Synthesis of Thiol, Selenol, and Tellurol Esters from Aldehydes by the Reaction with $^{i}Bu_2AlYR$ (Y = S, Se, Te)

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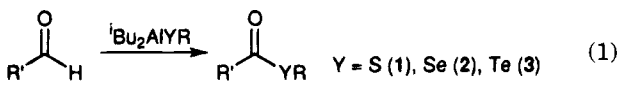
Chalcogenoesters (thiol (**1**), selenol (**2**) and tellurol esters (**3**)) are useful synthetic intermediates having been employed, for example, as mild acyltransfer reagents,[1] building blocks of heterocyclic compounds (oxazole,[2] β-lactone[3]), precursors of acyl radicals[4] or anions,[5] and for asymmetric aldol reactions.[6] In spite of the growing interest in new organic transformations of these compounds, preparative methods available are still limited, with few exceptions,[7] to those based on conventional methodology (i.e. formal substitution at the carbonyl carbon of carboxylic acids and their derivatives or addition to nitriles).[8] Here we report a new synthetic method for chalcogenoesters **1**–**3** from aldehydes via a Tishchenko-type reaction using diisobutylaluminum chalcogenoate ($^{i}Bu_2AlYR$, Y = S, Se, Te) as shown in eq 1.



(1)

During the course of our study on generation of acyl- and aroyllithiums from tellurol esters by lithium–tellurium exchange reactions, we needed a practical and convenient preparative method for tellurol esters from synthetic sources other than acid halides or acid anhydrides.[1d,9] Of a number of reactions developed for construction of the ester skeleton, we became interested in the Tishchenko reaction which affords esters from aldehydes in the presence of aluminum alkoxides.[10] Since this reaction involves transfer of an alkoxy moiety from aluminum alkoxides to the carbonyl carbon of aldehydes,[10b] we examined the reaction of aldehydes with $^{i}Bu_2AlTeBu^{n}$. When 2 mol equiv of benzaldehyde was treated in hexane with $^{i}Bu_2AlTeBu^{n}$ prepared in situ from $^{n}BuTeTeBu^{n}$ and $^{i}Bu_2AlH$ (1 N in hexane) according to Ogura's procedure,[11] a tellurol ester (**3a**, R′ = Ph) was obtained in 25% yield along with benzyl benzoate (**4**) formed by the usual Tishchenko reaction. Table 1 summarizes representative results obtained under different conditions. Extension of the reaction time and use of toluene as a solvent had little effect on the yield and product selectivity (runs 2, 3). However when the reaction was conducted in a THF/hexane mixture, **3a** was obtained selectively in 52% yield (run 4). GLC analysis of the resulting mixture after workup with aqueous NH_4Cl showed the formation of benzyl alcohol in 138% yield based on $^{i}Bu_2AlTeBu^{n}$ used. The result that more than an equal amount of benzyl alcohol formed with respect to **3a** suggests the presence of an alternative pathway for the reduction of benzaldehyde which may compete with the formation of **3a**. Although 28% of the benzaldehyde remained unreacted in this case, prolonged reaction time did not increase the formation of **3a** but did affect that of **4** (run 5). Addition of Et_2AlCl improved the yield of **3a** and completely suppressed the formation of **4** (run 6).

Table 1. Reaction of Benzaldehyde with $^{i}Bu_2AlTeBu^{n}$ [a]

run	solvent	time (h)	isolated yield (%) **3a**	isolated yield (%) **4**
1	hexane	7	25	26
2	hexane	48	25[b]	37[b]
3	toluene	2	22[b]	25[b]
4	THF/hexane[c]	1	52	trace
5	THF/hexane[c]	20	53[d]	28[d]
6[e]	THF/hexane[c]	1	71	0

[a] Conditions: benzaldehyde (2 mmol), $^{i}Bu_2AlTeBu^{n}$ (1 mmol), solvent (1 mL), −23 to 25 °C. [b] NMR yield. [c] In a mixed solvent of THF (2 mL) and hexane (1 mL). [d] GLC yield. [e] In the presence of 0.5 mmol of Et_2AlCl (1 N in hexane, 0.5 mL).

This reaction proceeded efficiently to give thiol and selenol esters when $^{i}Bu_2AlSR$ and $^{i}Bu_2AlSeR$ were used, respectively, under similar conditions. Results are summarized in Table 2. Thiol and selenol esters were obtained in good yields from both aromatic and aliphatic aldehydes except for the case of pivalaldehyde. Under similar conditions *S*- and *Se*-Ph esters were formed in moderate yields. *Te*-Bu esters were obtained satisfactorily from aromatic aldehydes. The yields of **2b**, **3a**,**d** were improved appreciably by the addition of Et_2AlCl. Aliphatic aldehydes were converted to corresponding tellurol esters less efficiently and Et_2AlCl was ineffective in these cases. When arenetellurolate ($^{i}Bu_2AlTeAr$) was employed, reduction of aldehydes to alcohols predominated, and *Te*-Ar esters could not be obtained.

