

# Selenothioic Acid *S*-Esters: Synthesis, Characterization, and Trend for Stability

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**Abstract:** Selenothioic acid *S*-alkyl esters were synthesized from the reaction of terminal acetylenes with *n*-butyllithium, selenium, and alkanethiols in moderate to high yields. The use of substituted benzenethiols or (triphenylsilyl)-acetylene allowed for the isolation of *S*-aryl esters. The synthesis of  $\alpha$ -aryl selenothioic acid *S*-alkyl esters was attained by the acid-catalyzed reaction of selenoacetic acid *Se*-alkynyl esters with thiols in good yields. <sup>77</sup>Se NMR studies showed that the chemical shifts in a series of the esters were downfield of that in selenoester by about 500 ppm and were upfield of that in selenoketone by about 600 ppm. In the visible spectra the absorptions of the esters were observed at about 340 and 568 nm. X-ray molecular structure analyses of  $\alpha$ -silyl esters showed that the bond distances in the selenocarbonyl group were 1.792 and 1.785 Å, respectively. The formation of 1,3-diselenetane was confirmed from the decomposed products of *S*-phenyl ester. The trend for the stability of selenothioic acid *S*-esters is discussed on the basis of these synthetic results.

Organoselenium compounds<sup>1</sup> have played important roles in biological systems<sup>1d</sup> and organic syntheses<sup>1e</sup> as well as materials-related chemistry.<sup>1f</sup> They are also used as spectroscopic probes (for example, chiral derivatizing agents).<sup>1g</sup> This is mainly due to the properties of the compounds, since their stability and reactivity are variable even by subtle change of the structures. To fully utilize these properties, it is of great importance to design and synthesize new selenium-containing compounds having appropriate stabilities and reactivities. Selenocarbonyl compounds can be good candidates for this purpose. However, recent studies on selenoaldehydes and selenoketones<sup>2</sup> have disclosed that these are too labile to be isolated unless they are stabilized by resonance effects of heteroaromatic rings<sup>3a</sup> or are protected by sterically bulky groups.<sup>3b,4</sup> As a result, unprotected selenoaldehydes<sup>5</sup> and selenoketones<sup>6</sup> have been obtained only as their dimers or Diels–Alder adducts with dienes. Selenocarbonyl compounds substituted with nitrogen- and oxygen-containing functional groups, i.e. selenoamides (RC(Se)NR'<sub>2</sub>) and selenoesters (RC(Se)OR'),<sup>7</sup> have been known to be much more stable than selenoaldehydes and selenoketones. Even enolizable derivatives<sup>8,9</sup> have been isolated, but the purification is fairly cumbersome because they are highly polar and thermally labile.

In contrast, the chemistry of selenothioic acid *S*-esters, i.e. selenocarbonyl compounds substituted with an organosulfur group (RC(Se)SR'), has remained elusive.<sup>10</sup> Attempts to synthesize selenothioic acid *S*-esters were reported as early as 1962, and the esters have been noted to be unstable.<sup>11</sup> Jensen briefly described methods for synthesizing these esters using selenoiminonium salts and hydrogen selenide,<sup>12</sup> but no details were made available. Since then, the only examples of such esters have been two cyclic compounds with a selenothiocarbonyl group.<sup>13</sup> Transition metal complexes of selenothioic acid *S*-esters, which are generally more stable than uncomplexed selenocarbonyl compounds, were not prepared until recently.<sup>14</sup> Nonetheless, an organosulfur group is expected to have a stabilizing effect, since dithioic acid esters (RC(S)SR') are much more stable than thioaldehydes and thioketones and have been

