Notes

Selenotellurocarbamic Acid *Te*-Alkyl Esters: First Isolation and Characterization

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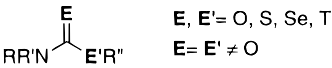
Summary: Selenotellurocarbamic acid Te-alkyl esters were isolated for the first time in yields of 20−40% from the reaction of acyl isoselenocyanates with tellurols.

Introduction

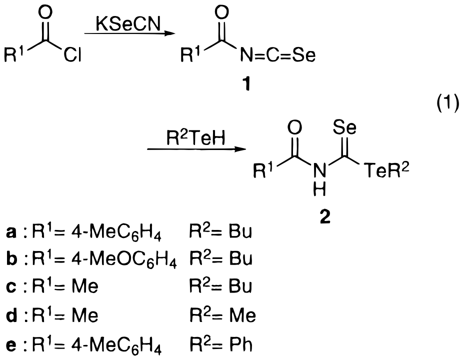
Chalcogen isologues of carbamic acid esters consist of 15 kinds of congeners formulated in Chart 1. Among these, thio- and dithioesters (E, E′ = O, S) have been extensively studied and are widely used as fungicides, pesticides, vulcanization accelerators, and antioxidants of rubber.[1−3] However, little is known about the selenium and tellurium isologues.[4] To the best of our knowledge, there are no previously reported methods for the synthesis of telluro- ($R_2NC(Te)OR'$), tellurothio- ($R_2NC(Te)SR'$), selenotelluro- ($R_2NC(Se)TeR'$, $R_2NC(Te)SeR'$), and ditellurocarbamates ($R_2NC(Te)TeR'$), despite great interest from both synthetic and spectroscopic perspectives. In our study of new chalcogenocarboxylic acid derivatives, we found that treatment of acetylenic selenides (RC⋮CSeC(O)Me or RC⋮CSeLi) with alcohols or thiols gave selenoic acid *O*-esters ($RCH_2C(Se)OR'$)[5] and selenothioic acid *S*-esters ($RCH_2C(Se)SR'$),[6] which strongly suggested the generation of selenoketene intermediates. However, several attempts to prepare diseleno- and selenotelluroesters using selenols and tellurols under various conditions were unsuccessful, most likely due to their extreme instability. Organoisoselenocyanates are believed to be more suitable starting reagents for the construction of the selenotellurocarboxyl framework (−C(Se)Te−). We describe herein the first isolation and characterization of crystalline selenotellurocarbamic acid *Te*-alkyl esters **2**.

Chart 1



Results and Discussion

Synthesis of Selenotellurocarbamic Acid *Te*-Esters 2. This synthesis was achieved by the reaction of acyl isoselenocyanates **1** with tellurols (eq 1). For



example, in situ generated 4-methylbenzoyl isoselenocyanate (**1a**; R^1 = 4-MeC_6H_4)[7] was reacted in THF at −80 °C with 5 equiv of BuTeH, which was freshly prepared by treating BuTeLi with an ether solution of HCl. After the mixture was stirred for 30 min under the same conditions and warmed to 20 °C for another 1 h, chromatographic purification followed by aqueous workup gave *N*-(4-methylbenozyl)selenotellurocarbamic

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(1) For reviews on thio- and dithiocarbamates: (a) *Organic Compounds of Sulfur, Selenium, and Tellurium*; Special Periodical Reports 1−6; The Chemical Society: London, 1970−1981. (b) Coucouvanis, D. *Prog. Inorg. Chem.* **1979**, *26*, 301; **1972**, *11*, 233. (c) *The Dithiocarbamates and Related Compounds*; Thorn, G. D., Ludwig, R. A., Eds.; Elsevier: New York, 1962.

(2) For reviews on selenocarbamates: (a) Sonoda, N. *Pure Appl. Chem.* **1993**, *65*, 699. (b) Gysling, H. J. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1986; Vol. 1, p 679.

(3) For reviews on chalcogenoesters: (a) Ogawa, A.; Sonoda, N. In *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R., Meth-cohn, O., Rees, C. W., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 5, p 231. (b) Voss, J. In ref 3a, p 435. (c) Ishii, A.; Nakayama, J. In ref 3a, p 505. (d) Murai, T.; Kato, S. In ref 3a, p 545. (e) Ogawa, A.; Sonoda, N. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 6, p 461. (f) Reference 2b.