(1) Thiol esters: (a) Mukaiyama, T.; Araki, M.; Takei, H. *J. Am. Chem. Soc.* **1973**, *95*, 4763. (b) Anderson, R. J.; Henrick, C. A.; Rosenblum, L. D. *J. Am. Chem. Soc.* **1974**, *96*, 3654. Selenol esters: (c) Sviridov, A. F.; Ermolenko, M. S.; Yashunsky, D. V.; Kochetkov, N. K. *Tetrahedron Lett.* **1983**, *24*, 4355, 4359. Tellurol esters: (d) Sasaki, K.; Aso, Y.; Otsubo, T.; Ogura, F. *Chem. Lett.* **1986**, 977.

(2) Thiol esters: Alvarez-Ibarra, C.; Mendoza, M.; Orellana, G.; Quiroga, M. L. *Synthesis* **1989**, 560. Selenol esters: Kozikowski, A. P.; Ames, A. *J. Am. Chem. Soc.* **1980**, *102*, 860.

(3) Thiol esters: Danheiser, R. L.; Nowick, J. S. *J. Org. Chem.* **1991**, *56*, 1176.

(4) Selenol esters: (a) Pfenninger, J.; Heuberger, C.; Graf, W. *Helv. Chim. Acta* **1980**, *63*, 2328. (b) Boger, D. L.; Mathvink, R. J. *J. Org. Chem.* **1992**, *57*, 1429. (c) Batty, D.; Crich, D. *J. Chem. Soc., Perkin Trans. 1* **1992**, 3193, 3205 and references cited therein. Tellurol esters: (d) Chen, C.; Crich, D.; Papadatos, A. *J. Am. Chem. Soc.* **1992**, *114*, 8313.

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(6) Enol silyl ethers of thiol esters: Mukaiyama, T.; Uchiro, H.; Shiina, I.; Kobayashi, S. *Chem. Lett.* **1990**, 1019. Kobayashi, S.; Uchiro, H.; Fujishita, Y.; Shiina, I.; Mukaiyama, T. *J. Am. Chem. Soc.* **1991**, *113*, 4247.

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(9) (a) Piette, J. L.; Renson, M. *Bull. Soc. Chim. Belg.* **1970**, *79*, 383; *Chem. Abstr.* **1970**, *73*, 66201. (b) Piette, J. L.; Debergh, D.; Baiwir, M.; Llabres, G. *Spectrochim. Acta* **1980**, *36A*, 769. (c) Gardner, S. A.; Gysling, H. J. *J. Organomet. Chem.* **1980**, *197*, 111. (d) Kanda, T.; Nakaiida, S.; Murai, T.; Kato, S. *Tetrahedron Lett.* **1989**, *30*, 1829.

(10) (a) Tishchenko, W. *J. Russ. Phys. Chem. Soc.* **1906**, *38*, 355. (b) Ogata, Y.; Kawasaki, A.; Kishi, I. *Tetrahedron* **1967**, *23*, 825. (c) Ogata, Y.; Kawasaki, A. *Tetrahedron* **1969**, *25*, 929. For Tishchenko reactions catalyzed by other metals, see: Morita, K.-I.; Nishiyama, Y.; Ishii, Y. *Organometallics* **1993**, *12*, 3748. Onozawa, S.-y.; Sakakura, T.; Tanaka, M. *Chem. Lett.* **1994**, 531 and references cited therein.

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Scheme 1

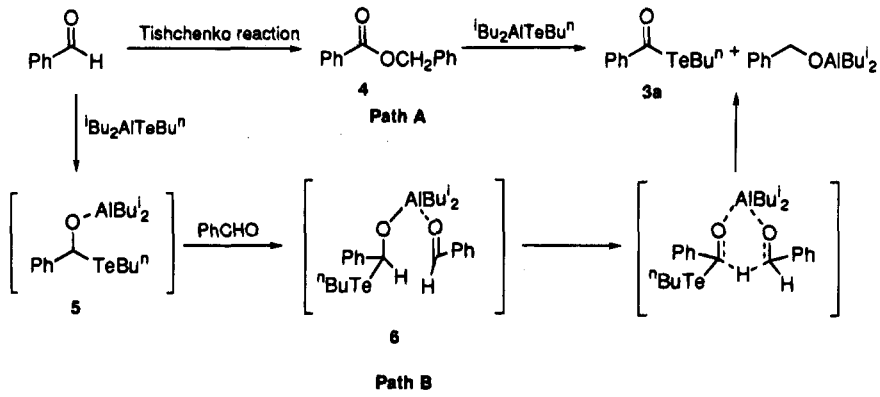
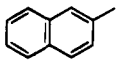
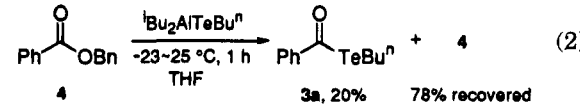


