the reaction of the esters **2** with aluminum methaneselenolate.[8] However, the ester **4a** was highly labile and easily susceptible to the air oxidation to give thiobenzoic acid *S*-methyl ester with the liberation of red selenium. Noteworthy is that this instability is in sharp contrast to that of the aliphatic selenothioic acid *S*-alkyl esters **3**, which can be handled under air at least for several hours.[9]

Second, the reaction of the ester **2a** with a variety of dimethylaluminum thiolates[11] prepared from trimethylaluminum and thiols was carried out. The results are shown in Table 1 along with the representative spectroscopic data. The reaction of the ester **2a** with aluminum thiolates proceeded smoothly, and the ester **2a** was completely consumed within 4 h. When aliphatic thiols were employed as a starting material, the intensive blue color of the reaction mixture was kept until the purification through column chromatography (runs 1−3), whereas in the reaction of aromatic thiols, the deep blue reaction mixture, which was indicative of the formation of the ester **4e**, turned yellow during the aqueous workup (run 4). The purity of the esters isolated by column chromatography was confirmed by the ^1H NMR spectra. However, their stability was very low.[12] Unless the esters were treated under the inert atmosphere, the signals due to thioesters were also observed together with the signals corresponding to the desired esters.

A substituent was introduced onto the aromatic ring to enhance the stability of the esters. As shown in Table 1, the reaction of the esters substituted with a methyl or a methoxy group at the 2- or 4-position of the aromatic ring has been carried out. Although the longer reaction time was necessary in the reaction using 1,1-dimethylethanethiol, the ester **4f** was obtained in 81% yield, but it was also sensitive to air. On the other hand, no appreciable decomposition was observed for the product **4g** prepared from 4-methoxy-substituted ester **2c** (run 6).[13] The stabilizing effect of the methyl group at the 2-position of the aromatic ring was also observed for the reaction of the ester **2d**, affording the esters **4h** and **4i** in high yields (runs 7 and 8). In UV−visible spectra of these products **4h** and **4i**, the absorptions attributed to $\pi-\pi^*$ transitions were shifted to shorter wavelengths that were similar to those of aliphatic esters **3**.[14]

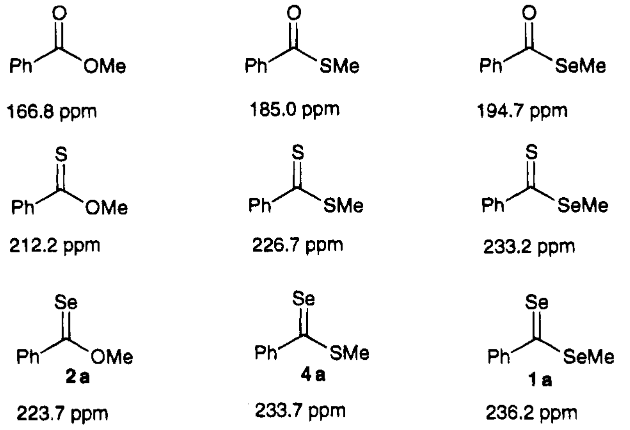

Figure 1. ^{13}C NMR spectral data of the series of chalcogenobenzoic acid methyl esters.

The signals of the carbonyl carbon of the series of chalcogenoesters have been compared in Figure 1. When the oxygen atom in the carbonyl group was replaced with the sulfur atom, the signal due to thiocarbonyl carbon was shifted to a lower field by about 40 ppm regardless of the substituents attached to the C=O group, whereas the substitution of a sulfur atom of the thiocarbonyl group with a selenium atom led to the low-field shift within 10 ppm. Among three esters containing the selenocarbonyl group, the value for C=Se was shifted to a lower field only by 10 ppm in going from the OCH_3 to the SCH_3 group. Moreover, no change was observed for the selenocarbonyl group between the esters **1a** and **4a**.

The UV−visible spectra of **1a**, **2a**, and **4a** are shown in Table 2 along with the color of these esters. When the oxygen atom of **2a** was replaced with the sulfur atom, the $\pi-\pi^*$ transitions at 327 nm were red-shifted by 31 nm. When the sulfur atom of **4a** was replaced with the selenium atom, the $\pi-\pi^*$ transitions were further red-shifted by 24 nm. The shift to a longer wavelength by ca. 100 nm was observed for $n-\pi^*$ transitions between **2a** and **4a**. The similar shift from **4a** to **1a** was at most 10 nm. These values were correlated to the color of the compounds. The color of **2a** was red, and the esters **1a** and **4a** showed the similar green color. The ester **2a** was the most stable among these three esters, and **2a** did not

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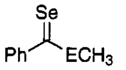
(12) The instability of the products **4** did not allow for their elemental analyses or the measurement of high-resolution mass spectroscopy except for the esters **4g**−**4i**.

(13) A similar enhancement of the stability of selenocarbonyl compounds by the methoxy group was observed for 4-methoxybenzoselenophenone; see ref 2k.

