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Telluration of seleno- and chloroiminium salts leading to various telluroamides, and their structure and NMR properties

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Abstract

The reaction of seleno- and chloroiminium salts with a tellurating agent derived from LiAlH$_4$ and elemental tellurium gave telluroamides in moderate to good yields. This new synthetic method enabled the isolation of the first aliphatic and secondary telluroamides. The molecular structure of an aromatic telluroamide was successfully revealed for the first time; the length of the C=Te bond in the aromatic telluroamide was the same as that in the telluroformamide–Cr complex, and the aromatic ring and Te=C–N moiety were not planar. Unlike the structure in the solid state, spectroscopic data of telluroamides suggest that there is conjugation between these two planes. The properties of the NMR spectra of a series of chalcogenoamides are also discussed.
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1. Introduction

Amides are some of the most ubiquitous compounds and are the least reactive among a series of carboxylic acid derivatives. In view of the central importance of carboxylic acids and their derivatives in organic chemistry, their heavier chalcogen isologues have recently been the subject of active research [1]. Thio- and selenoamides, which are sulfur and selenium isologues of amides, have also been investigated, and a variety of methods for their synthesis have been developed by many groups [2], including our group [3]. In contrast, there have been only a few studies on tellurium isologues of amides, i.e., telluroamides [4,5], probably because of the limited variety of synthetic routes to obtain them and their sensitivity toward oxygen, moisture, and light. In particular, simple aliphatic telluroamides have not yet been reported [6], although the preparation and

the molecular structure analyses of telluroformamides and a tellurolactam were reported [5c]. During the course of our studies on the selenoiminium salts, in which a selenenyl group (RSe–) is attached to the carbon atom of an iminium salt [7], the salts were found to be key starting materials for telluroamides. We report here the details of the synthesis and structure in the solid state and solutions of telluroamides bearing various types of substituents.

2. Results and discussion

2.1. Isolation of telluroamides

Selenoiminium salt **1a** was initially reacted with a tellurating agent prepared from lithium aluminum hydride and elemental tellurium [8] (Method A, Scheme 1). To a THF suspension of the tellurating agent was added selenoiminium salt **1a** at 0 °C. The color of the reaction mixture immediately changed from gray to wine red. The mixture was stirred at room temperature for an additional 3 h, and then passed through a sintered glass filter. After purification, tellurobenzamide **2a** was obtained as a wine red

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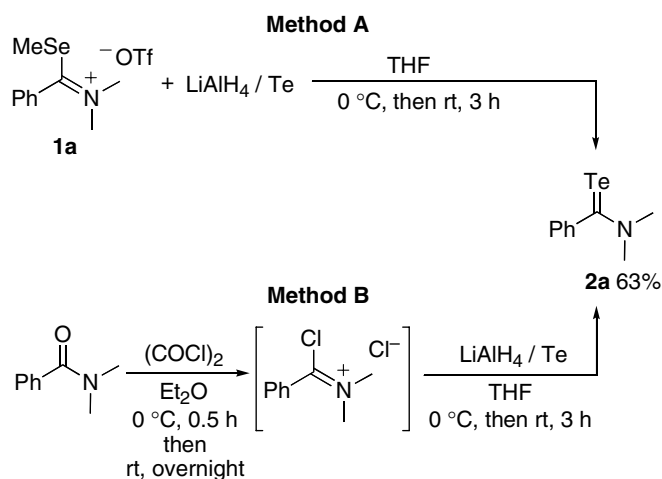
Method A

Scheme 1.

solid in 63% yield. Alternatively, the reaction of chloroiminium salt generated in situ from *N,N*-dimethyl benzamide and oxalyl chloride with the tellurating agent also gave **2a** in comparable yield (Method B, Scheme 1). These two reactions led to **2a** in much better yields than the reported method [5a]. Various telluroamides were then synthesized using these methods (Scheme 2, Table 1). Readily available benzamides with a substituent at the para position **1b–d** were successfully converted to tellurobenzamides **2b–d** by Method B in yields of about 40% (entries 1–3). Similarly, *N,N*-diallyl tellurobenzamide **2e** was isolated in 45% yield (entry 4). Telluroformamide **2f**, which is a known compound [5d], was synthesized by Method A in 21% yield (entry 5). The application of Method A to the reaction of aliphatic selenoiminium salts successfully gave the aliphatic telluroamides for the first time (entries 7 and 8). The reaction of selenoiminium salt **1h** gave α,α-disubstituted telluroamide **2h** in 61% yield (entry 7), whereas α-monosubstituted telluroamide **2i** was obtained in only low yield (entry 8). It is extremely labile at room temperature, and is easily decomposed during purification. Method A was further applied to the reaction of secondary selenoiminium salts **1g** and **1j** to lead to secondary telluroamides
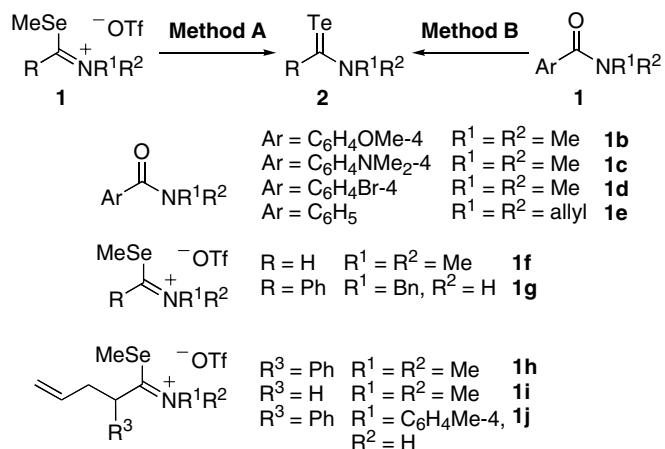
2g and **2j** as isolable compounds through column chromatography on Florisil for the first time (entries 6 and 9). The characteristic resonance signals assigned to their N–H protons were observed at 8.94 and 8.21 ppm, respectively, in the ^{1}H NMR spectra. In all cases, when the isolated telluroamides **2** were exposed to air, they gradually turned black, which is most likely due to the deposition of elemental tellurium. Nevertheless, tellurobenzamides **2a–e** and α,α-disubstituted telluroamide **2h** were more stable than telluroformamide **2f** and α-monosubstituted telluroamide **2i** under air.

