Se-Aryl Alkane- or Arenecarboselenothioates: Synthesis and Some Reactions[1)]

Shinzi Kato,* Eiji Yasui, Kiyomitsu Terashima, Hideharu Ishihara,
and Toshiaki Murai
Department of Chemistry, Faculty of Engineering, Gifu University, 1-1 Yanagido, Gifu 501-11

(Received March 30, 1988)

A series of *Se*-aryl carboselenothioates **3** (RCSSeAr, R=alkyl, aryl) were synthesized and characterized from the reaction of bis(thioacyl) sulfides **1** with sodium areneselenolates. The thionselenolesters **3** are stable (liquid or crystals) both thermally and to moisture. Reactions of **3** with aliphatic primary and secondary amines gave the corresponding ammonium carbodithioates **8** together with diphenyl diselenide **7**. In contrast, treatment with aromatic amines or sodium alcoholates afforded the corresponding thioamides or *O*-alkyl or *O*-aryl thionesters in good yields. The oxidation of **3** with *m*-chloroperbenzoic acid gave the corresponding sulfides **12** [RCS(O)SeAr] and acyl arylseleno sulfides **13** [RCOSSeAr] which are formed by a rearrangement of the ArSe group to the thiocarbonyl sulfur atom.

In the past decades, a number of esters of carboselenoic and carbotelluroic acids (RCOER′, E=Se, Te) have been prepared and their physical and chemical properties have been revealed.[2)] In contrast, the chemistry of carboselenothioic acid esters **3** (RCSSeR′)[3)] (hereafter cited as thionselenolesters) have virtually not been studied, because of their synthetic difficulty, though they are interesting compounds synthetically and spectroscopically. In earlier studies, we succeeded in isolating bis(thioacyl) sulfides **1**[4)] and demonstrated that they are very useful for the thioacylation of amines, alcoholates, and thiolates.[5)] We now wish to report on the synthesis of a series of thionselenolesters **3** from the reaction of bis(thioacyl) sulfides **1** with sodium areneselenolates and their various reactions.

Results and Discussion

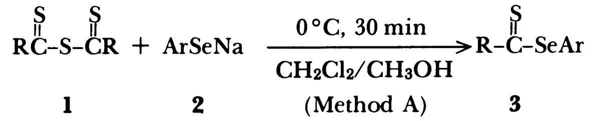
For the synthesis of thionselenolesters **3**, the reaction conditions (using bis[4-methyl(thiobenzoyl)] sulfide **1i** and sodium benzeneselenolate) have been preliminary investigated in detail. As a result, the reaction conditions of bis(thioacyl) sulfides with a large excess of sodium areneselenolate at 0 °C for 1 h seemed to be preferable. For example, when a dichloromethane solution of the sulfide **1i** was added to three equivalents of sodium benzeneselenolate in ethanol at 0 °C, the color of the mixture quickly changed from dark green to reddish pink. After the usual work-up of the reaction mixture, a chromatographic separation on silica gel afforded 73% of *Se*-

Table 1. Yields and Bp or Mp of *Se*-Aryl Alkane- and Arenecarboselenothioates **3**

No.	RCSSeAr R	Ar	Method[a)]	Yield[b)] %	Bp (°C/Torr)[c)] or Mp (°C)
3a	CH_3	C_6H_5	A	26	85 / 1.5
3b	C_2H_5	C_6H_5	A	51	114 / 3.5
3c	n-C_3H_7	C_6H_5	A	68	127 / 3.5
3d	i-C_3H_7	C_6H_5	A	77	111 / 3.0
3e	n-C_4H_9	C_6H_5	A	60	132 / 3.5
3f	n-C_5H_{11}	C_6H_5	A	69	152 / 3.5
3g	*cyclo*-C_6H_{11}	C_6H_5	A	83	119 / 1.0
3h	C_6H_5	C_6H_5	A	44	44—46
			B	60	
			C	12	
3i	4-$CH_3C_6H_4$	C_6H_5	A	73	83—84
			B	77	
			C	12	
3j	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	A	81	118—120
3k	4-$CH_3C_6H_4$	4-ClC_6H_4	A	70	96—97
3l	2,4,6-$(CH_3)_3C_6H_2$	C_6H_5	A	0	
3m	4-$CH_3OC_6H_4$	C_6H_5	A	68	63—65
			B	31	
			C	0	
3n	4-ClC_6H_4	C_6H_5	A	78	87—88
			B	80	
			C	37	

a) Method A: $(RCS)_2S$+ArSeNa; Method B: RCSCl+ArSeNa; Method C: RCSCl+$ArSeSi(CH_3)_3$. b) Isolated yield. c) Kugelrohr oven temp, 1 Torr≈133.322 Pa.

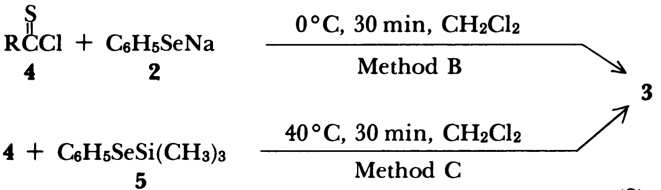
phenyl 4-methylbenzenecarboselenothioate **3i** as reddish-pink crystals. Through an analogous treatment of other bis(thioacyl) sulfides **1a—h, j—n** with sodium areneselenolates, the corresponding aliphatic and aromatic thionselenolesters **3a—h, j—n** were isolated in good yields[6] (Eq. 1, Table 1). However, a number of attempts to prepare a sterically hindered 2,4,6-trimethylphenyl derivative **3l** failed. In order to make a comparison with the above mentioned method, the following two synthetic methods were also examined: a) Reaction of thioacyl chloride with sodium benzeneselenolate (Method B) and b) with (phenylseleno)trimethylsilane (Method C) (Eq. 2). As shown in Table 1, the former method led to analogous yields of **3**, while the later to low yields, because of the unexpected low reactivity of (phenylseleno)trimethylsilane.[7] It is noted that both methods are limited to the synthesis of aromatic derivatives (**3**, R=aromatic), because of a synthetic difficulty involving aliphatic thioacyl chlorides.[8]



$$\underset{\mathbf{1}}{\mathrm{R}\overset{\overset{S}{\|}}{\mathrm{C}}\text{-}\mathrm{S}\text{-}\overset{\overset{S}{\|}}{\mathrm{C}}\mathrm{R}} + \underset{\mathbf{2}}{\mathrm{ArSeNa}} \xrightarrow[\mathrm{CH_2Cl_2/CH_3OH}]{0\,^\circ\mathrm{C},\ 30\ \mathrm{min}} \underset{\mathbf{3}}{\mathrm{R}\text{-}\overset{\overset{S}{\|}}{\mathrm{C}}\text{-}\mathrm{SeAr}} \quad (1)$$

(Method A)

No.	R	Ar
3a	CH_3	C_6H_5
3b	C_2H_5	C_6H_5
3c	n-C_3H_7	C_6H_5
3d	i-C_3H_7	C_6H_5
3e	n-C_4H_9	C_6H_5
3f	n-C_5H_{11}	C_6H_5
3g	*cyclo*-C_6H_{11}	C_6H_5
3h	C_6H_5	C_6H_5
3i	4-$CH_3C_6H_4$	C_6H_5
3j	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$
3k	4-$CH_3C_6H_4$	4-ClC_6H_4
3l	2,4,6-$(CH_3)_3C_6H_2$	C_6H_5
3m	4-$CH_3OC_6H_4$	C_6H_5
3n	4-ClC_6H_4	C_6H_5



$$\underset{\mathbf{4}}{\mathrm{R}\overset{\overset{S}{\|}}{\mathrm{C}}\mathrm{Cl}} + \underset{\mathbf{2}}{\mathrm{C_6H_5SeNa}} \xrightarrow[\text{Method B}]{0\,^\circ\text{C, 30 min, CH}_2\text{Cl}_2} \mathbf{3}$$

$$\mathbf{4} + \underset{\mathbf{5}}{\mathrm{C_6H_5SeSi(CH_3)_3}} \xrightarrow[\text{Method C}]{40\,^\circ\text{C, 30 min, CH}_2\text{Cl}_2} \mathbf{3} \quad (2)$$

The structures of the obtained thionselenolesters **3** were determined on the basis of mass, IR, UV/Vis, and ^{1}H and ^{13}C NMR spectroscopic data, and the results of microanalysis. The stretching frequencies, n-π^* transitions, and ^{13}C NMR spectra of the thiocarbonyl group of **3** are summarized in Table 2.

The thionselenolesters **3** are colored compounds: aliphatic derivatives (R=aliphatic) are yellow to orange and aromatic ones (R=aromatic) are red to reddish pink. They are stable both thermally and to moisture. They did not change at room temperaure for one week and can be storred in the refrigerator (0 °C) for over 3 years.

Spectra. It is known that νC=S bands of dithiocarboxylic acid esters appear in the region 1100—1200 cm^{-1} for the aliphatic derivatives and 1200—1250 cm^{-1} for the aromatic ones. As listed in Table 2, the characteristic thiocarbonyl stretching frequencies of **3** were observed in the 1220—1250 cm^{-1} region for the aliphatic derivatives and the 1000—1200 and/or 840—900 cm^{-1} regions for the aromatic derivatives. In the electron spectra of **3**, two characteristic absorption maxima were observed at 300—320 nm (π-π^*) and 480—495 nm (n-π^*,[10] C=S group) for the aliphatic derivatives and 530—540 nm (n-π^*,[10] C=S group) for the aromatic ones. The π-π^* and n-π^* transitions of the C=S group of *O*-phenyl 4-methylbenzenecarbothioate **11c**, phenyl 4-methylbenzenecarbodithioate **18**, and *Se*-phenyl 4-methylbenzenecarboselenothioate **3i** in both cyclohexane and ethanol are collected in Table 3. In going from E=*O*, to *S*, and *Se*, both absorption maxima shift to a longer-wavelength region. This is the first example of a bathochromic effect regarding the π-π^* and n-π^* transitions by an

Table 2. The IR, Visible, and ^{13}C NMR Spectra of the C=S Group of **3**

No.	RCSSeAr R	Ar	IR (neat) νC=S/cm^{-1}	Vis (hexane) λ_{max}/nm (log ε)	^{13}C NMR[c] [δ] (C=S)
3a	CH_3	C_6H_5	1195, 831	492	240.1
3b	C_2H_5	C_6H_5	1191, 860	486	246.4
3c	n-C_3H_7	C_6H_5	1184, 832	486	244.4
3d	i-C_3H_7	C_6H_5	1210	493	242.2
3e	n-C_4H_9	C_6H_5	1180, 867	486	244.3
3f	n-C_5clH_{11}	C_6H_5	1170, 878	486	245.4
3g	*cyclo*-C_6H_{11}	C_6H_5	1190, 860	488	250.2
3h	C_6H_5	C_6H_5	1245[a]	542 (1.92)	232.2
3i	4-$CH_3C_6H_4$	C_6H_5	1250[a]	541 (1.97)[b]	231.8
3j	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	1250[a]	528 (2.05)	232.4
3k	4-$CH_3C_6H_4$	4-ClC_6H_4	1223[a]	540 (1.99)	230.7
3m	4-$CH_3OC_6H_4$	C_6H_5	1240[a]	538 (2.09)	229.5
3n	4-ClC_6H_4	C_6H_5	1238[a]	542 (1.92)	230.5