(14) A representative UV−visible spectrum of aliphatic selenothioic acid *S*-alkyl esters is as follows: λ_{max} (log ϵ) 338 (4.12) and 572 nm (1.91) for $CH_3C(Se)SC_4H_9$-*n*.

Table 2. Spectroscopic Data of 1a, 2a, and 4a

		^{77}Se NMR^a (ppm)	UV–vis^b (nm)				color
					π–π*	n–π*	
O	**2a**	910.3	214	253	327	509	red
S	**4a**	1623.8	227	305	358	607	blue green
Se	**1a**	1786.8	211	317	382	616	green

^{a} In CDCl$_3$. ^{b} Cyclohexane.

decompose even upon exposure to air for 2 days at least.[15] When the esters **1a** and **4a** were exposed to air on the same vessel, the red selenium increasingly deposited in **4a** within 1 h whereas **1a** survived, although the slight change of the color from green to yellow was seen. This observation goes against the general tendency of the stability of selenocarbonyl compounds which holds that the selenium homologues are more reactive than the corresponding sulfur-containing compounds.[3] The tendency of the stability of these aromatic esters is also in sharp contrast to those of aliphatic esters. The aliphatic diselenoesters easily undergo self-oligomerization, whereas the aliphatic selenothioic acid *S*-alkyl esters **3** can be handled with usual operation under air.

The result of the ^{77}Se NMR spectra of C=Se is also shown in Table 2. Among three esters, the replacement of the oxygen atom of **2a** with sulfur resulted in the low-field shift of the signal of the ^{77}Se of the selenocarbonyl group by 800 ppm. On the other hand, for the ester **1a**, the value of the ^{77}Se NMR spectrum was nearly equal to that of the ester **4a**. Furthermore, these two values resemble those of better-known selenoketones[16] rather than that of ester **2a**. The sensitivity of ^{77}Se NMR spectra toward the electronic structure around the Se atom has been known to be high.[17] The observation of the signal of the ester **2a** in a higher field compared to that of the selenoketones has been understood through mesomeric effects where the lone pair electrons on the oxygen atom of **2a** efficiently delocalize on the carbon–selenium double bond. On the basis of the chemical shift of the ^{77}Se NMR spectra, the similar delocalizing effect of the lone pair electrons of the sulfur and selenium atoms in **1a** and **4a** appears to be less efficient, which may be one of the reasons for the low stability of these esters.

In summary, we have disclosed that the substitution reaction of a methoxy group of selenoesters with aluminum thiolates proceeded highly efficiently to give the corresponding selenothioic acid *S*-alkyl esters. The selenocarbonyl group remained intact during the reaction. However, the stability of the aromatic esters **4** produced was very low in the presence of air. They gradually decomposed to give the thioesters with the liberation of red selenium. The esters **4** have shown spectroscopic data similar to those of the esters **1**.

Experimental Section

General Procedure. Toluene was distilled from a sodium–lead alloy. The esters **2** were prepared according to the literature procedure.[5c] Trimethylaluminum *n*-hexane solution was purchased from Kanto Kagaku Co. All the thiols were purchased and used without further purification. The silica gel used in the column chromatography was run on BW-820 MH of Fuji Davison Chemical Co. Ltd. ^{1}H (270 MHz) and ^{13}C NMR (67.9 Hz) spectra were recorded using CDCl$_3$ as a solvent with tetramethylsilane as an internal standard. The sample for the ^{77}Se NMR (51.5 MHz) spectra was prepared by dissolving ca. 0.4 mmol of the ester in ca. 1.3 mL of CDCl$_3$, and Me$_2$Se was used as an external standard.

Preparation of Benzenecarboselenothioic Acid *S*-Methyl Ester (4a). In a 20 mL two-necked flask was placed sulfur powder (0.096 g, 3.0 mmol) under an argon atmosphere. To this was added Me$_3$Al (3.00 mL, 3.0 mmol, 1.0 M in hexane). After the mixture was stirred at 69 °C for 2 h, selenobenzoic acid *O*-methyl ester (**2a**) (0.40 g, 2.0 mmol) was added, and the mixture was stirred for 30 min at 0 °C. The reaction mixture was allowed to warm to 20 °C, and the stirring was continued for 1 h. The reaction mixture was poured onto water. The organic layer was dried over Na$_2$SO$_4$ and concentrated in vacuo. The residue was chromatographed through a silica gel column using hexane as eluent to give 0.356 g (82%) of **4a** as a blue-green liquid: IR (neat) 3055, 2906, 1662, 1588, 1481, 1443, 1401, 1331, 1223, 1180, 1030, 982, 948, 917, 883, 759, 725, 686, 628, 557 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.79 (s, 3H), 7.25–7.45 (m, 2H), 7.50–7.65 (m, 1H), 7.9–8.1 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 25.4, 126.3, 128.8, 131.7, 150.9, 233.7; MS *m/z* CI 217 (M$^+$ + 1).