2.2. Molecular structure of telluroamides

The structural features of the telluroamides in the solid state were elucidated by X-ray molecular structure analysis.

Table 1
Synthesis of Telluroamides **2**[a]

Entry	Method	Telluroamide **2**		Yield[b] (%)
1	B		**2b**	43
2	B		**2c**	41
3	B		**2d**	26
4	B		**2e**	45
5	A		**2f**	21
6	A		**2g**	61
7	A		**2h**	80
8	A		**2i**	8
9	A		**2j**	223

[a] Telluroamides were synthesized by using Methods A or B shown in Scheme 1.
[b] Isolated yield.

Scheme 2.

An ORTEP drawing of **2d** is shown in Fig. 1, and this is the first example of the X-ray molecular structure of a simple aromatic telluroamide. Selected bond lengths and angles and torsion angles are also shown in Table 2. There are two crystallographically independent molecules of **2d** in the unit cell, and both molecular structures are almost identical. The length of the Te1–C1 bond in **2d** is
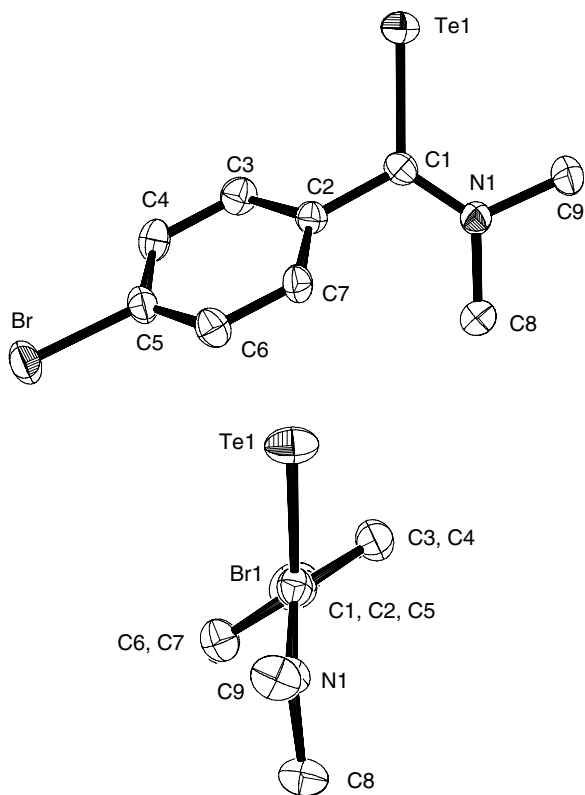

Fig. 1. ORTEP drawing of telluroamide **2d** (top, general view; bottom, the view along the C1–C2 bond). Only one of the two molecules in the unit cell is shown. Hydrogen atoms are omitted for clarity.

2.056(4) Å and almost the same as those in telluroformamide **2k**, tellurolactam **2l**, and telluroformamide–Cr complex **3a** (Table 3), but clearly shorter than those in tellurourea **4** and its Cr complex **5**. The length of the N1–C1 bond in **2d** is 1.316(5) Å, which is almost the same as those in the telluroamide derivatives **2k**, **2l**, and **3a**, and telluroiminium salts **3b** but slightly longer than that in telluroimidate **6a**. The torsion angle Te1–C1–N1–C8 in **2d** is −173.2(3)°, and the four atoms are located in almost the same plane. In contrast, the torsion angle Te1–C1–C2–C7 is −121.1(3)°, and the aromatic ring deviates from the plane that is formed by the Te1, C1, and N1 atoms [10]. These results suggest that the benzene ring in **2d** is almost not conjugated with the C=Te double bond.