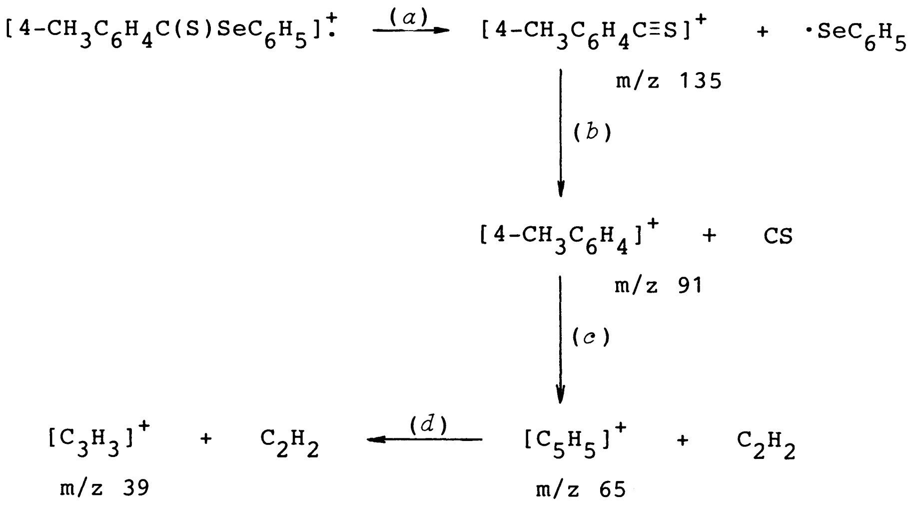
a) KBr. b) CH_2Cl_2. c) $CDCl_3$.

Table 3. The π-π* and n-π* Transitions of *O*-Phenyl 4-Methylbenzenecarbothioate (**11c**), Phenyl 4-Methylbenzenecarbodithioate (**18**), and *Se*-Phenyl 4-Methylbenzenecarboselenothioate (**3i**) and ^{13}C NMR Spectra of the Thiocarbonyl Groups

No.	$\mathrm{R{-}\overset{\overset{S}{\|}}{C}{-}E{-}C_6H_5}$ R	E	λ_{max}/nm				^{13}C=S ($CDCl_3$) [δ]
			π-π*		n-π*		
			cyclo-C_6H_{12}	C_2H_5OH	*cyclo*-C_6H_{12}	C_2H_5OH	
11c	4-$CH_3C_6H_4$	O	297	301	438	431	210.9
18	4-$CH_3C_6H_4$	S	310	314	528	518	227.6
3i	4-$CH_3C_6H_4$	Se	314	319	540	533	231.8
	4-$CH_3C_6H_4$	Te	318 (?)		550 (?)		236 (?)

Table 4. Selected Ions from Mass Spectra (70 eV) of *Se*-Phenyl 4-Methylbenzenecarbothioselenoate (**3i**), and *O*-Phenyl 4-Methylbenzenecarbothioate (**11c**), and Phenyl 4-Methylbenzenecarbodithioate (**18**)

4-$CH_3C_6H_4C(S)SeC_6H_5$	*m/z*	RI	4-$CH_3C_6H_4C(S)OC_6H_5$	*m/z*	RI	4-$CH_3C_6H_4CS_2C_6H_5$	*m/z*	RI
$[C_3H_3]^+$	39	9	$[C_3H_3]^+$	39	31	$[C_3H_3]^+$	39	14
$[C_4H_3]^+$	51	12	$[C_4H_3]^+$	51	17	$[C_4H_3]^+$	51	9.5
$[C_5H_5]^+$	65	14	$[C_5H_5]^+$	65	35	$[C_5H_5]^+$	65	25
$[C_6H_5]^+$	77	13	$[C_6H_5]^+$	77	10.5	$[C_6H_5]^+$	77	4.5
$[CH_3C_6H_4]^+$	91	30	$[CH_3C_6H_4]^+$	91	61.5	$[CH_3C_6H_4]^+$	91	39.5
$[C_6H_5S]^+$	109	2.5	$[C_6H_5O]^+$	93	5.5	$[C_6H_5S]^+$	109	13.5
$[CH_3C_6H_4C{\equiv}S]^+$	135	100	$[C_6H_5S]^+$	109	7	$[CH_3C_6H_4C{\equiv}S]^+$	135	100
$[C_6H_5Se]^+$	157	7	$[CH_3C_6H_4C{\equiv}O]^+$	119	53	$[M]^{+\cdot}$	244	
$[CH_3C_6H_4C{\equiv}Se]^+$	183	2.5	$[CH_3C_6H_4C{\equiv}S]^+$	135	100			
$[M]^{+\cdot}$	292		$[M]^{+\cdot}$	228				

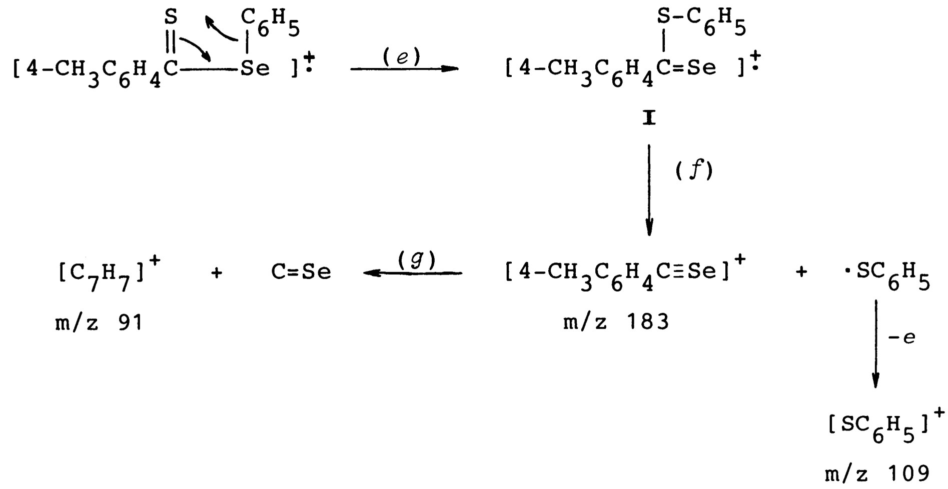


Scheme 1.

adjacent chalcogen element. In ^{13}C NMR spectra, ^{13}C=S values appear at δ 240—246 for the aliphatic derivatives and at 229—233 for the aromatic derivatives, respectively. As shown in Table 3, lower-field shifts of the thiocarbonyl carbon of the thion- **11c**, dithio- **18**, and thionselenolesters **3i** were observed in going from E=*O*, to *S*, and *Se*. Analogous lower shifts of the carbonyl carbon were observed for chalcogeno esters (RCOER′, E=*O*, *S*, *Se*, *Te*).[2]

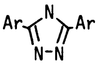
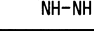
It is well-known that *S*-alkyl benzenecarbothioates undergo a rearrangement of the alkyl group to the carbonyl oxygen atom, while the alkyl group of *O*-alkyl benzenecarbothioates migrates to the thiocarbonyl sulfur atom.[11–14] The obtained thionselenolesters **3** all afforded molecular ions. The fragment ions and the relative intensity of the 4-methyl derivative **3i** together with those of the corresponding thion- **11c** and dithioester **18** are shown in Table 4. As shown in the table, the cleavage pattern of the thionselenolester is substantially similar to those of the corresponding thion- and dithioesters.[15] Thus, the base peak is $[4\text{-}CH_3C_6H_4C{\equiv}S]^+$ peak at *m/z* 135 and the second highest one is the $[C_7H_7]^+$ peak at *m/z* 91; other significant peaks are those of the $[C_5H_5]^+$, $[C_6H_5]^+$, $[C_4H_3]^+$, $[C_3H_3]^+$, and $[C_6H_5Se]^+$, ions at *m/z* 65, 77, 51, 39, and 157, respectively. The most important successive fragmentations are (*a*)→(*b*)→(*c*), and→(*d*) (Scheme 1). In addition to these peaks, two characteristic peaks at *m/z* 183 and 109 can be observed corresponding to $[CH_3C_6H_4C{\equiv}Se]^+$ and $[C_6H_5S]^+$, respectively. This fact suggests a possible rearrangement of the phenyl group to the thiocarbonyl sulfur atom, followed by a fragmentation ion (**I**), though no metastable peaks corresponding to the fragmentation from the ion (**I**) could be observed (Scheme 2). Such a migration of the phenyl group bonded to a Se atom to the thiocarbonyl sulfur atom is the first example.

Reactions: In general, thion-[16] and dithioesters[17,18] react with primary and secondary amines to give the corresponding thioamides. In order to clarify the reactivity of the thionselenolester **3i**, several reactions with nucleophiles, such as amines and alcoholates, and oxidation by *m*-chloroperbenzoic acid were carried out using the 4-methyl derivative **3i** as the model thionselenolester. In Table 5, the reaction conditions of **3i** with primary and secondary amines and the products are summarized. At room temperature, **3i** does not react with an aromatic amine, such as aniline, though the reaction does occur under reflux in hexane to afford the corresponding thioanilide **6a** and diphenyl diselenide **7** in 68 and 99%, respectively. In contrast, the reaction with aliphatic amines, such as cyclohexylamine, diethylamine, and piperidine, occurrs at room temperature to give the corresponding ammonium salts **8** in 30—40% yields together with diselenide **7** and a dark-brown oil. No formation of the expected thioamides was observed.[18] In these reactions, the yields of diphenyl diselenide were quantitative. Over 60% the sulfur in the used **3i** was recovered as a dithio salt **8**, while the recovery of the $CH_3C_6H_4$ moiety was less than 45%. In order to elucidate the formation mechanism of **8**, a number of attempts to analyze the dark-brown oily substances have been undertaken. However, at the present stage, no appropriate explanation has been found regarding the formation of the ammonium dithiocarboxyates **8**.