Table 2. Synthesis of Chalcogenoesters by the Reaction of Aldehydes with Diisobutylaluminum Chalcogenoates

R'	R	time (h)	Y	isolated yield of 1, 2, or 3 (%)
Ph	^{n}Bu	2	S	**1a**, 83
		2	Se	**2a**, 79
		1	Te	**3a**, 52
		1[a]	Te	**3a**, 71
	Ph	20	S	**1b**, 61
		20	Se	**2b**, 29
		10[a]	Se	**2b**, 44
	Bn	2	S	**1c**, 83
	^{n}Bu	2	S	**1d**, 87
		2	Se	**2d**, 73
		1	Te	**3d**, 27
		10	Te	**3d**, 41
		10[a]	Te	**3d**, 73
		2	S	**1e**, 86
		2	Se	**2e**, 82
		10	Te	**3e**, 35
$^{n}C_8H_{17}$		2	S	**1f**, 81
		20	Te	**3f**, 35
cyclo-C_6H_{11}		2	S	**1g**, 96
		2	Se	**2g**, 82
^{i}Bu		2	S	**1h**, 46
		10	Se	**2h**, 20
		20	Te	**3h**, 27

Conditions: aldehyde (2 mmol), $^{i}Bu_2AlYR$ (1 mmol), THF (2 mL), hexane (1 mL), -23 ~ 25 °C. [a] In the presence of 0.5 mmol of Et_2AlCl (1 N in hexane, 0.5 mL).

Two possible reaction pathways are shown in Scheme 1. Path A involves Tishchenko reaction to give benzyl benzoate (**4**) followed by transesterification with $^{i}Bu_2AlTeBu^{n}$. The latter step is known for R''_2AlYR (Y = S, Se) which affords thiol[12] and selenol esters[1c,13] by the reaction with esters. In path B, $^{i}Bu_2AlTeBu^{n}$ adds to benzaldehyde to form an adduct **5** which then undergoes intramolecular hydride shift to give a tellurol ester **3a** via **6**. In order to reveal which pathway, if either, is operative, we carried out some control experiments. When benzyl benzoate was treated with $^{i}Bu_2AlTeBu^{n}$ under the same conditions as employed in run 4 of Table 1, only 20% of **3a** was obtained with 78% recovery of **4** (eq 2).[14] This result may indicate that path A via transesterification of esters with $^{i}Bu_2AlTeBu^{n}$ cannot be the main pathway.



(2)

In order to shed light on the intermediacy of an adduct **5**, we examined the reaction of benzaldehyde with an equimolar amount of $^{i}Bu_2AlTeBu^{n}$ at 25 °C for 1 h. In this reaction neither a tellurol ester **3a** nor **4** was formed and benzaldehyde was recovered after workup with aqueous NH_4Cl. Under the assumption that the adduct **5** was formed at this stage, we added ^{n}BuLi to the mixture at −78 °C and then quenched the products by D_2O. After usual workup, d_1-benzyl alcohol (**7**) and $^{n}Bu_2Te$ were obtained quantitatively but 1-phenylpentanol, which was expected to be formed by the addition of ^{n}BuLi to benzaldehyde, was not detected (eq 3). These results can be explained as follows: benzaldehyde reacted with $^{i}Bu_2AlTeBu^{n}$ to form an adduct **5** and this then underwent lithium−tellurium exchange to give **7** via **8** by the trapping with D_2O.[15] These evidences lead to the conclusion that tellurol esters are formed probably by path B. A similar intramolecular hydride shift has been proposed for Tishchenko reaction.[10b]

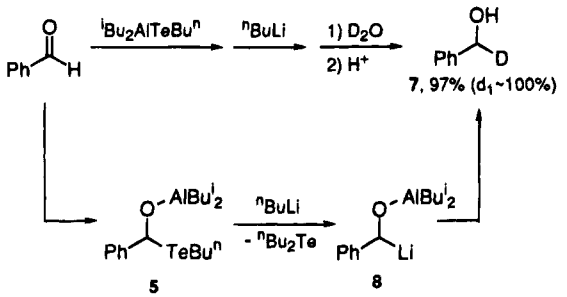
Although the effect of Et_2AlCl was noticeable in some cases, its role is still unclear. A possibility is that it activates an aldehyde as a hydride acceptor either by coordination to the carbonyl oxygen of **6**, or to the free aldehyde if the reaction proceeds intermolecularly, but unfortunately we have no further information on this matter.