2.3. Spectroscopic properties

Spectroscopic data of selected telluroamides **2** are shown in Table 4 along with those of telluroimidates **6b** and **6c** [11]. In the ^{13}C NMR spectra, the signals of the carbon

Table 2
Selected bond lengths (Å) and angles (°), and torsion (°) for **2d**

Bond lengths			
Te1–C1	2.056(4)	Te2–C10	2.067(4)
N1–C1	1.316(5)	N2–C10	1.309(4)
N1–C8	1.474(5)	N2–C17	1.478(5)
C1–C2	1.486(5)	C10–C11	1.488(5)
Bond angles			
Te1–C1–C2	117.9(2)	Te2–C10–C11	116.7(2)
Te1–C1–N2	124.0(2)	Te2–C10–N2	123.3(2)
N1–C1–C2	118.0(3)	N2–C10–C11	120.0(2)
C1–N1–C8	125.3(3)	C10–N2–C17	124.5(3)
C1–N1–C9	121.1(3)	C10–N2–C18	121.1(3)
C8–N1–C9	113.6(3)	C17–N2–C18	114.2(3)
Torsion angles			
Te1–C1–N1–C8	−173.2(3)	Te2–C10–N2–C17	172.7(3)
Te1–C1–C2–C7	−121.1(3)	Te2–C10–C11–C16	−60.8(4)
C2–C1–N1–C8	9.1(5)	C11–C10–N2–C17	−7.3(5)

Table 3
C–Te and C–N bond lengths of telluroamides and related compounds

Compounds		C–Te (Å)	C–N (Å)	Reference
	2k	2.04	1.30	[5c]
	2l	2.05	1.32	[5c]
4-BrC$_6$H$_4$	**2d**	2.06	1.31	This work
(OC)$_5$Cr	**3a**	2.06	1.30	[9a]
MeTe, $^-$OTf	**3b**	2.09 2.12 (Me–Te)	1.30	[9b]
	4	2.09	1.36	[9c]
(OC)$_5$Cr	**5**	2.12	1.33	[9d]
p-tolTe	**6a**	2.17 2.12 (ptol–Te)	1.28	[9e]

Bt = benzotriazolyl

atom of the tellurocarbonyl group were observed at around 200 ppm, and were shifted upfield compared to those of the telluroimidates **6b** and **6c**. In the ^{125}Te NMR spectra, the signals of the tellurium atom of tertiary telluroamides **2a**–**e** were observed in a region of 850–980 ppm, whereas the signals of secondary and aliphatic telluroamides **2g**, **2h**, and **2j** were at higher fields by about 200–300 ppm, but still lower than those of telluroimidates. The signals in aromatic telluroamides are sensitive to the electronic effects on the aromatic ring. In the contrast, the coupling constants between the carbon and tellurium atoms of **2** were 562 ± 17 Hz, and were almost independent of the substituents on the nitrogen atom and on the tellurocarbonyl carbon atom.

Finally, the signals of a series of chalcogenoamides were compared (Table 5). In the ^{1}H NMR spectra of **2a**, **7–9**, the signals due to the methyl groups on the nitrogen atom were observed as two separate signals at a region of 3–4 ppm, which is ascribed to the rotational barriers of the carbon–nitrogen bond of amides and their chalcogen isologues. Notably, the difference in the chemical shifts of these methyl groups increases on going from amide **7** to **8**, **9**, and **2a**. Similarly, for telluroamide **2a**, the signal of one methyl group was at a higher region than that of the other methyl group by more than 10 ppm in ^{13}C NMR spectra. These results may be because one of the methyl groups is highly effectively deshielded by a C=Te group. The lower shift of the signal of the *ipso*-carbon atom of telluroamide **2a** may also be attributed to this effect.

Table 4
Typical spectroscopic data of selected telluroamides **2**, and telluroimidate **6**

Compound	^{13}C NMR[a,b] (ppm)	^{125}Te NMR[a,c] (ppm)	$^1J_{C(sp^2)-Te}$[d] (Hz)
2a	197.5	913.4	557.2
2b	197.6	915.9	553.8
2c	196.9	849.2	545.5
2d	196.4	978.7	559.7
2e	200.2	957.3	561.6
2g	198.3	668.4	567.5
2h	205.7	660.2	572.3
2j	206.3	589.5	579.6
MeTe Ph—=N—Ph **6b**[e]	159.8	325.9	342.7
PhTe Ph—=N—Xy-o NHBn **6c**[f]	167.3	–[g]	356.4

[a] CDCl$_3$ as used as a solvent.
[b] The signals of the carbon atom of the telluro-carbonyl or -imidate group are shown.
[c] The signals were measured at 50 °C.
[d] Coupling constants were determined by ^{13}C NMR.
[e] Crude product.
[f] Ref. [11].
[g] Not observed.

Table 5
NMR data of a series of chalcogenoamides **2d**, **7**, **8**, and **9**

Ch		^{1}H NMR[a] (ppm)		^{1}H NMR[a] (ppm)			
		N(CH$_3$)$_2$	$\Delta\delta$	N(CH$_3$)$_2$	$\Delta\delta$	Ph(*ipso*)	C=Ch
O	**7**	2.98, 3.29	0.13	35.3, 39.6	4.6	136.4	171.6
S	**8**	3.14, 3.58	0.44	43.0, 44.0	1.0	143.2	201.0
Se	**9**	3.10, 3.70	0.60	44.8, 47.3	2.5	146.1	205.2
Te	**2a**	2.96, 3.78	0.82	44.7, 55.2	10.5	152.6	197.5

[a] CDCl$_3$ as used as a solvent.