(4) For the synthesis of chalcogenocarbamates, see the following. $R_2NC(S)TeR'$: (a) Wudl, F.; Nalewajek, D. *J. Organomet. Chem.* **1981**, *217*, 329. $R_2NC(Se)SR'$ and $R_2NC(Se)SeR'$: (b) Shu, P.; Bloch, A. N.; Carruthers, T. F.; Cowan, D. O. *J. Chem. Soc., Chem. Commun.* **1977**, 505. (c) Klayman, D. L.; Shine, R. J. *J. Org. Chem.* **1969**, *34*, 3459. (d) Rosenbaum, V. A.; Kirchberg, H.; Leibnitz, E. *J. Prakt. Chem.* **1963**, *19*, 1. $R_2NC(Se)OR'$: (e) Bulka, E. In *The Chemistry of Cyanates and Their Thio Derivatives*; Patai, S., Ed.; Wiley: New York, 1977; Vol. 2, p 915. (f) Jensen, K. A.; Due, M.; Holm, A.; Wentrup, C. *Acta Chem. Scand.* **1966**, *20*, 2091.

(5) Ishihara, H.; Yoshimi, M.; Hara, N.; Ando, H.; Kato, S. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 835.

(6) (a) Murai, T.; Kakami, K.; Itoh, N.; Kanda, T.; Kato, S. *Tetrahedron* **1996**, *52*, 2839. (b) Murai, T.; Hayashi, A.; Kanda, T.; Kato, S. *Chem. Lett.* **1993**, 1469. (c) Kato, S.; Komuro, T.; Kanda, T.; Ishihara, H.; Murai, T. *J. Am. Chem. Soc.* **1993**, *115*, 3000.

(7) The starting **1** was used without isolation. The reaction of $R^1C(O)Cl$ with KSeCN was completed within 30 min under the conditions described as a footnote of Table 1.

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Table 1. Synthesis of *N*-Acylselenotellurocarbamic Acid Esters 2 from Acyl Isoselenocyanates 1 and Tellurols[a]

entry no.	R^1 of $R^1C(O)N{=}C{=}Se$ (**1**)	R^2 of R^2TeH	product **2**	 yield, %[b]
1	4-MeC_6H_4	Bu	**2a**	42
2	4-$MeOC_6H_4$	Bu	**2b**	35
3	Me	Bu	**2c**	36
4	Me	Me	**2d**	29
5	4-MeC_6H_4	Ph	**2e**	*c*

[a] Reaction conditions: $R^1C(O)Cl$ (1 mmol), KSeCN (1 mmol), THF (5 mL), 20 °C, 30 min; R^2TeH (5 mmol), −80 °C, 0.5 h; −80 to +20 °C, 1 h. [b] Isolated yield based on $R^1C(O)Cl$. [c] Not obtained.

acid *Te*-butyl ester (**2a**) in a yield of 42% as reddish yellow needles. Similarly, the reaction of other acyl isoselenocyanates with alkanetellurols led to the isolation of the corresponding selenotellurocarbamates **2b**−**d** in yields of 20−40% (Table 1, entries 2−4). This is the first example of compounds containing the selenotellurocarboxyl framework (−C(Se)Te−). Unfortunately, the reaction with benzenetellurol resulted in a complex mixture (entry 5). Furthermore, the use of lithium tellurolates (R^2TeLi) instead of R^2TeH as nucleophiles predominantly resulted in the formation of telluroesters [$R^1C(O)TeR^2$].[8]

The structures of **2** were determined by IR and ^1H, ^{13}C, ^{77}Se, and ^{125}Te NMR spectra and elemental analysis. For example, in the case of **2a**, the ^{13}C NMR spectra show signals at δ 164.8 and 195.5 ($^1J_{C-Se} = 199.4$ Hz) due to the C═O and C═Se moieties, respectively.[9] In the ^1H NMR spectra, a broad signal is observed at δ 11.38 and is ascribed to the N−H proton.[10] The ^{77}Se NMR spectra also show a characteristic signal due to the C−Se moiety at δ 1119.3. Furthermore, the ^{125}Te NMR spectra show a signal at δ 596.1. In the IR spectra, absorptions of C═O and N−H stretches are observed at 1684 and 3103 cm^{-1}, respectively.[11] Moreover, the results of elemental analysis were consistent with the calculated values.

The resulting selenotellurocarbamates **2** are reddish yellow needles that are extremely labile toward oxygen. Upon exposure to air, the esters **2** completely decompose within a few minutes into a complex mixture containing elemental tellurium. In particular, the ester **2d** is too sensitive toward oxygen to isolate.