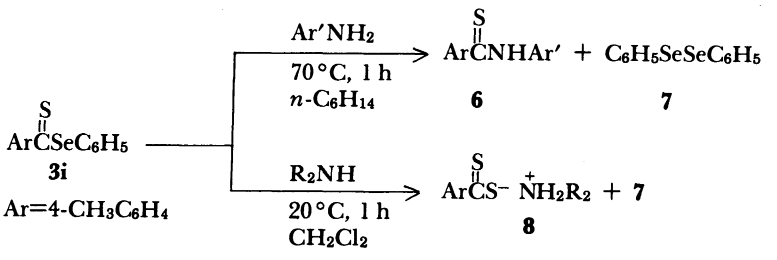


Scheme 2.

Table 5. Reaction of Thionselenolesters **3i** with Amines[a)]

$ArCSSeC_6H_5$	Ar′ or R_2NH	Solvent	Temp	Time		Product/%	
Ar			°C	h	ArCSNHAr′ (**6**)	$ArCS_2^-\overset{+}{N}H_2R_2$ (**8**)	$C_6H_5SeSeC_6H_5$ (**7**)
$4\text{-}CH_3C_6H_4$ **3i**	$C_6H_5NH_2$	$n\text{-}C_6H_{14}$	69	24	68 (**6a**)		99
	cyclo-$C_6H_{11}NH_2$	$n\text{-}C_6H_{14}$	20	5		40 (**8a**)	90
	$(C_2H_5)_2NH$	$n\text{-}C_6H_{14}$	25	24		44 (**8b**)	94
		$n\text{-}C_6H_{14}$	20	0.5		31 (**8c**)	97
	NH_2NH_2	$n\text{-}C_6H_{14}$	18	1	29 (**6b**)		
		C_2H_5OH	20	1	78 (**6b**)		98
		C_2H_5OH	78	24	 (**9**) (84%)		
	$NH_2CSNHNH_2$	C_2H_5OH	78	6	 (**10**) (89%)		

a) Mole ratio: **3i**/NH_2NH_2=1:2.



$$\underset{\substack{\mathbf{3i}\\ Ar=4\text{-}CH_3C_6H_4}}{Ar\overset{S}{\overset{\|}{C}}SeC_6H_5} \xrightarrow[\substack{70\,°C,\ 1\,h\\ n\text{-}C_6H_{14}}]{Ar'NH_2} \underset{\mathbf{6}}{Ar\overset{S}{\overset{\|}{C}}NHAr'} + \underset{\mathbf{7}}{C_6H_5SeSeC_6H_5} \qquad (3)$$

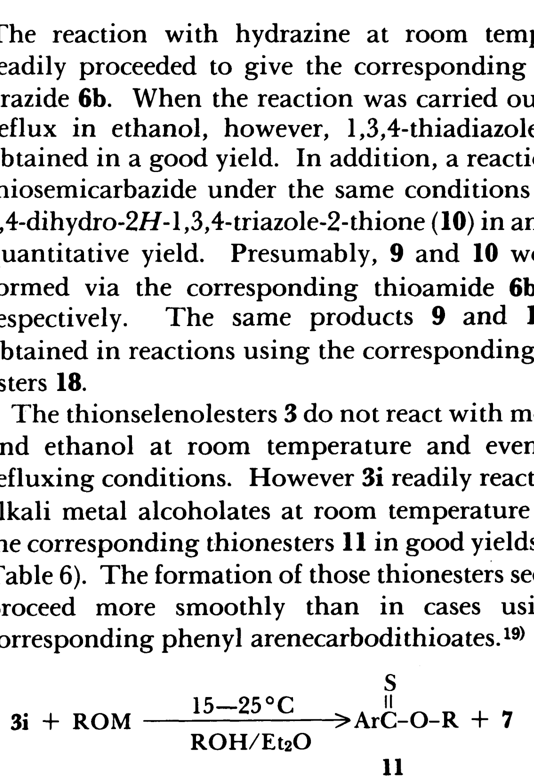
$$\mathbf{3i} \xrightarrow[\substack{20\,°C,\ 1\,h\\ CH_2Cl_2}]{R_2NH} \underset{\mathbf{8}}{Ar\overset{S}{\overset{\|}{C}}S^-\ \overset{+}{N}H_2R_2} + \mathbf{7} \qquad (4)$$

No.	Ar′
6a	C_6H_5
6b	NH_2
6c	NH_2CSNH

No.	R_2NH
8a	*cyclo*-$C_6H_{11}NH_2$
8b	$(C_2H_5)_2NH$
8c	

The reaction with hydrazine at room temperature readily proceeded to give the corresponding thiohydrazide **6b**. When the reaction was carried out under reflux in ethanol, however, 1,3,4-thiadiazole **9** was obtained in a good yield. In addition, a reaction with thiosemicarbazide under the same conditions yielded 3,4-dihydro-2*H*-1,3,4-triazole-2-thione (**10**) in an almost quantitative yield. Presumably, **9** and **10** would be formed via the corresponding thioamide **6b** or **6c**, respectively. The same products **9** and **10** were obtained in reactions using the corresponding dithioesters **18**.

The thionselenolesters **3** do not react with methanol and ethanol at room temperature and even under refluxing conditions. However **3i** readily reacted with alkali metal alcoholates at room temperature to give the corresponding thionesters **11** in good yields (Eq. 5, Table 6). The formation of those thionesters seemed to proceed more smoothly than in cases using the corresponding phenyl arenecarbodithioates.[19]



$$\mathbf{3i} + ROM \xrightarrow[ROH/Et_2O]{15\text{—}25\,°C} \underset{\mathbf{11}}{Ar\overset{S}{\overset{\|}{C}}\text{-}O\text{-}R} + \mathbf{7} \qquad (5)$$

$$M=Na,\ K$$

No.	R
11a	CH_3
11b	C_2H_5
11c	C_6H_5

The oxidation of dithioesters with peroxy acid provides a route to (alkyl- or arylthio)-, (alkyl- or arylsulfinyl)-, and (alkyl- or arylsulfonyl)sulfines.[20] The thionselenolesters **3i** upon treatment with peroxy acids are expected to produce the corresponding sulfines. In fact, the treatment of *Se*-phenyl 4-methylbenzenecarboselenothioate **3i** with one equivalent of *m*-chloroperbenzoic acid (mCPBA) in ether at 0 °C gave a 34% yield of a mixture of two isomeric phenylseleno(4-methylphenyl)sulfines (**12i** and **12′i**). No formation of the expected phenyl selenenyl ($PhSeO\text{–}CSO\text{–}C_6H_4CH_3\text{-}4$) and phenylselenonylsulfines ($PhSeO_2\text{–}CSO\text{–}C_6H_4CH_3\text{-}4$) were observed. Instead, phenylseleno 4-methylbenzoyl sulfides (**13i**), bis(4-methylbenzoyl) disulfide (**14**, $R=4\text{-}CH_3C_6H_4$), and diphenyl diselenide (**7**) were obtained in 11, 3, and 14% yields, respectively. Similarly, the oxidation of the aliphatic thionselenolesters, **3d** and **3e** afforded the corresponding sulfines as a mixture of the trans- (**12d**, **12e**) and cis-isomer (**12′d**, **12′e**), phenylseleno acyl sulfides **13d**, **13e**,[1] and diphenyl diselenide **7** in analogous yields.[21] The trans- **12** and cis-isomer **12′** were separated by thin-layer chromatography. The structures of the products, **12**, **13**, **14**, were established on the basis of the IR, ^1H and ^{13}C NMR, and mass spectra, and/or by comparisons of the spectra with those of authentic samples. In addition, the conformation of the trans- **12e** and cis-isomer **12′e** were deduced by the ^1H NMR spectra. For example, the methine and methylene protons of the trans- **12e** were shifted down field, compared with those of the cis-isomers **12′d** and **12′e**, respectively. In addition, the ortho-protons on the 4-methylbenzene ring of the trans-isomer **12i** showed a broad multiplet without

Table 6. Reaction of Thionselenolesters **3i** with Sodium Alcoholates

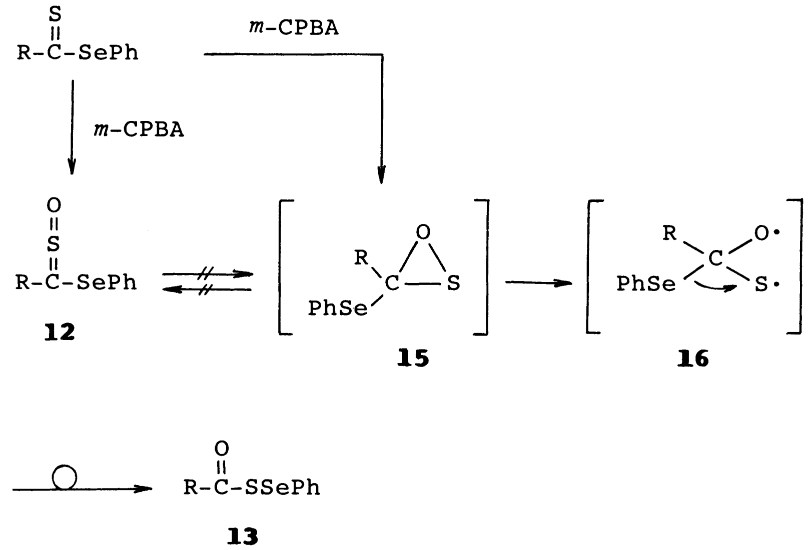
$ArCSSeC_6H_5$ Ar	ROM[a)]	Solvent	Temp °C	Time h	Product/% ArCSOR (**11**)	$C_6H_5SeSeC_6H_5$ (**7**)
$4\text{-}CH_3C_6H_4$	CH_3ONa	$(C_2H_5)_2O/CH_3OH$	20	2	86 (**11a**)	90
3i	C_2H_5ONa	$(C_2H_5)_2O/C_2H_5OH$	22	2	91 (**11b**)	95
	C_6H_5ONa	$(C_2H_5)_2O$	18	24	79 (**11c**)	90

a) Mole ratio: **3i**/ROM=1:1.

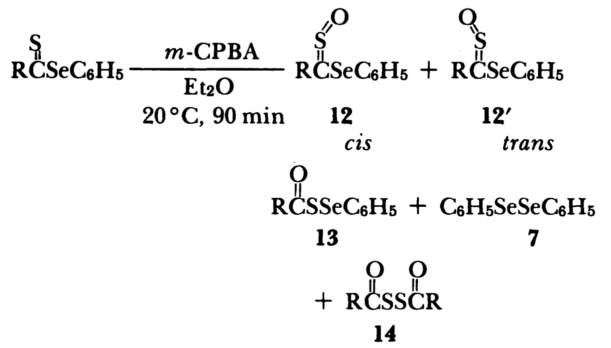
Table 7. Reaction of Thionselenolesters **3** with *m*-Chloroperbenzoic Acid[a)]

$RCSSeC_6H_5$ (**3**) R	Diselenide (**7**)	Product/% *trans*-Sulfine (**12**)	 *cis*-Sulfine (**12′**)	 $RCOSSeC_6H_5$	 Disulfide (**14**)
i-C_3H_7 (**3d**)	35	13 (**12d**)	13 (**12′d**)	19 (**13d**)	—
n-C_4H_9 (**3e**)	Trace	32 (**12e**)	21 (**12′e**)	38 (**13e**)	—
4-$CH_3C_6H_4$ (**3i**)	14	26 (**12i**)	8 (**12′i**)	11 (**13i**)	3

a) Reaction conditions: 0 °C, 90 min in ether; mole ratio **3**/*m*-CPBA=1 : 1.