3. Conclusion

We have successfully isolated a variety of telluroamides by reacting seleno- and chloroiminium salts with a tellurating agent derived from LiAlH$_4$ and elemental tellurium. X-ray molecular structure analysis of the aromatic telluroamide was carried out. The benzene ring in the aromatic telluroamide in the solid state does not necessarily conjugate with a tellurocarbonyl group. The spectroscopic properties of telluroamides show that their tellurium atoms are sensitive to electronic effects, and there is conjugative interaction between the benzene ring and C=Te double bond in solution. Based on the difference in the chemical shifts of methyl groups in a series of chalcogenoamides, C=Te appeared to have the greatest deshielding effect among C=Ch (Ch=O, S, Se, Te) groups.

4. Experimental

4.1. General considerations

Melting points were measured by a Yanagimoto micro melting point apparatus (uncorrected). IR spectra were obtained on a JASCO FT/IR 410 spectrophotometer. ^{1}H (399.7 MHz), ^{13}C (100.4 MHz), and ^{125}Te (126.0 MHz) NMR spectra were measured on a JEOL a-400 spectrometer. The ^{1}H and ^{13}C chemical shifts are reported in δ values with reference to Me$_4$Si and CDCl$_3$ as internal standards, respectively. The ^{125}Te chemical shifts are expressed in δ values deshielded with respect to Me$_2$Te as an external standard. All spectra were acquired in the proton-decoupled mode. Mass (MS) and high-resolution mass spectra (HRMS) were measured on a JEOL GC-mate II mass spectrometer or a JEOL JMS-700 spectrometer.

Diethyl ether (Et$_2$O) and tetrahydrofuran (THF) were distilled from sodium/benzophenone ketyl prior to use, or anhydrous Et$_2$O and THF were purchased from Kanto Chemical Co., Inc. Dichloromethane (CH$_2$Cl$_2$) was distilled over diphosphorus pentoxide after refluxing for 5 h. Hexane was distilled from sodium metal. Tellurium was purchased from Nacalai Tesque, Inc. and finely crushed, prior to use. Lithium aluminum hydride (LiAlH$_4$) was purchased from Nacalai Tesque, Inc. and Wako Pure

Chemical Industry Co., Ltd., and used without further purification. Selenoiminium salts **1** were prepared as described in the literature [7]. Florisil used in column chromatography was Florisil (150–250 μm) from Kanto Chemical Co., Inc.

All reactions were carried out under dry argon atmosphere, and all handling should be carried out in a well-ventilated hood. All glassware was wrapped with aluminum foil because of the characteristic photosensitivity of tellurium compounds, and laboratory lights were extinguished to minimize any illumination. All solvents were degassed by bubbling with argon or by the freeze-pump-thaw method.

4.2. Synthesis of Telluroamides 2

4.2.1. N,N-Dimethyl benzenecarbotelluroamide (2a)

To a THF suspension (15 mL) of tellurium (0.459 g, 3.6 mmol) was added LiAlH$_4$ (0.138 g, 3.6 mmol) at 0 °C, and this was stirred at the temperature for 1 h. Then, to an Et$_2$O suspension (15 mL) of selenoiminium salt **1a** (1.128 g, 3.0 mmol) was cannulated the gray THF suspension at 0 °C, and the mixture was stirred at room temperature for 3 h. The mixture was passed through a sintered glass filter (G4), and the solvent was removed under reduced pressure. The residue was purified by column chromatography (Florisil, CH$_2$Cl$_2$) to give telluroamide **2a** (0.492 g, 63%) as a wine-red solid: ^{1}H NMR (CDCl$_3$) δ 2.96 (s, 3H, CH$_3$), 3.78 (s, 3H, CH$_3$), 7.23–7.36 (m, 5H, Ar); ^{13}C NMR (CDCl$_3$) δ 44.7, 55.2 (NCH$_3$), 123.1, 128.0, 128.3, 152.6 (Ar), 197.5 (C=Te); ^{125}Te NMR (CDCl$_3$, 50 °C) δ 913.4. ^{1}H NMR spectroscopic data matched the data reported previously [5a].