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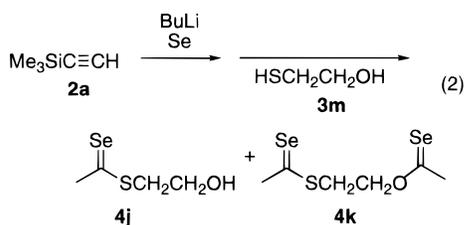
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mixture turned dark pink via orange during the reaction.<sup>19</sup> Purification of the mixture by column chromatography on silica gel using hexane as the eluent gave a 98% yield of selenothioacetic acid *S*-butyl ester (**4b**) as a deep pink oil (entry 2). The ester **4b** could be handled even at room temperature, in marked contrast to a previous report that **4b** was unstable.<sup>10</sup> Upon the exposure of **4b** to air for more than 8 h, red selenium began to deposit. Similarly, the reaction with thiols **3a,c–e** gave selenothioacetic acid *S*-alkyl esters **4a,c–e** in good to high yields. In these cases, the trimethylsilyl group of **2a** was completely removed during chromatographic purification (entries 1–5 and 7–9). Thus, the system of **2a**, *n*-butyllithium, and selenium can be regarded as an agent for selenoacetylation of thiols. The use of (triphenylsilyl)acetylene **2b** gave  $\alpha$ -silyl esters **5** in moderate to good yields (entries 10–14). The esters **4a–c** and **5a,b** were obtained as deep pink liquids or solids and could be stored below  $-10^\circ\text{C}$  for more than 1 year, whereas *S*-*tert*-butyl ester **4d** and *S*-benzyl ester **4e** gradually decomposed after purification. The reaction of **2a** with benzenethiol **3f** gave rise to a blue solution, which was indicative of the formation of **4f**, but this instantly turned yellow in aqueous workup (entry 6). To enhance the stability of *S*-aryl esters, substituted benzenethiols were used. Bulky substituents were also introduced to the  $\alpha$ -carbon atom of the selenocarbonyl group of the esters. After several disappointing results, the reaction with thiols **3g–i** or the use of silylacetylene **2b** gave *S*-aryl esters **4g–i**, and **5c–e** (entries 7–9 and 12–14). Nevertheless, deep violet blue *S*-aryl esters **4g–i** and **5c–e** turned yellow much more quickly than *S*-alkyl esters **4a–c** and **5a,b**, even at low temperature.

Both 2-hydroxyethanethiol (**3m**) and 1,2-ethanedithiol (**3n**) were also reacted. Although the reaction with **3n** gave a complex mixture, the reaction with **3m** produced a 44% yield of selenothioacetic acid *S*-2-hydroxyethyl ester (**4j**) together with a 41% yield of ester **4k** (eq 2). A selenoacetyl group was



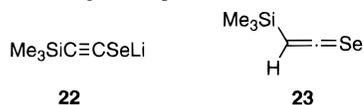
introduced not only to a mercapto group but also to a hydroxyl group. The use of 2 equiv of **3m** decreased the yield of **4k**, whereas the reaction with 0.5 equiv of **3m** predominantly gave **4k**. These results are in sharp contrast to the reaction using alcohols instead of thiols, in which no selenoacetylation of hydroxyl group took place.

This synthetic method was applied to the reaction of terminal acetylenes **2c–e** (Table 1, entries 15–17). The use of Et<sub>2</sub>O as

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(19) The reaction in eq 1 may begin with the generation of lithium alkyneselenolate **22** from silylacetylene **2a**, *n*-butyllithium, and selenium. Then, the protonation of **22** with **3** may give rise to selenoketene intermediate **23**,<sup>8d,f,16</sup> followed by the nucleophilic attack of lithium thiolates derived from **3** on **23** to give the products.

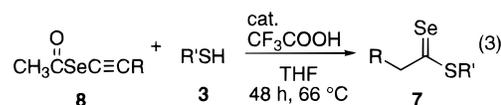


**Table 2.** Synthesis of Selenothioic Acid *S*-Esters from **8**<sup>a</sup>

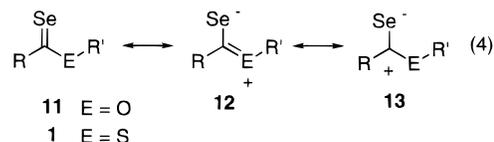
compd	ester		yield <sup>b</sup> (%)
	R	R'	
<b>7a</b>	C <sub>6</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	48
<b>7b</b>	C <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	70
<b>7c</b>	C <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	55
<b>7d</b>	4-ClC <sub>6</sub> H <sub>4</sub>	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	46
<b>7e</b>	1-naphthyl	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	40