Scheme 3.

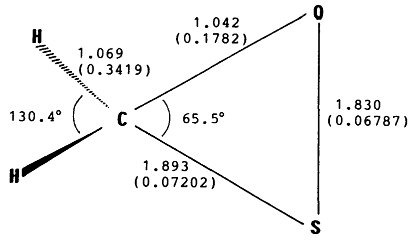


$$\mathrm{R\overset{S}{\overset{\|}{C}}SeC_6H_5} \xrightarrow[\mathrm{Et_2O}]{m\text{-CPBA}} \underset{\substack{\mathbf{12}\\ cis}}{\mathrm{R\overset{S\nearrow O}{\overset{\|}{C}}SeC_6H_5}} + \underset{\substack{\mathbf{12'}\\ trans}}{\mathrm{R\overset{O\searrow S}{\overset{\|}{C}}SeC_6H_5}}$$

$$20\,^\circ\mathrm{C},\ 90\ \mathrm{min}$$

$$\underset{\mathbf{13}}{\mathrm{R\overset{O}{\overset{\|}{C}}SSeC_6H_5}} + \underset{\mathbf{7}}{\mathrm{C_6H_5SeSeC_6H_5}} + \underset{\mathbf{14}}{\mathrm{R\overset{O}{\overset{\|}{C}}SS\overset{O}{\overset{\|}{C}}R}} \qquad (6)$$

No.	R
12d, 12′d, 13d	*i*-C_3H_7
12e, 12′e, 13e	*n*-C_4H_9
12i, 12′i, 13i, 14	4-$CH_3C_6H_4$



17

Fig. 1. Optimized geometry, bond lengths in Å, angles in deg. and bond populations in parentheses from 3-21G level MO calculations.

any downfield shift, while those of the cis-isomer **12′i** showed a singlet.[22)] Presumably, one of the reasons for such downfield shifts of the methine and methylene protons seems to be due to a deshielding action of the sulfinyl group.[23)] It is noted that the methine, methyl, and sulfine carbons of the *trans*-isopropyl(phenylseleno)sulfine **12d** were shifted upfield compared with those of the cis-isomer **12′i**. Similar upfield shifts of trans-isomer were observed for the ^{13}C NMR spectra of butyl(phenylseleno)sulfine, **12e** and **12′e**.

For the formation of phenylseleno acyl sulfides **13**, the possibility via the sulfine **12** and then 2-phenylseleno-3-alkyl (or aryl) oxathiirane **15** as intermediates can be considered (Scheme 3). However, after stirring trans- **12** or cis-isomer **12″** in dichloromethane at 20 °C for 2 h, no conversion between the trans- **12** and cis-isomers **12′** was observed. This result suggests that the possibility of a formation roue of **13** via the sulfine **12**, can be ruled out. In order to obtain additional information regarding the formation of the sulfine **12** via the oxathiirane **15**, an ab initio molecular orbital study was carried out by employing oxathiirane **17** as a model. The optimized molecular geometries[24)] of **17** were calculated by ab initio MO calculations at the 3-21G level using on energy-gradient method. As illustrated in Fig. 1, the bond population between sulfur and oxygen was smaller than those of the carbon–oxygen and carbon–sulfur bonds. Thus, the S–O bond of the oxathiirane ring is weaker than the C–O and C–S bonds. Most probably, phenylseleno acyl sulfide **13** is formed by a migration of the phenylseleno group of the opening intermediate **16**.

Experimental

The melting points were obtained by using a Yanagimoto micromelting point apparatus and are uncorrected. The IR spectra were measured on a JASCO grating IR spectrophotometer (IR-G and A-302). The UV/Vis spectra were taken from a Hitachi 124 and 330 spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded on Hitachi R-24 (60 MHz), R-22 (90 MHz), and JEOL JNM GX-270 (270 MHz) with tetramethylsilane as an internal standard.

The mass spectra were taken from a Hitachi RMU-6M mass spectrometer (70 eV, 180—190 °C). High-resolution mass spectroscopy was taken by a Shimazu high-resolution mass spectrometer (GCMS 9020-DF/PAC-1100). Elemental analyses were carried out by Elemental Analyses Center of Kyoto University and Alfred Bernhardt Analytical Laboratory, Engelskirhen (Germany).

Materials: Bis(thioacyl) sulfides,[4] piperidinium carbodithioates,[25] thioacyl chlorides,[26] phenylselenotrimethylsilanes,[27] diphenyl-,[27] bis(4-methylphenyl)-,[28] and bis(4-chlorophenyl) diselenides,[29] were prepared according to methods described in the literature. Sodium areneselenolates were prepared by a treatment of the corresponding diaryl diselenides with sodium borohydride, respectively.[30] Aniline, cyclohexylamine, diethylamine, and piperidine were dried by refluxing with potassium hydroxide, and distilled before use. Hydrazine hydrate, thiosemicarbazide, and *m*-chloroperbenzoic acid (80%) were of commercial grade and were used without further purification. The solvents were dried by the use of sodium metal or calcium chloride. Column chromatography was performed on Wako Gel 200.

The preparation methods of *Se*-phenyl 2-propane- (**3d**) and 4-methylbenzenecarboselenothioate (**3i**) (as typical procedures) are described in detail. All manipulations are carried out under nitrogen.

***Se*-Phenyl Methanecarboselenothioate (3a):** In a manner similar to the synthesis of **3d**, the reaction of bis[methyl(thiocarbonyl)] sulfide (**1a**, 3 mmol) in hexane (20 ml), freshly prepared from ethanedithioic acid (533 mg, 6 mmol) and dicyclohexylcarbodiimide (619 mg, 3 mmol), with a solution of sodium benzeneselenolate (3 mmol) in dichloromethane/methanol (3:1, 20 ml) at −60 °C for 30 min, followed by silica-gel column chromatography (hexane) and then bulb-to-bulb distillation yielded 170 mg (26%) of **3a** as orange liquid: bp 85 °C/1.5 Torr. IR (neat), 3047, 1582, 1480, 1442, 1359, 1208, 1195 (C=S), 1092, 1070, 1021, 1001, 831 (C=S) 737, 688, 494, and 468 cm^{-1}. UV/Vis (hexane) 258, 328, and 492 nm. ^{1}H NMR (CDCl$_3$) δ=2.84 (3H, s, CH$_3$), and 7.4—7.6 (5H, m, Ar). ^{13}C NMR (CDCl$_3$) δ=42.3 (CH$_3$), and 240.1 (C=S). MS (70 eV) *m/z* (rel intensity), 216 (M$^+$; 12), 157 ($C_6H_5Se^+$, 24), and 59 (CH_3CS^+, 100). Found: *m/z* 215.9503. Calcd for C_8H_8SSe: M, 215.9512.

***Se*-Phenyl Ethanecarboselenothioate (3b):** In a manner similar to the synthesis of **3d**, the reaction of bis[ethyl(thiocarbonyl)] sulfide (**1b**) (3 mmol) in hexane (20 ml), freshly prepared from propane dithioic acid (637 mg, 6 mmol) and dicyclohexylcarbodiimide (619 mg, 3 mmol), with a solution of sodium benzeneselenolate (3 mmol) in a mixed solvent of dichloromethane/methanol (3:1, 20 ml) at −10 °C for 30 min, followed by silica-gel column chromatography (hexane) and then bulb-to-bulb distillation yielded 353 mg (51%) of **3b** as orange liquid: bp 114 °C/3.5 Torr. IR (neat), 3025, 2950, 2290, 1577, 1480, 1441, 1280, 1191 (C=S), 1067, 1022, 1002, 968, 860 (C=S), 744, 691, and 471 cm^{-1}. UV/Vis (hexane) 258, 328, and 486 nm. ^{1}H NMR (CDCl$_3$) δ=1.35 (3H, t, CH$_3$), 3.04 (2H, q, CH$_2$), and 7.3—7.6 (5H, m, Ar). ^{13}C NMR (CDCl$_3$) δ=15.0 (CH$_3$), 47.1 (CH$_2$), and 246.4 (C=S). MS (70 eV) *m/z* (rel intensity), 230 (M$^+$; 5), 157 ($C_6H_5Se^+$, 5), and 73 ($C_2H_5CS^+$, 100). Found: *m/z* 229.9661. Calcd for $C_9H_{10}SSe$: M, 229.9668.

***Se*-Phenyl 1-Propanecarboselenothioate (3c):** In a manner similar to the synthesis of **3d**, bis[propyl(thiocarbonyl)] sulfide (**1c**) (3 mmol) in hexane (20 ml), freshly prepared from butanedithioic acid (721 mg, 6 mmol) and dicyclohexylcarbodiimide (619 mg, 3 mmol), was added to a solution of sodium benzeneselenolate (3 mmol) in a mixed solvent of dichloromethane/methanol (3:1, 20 ml) at 0 °C for 30 min, followed by silica-gel column chromatography and then bulb-to-bulb distillation yielded 496 mg (68%) of **3c** as orange liquid: bp 127 °C/3.5 Torr. IR (neat) 3025, 2980, 2950, 2880, 1580, 1478, 1460, 1440, 1380, 1240, 1184 (C=S), 1063, 1020, 1000, 922, 832 (C=S), 737, 687, and 468 cm^{-1}; UV/Vis (hexane) 258, 330, and 486 nm. ^{1}H NMR (CDCl$_3$) δ=0.99 (3H, t, CH$_3$), 1.88 (2H, m, CH$_2$), 3.04 (2H, t, CH$_2$), and 7.34—7.57 (5H, m, Ar). ^{13}C NMR (CDCl$_3$) δ=13.0 (CH$_3$), 23.7 (CH$_2$), 55.6 (CH$_2$), and 244.4 (C=S). MS (70 eV) *m/z* (rel intensity), 244 (M$^+$; 12), 157 ($C_6H_5Se^+$, 12), and 87 ($C_3H_7CS^+$, 100). Found: *m/z* 243.9836. Calcd for $C_{10}H_{12}SSe$: M, 243.9825.