4.2.2. N,N-Dimethyl 4-methoxybenzenecarbotelluroamide (2b)

To an Et$_2$O solution (15 mL) of N,N-dimethyl 4-methoxybenzamide (0.895 g, 5.0 mmol) was added oxalyl chloride (0.45 mL, 5.0 mmol) at 0 °C, and the mixture was stirred at this temperature for 0.5 h. The reaction mixture was further stirred at room temperature overnight. On the other hand, to a THF suspension (15 mL) of tellurium (0.638 g, 5.0 mmol) was added LiAlH$_4$ (0.19 g, 5.0 mmol) at 0 °C, and this was stirred at the same temperature for 1 h. To the white Et$_2$O suspension was then cannulated the gray THF suspension at 0 °C, and the mixture was stirred at room temperature for 3 h. The mixture was passed through a sintered glass filter (G4), and the solvent was removed under reduced pressure. The residue was purified by column chromatography (Florisil, CH$_2$Cl$_2$) to give telluroamide **2b** (0.623 g, 43%) as a wine-red solid: mp 67.0–70.5 °C; IR (Nujol) 1626, 1601, 1571, 1531, 1504, 1438, 1393, 1296, 1247, 1175, 1129, 1110, 1082, 1026, 831, 593 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.07 (s, 3H, CH$_3$), 3.809 (s, 3H, CH$_3$), 3.812 (s, 3H, CH$_3$), 6.83 (d, J = 8.8 Hz, 2H, Ar), 7.29 (d, J = 8.8 Hz, 2H, Ar); ^{13}C NMR (CDCl$_3$) δ 44.6 (CH$_3$), 55.4, 55.4 (CH$_3$), 113.2, 125.3, 144.7, 159.6

(Ar), 197.6 (C=Te, $^1J_{C=Te}$ = 553.8 Hz); ^{125}Te NMR (CDCl$_3$, 50 °C) δ 915.9; MS (EI) m/z 293 (M$^+$, ^{130}Te); HRMS (EI) calcd for C$_{10}$H$_{13}$NO^{130}Te 293.0059, found: 293.0065.

4.2.3. N,N-Dimethyl 4-dimethylaminobenzenecarbotelluroamide (2c)

Telluroamide **2c** was prepared by utilizing the procedure described for **2b**. The title compound was obtained in 41% yield as a wine red solid: mp 64.5–69.0 °C; IR (Nujol) 1607, 1511, 1284, 1230, 1186, 1121, 1084, 946, 903, 813, 765 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.89 (s, 6H, N(CH$_3$)$_2$), 3.07 (s, 3H, NCH$_3$), 3.72 (s, 3H, NCH$_3$), 6.49 (d, J = 8.6 Hz, 2H, Ar), 7.23 (d, J = 8.6 Hz, 2H, Ar); ^{13}C NMR (CDCl$_3$) δ 40.0 (NCH$_3$)$_2$), 44.6, 55.5 (NCH$_3$), 110.2, 126.3, 139.0, 150.2 (Ar), 196.9 (C=Te, $J_{C=Te}$ = 545.5 Hz); ^{125}Te (CDCl$_3$, 50 °C) δ 849.2; MS (EI) m/z 306 (M$^+$, ^{130}Te); HRMS (EI) calcd for C$_{11}$H$_{16}$N$_2$^{130}Te (M$^+$) 306.0376, found: 306.0357.

4.2.4. N,N-Dimethyl 4-bromobenzenecarbotelluroamide (2d)

Telluroamide **2d** was prepared by utilizing the procedure described for **2b**. The title compound was obtained in 26% yield as a wine red solid: mp 116.5–129.0 °C; IR (Nujol) 1578, 1525, 1389, 1254, 1130, 1103, 1007, 906, 870, 817 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.93 (s, 3H, NCH$_3$), 3.73 (s, 3H, NCH$_3$), 7.11 (d, J = 8.8 Hz, 2H, Ar), 7.22 (d, J = 8.8 Hz, 2H, Ar); ^{13}C NMR (CDCl$_3$) δ 44.6, 55.0 (NCH$_3$), 122.3, 124.5, 131.0, 150.8 (Ar), 196.4 (C=Te, $J_{C=Te}$ = 559.7 Hz); ^{125}Te (CDCl$_3$, 50 °C) δ 978.7; MS (EI) m/z 341 (M$^+$, ^{130}Te); HRMS (EI) calcd for C$_9$H$_{10}$BrN^{130}Te (M$^+$) 340.9059, found: 340.9032.

4.2.5. N,N-Di-2-propenyl benzenecarbotelluroamide (2e)

Telluroamide **2e** was prepared by utilizing the procedure described for **2b**. The title compound was obtained in 45% yield as a wine red solid: IR (neat) 3079, 2985, 1701, 1638, 1494, 1477, 1410, 1257, 1202, 1156, 1028, 991, 756, 698, 657 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.89 (d, J = 5.6 Hz, 2H, NCH$_2$), 4.89 (d, J = 6.0 Hz, 2H, NCH$_2$), 5.10 (d, J = 17.2 Hz, 1H, CH$_2$=CH), 5.21 (d, J = 10.0 Hz, 1H, CH$_2$=CH), 5.32 (d, J = 17.2 Hz, 1H, CH$_2$=CH), 5.35 (s, 1H, 5.83 CH$_2$=CH), 5.65 (ddt, J = 7.8, 10.1, 17.2 Hz, 1H, CH$_2$=CH), 6.01 (ddt, J = 7.8, 10.1, 17.2 Hz, 1H, CH$_2$=CH), 7.16–7.26 (m, 5H, Ar); ^{13}C NMR (CDCl$_3$) δ 55.6, 64.0 (NCH$_2$), 120.0, 120.2 (CH$_2$=CH), 122.1, 127.6, 128.1 (Ar), 129.8 (CH$_2$=CH × 2), 152.0 (Ar), 200.2 (C=Te, $^1J_{C=Te}$ = 561.6 Hz); ^{125}Te NMR (CDCl$_3$, 50 °C) δ 957.3; MS (EI) m/z 315 (M$^+$, ^{130}Te); HRMS (EI) calcd for C$_{13}$H$_{15}$N^{130}Te (M$^+$) 315.0267, found: 315.0282.

