Organotellurium Compounds Involving Tellurium(II)–Nitrogen Bonds. Synthesis of Arenetellurenamides and Their Reactions with Acetylenes

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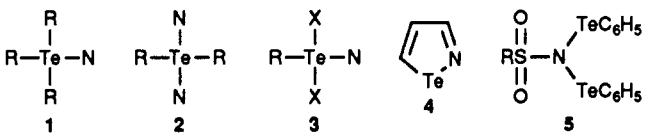
Arenetellurenamides have been prepared by the reaction of arenetellurenyl iodide with lithium amides. The *N,N*-dialkyl derivatives generally decompose above 0 °C, whereas the *N,N*-disilyl ones are thermally stable enough to distill or recrystallize unless exposed to air. Attempts to prepare arenetellurenamides via hydrolysis of disilylamides have failed and resulted in only diaryl ditellurides and tellurinic acid anhydrides. The *N,N*-diisopropylbenzenetellurenamide reacts with terminal acetylenes to give acetylenyl tellurides. *N,N*-diisopropyl- and *N,N*-disilyltellurenamides were found to add to dimethyl acetylenedicarboxylate to give a 1:1 adduct. The cis isomer was selectively obtained in high yield after the purification by silica gel column chromatography. It was isomerized by distillation to give a mixture of cis and trans isomers.

Introduction

Among the chemistry of organotellurium compounds that have been widely studied for over 20 years,[1] relatively less attention has been paid to those containing Te–N bonds.[2] Although organotellurium compounds bearing structure 1,[3] 2,[4] and 3,[5] where Te is tetravalent have been

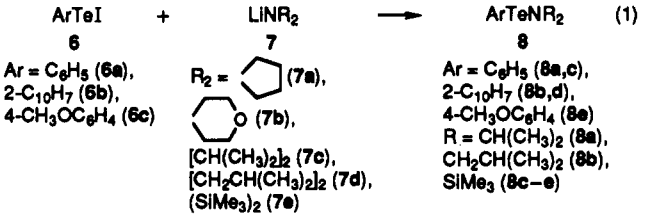


1 2 3 4 5

extensively studied,[6] only cyclic tellurazoles 4[7] have been reported as compounds bearing Te(II)–N bonds. In contrast, acyclic derivatives, i.e. tellurenamides, have so far not been reported, except for ditellurenylsulfonamide (5),[8] to the best of our knowledge. However, since the syntheses of chalcogeno isologues such as sulfenamides[9] and selenamides[2a,10] and their applications not only to organic synthesis but also to industrial materials have been well developed, tellurenamides should provide a new insight into chalcogenoamide chemistry. In this paper we report the details of our study on the synthesis of arenetellurenamides and their reactions with acetylenes.[11]

Results and Discussion

Synthesis of Arenetellurenamides. The synthesis of arenetellurenamides has been examined by the reaction of arenetellurenyl iodide (6) with lithium amides (7) (eq 1). Benzene (6a), naphthalene (6b), and 4-methoxybenzene (6c) derivatives were used as 6. Lithium piperidide (7a), morphoride (7b), diisopropylamide (7c), diisobutylamide (7d), and bis(trimethylsilyl)amide (7e) were employed as 7. In all cases, the dark bluish color of 6 disappeared within 4 h below 0 °C in THF or petroleum ether to give a light yellow solution. Although this was indicative of the formation of the desired product, the reaction mixtures of 6a and 7a, 6a and 7b, and 6b and 7b instantly changed to orange to give only diaryl ditelluride 9 when raised to room temperature. The formation of *N,N*-diisopropylbenzenetellurenamide (8a) in THF at −70 °C from 6a and 7c was detected by mass spectroscopy. But attempts to purify the crude product resulted in the



(1)

(1) For reviews, see: (a) Irgolic, K. J. *The Chemistry of Tellurium*; Gordon and Breach Science: New York, 1974. (b) Engman, L. *Acc. Chem. Res.* **1985**, 18, 274. (c) Petragnani, N.; Comasseto, J. V. *Synthesis* **1986**, 1. (d) Du Mont, W.-W.; Hensel, R.; Kubiniok, S.; Lange, L.; Severengiz, T. *Phosphorus Sulfur Relat. Elem.* **1988**, *38*, 85. (e) Engman, L. *Phosphorus Sulfur Relat. Elem.* **1988**, *38*, 105. (f) Sadekov, I. D.; Maksimenko, A. A.; Minkin, V. I. *Sulfur Rep.* **1990**, *9*, 359.