***Se*-Phenyl 2-Propanecarboselenothioate (3d):** A solution of bis[isopropyl(thiocarbonyl)] sulfide (**1d**, 3 mmol) in hexane (20 ml), freshly prepared by a reaction of 2-methylpropanedithioic acid (721 mg, 6 mmol) with dicyclohexylcarbodiimide (619 mg, 3 mmol) in hexane (20 ml) at −70 °C for 30 min, was added to a solution of freshly prepared sodium benzeneselenolate (3 mmol) in a mixed solvent of dichloromethane/methanol (3:1, 20 ml) at 0 °C. The reaction mixture was then stirred at this temperature for 30 min. The color of the solution quickly changed from violet to orange. Hexane (15 ml) was added; the mixture was then washed with water (3×50 ml), followed by drying with anhydrous sodium sulfate. The solvent was evaporated in vacuo. The residue was chromatographed on silica gel [hexane/dichloromethane (9:1)]; then, a bulb-to-bulb distillation of the resulting orange eluent yielded 560 mg (77%) of **3d** as orange liquid: bp 111 °C/3.0 Torr. IR (neat) 3045, 3000, 2950, 2900, 1581, 1480, 1441, 1384, 1210 (C=S), 1160, 1067, 1031, 1021, 1001, 905, 815, 738, 688, and 470 cm^{-1}. UV/Vis (hexane) 258, 328, and 493 nm. ^{1}H NMR (CDCl$_3$) δ=1.36 (6H, d, CH$_3$), 3.59 (1H, m, CH), and 7.41—7.53 (5H, m, Ar). ^{13}C NMR (CDCl$_3$) δ=23.9, 50.8, and 242.2 (C=S). MS (70 eV) *m/z* (rel intensity), 244 (M$^+$; 12), 157 ($C_6H_5Se^+$, 42), and 87 (i-$C_3H_7CS^+$, 100). Found: *m/z* 243.9825. Calcd for $C_{10}H_{12}SSe$: M, 243.9825.

***Se*-Phenyl 1-Butanecarbothioselenoate (3e):** In a manner similar to the synthesis of **3d**, bis[butyl(thiocarbonyl)] sulfide (**1e**, 3 mmol) in hexane (20 ml), freshly prepared from pentanedithioic acid (806 mg, 6 mmol) and dicyclohexylcarbodiimide (619 mg, 3 mmol), was added to a solution of sodium benzeneselenolate (3 mmol) in a mixed solvent of dichloromethane/methanol (3 : 1, 20 ml) at 0 °C for 30 min, followed by silica-gel column chromatography (hexane) and then bulb-to-bulb distillation of the resulting orange eluent yielded 460 mg (60%) of **3e** as orange liquid: bp 132 °C/3.5 Torr. IR (neat) 3050, 2970, 2950, 2580, 1580, 1478, 1440, 1380, 1300, 1220, 1180 (C=S), 1091, 1064, 1021, 1000, 867, 732, 688, and 468 cm^{-1}. UV/Vis (hexane) 258, 330, and 486 nm. ^1H NMR ($CDCl_3$) δ=0.91 (3H, t, CH_3), 1.39 (2H, m, CH_2), 1.82 (2H, m, CH_2), 3.06 (2H, t, CH_2), and 7.34—7.54 (5H, m, Ar). ^{13}C NMR ($CDCl_3$) δ=13.6, 21.6, 32.7, 53.5, and 244.3 (C=S). MS (70 eV) *m/z* (rel intensity), 258 (M^+; 10), 156 ($C_6H_5Se^+$, 50), and 101 (*n*-$C_4H_9CS^+$, 100). Found: *m/z* 257.9987. Calcd for $C_{11}H_{14}SSe$: M, 257.9987.

***Se*-Phenyl 1-Pentanecarboselenothioate (3f):** In a manner similar to the synthesis of **3d**, bis[1-pentyl(thiocarbonyl)] sulfide (**1f**, 3 mmol) in hexane (20 ml), freshly prepared from 1-hexanedithioic acid (890 mg, 6 mmol) and dicyclohexylcarbodiimide (619 mg, 3 mmol), was added to a solution of sodium benzeneselenolate (3 mmol) in dichloromethane/methanol (3 : 1, 20 ml) at 0 °C for 30 min, followed by silica-gel column chromatography [hexane/carbon tetrachloride (2 : 1)] and then bulb-to-bulb distillation yielded 560 mg (69%) of **3f** as orange liquid: bp 152 °C/3.5 Torr. IR (neat) 3027, 2990, 2950, 2880, 1578, 1475, 1460, 1448, 1376, 1210 (C=S), 1070, 1061, 1019, 999, 878, 821, 730, 681, and 464 cm^{-1}. UV/Vis (hexane) 258, 332, and 486 nm. ^1H NMR ($CDCl_3$) δ=0.90 (3H, t, CH_3), 1.33 (4H, m, CH_2), 1.84 (2H, m, CH_2), 3.06 (2H, t, CH_2), and 7.33—7.57 (5H, m, Ar). ^{13}C NMR ($CDCl_3$) δ=13.9 (CH_3), 22.3 (CH_2), 30.7 (CH_2), 30.9 (CH_2), 54.1 (CH_2), and 245.4 (C=S). MS (70 eV) *m/z* (rel intensity), 272 (M^+; trace), 157 ($C_6H_5Se^+$, 32), and 115 (*n*-$C_5H_{11}CS^+$, 100). Found: *m/z* 272.0147. Calcd for $C_{12}H_{16}SSe$: M, 272.0138.

***Se*-Phenyl Cyclohexanecarbothioselenoate (3g):** In a manner similar to the synthesis of **3d**, bis[cyclohexyl(thiocarbonyl)] sulfide (**1g**) (3 mmol) in hexane (20 ml), freshly prepared from cyclohexanecarbodithioic acid (962 mg, 6 mmol) and dicyclohexylcarbodiimide (619 mg, 3 mmol), was added to a solution of sodium benzeneselenolate (3 mmol) in dichloromethane/methanol (3 : 1, 20 ml) at 0 °C for 30 min. Silica-gel column chromatography [hexane/dichloromethane (3 : 1)] and then bulb-to-bulb distillation of the resulting orange eluent yielded 705 mg (83%) of **3g** as orange liquid: bp 119 °C/1.0 Torr. IR (neat) 3030, 2950, 2880, 1583, 1478, 1450, 1440, 1241, 1190 (C=S), 1131, 1066, 1020, 1001, 990, 919, 888, 860, 845, 780, 736, 687, and 470 cm^{-1}. UV/Vis (hexane) 261, 331, and 488 nm. ^1H NMR ($CDCl_3$) δ=1.15—2.03 (10H, m, CH_2), 3.25 (1H, tt, CH), and 7.4—7.6 (5H, m, Ar). ^{13}C NMR ($CDCl_3$) δ=25.5, 26.0, 34.6, 61.9, and 250.2 (C=S). MS (70 eV) *m/z* (rel intensity), 284 (M^+; 9), 157 ($C_6H_5Se^+$, 5) 127 (*cyclo*-$C_6H_{11}CS^+$, 100), and 83 (*cyclo*-$C_6H_{11}^+$, 51). Found: *m/z* 284.0133. Calcd for $C_{13}H_{16}SSe$: M, 284.0138.

***Se*-Phenyl Benzenecarboselenothioate (3h) (Method A):** In a manner similar to synthesis Method A of **3i**, the reaction of bis(thiobenzoyl) sulfide (**1h**, 3 mmol) in hexane (50 ml) with sodium benzeneselenolate (3 mmol), followed by silica-gel column chromatography [hexane/dichloromethane (5 : 1)], yielded 122 mg (44%) of chemically pure **3h** as violet crystals: mp 44—46 °C. IR (neat) 3120, 3100, 1595, 1582, 1578, 1480, 1444, 1318, 1245 (C=S), 1186, 1160, 1109, 1086, 1045, 1022, 1003, 836, 759, 738, 685, 622, 611, 560, and 471 cm^{-1}. UV/Vis (hexane) 302 (4.18), and 542 (1.92) nm. ^1H NMR ($CDCl_3$) δ=7.0—8.0 (10H, m, Ar). ^{13}C NMR ($CDCl_3$) δ=126.3—146.6 (Ar), and 232.2 (C=S). MS (70 eV) *m/z* (rel intensity), 278 (M^+; 3), 121 ($C_6H_5CS^+$, 100), and 77 ($C_6H_5^+$, 5). Found: *m/z* 277.9668. Calcd for $C_{13}H_{10}SSe$: M, 277.9668.

Method B: In a manner similar to synthesis Method B of **3i**, the reaction of thiobenzoyl chloride (**4a**, 386 mg, 2 mmol) with sodium benzeneselenolate (2 mmol), followed by silica-gel column chromatography [hexane/dichloromethane (5 : 1)], yielded 330 mg (60%) of **3h**.

Method C: In a manner similar to synthesis Method C of **3i**, the treatment of thiobenzoyl chloride (**4a**, 156 mg, 1 mmol) with (phenylseleno) trimethylsilane (229 mg, 1 mmol) in hexane (15 ml) at 20 °C for 1 h, followed by silica-gel column chromatography [hexane/dichloromethane (5 : 1)], yielded 33 mg (12%) of **3h** and 119 mg (76%) of diphenyl diselenide.

***Se*-Phenyl 4-Methylbenzenecarboselenothioate (3i) (Method A):** A solution of bis[4-methyl(thiobenzoyl)] sulfide (**1i**, 302 mg, 1 mmol) in dichloromethane (3 ml) was added to sodium benzeneselenolate (1 mmol) in a mixed solvent of dichloromethane and methanol (2 : 1, 15 ml) at 0 °C; the reaction mixture was then stirred at this temperature for 30 min. The color of the reaction mixture quickly changed from dark green to red. Dichloromethane (20 ml) was added; the mixture was then washed with water (3×30 ml), followed by drying with anhydrous sodium sulfate. After the solvent had been evaporated in vacuo, the residue was chromatographed on silica-gel column [hexane/dichloromethane (5 : 1)] to yield 213 mg (73%) of **3i** as reddish-pink crystals: mp 83—84 °C. IR (KBr) 1600, 1475, 1440, 1309, 1250 (C=S), 1181, 1045, 1020, 1010, 848, 817, 767, 732, 684, 630, 554, 471, and 458 cm^{-1}. UV/Vis (hexane) 265 (3.83), 315 (4.23), and 541 (1.97) nm. ^1H NMR ($CDCl_3$) δ=2.30 (3H, s, CH_3) and 7.22—7.93 (9H, m, Ar). ^{13}C NMR ($CDCl_3$) δ=21.6 (CH_3), 126.7—144.5 (Ar), and 231.8 (C=S). MS (70 eV) *m/z* (rel intensity), 292 (M^+; 12), 135 (4-$CH_3C_6H_4CS^+$, 100), and 91 (4-$CH_3C_6H_4^+$, 64). Found: C, 57.82; H, 4.49; S, 11.13; Se, 27.26%. Calcd for $C_{14}H_{12}SSe$: C, 57.57; H, 4.42; S, 10.99; Se, 27.03%.