Experimental Section

General Comments. All reactions were performed under an argon atmosphere by using a NESLAB Cryobath (CB-80) equipped with a Cryotrol. Melting points were measured by a Yanagimoto micro melting point apparatus (uncorrected). IR spectra were measured on a Perkin-Elmer 1640 infrared spectrophotometer. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a JEOL α-400 instrument using $CDCl_3$ or $(CD_3)_2CO$ and Me_4Si as internal standards. UV−vis spectra were obtained from a JASCO Ubest-55 photometer using $CHCl_3$ as a solvent. Microanalyses were performed by the Analytical Center of Kyoto University. Column chromatography was run by using Sephadex (LH-20).

Materials. Tellurium (99.999%) and CH_2Cl_2 were purchased from Nacalai Tesque Inc. KSeCN and an ether solution of hydrogen chloride (1.0 M) were purchased from Aldrich Chemical Co. A hexane solution of BuLi (1.6 M) and an ether solution of MeLi (1.0 M) were purchased from Kanto Chemical Co. These elements and compounds were used without further purification. Acetyl chloride was purchased from Nacalai Tesque Inc. and purified by the published literature.[12] Other acyl chlorides were synthesized from $SOCl_2$ and the corresponding carboxylic acids in the presence of DMF as a catalyst and then distilled. Ether, THF, and hexane were purchased from Nacalai Tesque Co. and freshly distilled over sodium turnings under a nitrogen atmosphere prior to use. The starting acyl isoselenocyanates, except the 4-methylbenzoyl derivative (**1a**), were not characterized spectroscopically.

4-Methylbenzoyl isoselenocyanate (1a; R^1 = 4-MeC_6H_4): IR (neat) 1958 (ν(N═C═Se)), 1700 (ν(C═O)) cm^{-1}; ^1H NMR (400 MHz, $(CD_3)_2CO$) δ 2.47 (s, 3 H), 7.45 (d, 2 H, $J = 8.3$ Hz), 7.97 (d, 2 H, $J = 8.3$ Hz); ^{77}Se NMR (76 MHz, $(CD_3)_2CO$) δ 1016.5. The IR spectrum of MeC(O)N═C═Se (1960 (ν(N═C═Se)), 1740 (ν(C═O)) cm^{-1}) has already been reported.[13]

Typical Procedure for the Synthesis of 2a (Entry 1 in Table 1). Into a dried and cooled (−80 °C) two-necked flask (50 mL) was placed a THF solution (10 mL) of **1a** (R^1 = 4-MeC_6H_4, 1 mmol), prepared at 20 °C from KSeCN and 4-methylbenzoyl chloride, and a stirring bar. A mixed solution (THF/Et_2O/hexane (ca. 15 mL, ca. 5/7/3)) of BuTeH (5 mmol) prepared in a dried two-necked flask (50 mL, −80 °C) from the reaction of BuLi/hexane (1.6 M, 3.1 mL), elemental tellurium, and HCl/Et_2O (1 M, 6.5 mL) in the dark was added at the same temperature through a glass tube into the above reaction vessel. After it was stirred for 30 min under the same conditions, the resulting solution was warmed to 20 °C (1 h). The reaction was quenched by addition of water (10 mL), and the mixture was extracted with ether (30 mL × 2). The combined organic layer was dried over anhydrous $MgSO_4$ under an argon atmosphere, filtered, and concentrated under reduced pressure. Flash column chromatography (20 mm i.d. × 15 cm, Sephadex LH-20, 1/1 CH_2Cl_2/hexane) of the residual oil gave **2a** in 42% isolated yield as reddish yellow needles after removal of the solvent. The product must be stored under argon below −15 °C as quickly as possible.

***Te*-Butyl *N*-(4-methylbenzoyl)selenotellurocarbamate (2a):** reddish yellow needles; mp 92−93 °C dec; IR (KBr) 3103 (ν(N−H)), 1684 cm^{-1} (ν(C═O)); ^1H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, 3 H, $J = 7.5$ Hz), 1.50 (sextet, 2 H, $J = 7.5$ Hz), 1.93 (quintet, 2 H, $J = 7.5$ Hz), 2.44 (s, 3 H), 3.15 (t, 2 H, $J = 7.5$ Hz, $^2J_{Te-H} = 27.8$ Hz), 7.34 (d, 2 H, $J = 8.3$ Hz), 7.86 (d, 2 H, $J = 8.3$ Hz), 11.38 (br s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 21.7, 23.5, 25.7, 31.1, 127.7, 127.9, 130.0, 145.0, 164.8 (C═O), 195.5 (C═Se, $^1J_{C-Se} = 199.4$ Hz); ^{77}Se NMR (76 MHz, $CDCl_3$) δ 1119.3; ^{125}Te NMR (126 MHz, $CDCl_3$) δ 596.1; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 231 (4.82), 324 (4.25), 424 (3.88), 509 (2.32) nm. Anal. Calcd for $C_{13}H_{17}NOSeTe$: C, 38.10; H, 4.18. Found: C, 38.47; H, 4.12.