4.2.6. N-(Phenylmethyl)benzenecarbotelluroamide (2g)

Telluroamide **2g** was prepared by utilizing the procedure described for **2a**. The title compound was obtained in 80% yield as a chocolate viscous oil: IR (neat) 3026, 2917, 2849, 1607, 1524, 1493, 1443, 1384, 1341, 1027, 693 cm^{-1}; ^{1}H

NMR (CDCl$_3$) δ 4.93 (br, 2H, CH$_2$), 7.31 (t, $J = 7.2$ Hz, 2H, Ar), 7.44–7.52 (m, 6H, Ar), 7.68 (d, $J = 7.2$ Hz, 2H, Ar), 8.94 (br, 1H, NH); ^{13}C NMR (CDCl$_3$) δ 60.5 (CH$_2$), 125.9, 128.1, 128.2, 128.6, 130.4, 149.6 (Ar, the signal of two aromatic carbon atoms were overlapped), 198.3 (C=Te, $^1J_{C=Te} = 567.5$ Hz); ^{125}Te NMR (CDCl$_3$, 50 °C) δ 668.4; MS (EI) m/z 325 (M$^+$, ^{130}Te); HRMS (EI) calcd for C$_{14}$H$_{13}$N^{130}Te (M$^+$) 325.0110, found: 325.0098.

4.2.7. N,N-Dimethyl 2-phenyl-4-pentenetelluroamide (2h)

To an Et$_2$O solution (15 mL) of *N,N*-dimethyl 2-phenyl-4-penteneselenoamide [12] (1.33 g, 5.0 mmol) was added methyl triflate (0.575 mL, 5.0 mmol) at room temperature, and the mixture was stirred at the temperature for 30 s. On the other hand, to a THF suspension (15 mL) of tellurium (0.638 g, 5.0 mmol) was added LiAlH$_4$ (0.19 g, 5.0 mmol) at 0 °C, and this was stirred at the same temperature for 1 h. To the white Et$_2$O suspension was then cannulated the gray THF suspension at 0 °C, and the mixture was stirred at room temperature for 3 h. The mixture was passed through a sintered glass filter (G4), and the solvent was removed under reduced pressure. The residue was purified by column chromatography (Florisil, CH$_2$Cl$_2$) to give telluroamide **2h** (0.96 g, 61%) as a reddish-orange solid: IR 3060, 2924, 1638, 1598, 1511, 1493, 1389, 1250, 1151, 1054, 998, 916, 766, 701 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.84 (dt, $J = 7.6$, 14.0 Hz, 1H, CH$_2$=CHCH), 3.13–3.22 (m, 4H, CH$_2$=CHCH_2, NCH_3), 3.69 (s, 3H, NCH$_3$), 3.90 (t, $J = 7.2$ Hz, 1H, PhCH), 4.97 (dt, $J = 2.5$, 10.4 Hz, 1H, CH$_2$=CHCH_2), 5.06 (dq, $J = 1.6$, 17.3 Hz, 1H, CH_2=CHCH$_2$), 5.77 (ddt, $J = 6.4$, 10.4, 17.2 Hz, 1H, CH$_2$=CHCH$_2$), 7.23–7.32 (m, 3H, Ar), 7.51–7.53 (m, 2H, Ar); ^{13}C NMR (CDCl$_3$) δ 42.8 (NCH$_3$), 47.8 (CH$_2$=CHCH$_2$), 58.1 (NCH$_3$), 60.7 (PhCH), 116.9 (CH$_2$=CHCH$_2$), 127.4, 128.7, 129.1 (Ar), 136.4 (CH$_2$=CHCH$_2$), 138.9 (Ar), 205.7 (C=Te, $^1J_{C=Te} = 572.3$ Hz); ^{125}Te NMR (CDCl$_3$, 50 °C) δ 660.2; MS (EI) m/z 317 (M$^+$, ^{130}Te); HRMS (EI) calcd for C$_{13}$H$_{17}$N^{130}Te (M$^+$) 317.0423, found: 317.0420.