(12) Synthesis of thiol esters by the reaction of R''_2AlSR with esters: Corey, E. J.; Beames, D. J. *J. Am. Chem. Soc.* **1973**, *95*, 5829. Warwel, S.; Ahlfaenger, B. *Chem. Ztg.* **1977**, *101*, 103. Hatch, R. P.; Weinreb, S. M. *J. Org. Chem.* **1977**, *42*, 3960. Cohen, T.; Gapinski, R. E. *Tetrahedron Lett.* **1978**, *45*, 4319.

(13) Synthesis of selenol esters by the reaction of R''_2AlSeR with esters: Kozikowski, A. P.; Ames, A. *J. Org. Chem.* **1978**, *43*, 2735. Kozikowski, A. P.; Ames, A. *Tetrahedron* **1985**, *41*, 4821. Khalid, M.; Ripoll, J.-L.; Vallée, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 964. Lemarié, M.; Vallée, Y.; Worrell, M. *Tetrahedron Lett.* **1992**, *33*, 6131. Murai, T.; Mizutani, T.; Kanda, T.; Kato, S. *J. Am. Chem. Soc.* **1993**, *115*, 5823.

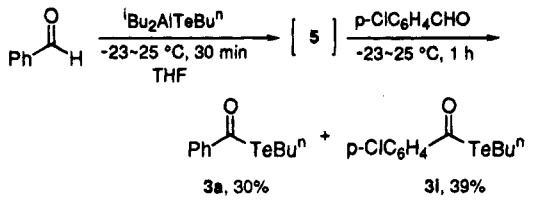
(14) Optimization of the reaction conditions led to improvement of the yield. Results will be published in due course.

(15) The anion **8** generated by lithium−tellurium exchange reaction might form an aluminum ate complex with intramolecular and/or intermolecular coordination.



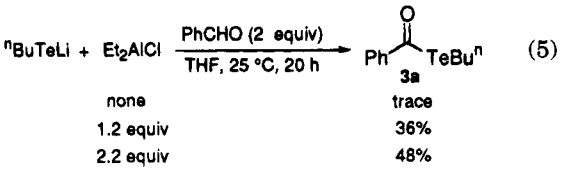
(3)

When *p*-chlorobenzaldehyde was added to the adduct **5**, prepared from benzaldehyde and $^{i}Bu_2AlTeBu^{n}$ in THF/hexane, both tellurol esters **3a** and **3i** were formed in almost equal amounts (eq 4). This may indicate that addition of $^{i}Bu_2AlTeBu^{n}$ to aldehydes is an equilibrium process heavily favoring the adduct. Attempts to use benzoquinone, chloral, acetone, or benzophenone as a hydride acceptor in the reaction with **5** were unsuccessful, leading to the formation of **3a** in only poor yields.



(4)

Quintard et al. have reported that acylstannanes are formed by the reaction of $^{n}Bu_3SnMgCl$ with aldehydes.[16] Although a similar reaction of $^{n}BuTeLi$ with 2 equiv of benzaldehyde gave only a trace amount of **3a**, addition of Et_2AlCl improved the yield to some extent (eq 5). Since lithium telluroates (RTeLi) can be prepared directly from metallic tellurium and organolithium reagents (RLi) in THF at ambient temperature, this can be a convenient one-pot preparative method without isolation of ditellurides, although the yield is moderate.



(5)

Experimental Section

General Procedure. THF was distilled from sodium benzophenone ketyl. All aldehydes and thiols were purchased and aldehydes were dried over $CaSO_4$ and distilled. $^{i}Bu_2AlH$ (1 N in hexane or toluene) and Et_2AlCl (1 N in hexane) were purchased from Kanto Chemical Co., Inc. Diphenyl diselenide[17] and diphenyl ditelluride[18] were prepared according to the literature and were purified by recrystallization from hexane. Dibutyl diselenide and dibutyl ditelluride were synthesized by the air oxidation of $^{n}BuSeLi$ and $^{n}BuTeLi$, respectively, prepared by the reaction of $^{n}BuLi$ with equimolar amounts of metallic selenium or tellurium.[19] Selenium and tellurium metal were ground with a mortar and pestle just before use. Medium pressure liquid chromatography (MPLC) were performed using Merck 25–40 μm mesh silica gel. ^1H and ^{13}C NMR spectra were recorded using $CDCl_3$ as solvent with Me_4Si as an internal standard.