<sup>a</sup> The reaction was carried out as follows: *Se*-alkynyl selenoester (1 mmol) was stirred with CF<sub>3</sub>COOH (0.3 mmol) and thiol (6 mmol) in THF (2 mL) at 66 °C for 48 h. <sup>b</sup> Isolated yield.

a solvent did not give the corresponding esters, unlike the reaction of silylacetylenes **2a,b**, but the reaction of **2c** and **2d** in THF proceeded smoothly to give **6a** and **6b** in yields of 34% and 58%, respectively (entries 15 and 16). In contrast, the reaction of **2e** gave the corresponding  $\alpha$ -phenyl ester **7a** at most in 10% yield (entry 17). The synthesis of  $\alpha$ -aryl esters **7** was attained by the acid-catalyzed reaction of *Se*-alkynyl esters **8** with thiols **3** in better yields (eq 3, Table 2). Although this reaction required a high reaction temperature and longer reaction time, it demonstrated the thermal stability of **7** under acidic conditions.



Selected spectroscopic data for the esters are summarized in Table 3. The data for selenoester **9**<sup>8f</sup> and selenoketone **10**<sup>20</sup> are also listed. In the <sup>13</sup>C NMR spectra of esters **4b,d**, **5a,c,d**, and **7c**, the C=Se signal was observed in the range of 238.0  $\pm$  2.4 ppm, which is close to that of **9**.<sup>8f</sup> In contrast, the C=Se signal in the <sup>77</sup>Se NMR spectra of **4b**, **5a,c,d**, and **7c** (1487  $\pm$  64 ppm) was shifted to lower fields by about 500 ppm compared to that of **9**. In **4k**, two signals, which are characteristic of selenocarboxyl (Se=C–O) and selenothiocarboxyl (Se=C–S) groups, were observed at 952.0 and 1557.4 ppm, respectively. This difference may be explained by noting the degree to which the lone-pair electrons on the oxygen or sulfur atom delocalize on the selenocarbonyl group (eq 4).<sup>21</sup> The contribution of



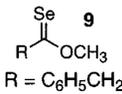
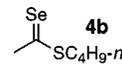
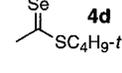
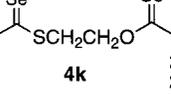
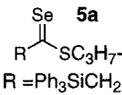
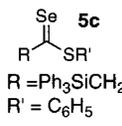
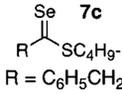
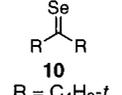
resonance structures **12** and **13** is more important in **11** than in **1** but is still present in **1**. In fact, the selenium atom in selenoketone **10**, which has no resonance structures of type **12** and type **13**, appears at lower field than those of these esters. In a series of *S*-alkyl esters, the chemical shift of *tert*-butyl ester **4d** was further downfield than that in *n*-butyl ester **4b** in the <sup>77</sup>Se NMR spectra.

In the visible spectra of esters **4b,d**, **5a,c,d**, and **7c**, the absorptions were observed at about 340 and 574  $\pm$  20 nm. Absorption at longer wavelengths which may be ascribed to  $n-\pi^*$  transitions of the selenocarbonyl group of the esters were substantially red-shifted by ca. 100 nm compared with that for **9**. In the ester **4k**, typical bathochromic shifts of the absorptions in the UV–visible spectra were observed between Se=C–O and Se=C–S (Figure 1), analogous to the findings with thioic

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**Table 3.** Selected Spectroscopic Data of Selenothioic Acid *S*-Esters

compound	$^{13}\text{C}$ NMR $\delta$ [ppm] <sup>a</sup>	$^{77}\text{Se}$ NMR $\delta$ [ppm] <sup>a</sup>	$\lambda_{\text{max}}^{\text{vis}^b}$ [nm] (log $\epsilon$ )	
<b>9</b> 	232.8	955.9	465	
<b>4b</b> 	237.8	1510.0	338 (4.12)	571 (2.37)
<b>4d</b> 	236.4	1634.0	340 (4.04)	594 (2.75)
<b>4k</b> 	230.9 236.1	952.0 1557.4	273 (4.08) 341 (3.98)	467 (2.84) 571 (2.84)
<b>5a</b> 	235.6	1423.2	341 (3.98)	554 (2.31)
<b>5c</b> 	238.3	1485.8	348 (3.78)	584 (2.24)
<b>5d</b> 	237.6	1465.4	341 (3.90)	581 (2.30)
<b>7c</b> 	240.4	1550.0	340 (3.94)	578 (2.34)
<b>10</b> 	291.4	2131	710	

<sup>a</sup> In  $\text{CDCl}_3$ . <sup>b</sup> In cyclohexane. <sup>c</sup> Not observed.