Benzenecarboselenothioic acid *S*-butyl ester (4b): IR (neat) 3057, 2956, 2925, 2869, 1662, 1589, 1443, 1418, 1296, 1373, 1332, 1311, 1268, 1219, 1180, 1076, 1048, 999, 962, 916, 883, 758, 686, 616, 558 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.98 (t, *J* = 7.5 Hz, 3H), 1.50 (sextet, *J* = 7.5 Hz, 2H), 1.87 (quintet, *J* = 7.5 Hz, 2H), 3.37 (t, *J* = 7.5 Hz, 2H), 7.2–7.4 (m, 2H), 7.50–7.65 (m, 1H), 7.90–8.10 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 13.7, 22.4, 29.1, 41.8, 126.3, 128.5, 131.6, 151.2, 233.0; MS *m/z* CI 259 (M$^+$ + 1).

Benzenecarboselenothioic acid *S*-1-methylpropyl ester (4c): IR (neat) 2964, 1660, 1447, 1378, 1206, 1175, 967, 912, 772, 690, 648 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.07 (t, *J* = 7.1 Hz, 3H), 1.49 (d, *J* = 7.1 Hz, 3H), 1.85 (m, 2H), 4.05 (m, 1H), 7.25–7.40 (m, 2H), 7.50–7.65 (m, 1H), 7.9–8.1 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 11.6, 18.7, 28.3, 52.4, 126.4, 128.5, 131.6, 151.2, 232.4; MS *m/z* CI 259 (M$^+$ + 1).

Benzenecarboselenothioic acid *S*-ethyl ester (4d): IR (neat) 3057, 2956, 2925, 2869, 1662, 1589, 1443, 1418, 1396, 1373, 1332, 1311, 1268, 1219, 1180, 1076, 1048, 999, 962, 916, 883, 758, 686, 626, 558 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.49 (t, *J* = 7.5 Hz), 3.40 (q, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.60 (t, *J* = 7.7 Hz, 1H), 8.03 (d, *J* = 7.7 Hz); ^{13}C NMR (CDCl$_3$) δ 11.9, 36.1, 126.3, 128.5, 131.7, 151.1, 232.8; MS *m/z* CI 231 (M$^+$ + 1).

4-Methylbenzenecarboselenothioic acid *S*-1,1-dimethylethyl ester (4f): IR (neat) 2960, 1655, 1603, 1453, 1390, 1362, 1223, 1179, 1019, 966, 910, 878, 814, 779, 639, 593, 557 cm^{-1}; ^{1}H NMR (CDCl$_3$) 1.75 (s, 9H), 2.28 (s, 3H), 7.10 (d, *J* = 8.1 Hz), 7.82 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 21.5, 28.4, 53.5, 126.0, 129.0, 141.9, 151.1, 232.3; MS *m/z* CI 273 (M + 1).

4-Methoxybenzenecarboselenothioic acid *S*-methyl ester (4g): IR (neat) 2926, 2361, 1596, 1501, 1418, 1260, 1170, 1129, 887, 831, 573 cm^{-1}; ^{1}H NMR (CDCl$_3$) 2.81 (s, 3H), 3.85 (s, 3H), 6.83 (d, *J* = 9.0 Hz, 2H), 8.14 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 23.6, 55.6, 113.8, 128.7, 143.9, 131.9, 231.5; HRMS calcd for C$_9$H$_{10}$OSSe 245.961 71, found 245.960 08.

2-Methylbenzenecarboselenothioic acid *S*-methyl ester (4h): IR (neat) 3060, 3016, 2976, 2908, 1596, 1478, 1453, 1412, 1379, 1287, 1260, 1225, 1147, 1114, 1036, 1012, 989, 949, 936, 887, 753, 724, 632, 583, 528 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.35 (s, 3H), 2.75 (s, 3H), 7.2–7.8 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 19.7, 25.3, 126.2, 126.7, 128.2, 128.4, 131.6, 150.6, 237.9; MS *m/z* EI 230 (M$^+$); HRMS calcd for C$_9$H$_{10}$SSe 229.966 79, found 229.966 93.

2-Methylbenzenecarboselenothioic acid *S*-butyl ester (4i): IR (neat) 3061, 3016, 2957, 2871, 2360, 1911, 1793, 1663, 1596, 1445, 1379, 1286, 1233, 1153, 1115, 1036, 973, 886, 861, 751, 717, 632, 583 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.98 (t, *J* = 7.4 Hz, 3H), 1.51 (sextet, *J* = 7.4 Hz, 2H), 1.82 (quintet, *J* = 7.4 Hz,

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2H), 2.35 (s, 3H), 3.35 (t, $J = 7.4$ Hz, 2H), 7.1–7.3 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.7, 19.6, 22.3, 28.9, 41.4, 124.8, 125.3, 128.8, 130.8, 131.3, 152.8, 237.0; MS *m*/*z* CI 273 ($M^+ + 1$); HRMS calcd for $C_{12}H_{16}SSe$ 272.013 71, found 272.009 30.

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Supplementary Material Available: ^{1}H NMR spectra of **4a–d** and **4f–i** (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; *see any current masthead page for ordering information.*

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