A Typical Experiment. Reaction of Benzaldehyde with $^{i}Bu_2AlTeBu^{n}$. In a flame-dried flask equipped with an Ar inlet and a rubber septum was placed $^{n}BuTeTeBu^{n}$ (185 mg, 0.5 mmol). After $^{i}Bu_2AlH$ (1 N in hexane, 1 mL) was added under Ar, the solution was stirred at 25 °C for 1 h and then 2 mL of THF was added. The solution was cooled to −23 °C and 2 mmol of benzaldehyde and 0.5 mL of Et_2AlCl (1 N in hexane) were injected. The mixture was gradually warmed to 25 °C, stirred for another 1 h, and poured into saturated NH_4Cl solution. Products were extracted with Et_2O (30 mL × 3), dried over $MgSO_4$, and concentrated in vacuo. MPLC of the residue gave pure *Te*-butyl tellurobenzoate (**3a**) in 71% yield (205 mg) in a hexane/Et_2O (100/1) fraction: ^1H NMR (270 MHz, $CDCl_3$) δ 0.94 (t, J = 7.45 Hz, 3 H), 1.43 (sextet, J = 7.45 Hz, 2 H), 1.84 (quint, J = 7.45 Hz, 2 H), 3.06 (t, J = 7.45 Hz, 2 H), 7.40 (t, J = 7.57 Hz, 2 H), 7.55 (t, J = 7.57 Hz, 1 H), 7.75 (d, J = 7.57 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.4 (J_{C-Te} = 76.30 Hz), 13.5, 25.4, 34.0, 126.9, 128.8, 133.6, 143.1, 196.2; IR (neat) 2956, 1662, 1446, 1200, 1168, 863, 762, 685, 665 cm^{-1}; MS *m/z* (relative intensity) 292 (M^+, 1.6), 105 (100), 77 (55), 57 (5). Anal. Calcd for $C_{11}H_{14}OTe$: C, 45.57; H, 4.87. Found: C, 45.79; H, 4.77.

One-Pot Preparation of 3a from Benzaldehyde, Tellurium, and $^{n}BuLi$. Into a suspension of finely ground elemental tellurium (1 mmol, 127 mg) in 3 mL of THF was added $^{n}BuLi$ (ca. 1 mmol) at 25 °C under Ar with stirring until the mixture turned to a homogeneous pale yellow solution. After stirring for 10 min, Et_2AlCl (1 N in hexane, 2 mL) was added, the solution was stirred for 15 min, and 2 mmol of benzaldehyde was added. The solution was stirred for 4 h and poured into cold NH_4Cl solution. The mixture was extracted with Et_2O (30 mL × 3), dried over $MgSO_4$, and concentrated. MPLC of the residue gave pure **3a** (139 mg, 48%).

***Te*-Butyl 2-naphthalenecarbotelluroate (3d)**: ^1H NMR (270 MHz, $CDCl_3$) δ 0.95 (t, J = 7.33 Hz, 3 H), 1.44 (sextet, J = 7.33 Hz, 2 H), 1.86 (quint, J = 7.33 Hz, 2 H), 3.10 (t, J = 7.33 Hz, 2 H), 7.45–7.56 (m, 2 H), 7.76–7.78 (m, 3 H), 7.91 (d, J = 7.93 Hz, 1 H), 8.23 (s, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.5 (J_{C-Te} = 76.90 Hz), 13.5, 25.4, 34.1, 122.3, 127.0, 127.8, 128.5, 128.7, 129.0, 129.6, 132.5, 135.9, 140.3, 195.9; IR (neat) 2956, 2927, 1661, 1163, 1116, 802 cm^{-1}; MS *m/z* (relative intensity) 342 (M^+, 1) 155 (100), 127 (44); HRMS calcd for $C_{15}H_{16}OTe$ 342.0263, found 342.0275.

***Te*-Butyl 2-furancarbotelluroate (3e)**: ^1H NMR (270 MHz, $CDCl_3$) δ 0.94 (t, J = 7.33 Hz, 3 H), 1.42 (sextet, J = 7.33 Hz, 2 H), 1.85 (quint, J = 7.33 Hz, 2 H), 3.02 (t, J = 7.33 Hz, 2 H), 6.57 (dd, J = 3.51, 1.68 Hz, 1 H), 7.11 (d, J = 3.51 Hz, 1 H), 7.62 (d, J = 1.68 Hz, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 10.0 (J_{C-Te} = 74.46 Hz), 13.5, 25.3, 34.0, 112.0, 113.0, 146.3, 156.2, 181.4; IR (neat) 2959, 2928, 1655, 1459, 1244, 1012, 802 cm^{-1}; MS *m/z* (relative intensity) 282 (M^+, 5), 95 (100). Anal. Calcd for $C_9H_{12}O_2Te$: C, 38.63; H, 4.32. Found: C, 38.80; H, 4.45.