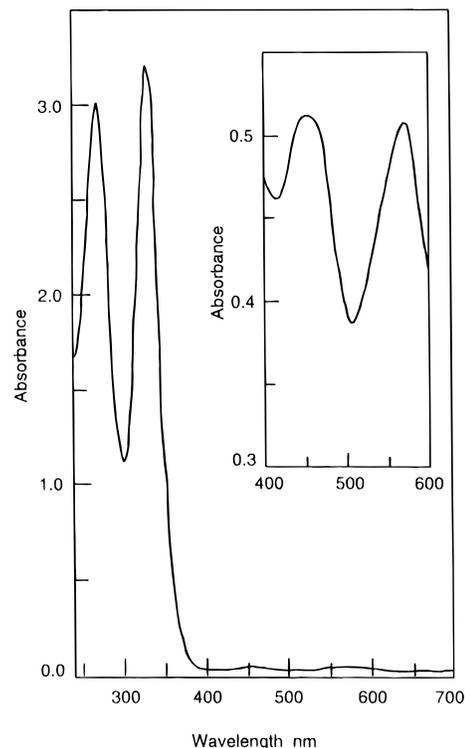
acid *O*-esters and dithioic acid esters.<sup>15a</sup> The absorptions due to  $\text{Se}=\text{C}-\text{O}$  in **4k** were at 273 and 467 nm, and those due to  $\text{Se}=\text{C}-\text{S}$  in **4k** were at 341 and 571 nm.

The molecular structures of **5a,d** were determined by X-ray crystallography. For **5a**, two independent molecules were present in one asymmetric unit and their average data are shown. ORTEP drawings of **5a** and **5d** are shown in Figures 2 and 3, respectively. Selected bond distances and angles are listed in Tables 4 and 5.

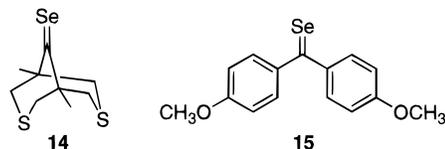
This is the first example of the X-ray molecular structure analysis of selenothioic acid *S*-esters. We have observed several characteristic features. First, the selenium atom and the alkyl or aryl group adopt a *cis* conformation with respect to the  $\text{C}-\text{S}$  bond, similar to ordinary esters,<sup>22</sup> even if steric and possibly electronic repulsion appear to exist between the selenium atom and the substituents on the sulfur atom. Second, the torsion angles of  $\text{Si}-\text{C}-\text{C}=\text{Se}$  of **5a** and **5d** are  $76.0(6)$  and  $68.9(4)^\circ$ , respectively. Thus, the esters exist in a bisecting conformation in the solid state, whereas  $\alpha$ -silyl acetic acid *S*-butyl ester has been reported to exist in an eclipsed conformation.<sup>23</sup> Third,

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**Figure 1.** UV-visible spectrum of **4k** in cyclohexane.

**5d** is thermally more labile than **5a**, but no differences were observed between **5a** and **5d** except that the  $\text{Se}=\text{C}-\text{S}$  bond in **5a** ( $1.724(6)$  Å) is shorter than that in **5d** ( $1.741(4)$  Å). Finally, the bond distances in  $\text{C}=\text{Se}$  should be noted. The average values of the bond distances in the selenocarbonyl group of selenoformaldehyde and selenoacetaldehyde have been estimated to be  $1.739-1.76$  Å by microwave spectroscopy<sup>24</sup> and molecular orbital calculations.<sup>25</sup> X-ray structure analyses have revealed that the bond distance of  $\text{C}=\text{Se}$  in selenoketone **14** is  $1.774(6)$  Å,<sup>4h</sup> and that in **15** is  $1.790(4)$  Å,<sup>4i</sup> whereas those in seleno-