Method B: A solution of 4-methyl(thiobenzoyl) chloride (**4b**, 341 mg, 2 mmol) in benzene (3 ml) was added to sodium benzeneselenolate (2 mmol) in a mixed solvent of benzene/methanol (1 : 1, 10 ml) at 0 °C; the mixture was stirred at this temperature for 30 min. Dichloromethane (50 ml) was added; the mixture was then washed with water (3×30 ml), followed by drying over anhydrous sodium sulfate. The solvent was evaporated using a rotary evaporator. The residue was chromatographed on a silica-gel column [hexane/dichloromethane (5 : 1)] to yield 330 mg (60%) of **3i**.

Method C: A solution of 4-methyl(thiobenzoyl) chloride (**4b**, 171 mg, 1 mmol) in hexane (3 ml) was added to (phenylseleno)trimethylsilane (229 mg, 1 mmol) in hexane (15 ml); the mixture was then stirred at 20 °C for 1 h. The solvent was evaporated in vacuo and the residue chromatographed on silica gel [hexane/dichloromethane (5 : 1)] the second red eluent)] to yield 34 mg (12%) of **3i** and 127 mg (81%) of diphenyl diselenide.

***Se*-(4-Methylphenyl) 4-Methylbenzenecarboselenothioate (3j) (Method A):** In a manner similar to synthesis Method A of **3i**, the reaction of sodium 4-methylbenzeneselenolate (1 mmol) in 15 ml of dichloromethane/methanol (2 : 1) with bis[4-methyl(thiobenzoyl)] sulfide (**1i**, 302 mg, 1 mmol) in dichloromethane (5 ml) yielded 247 mg (81%) of **3j** as reddish-pink crystals: mp 118—120 °C. IR (KBr) 2920, 1595, 1485, 1305, 1250 (C=S), 1235, 1208, 1176, 1040, 1036, 1008, 890, 811, 800, 757, 629, 552, 485, and 467 cm^{-1}. UV/Vis (CH_2Cl_2) 226 (4.45), 258 (4.02), 323 (4.34), and 528 (2.05) nm. ^{1}H NMR ($CDCl_3$) δ=2.17 (3H, s, CH_3ArSe), 2.38 (3H, s, CH_3ArCS), and 7.2—8.0 (8H, m, Ar). ^{13}C NMR ($CDCl_3$) δ=21.5 (CH_3), 21.6 (CH_3), 126.6—144.5 (Ar), and 232.4 (C=S). MS (70 eV) *m/z* (rel intensity), 306 (M^+; 3), 171 ($CH_3C_6H_4Se^+$, <1), 135 ($CH_3C_6H_4CS^+$, 100), and 91 ($CH_3C_6H_4^+$, 3). Found: C, 59.11; H, 4.49%. Calcd for $C_{15}H_{14}SSe$: C, 59.01; H, 4.62%.

***Se*-(4-Chlorophenyl) 4-Methylbenzenecarboselenothioate (3k) (Method A):** In a manner similar to synthesis Method A of **3i**, the reaction of 4-chlorobenzeneselenolate (1 mmol) in 15 ml of dichloromethane/methanol (2:1) with bis[4-methyl(thiobenzoyl)] sulfide (**1i**, 302 mg, 1 mmol) in dichloromethane (5 ml) yielded 229 mg (70%) of **3k** as reddish pink needles: mp 96—97 °C. IR (KBr) 2980, 1594, 1468, 1384, 1306, 1253, 1223, 1177, 1086, 1036, 1005, 850, 839, 812, 760, 721, 621, 550, 490, 478, and 448 cm^{-1}. UV/Vis (hexane) 227 (4.61), 269 (4.11), 316 (4.48), and 540 (1.99) nm. ^{1}H NMR ($CDCl_3$) δ=2.38 (3H, s, CH_3), and 7.2—8.0 (8H, m, Ar). ^{13}C NMR ($CDCl_3$) δ=21.6 (CH_3), 126.7—144.2 (Ar), and 230.7 (C=S). MS (70 eV) *m/z* (rel intensity), 326 (M^+; 2), 191 ($ClC_6H_4Se^+$, <1), 135 ($CH_3C_6H_4CS^+$, 100), and 91 ($CH_3C_6H_4^+$, 5). Found: C, 51.63; H, 3.32%. Calcd for $C_{14}H_{11}SSeCl$: C, 51.62; H, 3.40%.

Attempt to Synthesize *Se*-Phenyl 2,4,6-Trimethylbenzenecarboselenothioate (3l) (Method A): A dichloromethane solution (5 ml) of bis[2,4,6-trimethyl(thiobenzoyl) sulfide (**1l**, 359 mg, 1 mmol) was added to a solution of freshly prepared sodium benzeneselenolate (1 mmol) in dichloromethane/methanol (1:1); the reaction mixture was then stirred at 0 °C for 30 min. After the usual work-up of the reaction mixture, the resulting residue was chromatographed on a silica-gel column [hexane/dichloromethane (10:1)] to give 150 mg (96%) of diphenyl diselenide **7** and 183 mg (51%) of the starting sulfide **1l**.

***Se*-Phenyl 4-Methoxybenzenecarboselenothioate (3m) (Method A):** In a manner similar to synthesis Method A of **3i**, the reaction of sodium benzeneselenolate (1 mmol) in dichloromethane/methanol(1:1) with bis[4-methoxy(thiobenzoyl)] sulfide (**1j** 334 mg, 1 mmol) in dichloromethane (3 ml) yielded 155 mg (51%) of **3m** as reddish-pink crystals: mp 63—65 °C. IR (KBr) 1595, 1568, 1501, 1440, 1310, 1259, 1240 (C=S), 1186, 1174, 1034, 1020, 845, 830, 737, 688, 627, 570, and 553 cm^{-1}. UV/Vis (hexane) 240 (4.05), 264 (3.77), 339 (4.38), and 538 (2.09) nm. ^{1}H NMR ($CDCl_3$) δ=3.85 (3H, s, CH_3O), and 6.9—8.1 (9H, m, Ar). ^{13}C NMR ($CDCl_3$) δ=55.6 (CH_3O), 113.7—163.9 (Ar), and 229.5 (C=S). MS (70 eV) *m/z* (rel intensity), 308 (M^+; 2), 151 ($4\text{-}CH_3OC_6H_4CS^+$, 100), and 107 ($4\text{-}CH_3OC_6H_4^+$, 5). Found: C, 54.40; H, 4.33%. Calcd for $C_{14}H_{12}OSSe$: C, 54.58; H, 4.19%.

Method B: In a manner similar to synthesis Method B of **3i**, treatment of 4-methoxy(thiobenzoyl) chloride (**4c**, 374 mg, 2 mmol) in benzene (3 ml) with sodium benzeneselenolate (2 mmol) in a mixed solvent (1:1, 10 ml) at 0 °C for 30 min, followed by silica-gel column chromatography [hexane/dichloromethane (10:1)] yielded 188 mg (31%) of **3m**.

Method C: In a manner similar to synthesis Method C of **3i**, the reaction of 4-methoxy(thiobenzoyl) chloride (**4c**, 187 mg, 1 mmol) with phenylselenotrimethylsilane (229 mg, 1 mmol) in hexane (18 ml) at 0 °C for 1 h, followed by silica-gel column chromatograpy [hexane/dichloromethane (10:1)], gave 129 mg (82%) of diphenyl diselenide (**7**).

***Se*-Phenyl 4-Chlorobenzenecarboselenothioate (3n) (Method A):** In a manner similar to synthesis Method A of **3i**, the reaction of sodium benzeneselenolate (1 mmol) in a mixed solvent of dichloromethane/methanol (3:1, 20 ml) with bis[4-chloro(thiobenzoyl)] sulfide (**1i**, 1.1 mmol) in hexane (50 ml) at 0 °C for 30 min, followed by column chromatography on silica gel [hexane/dichloromethane (10:1)] yielded 244 mg (78%) of **3n** as reddish-pink crystals: mp 87—88 °C. IR (KBr) 1580, 1479, 1448, 1396, 1298, 1238 (C=S), 1173, 1090, 1041, 1018, 1009, 891, 822, 731, 691, 681, 621, 550, 490, 420, and 400 cm^{-1}. UV/Vis (hexane) 230sh (4.12), 312 (4.17), and 542 (1.92) nm. ^{1}H NMR ($CDCl_3$) δ=7.0—7.8 (9H, m, Ar). ^{13}C NMR ($CDCl_3$) δ=127.8—145.1 (Ar) and 230.5 (C=S). MS (70 eV) *m/z* (rel intensity), 312 (M^+; 8), 155 ($4\text{-}ClC_6H_4CS^+$, 100), and 111 ($4\text{-}ClC_6H_4^+$, 5). Found: C, 50.37; H, 3.09%. Calcd for $C_{13}H_9SSeCl$: C, 50.10; H, 2.96%.

Method B: In a manner similar to synthesis Method B of **3i**, treatment of 4-chloro(thiobenzoyl) chloride (**4d**, 382 mg, 2 mmol) in benzene (3 ml) with sodium benzeneselenolate (2 mmol) in a mixed solvent of benzene/methanol (1:1, 10 ml) at 0 °C for 30 min, followed by silica-gel column chromatography [hexane/dichloromethane (5:2)] yielded 500 mg (80%) of **3n**.

Method C: In a manner similar to synthesis Method C of **3g**, the reaction of 4-chloro(thiobenzoyl) chloride (**4d**, 191 mg, 1 mmol) with phenylselenotrimethylsilane (229 mg, 1 mmol) in 20 °C for 1 h, followed by silica-gel column chromatography [hexane/dichloromethane (10:1)] yielded 115 mg (37%) of **3n** and 62 mg (32%) of diphenyl diselenide (**7**).

For the reaction of thionselenolester **3** with amine, sodium alcoholates, typical procedures are described. The products were confirmed by comparisons of the melting point and IR or NMR spectra with those of authentic sample.

Reaction with Aniline: Aniline (93 mg, 1 mmol) was added to a solution of *Se*-phenyl 4-methylbenzenecarboselenothioate (**3i**, 291 mg, 1 mmol) in hexane (30 ml); the reaction mixture was then refluxed for 24 h. Filtration of the resulting precipitates gave 154 mg (68%) of 4-methylthiobenzanilide **6a**. The solvent was evaporated by a rotary evaporator then the residue was chromatographed on a silica-gel column (hexane), giving 152 mg (98%) of diphenyl diselenide (**7**).