***Te*-Butyl nonanetelluroate (3f)**: ^1H NMR (270 MHz, $CDCl_3$) δ 0.88 (t, J = 7.33 Hz, 3 H), 0.92 (t, J = 7.33 Hz, 3 H), 1.27~1.41 (m, 12 H), 1.63 (quint, J = 7.33 Hz, 2 H), 1.77 (quint, J = 7.33 Hz, 2 H), 2.61 (t, J = 7.33 Hz, 2 H), 2.86 (t, J = 7.33 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 10.8 (J_{C-Te} = 75.80 Hz), 13.4, 14.1, 22.6, 25.1, 25.3, 28.6, 29.0, 29.2, 31.8, 34.1, 56.0, 202.9; IR (neat) 2956, 2926, 2855, 1702, 1460 cm^{-1}; MS *m/z* (relative intensity) 328 (M^+, 0.6), 141 (62), 71 (68), 57 (100). Anal. Calcd for $C_{13}H_{26}OTe$: C, 47.90; H, 8.04. Found: C, 47.71; H, 8.39.

***Te*-Butyl 2,2-dimethylpropanetelluroate (3h)**: ^1H NMR (270 MHz, $CDCl_3$) δ 0.92 (t, J = 7.49 Hz, 3 H), 1.14 (s, 9 H), 1.38 (sextet, J = 7.49 Hz, 2 H), 1.75 (quint, J = 7.49 Hz, 2 H), 2.83 (t, J = 7.49 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 9.9 (J_{C-Te} = 76.9 Hz), 13.5, 25.4, 26.4, 34.2, 52.9, 212.8; IR (neat) 2959, 2728, 1702, 1674, 1461, 898, 789 cm^{-1}; MS *m/z* (relative intensity) 272 (M^+, 3.7), 85 (48), 57 (100). Anal. Calcd for $C_9H_{18}OTe$: C, 40.06; H, 6.72. Found: C. 40.15; H, 6.90.

***Te*-Butyl *p*-chlorotellurobenzoate (3i)**: ^1H NMR (270 MHz, $CDCl_3$) δ 0.95 (t, J = 7.45 Hz, 3 H), 1.42 (sextet, J = 7.45 Hz, 2 H), 1.86 (quint, J = 7.45 Hz, 2 H), 3.08 (t, J = 7.45 Hz, 2 H), 7.39 (d, J = 8.24 Hz, 2 H), 7.67 (d, J = 8.24 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.8 (J_{C-Te} = 75.69 Hz), 13.5, 25.4, 34.0, 128.1, 129.1, 140.0, 141.5, 194.7; IR (neat) 2957, 2927, 1663, 1196, 1165, 866 cm^{-1}; MS *m/z* (relative intensity) 326 (M^+, 1), 141 (37), 139 (100), 111 (28). Anal. Calcd for $C_{11}H_{13}ClOTe$: C, 40.74; H, 4.04. Found: C, 40.70; H, 4.15.

(16) Quintard, J.-P.; Elissondo, B.; Mouko-Mpegna, D. *J. Organomet. Chem.* **1983**, *251*, 175.
(17) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434.
(18) Haller, W. S.; Irgolic K. J. *J. Organomet. Chem.* **1972**, *38*, 97.
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The following thiol and selenol esters were prepared by a similar method as described in the synthesis of tellurol esters. The reagents, $^{i}Bu_2AlSR$ and $^{i}Bu_2AlSeR$, were prepared by the reaction of RSH (1 mmol) or RSeSeR (0.5 mmol) with 1 mL of $^{i}Bu_2AlH$ (1 N in hexane).

***S*-Butyl thiobenzoate (1a)**:[20] ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.94 (t, J = 7.45 Hz, 3 H), 1.44 (sextet, J = 7.45 Hz, 2 H), 1.65 (quint, J = 7.45 Hz, 2 H), 3.07 (t, J = 7.45 Hz, 2 H), 7.41 (t, J = 7.81 Hz, 2 H), 7.53 (t, J = 7.81 Hz, 1 H), 7.97 (d, J = 7.81 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.5, 22.0, 28.6, 31.5, 127.1, 128.4, 133.1, 137.2, 191.9; IR (neat) 2959, 2931, 1665, 1448, 1207, 1176, 917, 773, 689, 648 cm^{-1}.

***S*-Phenyl thiobenzoate (1b)**:[21] ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.45–7.63 (m, 8 H), 8.03 (d, J = 7.32 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 127.3, 127.5, 128.7, 129.2, 129.5, 133.6, 135.1, 136.6, 190.1; IR (neat) 1664, 1439, 1200, 1176, 894, 750, 683 cm^{-1}.

***S*-Benzyl thiobenzoate (1c)**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.30 (s, 2 H), 7.22–7.41 (m, 7 H), 7.51 (t, J = 7.33 Hz, 1 H), 7.95 (d, J = 7.08 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 33.2, 127.2, 127.2, 128.5, 128.5, 128.9, 133.3, 136.6, 137.4, 191.0; IR (neat) 1662, 1581, 1495, 1448, 1207, 1175, 911, 772, 732, 689, 647 cm^{-1}; MS *m/z* (relative intensity) 228 (M^+, 10), 105 (100), 91 (10), 77 (34), 51 (11). Anal. Calcd for $C_{14}H_{12}OS$: C, 73.65; H, 5.30; S, 14.04. Found: C, 73.58; H, 5.39; S, 13.98.