(2) (a) Jennen, K. A.; Kjaer, A. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons Ltd.: Chichester, U.K., 1986; Vol. 1, p 1. (b) Kirsch, G.; Christiaens, L. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons Ltd.: Chichester, U.K., 1987; Vol. 2, p 421.

(3) (a) Ziolo, R. F.; Pritchett, K. *J. Organomet. Chem.* **1976**, *116*, 211. (b) Lee, J.-S.; Titus, D. D.; Ziolo, R. F. *J. Chem. Soc., Chem. Commun.* **1976**, 501. (c) Gunther, W. H. H.; Przyklek-Elling, R. Eur. Pat. Appl. 192466, 1986. (d) Raj, P.; Singhal, K.; Rastgi, R. *Polyhedron* **1986**, *5*, 677.

(4) (a) Musa, F. H.; Mcwhinue, W. R.; Downs, A. W. *J. Organomet. Chem.* **1977**, *134*, C43. (b) Srivastava, T. N.; Srivastava, R. C.; Singh, M. *J. Organomet. Chem.* **1978**, *160*, 449. (c) Musa, F. H.; Mcwhinnie, W. R. *J. Organomet. Chem.* **1978**, *159*, 37. (d) Srivastava, T. N.; Srivastava, R. C.; Singh, H. B. *Indian J. Chem., Sect. A* **1979**, *18A*, 71. (e) Srivastava, T. N.; Srivastava, R. C.; Singh, H. B.; Singh, M. *Indian J. Chem., Sect. A* **1979**, *18A*, 367. (f) Srivastava, T. N.; Srivastava, R. C.; Kumar, R. *J. Indian Chem. Soc.* **1982**, *59*, 186.

(5) (a) Mancinelli, C. S.; Titus, D. D.; Ziolo, R. F. *J. Organomet. Chem.* **1977**, *140*, 113. (b) Srivastava, T. N.; Srivastava, R. C.; Singh, M. *Inorg. Chim. Acta* **1979**, *33*, C99. (c) Miller, J. M.; Chadha, R. K. *J. Organomet. Chem.* **1981**, *216*, 177. (d) Srivastava, T. N.; Srivastava, R. C.; Srivastava, V. K. *Indian J. Chem., Sect. A* **1983**, *22A*, 503. (e) Kulkarni, Y. D.; Srivastava, S. *Indian J. Chem., Sect. A* **1985**, *24A*, 429. (f) Barton, D. H. R.; Finet, J. D.; Giannotti, C.; Thomas, M. *Tetrahedron Lett.* **1988**, *29*, 2671.

(6) The chemistry of tellurioimides ($R_2Te{=}NR'$) has also been developed; see ref 2b.

(7) (a) Waber, R.; Piette, J. L.; Renson, M. *J. Heterocycl. Chem.* **1978**, *15*, 865. (b) Campsteyn, H.; Dupont, L.; Lamotte-Brasseur, J.; Vermeire, M. *J. Heterocycl. Chem.* **1978**, *15*, 745. (c) Lucchesini, F.; Bertini, V. *Synthesis* **1983**, 824. (d) Guiliana, M.; El Jammal, T.; Mille, G. *Phosphorus Sulfur Relat. Elem.* **1984**, *20*, 21. (e) Lucchesini, F.; Bertini, V.; De Munno, A.; Pocci, M.; Dicci, N.; Liguori, M. *Heterocycles* **1987**, *26*, 1587.