Reaction with Cyclohexylamine: To a suspension of **3i** (291 mg, 1 mmol) in hexane (30 ml) was added cyclohexylamine (97 mg, 1 mmol). The reaction mixture was then stirred at 20 °C for 5 h. Filtration of the resulting red precipitates gave 96 mg (41%) of cyclohexylammonium 4-methylbenzenecarbodithioate (**8a**) as red crystals. Evaporation of the filtrate by a rotary evaporator, followed by a chromatographic separation of the resulting residue on silica gel (hexane), gave 140 mg (90%) of diphenyl diselenide (**7**).

Reaction with Diethylamine: The reaction of **3i** (291 mg, 1 mmol) with diethylamine (73 mg, 1 mmol) in hexane (30 ml) at 18 °C for 2 h, followed by silica-gel column chromatography (hexane), yielded 107 mg (44%) of diethylammonium 4-methylbenzenecarbodithioate (**8b**) as red crystals and 147 mg (94%) of **7**.

Reaction with Piperidine: The reaction of **3i** (291 mg, 1 mmol) with piperidine (85 mg, 1 mmol) in hexane (30 ml) at 20 °C for 30 min, followed by silica-gel column chromatograph (hexane), yielded 78 mg (31%) of piperidinium 4-methylbenzenecarbodithioate (**8c**) as red crystals and 151 mg (97%) of **7**.

Reaction with Hydrazine: (Conditions A): A solution of hydrazine hydrate (80%, 63 mg, 1 mmol) in hexane (5 ml) was added dropwise to *Se*-phenyl 4-methylbenzenecarboselenothioate (**3i**, 291 mg, 1 mmol) in hexane (40 ml); the mixture was then stirred at 18 °C for 1 h. Filtration of the resulting precipitates gave 48 mg (29%) of 4-methylbenzenecarbothionohydrazide (**6b**) as slightly yellow crystals. After evaporating the filtrate, the residue was chromatographed on silica-gel column [hexane/dichloromethane (5:1)] to give 151 mg (96%) of **7**.

6b: Mp 115—125 °C. IR (KBr) 3200, 1590, 1519, 1492, 1410, 1365, 1312, 1287, 1240, 1220, 1180, 1021, 1001, 937, 821, 719, 671, 629, and 612 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.38 (3H, s, CH_3), 4.99 (2H, br, NH_2), 7.1—7.7 (4H, m, Ar), and 8.74 (1H, br, NH). MS (70 eV) *m/z* (rel intensity), 166 (M$^+$; 26), 135 (4-$CH_3C_6H_4CS^+$, 96), 91 (4-$CH_3C_6H_4^+$, 100), and 65 ($C_5H_5^+$, 45).

(Conditions B): Hydrazine hydrate (80%, 63 mg, 1 mmol) and **3i** (291 mg, 1 mmol) was stirred in ethanol (40 ml) at 18 °C for 1 h. The solvent was removed by a rotary evaporator; then, hexane (30 ml) was added. Filtration of the precipitates yielded 130 mg (78%) of 4-methylbenzenecarboselenohydrazide (**6b**). Evaporation of the filtrate, followed by silica-gel column chromatography [hexane/dichloromethane (5:1)], gave 150 mg (96%) of **7**.

Reaction with Sodium Methanolate: A solution of sodium methanolate (27 mg, 0.5 mmol) in methanol (10 ml) was added dropwise to a solution of *Se*-phenyl 4-methylbenzenecarboselenothioate (**3i**, 146 mg, 0.5 mmol) in ether (10 ml). The reaction mixture was stirred at ca. 20 °C for 2 h. The solvent was evaporated and ether (20 ml) was added. The resulting precipitates (C_6H_5SeNa) was filtered, followed by acidlysis with 1 mol dm^{-3} HCl (5 ml) and by extraction with hexane (50 ml). Evaporation of the extract under reduced pressure gave 70 mg (90%) of diphenyl diselenide. The filtrate (ether soluble part) was concentrated to ca. 1 ml, followed by silica-gel column chromatography [hexane/dichloromethane (5:1)],to give 71 mg (86%) of *O*-methyl 4-methylbenzenecarbothioate (**11a**).

Reaction with Sodium Ethanolate: Similarly, the reaction of **3i** (146 mg, 0.5 mmol) with sodium ethanolate (34 mg, 0.5 mmol) in ethanol (10 ml) yielded 82 mg (91%) of *O*-ethyl 4-methylbenzenecarbothioate (**11b**) and 72 mg (95%) of **7**.

Reaction with Sodium Phenolate: The reaction of **3i** (146 mg, 0.5 mmol) with sodium phenolate (146 mg, 0.5 mmol) in ether at 20 °C for 24 h yielded 91 mg (79%) of *O*-phenyl 4-methylbenzenecarbothioate (**11c**) and 68 mg (90%) of **7**.

Reaction of *Se*-Phenyl 2-Propanecarboselenothioate (3d) with *m*-Chloroperbenzoic acid: A solution of *m*-chloroperbenzoic acid (217 mg, 1 mmol) in ether (10 ml) was added to *Se*-phenyl 2-propanecarboselenothioate (**3d**, 243 mg, 1 mmol) in the same solvent (30 ml); the mixture was then stirred at 0 °C for 90 min. The reaction mixture was washed with saturated aqueous sodium hydrogen carbonate (50 ml) and then water (3×50 ml), followed by drying using anhydrous sodium sulfate. After evaporating the solvent by a rotary evaporator, the residue was separated by thin-layer chromatography [hexane/dichloromethane (5:1)] to yield 50 mg (35%) of diphenyl diselenide (**7**, R_f=0.76), 52 mg (19%) of 2-methylpropionyl phenylseleno sulfide (**13d**, R_f=0.51) as slightly yellow oil, 34 mg (13%) of *trans*-isopropyl(phenylseleno)sulfine(**12d**, R_f=0.22) as yellow oil, and 33 mg (13%) of *cis*-isopropyl(phenylseleno)sulfine (**12′d**, R_f=0.11) as slightly yellow oil.

12′d: IR (neat) 3080, 3000, 2950, 1573, 1471, 1460, 1452, 1437, 1380, 1358, 1190, 1140, 1050, 1019, 998, 930, 738, and 687 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.08 (6H, d, CH_3), 4.07 (1H, m, CH), and 7.3—7.7 (5H, m, Ar). ^{13}C NMR ($CDCl_3$) δ=20.9 (CH_3), 32.5 (CH), 128.8—132.9 (Ar), and 197.9 (C=S=O). MS (70 eV) *m/z* (rel intensity), 260 (M$^+$; <1), 87 ($C_3H_7CS^+$, 62), 71 (*i*-$C_3H_7CO^+$, 100), and 43 (*i*-$C_3H_7^+$, 46).

12′d: IR (neat) 3080, 3000, 2950, 1573, 1471, 1460, 1452, 1437, 1205, 1190, 1140, 1070, 1050, 1019, 998, 930, 738, and 687 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.18 (6H, d, CH_3), 2.77 (1H, m, CH), and 7.3—7.8 (5H, m, Ar). ^{13}C NMR ($CDCl_3$) δ=23.3 (CH_3), 33.7 (CH), 125.2 (Ar), and 205.8 (C=S=O). MS (70 eV) *m/z* (rel intensity), 260 (M$^+$; 5), 87 (*i*-$C_3H_7CS^+$, 100), 71 (*i*-$C_3H_7CO^+$, 22), and 43 (*i*-$C_3H_7^+$, 18).

13d: IR (Neat) 2980, 2940, 1710 (C=O), 1570, 1470, 1451, 1433, 1087, 1015, 947, 845, 730, and 681 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.24 (6H, d, CH_3), 3.02 (1H, sept, CH), and 7.2—7.8 (5H, m, Ar). MS (70 eV) *m/z* (rel intensity), 260 (M$^+$; <1), 157 ($C_6H_5Se^+$, 21), 87 (*i*-$C_3H_7CS^+$, 5), 71 (*i*-$C_3H_7CO^+$, 100), and 43 (*i*-$C_3H_7^+$, 43).

Reaction of *Se*-Phenyl 1-Butanecarboselenothioate (3e) with *m*-Chloroperbenzoic Acid: In a manner similar to the reaction of **3d**, the reaction of *Se*-phenyl 1-butanecarboselenothioate (**3e**, 257 mg, 1 mmol) with *m*-chloroperbenzoic acid (217 mg, 1 mmol) at 0 °C for 90 min, followed by dry silica-gel column chromatography [hexane/dichloromethane (5:1)], yielded 20 mg (28%) of pentanoyl phenylseleno sulfide[†] (**13e**, the first eluent), as slightly yellow oil 89 mg (32%) of *trans*-1-butyl(phenylseleno)sulfine (**12e** the second eluent) as yellow oil, and 58 mg (21%) of *cis*-butyl(phenylseleno)sulfine (**12′e** the third eluent) as yellow oil.

12e: IR (neat) 3060, 2950, 2870, 1573, 1470, 1460, 1455, 1434, 1420, 1180, 1076, 1017, 998, 970, 733, and 684 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=0.87 (3H, t, CH_3), 1.28—1.81 (4H, m, CH_2), 2.94 (2H, t, CH_2), and 7.2—7.6 (5H, m, Ar). ^{13}C NMR ($CDCl_3$) δ=13.6 (CH_3), 21.9 (CH_2), 29.9 (CH_2), 32.1 (CH_2CSO), 128.8—136.9 (Ar), and 191.8 (C=S=O). MS (70 eV) *m/z* (rel intensity), 274 (M$^+$; 15), 181 ($C_4H_9CSSe^+$, 11), 117 ($C_4H_9CSO^+$, 9), 101 ($C_4H_9CS^+$, 100), 85 ($C_4H_9CO^+$, 28), and 57 ($C_4H_9^+$, 36).

12′e: IR (neat) 3060, 2950, 2870, 1573, 1479, 1460, 1455, 1434, 1420, 1375, 1300, 1228, 1160, 1138, 1070, 1017, 998, 970, 733, and 684 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=0.69 (3H, t, CH_3), 1.1—1.6 (4H, m, CH_2), 2.47 (2H, t, CH_2), and 7.3—7.7 (5H, m, Ar). ^{13}C NMR ($CDCl_3$) δ=13.2 (CH_3), 21.6 (CH_2), 29.9 (CH_2), 31.7 (CH_2CSO), 124.1—136.9 (Ar), and 197.2 (C=S=O). MS (70 eV) *m/z* (rel intensity), 274 (M$^+$; 10), 181 ($C_4H_9CSSe^+$, 10), 101 ($C_4H_9CS^+$, 100), 85 ($C_4H_9CO^+$, 28), and 57 ($C_4H_9^+$, 33).

13e: IR (neat) 3050, 2950, 2900, 2850, 1710, 1572, 1467, 1450, 1430, 1110, 1011, 990, 785, and 730 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=0.93 (3H, t, CH_3), 1.3—1.7 (4H, m, CH_2), 2.74 (2H, t, CH_2), and 7.1—7.8 (5H, m, Ar). MS (70 eV) *m/z* (rel intensity), 274 (M$^+$; 10), 157 ($C_6H_5Se^+$, 11), 101 ($C_4H_9CS^+$, 6), 85 ($C_4H_9CO^+$, 13), and 57 ($C_4H_9^+$, 100).