***Te*-Butyl *N*-(4-methoxybenzoyl)selenotellurocarbamate (2b):** mp 94−95 °C dec; IR (KBr) 3125 (ν(N−H)), 1680 (ν(C═O)) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.98 (t, $J = 7.5$ Hz, 3 H, CH_3), 1.50 (sextet, $J = 7.5$ Hz, 2 H, CH_2), 1.93 (quintet, $J = 7.5$ Hz, 2 H, CH_2), 3.15 (t, $J = 7.5$ Hz, $^2J_{Te-H} = 26.9$ Hz, 2 H, CH_2Te), 3.90 (s, 3 H, CH_3O), 7.02 (d, $J = 8.9$ Hz, 2 H, Ar),

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[8] In the case of aryl isoselenocyanates, the reaction with lithium chalcogenolates (RELi; E = S, Se) has been described: (a) Segi, M.; Nakajima, T. *J. Synth. Org. Chem. Jpn.* **1995**, *53*, 678. (b) Sakata, K.; Segi, M.; Nakajima, T. 21st Symposium on Heteroatom Chemistry, Toyama, Japan, 1993; Abstracts, p 231.

[9] ^{77}Se NMR spectra for selenoamides: (a) Sekiguchi, M.; Ogawa, A.; Fujiwara, S.-I.; Ryu, I.; Kambe, N. Sonoda, N. *Chem. Lett.* **1990**, 2053. (b) Cullen, E. R.; Guziec, F. S., Jr.; Murphy, C. J.; Wong, T. C.; Andersen, K. K. *J. Am. Chem. Soc.* **1991**, *103*, 7055.

[10] Also, *N*-acylthiocarbamic acid esters (RC(O)NHC(S)OR′) exist as a thioxo form in solution (characteristic broad signals due to the N−H proton are observed at δ 8.38−8.96): Oba, M.; Nishiyama, K. *Synthesis* **1994**, 624.

[11] No absorption band due to ν(Se−H) was observed at ca. 2300 cm^{-1}.

[12] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, U.K., 1980.

[13] Stec, W. J.; Lesiak, K.; Sudol, M. *Synthesis* **1975**, 785.

7.95 (d, $J = 8.9$ Hz, 2 H, Ar), 11.36 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.7, 23.4, 25.7, 31.1, 55.6, 114.6, 122.7, 129.9, 164.2, 164.2 (C=O), 195.5 (C=Se, $^1J_{C-Se} = 201.3$ Hz); ^{77}Se NMR ($CDCl_3$, 76 MHz) δ 1116.7; ^{125}Te NMR ($CDCl_3$, 126 MHz) δ 553.5. Anal. Calcd for $C_{13}H_{17}NO_2SeTe$: C, 36.70; H, 4.03. Found: C, 36.83; H, 3.91.

***Te*-Butyl *N*-ethanoylselenotellurocarbamate (2c):** mp 83.5−85 °C dec; IR (KBr) 3109 (ν(N−H), 1702 (ν(C=O)) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.96 (t, $J = 7.5$ Hz, 3 H, CH_3), 1.47 (sextet, $J = 7.5$ Hz, 2 H, CH_2), 1.89 (quintet, $J = 7.5$ Hz, 2 H, CH_2), 2.21 (s, 3 H, CH_3), 3.10 (t, $J = 7.5$ Hz, $^2J_{Te-H} = 27.2$ Hz, 2 H, CH_2Te), 11.08 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.7, 23.4, 23.8, 25.7, 31.1, 168.5 (C=O), 195.6 (C=Se, $^1J_{C-Se} = 201.6$ Hz); ^{77}Se NMR ($CDCl_3$, 76 MHz) δ 966.1; ^{125}Te NMR ($CDCl_3$, 126 MHz) δ 209.7. Anal. Calcd for $C_7H_{13}NOSeTe$: C, 25.19; H, 3.93. Found: C, 25.41; H, 4.02.

***Te*-Methyl *N*-Ethanoylselenotellurocarbamate (2d).** This compound was too labile to heat and toward oxygen to isolate: mp 102.5−103.5 °C dec; IR (KBr) 3101 (ν(N−H)), 1718 (ν(C=O)) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.22 (s, 3 H, CH_3C), 2.29 (s, $^2J_{Te-H} = 36.6$ Hz, 3 H, CH_3Te), 11.14 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 1.93 ($^1J_{C-Te} = 127.3$ Hz), 23.6, 168.7 (C=O), 195.9 (C=Se).

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for **1a** and **2d** (3 pages). Ordering information is given on any current masthead page.

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