(8) Naddaka, V. I.; Avanesyan, K. V.; Cherkinskaya, M. L.; Minkin, V. I. *Zh. Org. Khim.* **1987**, *23*, 2241.

(9) For a review, see: Craine, L.; Raban, M. *Chem. Rev.* **1989**, *89*, 689.

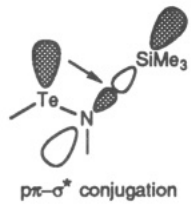
(10) Raulmier, C. In *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon Press: Oxford, U.K., 1986; p 38.

(11) Part of this work has appeared in a communication: Murai, T.; Kimura, K.; Kato, S. *Chem. Lett.* **1989**, 2017.

(12) Reich, H. J.; Renga, J. M. *J. Org. Chem.* **1975**, *40*, 3313.

0276-7333/91/2310-1095$02.50/0

Chart I



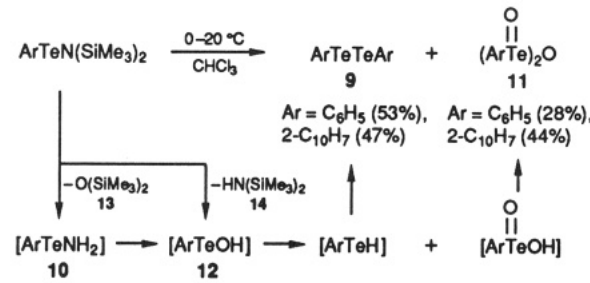
quantitative recovery of diphenyl ditelluride (**9a**). The instability of **8a** to heat was in sharp contrast to the corresponding selenamide, which was distillable under air.[10] On the other hand, when the reaction mixture obtained from **6b** and **7d** was filtered through a reversed glass filter to remove a white solid and concentrated, the yellow oil obtained did not decompose even at room temperature and showed a molecular ionic peak at m/e 386 corresponding to naphthalenetellurenamide **8b**. In the ^{1}H NMR spectrum, signals for the isobutyl groups at δ 0.88–2.94 and for the naphthyl group at δ 7.4–8.2 were observed in the ratio 18:7. The ^{13}C NMR spectrum showing ten aromatic carbons and four alkyl carbons also supported the structure of **8b**. The product **8b** was highly sensitive to moisture and decomposed to bis(2-naphthyl) ditelluride (**9b**) instantly when exposed to air. However, **8b** was relatively stable under an inert atmosphere and could be stored at 0 °C for at least several hours.

Interestingly, when lithium bis(trimethylsilyl)amide (**7e**) was employed, the crude products **8c** and **8d** obtained in THF or petroleum ether solution were thermally stable and survived at room temperature. Furthermore, when **8c** was carefully handled in an evacuated flask to remove air and moisture, distillation under reduced pressure became possible to give pure **8c** in ca. 70% yield. As for **7e**, recrystallization of **8d** from *n*-hexane at −20 °C under an argon atmosphere gave yellow needles melting at 63–65 °C in 61% yield. However, they also exhibited the much lower stability toward air than the corresponding *N,N*-disilylselenamides.[13] Furthermore, when a methoxy group was attached to the aromatic ring of **6**, the tellurenamide **8e** could not be detected unless it was trapped with DMAD (vide infra), although the color of **6c** completely disappeared during the reaction with **7e**.

^{125}Te NMR spectra of tellurenamides **8b** and **8c** have been measured. The observed chemical shift (δ 1209.9)[14,15] for **8c** is greater than that for **8b** (δ 741.6) by 468.3 ppm. These results indicate that the electron density of Te in **8c** is decreased, compared with that of Te in **8b**, and it is probably due to delocalization of a lone-pair electron of Te to the Si–N σ* orbital, enhancing the strength of the bond between Te and N, as shown in Chart I, which may be one of the reasons that **8c** is more stable than **8b** toward heat.