[†] Containing below 2% of diphenyl diselenide.

Reaction of *Se*-Phenyl 4-Methylbenzenecarboselenothioate (3i) with *m*-Chloroperbenzoic Acid: A solution of *m*-chloroperbenzoic acid (216 mg, 1 mmol) in ether (20 ml) was added to a solution of *Se*-phenyl 4-methylbenzenecarboselenothioate (**3i**, 291 mg, 1 mmol) in the same solvent (30 ml); the mixture was then stirred at 0 °C for 90 min. The reaction mixture was washed with saturated aqueous sodium hydrogen carbonate (50 ml) and then with water (3×50 ml), followed by drying with anhydrous sodium sulfate. The solvent was evaporated by a rotary evaporator. The residue was chromatographed on silica gel [hexane/dichloromethane (2:1)] to give a first eluent (orange), a second (pink), and third eluent (yellow). The repeated chromatographic separation of the first eluent [hexane/dichloromethane (20:1)] gave 22 mg (14%) of diphenyl diselenide (**7**). Similarly, a chromatographic separation of the second eluent [hexane/dichloromethane (5:1)] gave 34 mg (11%) of phenylseleno 4-methyl(thiobenzoyl) sulfide (**13i**) as slightly yellow crystals 9 mg (3%) of bis[4-methyl(thiobenzoyl)] disulfide (**14**). Thin-layer chromatography [20 cm×20 cm, hexane/dichloromethane (2:1)] of the third eluent gave 81 mg (26%) of *trans*-4-methylphenyl(phenylseleno) sulfine (**12i**, R_f=0.39) as yellow oil and 25 mg (8%) of *cis*-4-methylphenyl(phenylseleno) sulfine (**12′i**, R_f=0.07) as yellow oil.

12i: IR (neat) 3050, 1601, 1571, 1480, 1438, 1276, 1183, 1100, 1017, 995, 810, 740, 690, 618, 542, 471, 438, and 410 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.25 (3H, s, CH_3) and 6.9—7.5 (9H, m, Ar). ^{13}C NMR ($CDCl_3$) δ=21.7 (CH_3), 128.8—142.9 (Ar), and 178.5 (C=S=O). MS (70 eV) *m/z* (rel intensity), 308 (M^+; 7), 215 ($4\text{-}CH_3C_6H_4CSSe^+$, 79), 135 ($4\text{-}CH_3C_6H_4CS^+$, 100), 119 ($4\text{-}CH_3C_6H_4CO^+$, 28), and 91 ($4\text{-}CH_3C_6H_4^+$, 9).

12′i: IR (neat) 3050, 1601, 1571, 1480, 1438, 1276, 1201, 1183, 1170, 1100, 1017, 995, 810, 740, 690, 618, 542, 471, 438, and 410 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.35 (3H, s, CH_3), and 7.0—8.3 (9H, m, Ar). ^{13}C NMR ($CDCl_3$) δ=21.3 (CH_3), 126.1—141.1 (Ar), and 194.1 (C=S=O). MS (70 eV) *m/z* (rel intensity), 308 (M^+; 8), 215 ($4\text{-}CH_3C_6H_4CSSe^+$, 83), 135 ($4\text{-}CH_3CS^+$, 100), 119 ($4\text{-}CH_3C_6H_4CO^+$, 29), and 91 ($CH_3C_6H_4^+$, 23).

13i: Mp 86—88 °C (lit,[3] 86—88 °C). ^{1}H NMR ($CDCl_3$) δ=2.38 (3H, s, CH_3) and 6.9—8.1 (9H, m, Ar). IR (KBr) 1660 cm^{-1}.

14: Mp 117—119 °C. IR (KBr) 1693 cm^{-1}. UV/Vis (*cyclo*-C_6H_{12}) 250sh, 265 (4.55), and 267sh nm

We wish to thank Professor Satoshi Inagaki of Gifu University for his helpful suggestions to regarding the ab initio molecular orbital calculation.

References

1) The oral presentation of this work: K. Terashima, T. Katada, S. Kato, and M. Mizuta, The Central District Chemical Joint Meeting of The Japan Chemical Society, Nagoya, October, 1979, Abstr. No. 3F-08. It was taken for 9 years in order to confirm the curious experimental results, where the thionselenol esters react with primary and secondary amines to give the corresponding ammonium dithiocarboxylates; The formation of the sulfines **12** and sulfides **13** was presented at the First International Conference of Heteroatom Chemistry, Kobe, Japan, July 1987, Abstr. No. PS1026.

2) S. Kato, T. Murai, and M. Ishida, *Org. Prep. Proc. Int.*, **18**, 369 (1986).

3) Only three compounds have been described in literature—Selenothiophthalide from the reaction of iminoselenophthalide with hydrogen sulfide: a) M. Renson and R. Collinene, *Bull. Soc. Chim. Belg.*, **73**, 491 (1964). $C_6H_5CSSeCH_2CH_2\overset{+}{N}(CH_3)_2Cl^-$ from the reaction of thiobenzoyl chloride with 2-aminoethylselenomagnesium chloride, followed by treatment with hydrogen chloride: b) S. H. Chu and H. G. Mautner, *J. Med. Chem.*, **13**, 214 (1970). $(CF_3)_2CHCSSeC_6H_5$ from the reaction of bis(trifluoromethyl)thioketene with benzeneselenol: M. A. Raash, *J. Org. Chem.*, **37**, 1347 (1972).

4) a) S. Kato, T. Katada, and M. Mizuta, *Angew. Chem.*, **88**, 844 (1976); *Angew. Chem., Int. Ed. Engl.*, **15**, 766 (1976); b) S. Kato, K. Sugino, M. Yamada, T. Katada, and M. Mizuta, *Angew. Chem.*, **89**, 917 (1977); *Angew. Chem., Int. Ed. Engl.*, **16**, 788 (1977).

5) S. Kato, H. Shibahashi, T. Katada, T. Takagi, I. Noda, M. Mizuta, and M. Goto, *Liebigs Ann. Chem.*, **1982**, 1229.

6) The low yield of the methyl derivative **3a** seems to be due to decomposition of the starting sulfide **1a**, which is very unstable thermally.

7) The elevation of the reaction temperature over 40 °C leads to decomposition of (phenylseleno)trimethylsilane.

8) The synthesis of thioacyl chlorides are limited to the aromatic ones. The reaction of aliphatic dithiocarboxyl acid with sulfuryl chloride or phosphorus pentachloride to afford the sulfenyl chloride of structure $RCCl(SCl)_2$.

9) a) A. Bak, L. Hanzen-Nygarred, and C. Pedersen, *Acta Chem. Scand.*, **12**, 1451 (1958); b) L. T. Bellamy and P. F. Rogasch, *J. Chem. Soc.*, **1960**, 2218; c) S. Kato, M. Mizuta, and Y. Ishii, *J. Organometal. Chem.*, **55**, 121 (1973).

10) The hypsochromic shifts of these absorption maxima are observed by changing of the solvent from cyclohexane to ethanol, indicating the n-π^* transitions of the thioacyl group.

11) W. H. McFadden, R. M. Siefert, and J. Wasserman, *Anal. Chem.*, **32**, 1495 (1960).

12) A. Ohno, Y. Ohnishi, R. Koizumi, and G. Tsuchihashi *Tetrahedron Lett.*, **1968**, 4032.

13) A. Ohno, T. Koizumi, Y. Ohnishi, and G. Tsuchihashi, *Org. Mass Spec.*, **3**, 261 (1970).

14) S. Scheithauer and R. Mayer, "Thio- and Dithiocarboxylic Acids and Their Derivatives" in Topics in Sulfur Chemistry, ed by A. Senning, George Thieme, Stuttgartt (1979), p. 200.

15) It was reported that *O*-alkyl and *S*-alkyl thiobenzoates undergo the similar type of rearrangement thermally and under the conditions of electron impact: Y. Araki and A. Kaji, *Bull. Chem. Soc. Jpn.*, **43**, 3214 (1970).

16) P. Reynaud, R. C. Moreau, and J. P. Samana, *Bull. Soc. Chim. Fr.*, **1965**, 3628.

17) a) B. Holmberg, *Arkiv Kemi. Mineral. Geol. A*, **17** (No. 23), 1 (1944); b) A. Kjaer, *Acta Chem. Scand.*, **4**, 1437 (1950).

18) The reactions of *O*-phenyl 4-methylbenzenecarbothioate or *S*-phenyl 4-methylbenzenecarbodithioate with excess of piperidine gradually proceed at room temperature to give the corresponding thioamide in almost quantitative yields.

19) The reaction of phenyl benzenecarbodithioate with sodium ethanolate in ether does not occur at 10—25 °C.

20) a) B. Zwanenburg, L. Thijs, and J. Strating, *Tetrahedron Lett.*, **1967**, 3453; b) B. Zwanenburg, L. Thijs, and J. Strating, *Rec. Trav. Chim. Pays-Bas*, **90**, 614 (1971).

21) The low yields of the aliphatic esters are considered to be due to decomposition of the starting bis(thioacyl) sulfides **1**.

22) The ortho proton of the phenyl ring of *trans*-phenylthio(phenyl)sulfine (**12′**) shifted downfield compared with those of the corresponding cis-isomer **12**.

23) The similar downfield shifts were observed for the methyl protons of phenyl(methylthio)sulfine [$C_6H_5C(S{=}O)\text{-}SCH_3$].[19]

24) Karlström et al. obtained the similar result for decomposition of the oxathiirane **15** using the ab initio CASSCF method: G. Karlström, B. O. Roos, and L. Carlsen, *J. Am. Chem. Soc.*, **106**, 1557 (1984).

25) a) S. Kato and M. Mizuta, *Bull. Chem. Soc. Jpn.*, **45**, 3492 (1972); b) S. Kato, T. Mitani, and M. Mizuta, *Int. J. Sulfur Chem.*, **8**, 359 (1973).

26) a) R. Mayer and S. Scheithauer, *J. Prakt. Chem.*, **21**, 214 (1963); b) R. Mayer and S. Scheithauer, *Chem. Ber.*, **98**, 829 (1965).

27) J. E. Drake and R. T. Hemmings, *J. Chem. Soc., Dalton Trans.*, **1979**, 1730.

28) N. Marziano and R. Passerrini, *Gazz. Chim. Ital.*, **94**, 1137 (1964).

29) H. G. Mautner, *J. Am. Chem. Soc.*, **78**, 5292 (1956).

30) J. L. Piette and M. Renson, *Bull. Soc. Chim. Belg.*, **79** 360 (1970).