4.2.8. N-(4-Methylphenyl)methyl 2-phenyl-4-pentenetelluroamide (2j)

Telluroamide **2j** was prepared by utilizing the procedure described for **2h**. The title compound was obtained in 23% yield as a yellow solid: mp 98.5–101.5 (dec.); IR (KBr) 2861, 1636, 1616, 1541, 1525, 1453, 1123, 907, 802, 702 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.25 (s, 3H, CH$_3$), 2.70, (dt, $J = 7.6$, 14.6 Hz, 1H, CH$_2$=CHCH_2), 3.20 (dt, $J = 6.6$, 14.6 Hz, 1H, CH$_2$=CHCH_2), 4.16 (dd, $J = 6.0$, 8.8 Hz, 1H, PhCH), 4.57 (dd, $J = 5.3$, 16.1 Hz, 1H, CH$_2$Ar), 4.63 (dd, $J = 5.3$, 16.1 Hz, 1H, CH$_2$Ar), 4.90 (dq, $J = 1.4$, 10.2 Hz, 1H, CH_2=CHCH$_2$), 5.01 (dq, $J = 1.4$, 17.2 Hz, 1H, CH_2=CHCH$_2$), 5.66 (ddt, $J = 6.4$, 10.2, 17.2 Hz, 1H, CH$_2$=CHCH$_2$), 6.97 (d, $J = 8.0$ Hz, 2H, Ar), 7.05 (d, $J = 8.0$ Hz, 2H, Ar), 7.20–7.29 (m, 5H, Ar), 8.21 (br, 1H, NH); ^{13}C NMR (CDCl$_3$) δ 21.1 (CH$_3$), 40.2 (CH$_2$=CHCH$_2$), 60.1 (CH$_2$Ar), 69.3 (PhCH), 117.5

(CH$_2$=CHCH$_2$), 127.96, 127.98, 128.4, 129.1, 129.6, 131.2 (Ar), 134.9 (CH$_2$=CHCH$_2$), 137.5, 138.3 (Ar), 206.3 (C=Te, $^1J_{C=Te} = 579.6$ Hz); ^{125}Te NMR (CDCl$_3$, 50 °C) δ 589.5; MS (EI) m/z 393 (M$^+$, ^{130}Te); HRMS (EI) calcd for C$_{19}$H$_{21}$N^{130}Te (M$^+$) 393.0736, found: 393.0749.

4.3. X-ray structure analysis of telluroamide 2d

The measurement of telluroamide **2d** was carried out on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The structure was solved and refined using the teXsan® crystallographic software package from Molecular Structure Corporation. The X-ray quality crystal was obtained by slow diffusion of hexane into a CH$_2$Cl$_2$ solution of **2d** in a glovebox filled with argon. The crystal was cut from the grown crystals and mounted on a glass fiber. The structure was solved by the direct method using SIR92 [13] and expanded using DIRDIF94 [14]. Scattering factors for neutral atoms were from Cromer and Waber [15], and anomalous dispersion effects [16] were used. The function minimized was $\Sigma w(F_o^2 - F_c^2)^2$, and the weighting scheme used was $w = [\sigma_c^2(F_o^2) + (p(\max(F_o^2, 0) + 2F_c^2/3)^2)]^{-1}$. A full-matrix least-squares refinement was executed with non-hydrogen atoms considered to be anisotropic. The final-least square cycle included fixed hydrogen atoms at calculated positions for which each isotropic thermal parameter was set to 1.2 times that of the connecting atom. Crystal data and a description of the measurement are summarized in Table 6.

Table 6
Crystallography data for tellruroamide **2d**

	Tellruroamide **2d**
Empirical formula	C$_9$H$_{10}$NTe
Formula weight	339.69
Crystal size (mm)	$0.17 \times 0.20 \times 0.14$
Temperature (°C)	-80.0
Crystal color, habit	Red, prism
Crystal system	Monoclinic
Space group	$P2_1/c$ (#14)
a (Å)	11.120(3)
b (Å)	15.292(5)
c (Å)	13.018(4)
α (°)	90
β (°)	105.861(3)
γ (°)	90
Volume of unit cell (Å^3)	2129(1)
Z value	8
D_{calc} (g/cm^3)	2.119
No. of reflections (all, $2\theta < 54.97°$)	4852
No. of variables	217
Residuals: R, R_w	0.039, 0.076
Residuals: R_1 ($I > 2.0\sigma(I)$)	0.028
No. of reflections to calc. R_1	4048
Goodness-of-fit	0.81

Appendix A. Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC 295560. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: + 44 1223 336033; email: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.03.045.

References

[1] (a) M.F. Heaney, in: A.R. Katritzky, R.J.K. Taylor (Eds.), Comprehensive Organic Functional Group Transformations II, vol. 5, Elsevier Pergamon, Oxford, 2005, p. 435;
(b) A. Ishii, J. Nakayama, in: A.R. Katritzky, R.J.K. Taylor (Eds.), Comprehensive Organic Functional Group Transformations II, vol. 5, Elsevier Pergamon, Oxford, 2005, p. 459;
(c) T. Murai, in: A.R. Katritzky, R.J.K. Taylor (Eds.), Comprehensive Organic Functional Group Transformations II, vol. 5, Elsevier Pergamon, Oxford, 2005, p. 493;
(d) T. Muai, Synlett (2005) 1509;
(e) S. Kato (Ed.), Topics in Current Chemistry, vol. 251, Springer-Verlag, Berlin, 2005;
(f) J. Schmidt, L.A. Silks, in: A.B. Charette (Ed.), Science of Synthesis, vol. 18, Thieme, Stuttgart, 2005, p. 969;
(g) T. Wirth, in: A.B. Charette (Ed.), Science of Synthesis, vol. 22, Thieme, Stuttgart, 2005, p. 181.
[2] (a) J. Moore, in: A.R. Katritzky, R.J.K. Taylor (Eds.), Comprehensive Organic Functional Group Transformations II, vol. 5, Elsevier Pergamon, Oxford, 2005, p. 519;
(b) T. Murai, in: S. Kato (Ed.), Topics in Current Chemistry, vol. 251, Springer-Verlag, Berlin, 2005, p. 247.
[3] (a) For example, see: T. Murai, A. Suzuki, T. Ezaka, S. Kato, Org. Lett. 2 (2000) 311;
(b) T. Murai, Y. Mutoh, S. Kato, Org. Lett. 3 (2001) 1993;
(c) T. Murai, A. Suzuki, S. Kato, J. Chem. Soc., Perkin Trans. 1 (2001) 2711;
(d) T. Murai, H. Aso, S. Kato, Org. Lett. 4 (2002) 1407;
(e) T. Murai, M. Ishizuka, A. Suzuki, S. Kato, Tetrahedron Lett. 44 (2003) 1343;
(f) T. Murai, A. Fujishima, C. Iwamoto, S. Kato, J. Org. Chem. 68 (2003) 7979;
(g) T. Murai, H. Aso, Y. Tatematsu, Y. Itoh, H. Niwa, S. Kato, J. Org. Chem. 68 (2003) 8514;