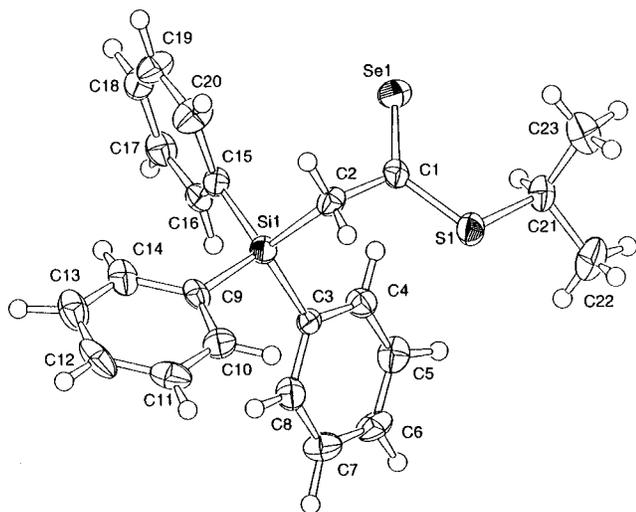
amides have been reported to be about  $1.83$  Å.<sup>26</sup> The bond distances of the  $\text{C}=\text{Se}$  in esters **5a** and **5d** are  $1.792(7)$  and  $1.785(4)$  Å, respectively, and are rather close to those of selenoketones.

Finally, the decomposition products of *S*-aryl esters **5c-e** were examined. These esters gradually turned from deep violet blue to yellow within 1 day even when they were stored below  $-10$  °C under Ar atmosphere, but no deposition of red selenium was observed. Although the NMR spectra of the yellow mixture derived from **5c-e** were less informative, X-ray molecular structure analysis<sup>27</sup> of a single crystal from the decomposed

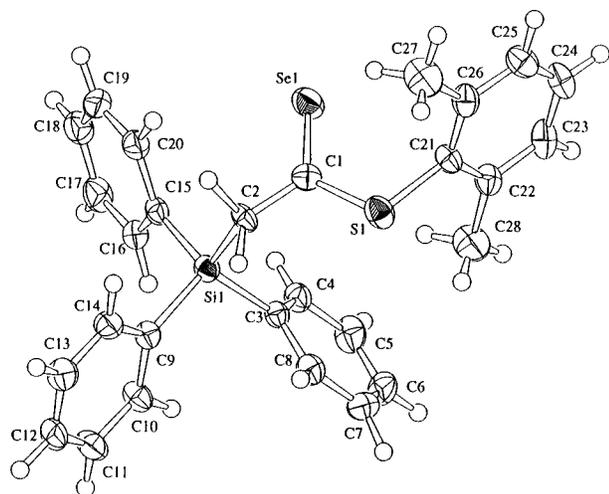
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**Figure 2.** ORTEP drawing of **5a**. Thermal ellipsoids are drawn at the 50% probability level.



**Figure 3.** ORTEP drawing of **5d**. Thermal ellipsoids are drawn at the 50% probability level.

**Table 4.** Selected Bond Distances and Angles of **5a**

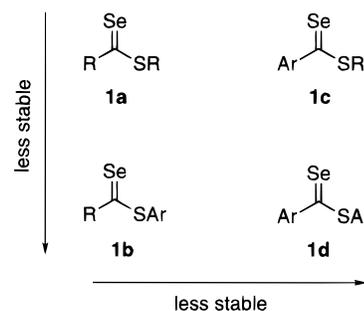
Bond Distance (Å)				
atom	atom	distance		
Se(1)	C(1)	1.792(7)		
S(1)	C(1)	1.724(6)		
S(1)	C(21)	1.833(7)		
Si(1)	C(2)	1.924(7)		
C(1)	C(2)	1.473(9)		
Bond Angle (deg)				
atom	atom	atom	angle	
Se(1)	C(1)	S(1)	125.1(4)	
Se(1)	C(1)	C(2)	122.6(5)	
S(1)	C(1)	C(2)	114.3(5)	
C(1)	S(1)	C(21)	106.3(3)	
Si(1)	C(2)	C(1)	114.3(5)	
Torsion Angle (deg)				
atom	atom	atom	atom	angle
Se(1)	C(1)	S(1)	C(21)	-5.3(5)
Se(1)	C(1)	C(2)	Si(1)	76.0(6)
C(1)	S(1)	C(21)	C(22)	-152.3(5)
C(1)	S(1)	C(21)	C(23)	85.4(6)