***S*-Butyl 2-naphthalenecarbothioate (1d)**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.95 (t, J = 7.33 Hz, 3 H), 1.47 (sextet, J = 7.33 Hz, 2 H), 1.68 (quint, J = 7.33 Hz, 2 H), 3.12 (t, J = 7.33 Hz, 2 H), 7.53 (t, J = 7.32 Hz, 2 H), 7.84 (d, J = 7.32 Hz, 2 H), 7.93 (d, J = 7.81 Hz, 1 H), 7.98 (d, J = 7.81 Hz, 1 H), 8.51 (s, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.6, 22.0, 28.8, 31.6, 123.1, 126.8, 127.7, 128.3, 128.3, 128.4, 129.5, 132.4, 134.5, 135.6, 191.9; IR (neat) 2958, 2931, 1657, 1173, 1161, 1122, 840, 800, 750 cm^{-1}; MS *m/z* (relative intensity) 244 (M^+, 11), 156 (19), 155 (100), 127 (67), 126 (11), 77 (9). Anal. Calcd for $C_{15}H_{16}OS$: C, 73.73; H, 6.60; S, 13.12. Found: C, 73.63; H, 6.84; S, 13.17.

***S*-Butyl 2-furancarbothioate (1e)**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.94 (t, J = 7.49 Hz, 3 H), 1.44 (sextet, J = 7.49 Hz, 2 H), 1.65 (quint, J = 7.49 Hz, 2 H), 3.06 (t, J = 7.49 Hz, 2 H), 6.53 (d, J = 3.42 Hz, 1H), 7.18 (d, J = 3.42 Hz, 1 H), 7.57 (brs, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.5, 22.0, 27.8, 31.6, 112.1, 115.1, 145.9, 151.1, 180.6; IR (neat) 1652, 1469, 1251, 1012, 954, 850, 758 cm^{-1}; MS *m/z* (relative intensity) 184 (M^+, 13), 142 (9), 129 (23), 128 (33), 124 (24), 95 (100), 67 (9), 55 (10). Anal. Calcd for $C_9H_{12}O_2S$: C, 58.66; H, 6.57; S, 17.40. Found: C, 58.85; H, 6.72; S, 17.64.

***S*-Butyl nonanethioate (1f)**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.90 (t, J = 7.33 Hz, 3 H × 2), 1.27–1.65 (m, 16 H), 2.53 (t, J = 7.33 Hz, 2 H), 2.87 (t, J = 7.33 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.5, 14.0, 21.9, 22.5, 25.6, 28.4, 28.9, 29.0, 29.1, 31.6, 31.7, 44.0, 199.5; IR (neat) 2957, 2927, 2857, 1693, 1466 cm^{-1}; MS *m/z* (relative intensity) 230 (M^+, 0.1), 173 (23), 141 (100), 57 (85), 55 (27). Anal. Calcd for $C_{13}H_{26}OS$: C, 67.76; H, 11.38; S, 13.92. Found: C, 67.36; H, 11.43; S, 13.90.

***S*-Butyl cyclohexanecarbothioate (1g)**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.91 (t, J = 7.32 Hz, 3 H), 1.25–1.93 (m, 14 H), 2.47 (m, 1 H), 2.86 (t, J = 7.32 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.4, 21.8, 25.4, 25.5, 28.0, 29.5, 31.6, 52.6, 202.9; IR (neat) 2932, 2856, 1690, 1450, 971 cm^{-1}; MS *m/z* (relative intensity) 200 (M^+, 3), 111 (84), 83 (100), 67 (16), 57 (9), 55 (94). Anal. Calcd for $C_{11}H_{20}OS$: C, 65.94; H, 10.06; S, 16.01. Found: C, 65.89; H, 10.32; S, 15.72.

***S*-Butyl 2,2-dimethylpropanethioate (1h)**:[22] ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.92 (t, J = 7.49 Hz, 3 H), 1.23 (s, 9 H), 1.39 (sextet, J = 7.49 Hz, 2 H), 1.54 (quint, J = 7.49 Hz, 2 H), 2.83 (t, J = 7.49 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.6, 22.0, 27.4, 28.2, 31.6, 46.4, 207.1; IR (neat) 2965, 2933, 1681, 953, 810 cm^{-1}.