In order to synthesize arenetellurenamide **10**, which has not so far been reported,[2] hydrolysis of disilylamino groups in **8c** and **8d** was carried out (Scheme I). To a $CHCl_3$ solution of **8c** was added 1 equiv of water at 0 °C,[16] and the temperature was raised to 20 °C. A white solid precipitated as the reaction mixture gradually changed from

Scheme I



yellow to orange. After stirring for 15 h at 20 °C, instead of **10**, ditelluride **9** and tellurinic acid anhydride **11** were formed in 53 and 28% yields, respectively. The similar reaction of **8e** with water also gave only the corresponding **9** and **11** in 47 and 44% yields.

The reaction pathway to **9** and **11** can be deduced on the basis of the similar alkali hydrolysis of **6b**.[17] As shown in Scheme I, it would involve the disproportionation of tellurenic acid **12** to tellurinic acid and tellurol. Two pathways to **12** may be possible. One would be hydrolysis of **8c** and **8d** to give **10** and hexamethyldisiloxane (**13**), followed by nucleophilic attack of water to **10**. The other would be direct nucleophilic attack of water to the Te–N bond of **8c** and **8d** to give **12** and hexamethyldisilazane (**14**). GLC analysis of the reaction mixture showed that **13** and **14** were formed in 42 and 52% yields, respectively. According to these results, both processes from **8** appear to result in **9** and **11** via **12**. Furthermore, the direct decomposition process of **10** to **9** and NH_3 cannot be excluded, since 1 equiv of water is not enough to convert **8** to **12** via **10**.[18]

Reaction of Arenetellurenamides with Acetylenes. Although the reactivity of **8** toward organic molecules, such as carbonyl compounds, olefins, and acetylenes,[19] was expected to be high on the basis of the instability mentioned above, the reaction of **8** with them usually resulted in the recovery of either the starting tellurenamides **8** or ditellurides **9**. But when **8a** formed in situ was reacted with terminal acetylenes at −70 to +20 °C, phenyl acetylenyl tellurides **15**[20,21] were formed in high yields (eq 2). Since

$$\underset{\textbf{8a}}{C_6H_5TeN[(CH(CH_3)_2]_2} + RC{\equiv}CH \xrightarrow[THF]{-70\ \text{to}\ +20\ ^\circ C} RC{\equiv}CTeC_6H_5 \quad (2)$$

$$\underset{}{\qquad\qquad} \underset{\textbf{15}}{\qquad\qquad}$$

$$R = C_6H_5\ (72\%),\ n\text{-}C_4H_9\ (85\%)$$

the similar reaction using pure $C_6H_5SeN(CH(CH_3)_2)_2$ did not take place in THF at 20 °C and both of the starting materials were recovered, the reaction in eq 2, which would involve hydrogen abstraction of acetylenes by chalcogenoamide, is specific with respect to tellurium.[22,23] The

(13) Dostal, K.; Cernik, M.; Sochorcova, M. *Z. Anorg. Allg. Chem.* **1975**, *417*, 143.

(14) The value of Te of **8c** in the ^{125}Te NMR spectrum is 1.77 times greater than that of Se (δ 683.4) of $C_6H_5SeN(SiMe_3)_2$ in the ^{77}Se NMR spectrum. This shift change is consistent with the relationship described by O'Brien et al.[15]

(15) O'Brien, D. H.; Dereu, N.; Huang, C.-K.; Irgolic, K. J. *Organometallics* **1983**, *2*, 305.

(16) Only the starting tellurenamide **8c** was recovered after the reaction with water at 0 °C for 20 h.

(17) Vincentini, G.; Giesbrecht, E.; Pitombo, L. R. M. *Chem. Ber.* **1959**, *92*, 40.

(18) The easiness of the hydrolysis of the Te(II)–N bond is in marked contrast to the stability of the Te(IV)–N bond. For example, $(C_6H_5)_3TeN_3$ has been prepared in a water/chloroform solution.[3a]

(19) Sulfen- and Selenamides have been reported to undergo addition reaction to olefins: Brownbridge, P. *Tetrahedron Lett.* **1984**, *25*, 3759.