products of **5c** revealed that *trans*-1,3-diselenetane **16** was formed, probably via the dimerization of **4f**, which was generated by the protodesilylation of **5c** (eq 5). A similar dimerized compound **19**, which was formed from selenoketone

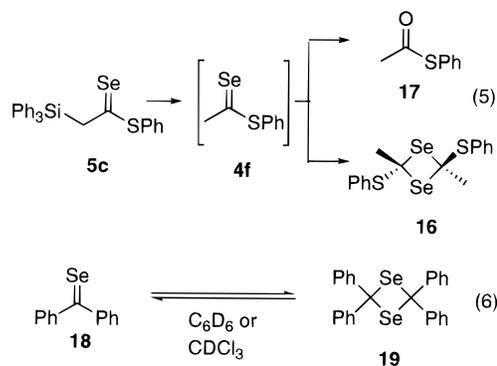
**Table 5.** Selected Bond Distances and Angles of **5d**

Bond Distance (Å)				
atom	atom	distance		
Se(1)	C(1)	1.785(4)		
S(1)	C(1)	1.741(4)		
S(1)	C(21)	1.771(4)		
Si(1)	C(2)	1.910(4)		
C(1)	C(2)	1.476(4)		
Bond Angle (deg)				
atom	atom	atom	angle	
Se(1)	C(1)	S(1)	123.5(2)	
Se(1)	C(1)	C(2)	124.5(3)	
S(1)	C(1)	C(2)	112.0(3)	
C(1)	S(1)	C(21)	105.1(2)	
Si(1)	C(2)	C(1)	114.8(3)	
Torsion Angle (deg)				
atom	atom	atom	atom	angle
Se(1)	C(1)	S(1)	C(21)	-1.1(3)
Se(1)	C(1)	C(2)	Si(1)	68.9(4)
C(1)	S(1)	C(21)	C(22)	-95.8(4)
C(1)	S(1)	C(21)	C(26)	88.7(4)

**Scheme 1**



**18**, was reported to be reversible with **18** when it was dissolved in  $C_6D_6$  or  $CDCl_3$  (eq 6).<sup>6d</sup> In contrast, **16** was highly stable in

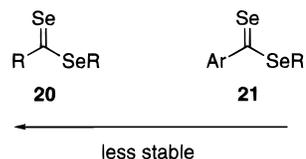


a solvent, and no reversible process was observed. These results suggest that *S*-aryl esters **1b** are thermally labile and undergo dimerization to 1,3-diselenethanes more easily than they undergo aerial oxidation leading to thioesters similar to **17** (eq 5). This is in sharp contrast to the case of aromatic selenothioic acid *S*-alkyl esters **1c**, which are easily oxidized to thioesters.<sup>17b</sup>

On the basis of the present and previous results,<sup>17b</sup> the general trend for the stability of selenothioic acid *S*-esters **1** is proposed in Scheme 1.

The aliphatic acid *S*-alkyl esters **1a** are the most stable among the four types of esters **1a–d**. The substitution of an alkyl group attached either to the selenocarbonyl group or to the sulfur atom with an aryl group reduces the stability of esters **1b,c**. The aliphatic acid *S*-aryl esters **1b** are prone to undergo dimerization, whereas the aromatic acid *S*-alkyl esters **1c** easily undergo aerial