***Se*-Butyl selenobenzoate (2a)**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.94 (t, J = 7.49 Hz, 3 H), 1.44 (sextet, J = 7.49 Hz, 2 H), 1.73 (quint, J = 7.49 Hz, 2 H), 3.09 (t, J = 7.49 Hz, 2 H), 7.42 (t, J = 7.81 Hz, 2 H), 7.56 (t, J = 7.81 Hz, 1 H), 7.90 (d, J = 7.81 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.5, 23.1, 25.4, 32.5, 127.0, 128.6, 133.3, 139.2, 194.8; IR (neat) 2957, 2931, 1672, 1202, 1173, 885, 767, 687, 674 cm^{-1}; MS *m/z* (relative intensity) 242 (M^+, 1.1), 105 (100), 77 (67), 51 (24). Anal. Calcd for $C_{11}H_{14}OSe$: C, 54.78; H, 5.85. Found: C, 54.62; H, 6.03.

***Se*-Phenyl selenobenzoate (2b)**:[4b] ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.42–7.62 (m, 8 H), 7.93 (d, J = 7.81 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 125.8, 127.3, 128.9, 129.0, 129.4, 133.9, 136.3, 138.6, 193.3; IR (neat) 3061, 1682, 1199, 1173, 876, 738, 687, 667 cm^{-1}.

***Se*-Butyl 2-naphthalenecarboselenoate (2d)**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.96 (t, J = 7.32 Hz, 3 H), 1.47 (sextet, J = 7.32 Hz, 2 H), 1.77 (quint, J = 7.32 Hz, 2 H), 3.15 (t, J = 7.32 Hz, 2 H), 7.52 (t, J = 7.81 Hz, 1H), 7.58 (t, J = 7.81 Hz, 1 H), 7.84 (d, J = 7.33 Hz, 2 H), 7.93 (t, J = 7.81 Hz, 2 H), 8.46 (s, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.6, 23.1, 25.6, 32.6, 122.9, 126.9, 127.8, 128.4, 128.5, 128.7, 129.6, 132.5, 135.8, 136.5, 194.8; IR (neat) 1671, 1168, 1157, 1120, 819, 784, 748 cm^{-1}; MS *m/z* (relative intensity) 294 (M^+, 0.5), 155 (100), 127 (61), 57 (11). Anal. Calcd for $C_{15}H_{16}OSe$: C, 61.86; H, 5.54. Found: C, 61.86; H, 5.74.

***Se*-Butyl 2-furancarboselenaote (2e)**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.94 (t, J = 7.32 Hz, 3 H), 1.44 (sextet, J = 7.32 Hz, 2 H), 1.73 (quint, J = 7.32 Hz, 2 H), 3.07 (t, J = 7.32 Hz, 2 H), 6.55 (d like, J = 1.95 Hz, 1 H), 7.17 (d, J = 3.42 Hz, 1 H), 7.60 (s like, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.5, 23.0, 24.4, 32.5, 112.5, 114.4, 146.1, 152.5, 182.3; IR (neat) 2958, 2932, 1673, 1652, 1639, 1566, 1465, 1246, 1012, 823, 758 cm^{-1}; MS *m/z* (relative intensity) 232 (M^+, 14), 95 (100), 67 (16), 55 (21). Anal. Calcd for $C_9H_{12}O_2Se$: C, 46.76; H, 5.23. Found: C, 46.93; H, 5.35.

***Se*-Butyl cyclohexanecarboselenoate (2g)**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.91 (t, J = 7.32 Hz, 3 H), 1.26–1.97 (m, 10 H), 1.39 (sextet, J = 7.33 Hz, 2 H), 1.63 (quint, J = 7.33 Hz, 2 H), 2.52 (m, 1 H), 2.87 (t, J = 7.33 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.5, 23.1, 24.6, 25.4, 25.7, 29.3, 32.7, 56.3, 206.1; IR (neat) 2931, 2855, 1698, 961, 757 cm^{-1}; MS *m/z* (relative intensity) 248 (M^+, 1.3), 111 (61), 83 (100), 57 (31), 55 (100). Anal. Calcd for $C_{11}H_{20}OSe$: C, 53.44; H, 8.15. Found: C, 53.39; H, 8.44.

***Se*-Butyl 2,2-dimethylpropaneselenoate (2h)**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.92 (t, J = 7.49 Hz, 3 H), 1.22 (s, 9 H), 1.39 (sextet, J = 7.49 Hz, 2 H), 1.67 (quint, J = 7.49 Hz, 2 H), 2.85 (t, J = 7.49 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.6, 23.2, 24.6, 27.2, 32.7, 49.4, 210.2; IR (neat) 2964, 2932, 1693, 923, 800 cm^{-1}; MS *m/z* (relative intensity) 222 (M^+, 0.8), 85 (17), 57 (100). Anal. Calcd for $C_9H_{18}OSe$: C, 48.87; H, 8.20. Found: C, 48.77; H, 8.24.

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Supplementary Material Available: Copies of ^{1}H and ^{13}C NMR spectra of **3d** (2 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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