(20) The acetylenyl tellurides have been prepared by treating terminal alkynes with EtMgBr or *n*-BuLi followed by tellurenylation.[21]

(21) (a) Petragnani, N.; Torres, L.; Wynne, K. J. *J. Organomet. Chem.* **1975**, *92*, 185. (b) Ohe, K.; Takahashi, H.; Uemura, S.; Sugita, N. *J. Org. Chem.* **1987**, *52*, 4859.

(22) In the present system containing **7c**, it can be another candidate as a reagent to abstract hydrogen. But **7c** seems to be consumed completely to form **8c** on the basis of the disappearance of **6a**, although the possibility that a small amount of **7c** catalyzed the reaction has still remained. Furthermore, **13** was never obtained when acetylene was added after stirring **8a**, formed in situ at 0 °C, for 30 min probably because of the decomposition of **8a**.

reaction of **8a** with acetophenone also proceeded through hydrogen abstraction to give α-(phenyltellurio)acetophenone (**16**) in moderate yield (eq 3).[24,25]

$$C_6H_5TeN[(CH(CH_3)_2]_2 + C_6H_5CCH_3 \xrightarrow[THF]{-70\ to\ +20\ ^\circ C} C_6H_5CCH_2TeC_6H_5 \quad (3)$$

8a — **16** (19%)

Finally, the reaction of **8a**, **8c**, and **8e** with DMAD was examined (eq 4). As expected from the known results of selenamides,[26] the reaction took place smoothly, and the

$$ArTeNR_2 + MeOCC{\equiv}CCOMe \longrightarrow \begin{matrix} MeOC & COMe \\ ArTe & NR_2 \end{matrix} \quad (4)$$

17a: Ar = C_6H_5, R = $CH(CH_3)_2$, 13%
17b: Ar = C_6H_5, R = $SiMe_3$, 10%
17c: Ar = 4-$CH_3OC_6H_4$, R = $SiMe_3$, 81%

formation of a 1:1 adduct was confirmed by mass spectroscopy. After several disappointing attempts to purify the products, the products **17a** and **17b** were obtained as a stereoisomeric mixture by either bulb to bulb distillation or Sephadex column chromatography, but in poor yields. In contrast, the cis isomer **17c** was selectively isolated in 81% yield after silica gel column chromatography when **8e** formed in situ was reacted with DMAD at 0 °C in THF, although it was isomerized during the distillation to give the mixture of cis and trans isomers.[27,28] The present reaction is a rare example of the addition of divalent organotellurium compounds to a carbon–carbon triple bond[29-31] and represents a new route to vinyl tellurides, which have recently become important intermediates in organic synthesis[32] but for which limited methods have been available.[31]

In conclusion, *N,N*-disilylarenetellurenamides **8c** and **8d**, obtained by the reaction of **6a** and **6b** with **7e**, were the first tellurenamides to be isolated in pure form under an inert atmosphere. Their sensitivity to air was in marked contrast to the corresponding selenamides. Attempts to afford the arenetellurenamides **10** via hydrolysis of **8c** and **8d** have failed and gave only **9** and **11**. New methods for the preparation of acetylenyl tellurides and alkenyl tellurides via **8a** and **8e** have been provided.

Experimental Section

Melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. The IR spectra were measured on a JASCO grating IR spectrophotometer IR-G. The ^1H NMR spectra were recorded on a JEOL JNM-GX-270 instrument (270 MHz) with tetramethylsilane or $CHCl_3$ as an internal standard, and the following abbreviations were used; s, singlet; t, triplet; m, multiplet. The ^{13}C NMR spectra were obtained from a JEOL JNM-GX-270 instrument (67.9 MHz). The ^{29}Si NMR, ^{125}Te NMR, and ^{77}Se NMR spectra were recorded on the JEOL JNM-GX-270 spectrometer (53.6 MHz, 85.3 MHz, and 51.5 MHz) with hexamethyldisilazane, diphenyl ditelluride, and diphenyl diselenide as external standards, respectively. Solutions for these NMR measurements were prepared by dissolving approximately 1.8 mmol of the tellurenamide in 4 mL of deuteriochloroform. The mass spectra in CI mode using isobutane and high-resolution mass spectra were recorded on SHIMADZU GCMS-QP1000 and GCMS 9020DF instrument. Elemental analyses were performed by the Elemental Analyses Center of Kyoto University. Analytical gas chromatography (GLC) was carried out on a Hitachi Model 263 apparatus equipped with a flame ionization detector, using a 3 m × 2 mm stainless steel column packed with 1% silicone SE-30 supported on 60–80 mesh Chromosorb G (AW). Benzenetellurenyl iodide (**6a**),[33] naphthalenetellurenyl iodide (**6b**),[17] and 4-methoxybenzenetellurenyl iodide (**6c**)[33] were prepared according to the literature.