## Scheme 2



oxidation. Attempts to isolate aromatic acid *S*-aryl esters **1d** have not yet been successful. It is also noteworthy that replacement of the *n*-butyl group attached to the sulfur atom in **1a** with a *tert*-butyl group reduces the stability of the esters. Accordingly, the introduction of a bulky group to esters **1** does not necessarily enhance their stability. This tendency is in sharp contrast to that in a series of better-known selenoesters<sup>7b,c</sup> and dithioic acid esters,<sup>15</sup> in which all types of derivatives with alkyl and aryl groups have been reported to be stable. It should also be noted that isolation of enolizable selenoaldehydes and selenoketones has not yet been reported, whereas aromatic derivatives can be isolated. More interestingly, the stability of a series of diselenoic acid esters (RC(Se)SeR') is also different (Scheme 2).<sup>26d,28</sup> Aliphatic diselenoic acid esters **20** are less stable than aromatic acid esters **21**.

## Conclusion

The synthesis, characterization, and general trend for the stability of selenothioic acid *S*-esters **1** have been demonstrated. The reaction of terminal acetylenes **2a**, **2b**, **2c**, and **2d** with selenium and thiols gave the corresponding esters **4–6** in good to high yields. Regarding the synthesis of  $\alpha$ -aryl esters, the acid-catalyzed reaction of *Se*-alkynyl selenoesters **8** with thiols **3** was effective. Although there were no critical differences in the spectroscopic data and structures of *S*-alkyl esters **1a** and *S*-aryl esters **1b**, **1b** was more labile than **1a**. From the decomposed products of **5c**, the formation of 1,3-*trans*-diselenetane was confirmed. Among four possible derivatives **1a–d**, *S*-alkyl esters **1a** and particularly selenothioacetic acid *S*-alkyl esters **4a–c** were found to be the most stable under air despite the fact that they were not protected either sterically or electronically.

## Experimental Section

**General Informations.** The materials are commercially available except for (triphenylsilyl)acetylene (**2b**)<sup>29</sup> and selenoacetic acid *Se*-alkynyl esters **8**.<sup>8f</sup> The <sup>77</sup>Se NMR (76 MHz) spectra were obtained from a JEOL  $\alpha$ -400 spectrometer, and <sup>77</sup>Se chemical shifts were expressed in parts per million deshielded with respect to neat Me<sub>2</sub>Se. All spectra were acquired in the proton-decoupled mode; generally 0.05–0.3 mmol solutions in CDCl<sub>3</sub> (0.4 mL) were used.

**General Procedure for the Synthesis of Selenothioic Acid S-Esters from Terminal Acetylenes: Synthesis of Ethaneselenothioic Acid S-Butyl Ester (4b).** To a solution of Et<sub>2</sub>O (60 mL) and (trimethylsilyl)acetylene (**2a**) (7.1 mL, 50.0 mmol) was added *n*-butyllithium (1.6 M in hexane, 31.3 mL, 50.0 mmol) at 0 °C. The solution was stirred at this temperature for 15 min, and selenium powder (3.95 g, 50.0 mmol) was added at 0 °C. The reaction mixture was warmed to 20 °C and stirred for 15 min. To this was added 1-butanethiol (11 mL, 100.0 mmol) at 0 °C. The reaction mixture gradually turned deep pink during the stirring at 0 °C for 30 min and at 20 °C for 1 h. Then, the resulting solution was poured onto water and extracted with Et<sub>2</sub>O. The organic layer was dried over anhydrous magnesium sulfate and concentrated. The residue was purified by column chromatography on silica gel using

hexane as the eluent to give 9.59 g (98%) of **4b** as deep pink oils: IR (neat) 2957, 2861, 1461, 1137, 1097, 827 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.95 (t, *J* = 7.4 Hz, 3H, CH<sub>3</sub>), 1.47 (sex, *J* = 7.4 Hz, 2H CH<sub>2</sub>), 1.72 (qui, *J* = 7.4 Hz, 2H, CH<sub>2</sub>), 2.57 (s, 3H, CH<sub>3</sub>), 3.23 (t, *J* = 7.4 Hz, 2H, SCH<sub>2</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  13.7 (CH<sub>3</sub>), 22.2 (CH<sub>2</sub>), 28.9 (CH<sub>2</sub>), 41.5 (SCH<sub>2</sub>), 44.9 (CH<sub>3</sub>), 237.8 (C=Se); CIMS (*m/z*) 197.0 (M<sup>+</sup> + 1). Anal. Calcd for C<sub>6</sub>H<sub>12</sub>SSe: C, 36.92; H, 6.20. Found: C, 36.74; H, 6.12.