(h) T. Murai, H. Sano, H. Kawai, H. Aso, F. Shibahara, J. Org. Chem. 70 (2005) 8148.
[4] T. Murai, in: A.B. Charette (Ed.), Science of Synthesis, vol. 22, Thieme, Stuttgart, 2005, p. 213.
[5] (a) K.A. Lerstrup, L. Henriksen, J. Chem. Soc., Chem. Commun. (1979) 1102;
(b) M. Segi, A. Kojima, T. Nakajima, S. Suga, Synlett (1991) 105;
(c) G.M. Li, R.A. Zingaro, M. Segi, J.H. Reibenspies, T. Nakajima, Organometallics 16 (1997) 756;
(d) G.M. Li, R.A. Zingaro, J. Chem. Soc., Perkin Trans. 1 (1998) 647.
[6] Attempts to isolate aliphatic telluroamides have been reported to give decomposed products: V.Z. Laishev, M.L. Petrov, A.A. Petrov, Zh. Org. Khim. 17 (1981) 2064.
[7] (a) Y. Mutoh, T. Murai, Org. Lett. 5 (2003) 1361;
(b) Y. Mutoh, T. Murai, Organometallics 23 (2004) 3907.
[8] A similar selenating agent was prepared from lithium aluminum hydride and elemental selenium: H. Ishihara, M. Koketsu, Y. Fukuta, F. Nada, J. Am. Chem. Soc. 123 (2001) 8408.
[9] (a) G.M. Li, J.H. Reibenspies, R.A. Zingaro, Heteroatom Chem. 9 (1998) 57;
(b) Y. Mutoh, T. Murai, S. Yamago, J. Am. Chem. Soc. 126 (2004) 16696;
(c) N. Kuhn, G. Henkel, T. Kartz, Chem. Ber. 126 (1993) 2047;
(d) M.F. Lappert, T.R. Martin, G.M. McLaughlin, J. Chem. Soc., Chem. Commun. (1980) 635;
(e) S. Yamago, H. Miyazoe, R. Goto, M. Hashidume, T. Sawazaki, J.-i. Yoshida, J. Am. Chem. Soc. 123 (2001) 3697.
[10] (a) Similarly, the benzene rings in the solid state of thio- and seleno-benzamide are almost not conjugated with the S=C–N and Se=C–N moieties: V.W. Walter, S. Harto, J. Voss, Acta Crystallogr. Sect. B 32 (1976) 2876;
(b) T. Murai, T. Mizutani, T. Kanda, S. Kato, Heteroatom Chem. 6 (1995) 241;
(c) P.A. Otten, S. Gorter, A. van der Gen Chem. Ber. 130 (1997) 49;
(d) G.M. Li, J. H Reibenspies, A. Derecskei-Kovacs, R.A. Zingaro, Polyhedron 18 (1999) 3391.
[11] S. Yamago, H. Miyazoe, T. Nakayama, M. Miyoshi, J. Yoshida, Angew. Chem., Int. Ed. 42 (2003) 117.
[12] T. Murai, T. Ezaka, S. Kato, Bull. Chem. Soc. Jpn. 71 (1998) 1193.
[13] A. Altomare, M.C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidori, J. Appl. Cryst. 27 (1994) 435.
[14] The DIRDIF94 program system was used: P.T. Beukskens, G. Admiraal, G. Beurskiens, W.P. Bosman, R. de Gelder, R. Israel, J.M.M. Smits, Technical Report of the Crystallography Laboratory; University of Nijmegen; The Netherlands, 1994.
[15] D.T. Cromer, J.T. Waber, in: J.A. Ibers, W.C. Hamilton (Eds.), International Tables for X-ray Crystallography, vol. IV, The Kynoch Press, Birmingham, England, 1974, Table 2.2A..
[16] D.C. Creagh, W.J. McAuley, in: A.J.C. Wilson (Ed.), International Tables for X-ray Crystallography, vol. C, Kluwer Academic Publishers., Boston, 1992, p. 219, Table 4.2.6.8.