Synthesis of *N,N*-Diisopropylbenzenetellurenamide (8a). Benzenetellurenyl iodide (**6a**) (663 mg, 2 mmol) was added to a THF solution (3 mL) of lithium diisopropylamide (**7c**) prepared from 2 mmol of diisopropylamine and 1.2 mL of a 1.62 M *n*-hexane solution of *n*-butyllithium in a 10-mL two-necked round-bottom flask at −70 °C. After stirring for 3 h at that temperature, the bluish color completely disappeared, and the resulting yellow reaction mixture was filtered through a reversed glass filter. Mass spectrum (*m/e*): 308 ($M^+ + 1$).

Synthesis of *N,N*-Diisobutyl-2-naphthalenetellurenamide (8b). 2-Naphthalenetellurenyl iodide (**6b**) (768 mg, 2 mmol) was added to a THF solution (3 mL) of lithium diisobutylamide (258 mg, 2 mmol) in a 10-mL two-necked round-bottom flask at −30 °C. The reaction mixture rapidly changed from blue-black to yellow. After stirring for 2 h at that temperature, the resulting yellow reaction mixture was filtered through a reversed glass filter and concentrated in vacuo to give 352 mg (46%) of *N,N*-diisobutyl-2-naphthalenetellurenamide (**8b**) as a yellow oil. IR (neat): 3050, 2950, 2850, 1623, 1582, 1500, 1464, 1388, 1367, 1337, 1270, 1156, 1130, 1070, 994, 939, 853, 810, 743, 629, 456 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.88 (d, J = 7 Hz, 12 H, CH_3), 1.93 (septet, J = 7 Hz, 2 H, CH), 2.94 (d, J = 7 Hz, 4 H, CH_2), 7.4–8.2 (m, 7 H, Ar). ^{13}C NMR ($CDCl_3$: δ 20.3 (CH_3), 29.4 (CH_2), 72.0 (CH), 116.8, 126.1, 126.3, 127.7, 127.8, 127.9, 132.8, 134.0, 134.3, 137.0 (Ar) ^{125}Te NMR ($CDCl_3$): δ 741.9. Mass spectrum (*m/e*): 386 ($M^+ + 1$).

Synthesis of *N,N*-Bis(trimethylsilyl)benzenetellurenamide (8c). Benzenetellurenyl iodide (**6a**) (663 mg, 2 mmol) was added to a petroleum ether solution (5 mL) of lithium bis(trimethylsilyl)amide (**7e**) (334 mg, 2 mmol) in a 10-mL two-necked round-bottom flask at 0 °C. After stirring for 4 h at that temperature, the resulting yellow reaction mixture was filtered through a reversed glass filter and concentrated in vacuo to give 638 mg (87%) of *N,N*-bis(trimethylsilyl)benzenetellurenamide (**8c**) as a yellow oil. It was placed via syringe into the distillation apparatus equipped with a stirring bar under nitrogen atmosphere and distilled under reduced pressure to give 521 mg (71%) of **8c**. Bp: 89–90 °C/0.2 Torr. IR (neat): 3000, 2850, 1570, 1475, 1433, 1250 (s), 1170, 1058, 1041, 905 (s), 860 (s), 835 (s), 730, 684, 642, 611 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.20 (s, 18 H, CH_3–Si), 7.2–7.4 (m, 5 H, Ar). ^{13}C NMR ($CDCl_3$): δ 3.3 (CH_3–Si), 122.5, 125.3, 127.7, 129.4 (Ar). ^{29}Si NMR ($CDCl_3$): δ 16.35; ^{125}Te NMR ($CDCl_3$): δ 1209.9. Mass spectrum (*m/e*): 368 ($M^+ + 1$). Anal. Calcd for $C_{12}H_{23}NSi_2Te$: C, 39.48; H, 6.35. Found: C, 39.50; H, 6.52.