**2-(Triphenylsilyl)ethaneselenothioic Acid S-1-Methylethyl Ester (5a):** IR (neat) 3044, 1426, 1111, 1086, 892, 699, 504, 487 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.10 (d, *J* = 6.9 Hz, 6H, CH<sub>3</sub>), 3.64 (m, *J* = 6.9 Hz, 1H, SCH), 3.83 (s, 2H, CH<sub>2</sub>), 7.25–7.41 (m, 9H, *m,p*-CH), 7.51–7.72 (m, 6H, *o*-CH); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  21.1 (CH<sub>3</sub>), 45.7 (SCH), 51.0 (CH<sub>2</sub>), 127.7, 129.9 (CH), 132.7 (*ipso*-C), 136.2 (CH), 235.6 (C=Se); EIMS (*m/z*) 440 (M<sup>+</sup>). Anal. Calcd for C<sub>23</sub>H<sub>24</sub>SSeSi: C, 62.85; H, 5.50. Found: C, 62.77; H, 5.46.

**2-(Triphenylsilyl)ethaneselenothioic Acid S-2,6-Dimethylphenyl Ester (5d):** IR (neat) 3051, 1428, 1110, 877, 733, 505, 490, 479 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.00 (s, 6H, CH<sub>3</sub>), 3.97 (br, 2H, CH<sub>2</sub>), 7.04 (d, *J* = 7.3 Hz, 2H, *m*-CH(SAr)), 7.19 (t, *J* = 7.6 Hz, 1H, *p*-CH(SPh)), 7.32–7.42 (m, 9H, *m,p*-CH), 7.66 (d, *J* = 6.8 Hz, 6H, *o*-CH); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  20.8 (CH<sub>3</sub>), 50.7 (CH<sub>2</sub>), 127.9, 128.4, 130.0, 130.5 (CH), 133.1 (*ipso*-C), 136.3 (CH), 136.4, 142.6 (*ipso*-C), 237.6 (C=Se); EIMS (*m/z*) 502 (M<sup>+</sup>). Anal. Calcd for C<sub>28</sub>H<sub>26</sub>SSeSi: C, 67.04; H, 5.22. Found: C, 66.68; H, 5.16.

**X-ray Measurements.** All measurement were carried out on a Rigaku AFC7R diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.710 69 Å). All of the structures were solved and refined using the teXsan crystallographic software package on an IRIS Indigo computer. X-ray quality crystals of **5a** were obtained by vaporization of the saturated hexane solution and of **5d** were obtained by vaporization of the diffused solution of hexane into dichloromethane solution of the samples. The crystals were cut from the grown needles. Each crystal mounted on a glass fiber was coated with an epoxy resin. The cell dimensions were determined by a least-squares refinement of the diffractometer angles for 25 automatically centered reflections. Three standard reflections were measured every 150 reflections, and no decay was detected. An empirical absorption correction (DIFABS<sup>30</sup>) was applied. The structures were solved by direct method SHELX86<sup>31</sup> and expanded using DIRDIF92.<sup>32</sup> Scattering factors for neutral atoms were from Cromer and Waber<sup>33</sup> and anomalous dispersion was used. The weighting scheme employed was  $w = [\sigma^2(F_o) + p^2(F_o)^2/4]^{-1}$ . A full-matrix least-squares refinement was executed with non-hydrogen atoms being anisotropic. The final least-squares cycle included fixed hydrogen atoms at calculated positions of which each isotropic thermal parameter was set to 1.2 times of that of the connecting atom. Crystal data, measurement description, data collection, and refinement parameters are available as a Supporting Information.

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**Supporting Information Available:** Experimental procedure for eq 3, characterization data for **4a,c–e,g–k**, **5b,c,e**, **6**, and **7**, and complete tables of crystallographic data, final atomic coordinates and equivalent isotropic thermal parameters, bond distances, bond angles, and torsion angles (23 pages). See any current masthead page for ordering and Internet access instructions.

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