Synthesis of *N,N*-Bis(trimethylsilyl)-2-naphthalenetellurenamide (8d). 2-Naphthalenetellurenyl iodide (**6b**) (768 mg, 2 mmol) was added to a petroleum ether solution (5 mL) of lithium bis(trimethylsilyl)amide (**7e**) (334 mg, 2 mmol) in a 10-mL

(23) The reaction of $C_6H_5SeN(CH(CH_3)_2)_2$ in the presence of a catalytic amount of **7c** resulted in the formation of the complex mixture involving diselenide.

(24) Hiiro, T.; Kambe, N.; Ogawa, A.; Miyoshi, N.; Murai, S.; Sonoda, N. *Synthesis* **1987**, 1096.

(25) Phenylselenylation of carbonyl compounds using selenamides has been known: (a) Jefson, M.; Meinwald, J. *Tetrahedron Lett.* **1981**, *22*, 3561. (b) Paulmier, C.; Leronge, P. *Tetrahedron Lett.* **1982**, *23*, 1557 (see also ref 11).

(26) Reich, H. J.; Renga, J. M.; Trend, J. E. *Tetrahedron Lett.* **1976**, *17*, 2217.

(27) A similar type of the isomerization and the kinetic studies have been reported in the case of the adduct of $C_6H_5SeN(CH(CH_3)_2)_2$ to DMAD.[28]

(28) The stereochemistry of **17c** was estimated by NOE analysis of the mixture of cis and trans isomers; for details see the Experimental Section.

(29) As another example, the addition of C_6H_5TeH to terminal acetylenes has been known.[30,31]

(30) Uemura, S.; Fukuzawa, S. *Tetrahedron Lett.* **1982**, *23*, 1181.

(31) Barros, S. M.; Dabdoub, M. J.; Dabdoub, V. M. B.; Comasseto, J. V. *Organometallics* **1989**, *8*, 1661 and references cited therein.

(32) (a) Ohe, K.; Takahashi, H.; Uemura, S.; Sugita, N. *Nippon Kagaku Kaishi* **1987**, 1469. (b) Hiiro, T.; Kambe, N.; Ogawa, A.; Miyoshi, N.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1187. (c) Barros, S. M.; Comasseto, J. V.; Berriel, J. *Tetrahedron Lett.* **1989**, *30*, 7353.

(33) Schulz, P.; G. Klar, *Z. Naturforsch.* **1975**, *30B*, 40.

two-necked round-bottom flask at 0 °C. After stirring for 4 h at 0 °C, the resulting yellow reaction mixture was filtered through a reversed glass filter and concentrated in vacuo to give 785 mg (94%) of *N,N*-bis(trimethylsilyl)-2-naphthalenetellurenamide (**8d**) as a yellow solid. To this was added *n*-hexane under a nitrogen atmosphere, and it was allowed to stand at −20 °C for 12 h to give **8d** as yellow needles in 66% yield. Mp: 63–65 °C dec. IR (KBr): 3050, 2950, 2850, 2800, 1619, 1583, 1498, 1465, 1255, 1245, (s), 1128, 903 (s), 860, 835, 820, 781, 726 (s), 671, 640, 618, 467 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.35 (s, 18 H, CH_3–Si), 7.51–8.00 (m, 7 H, Ar). ^{13}C NMR ($CDCl_3$): δ 4.7 (CH_3–Si), 121.5, 125.7, 126.2, 127.1, 127.8, 128.0, 128.4, 130.1, 132.6, 134.3 (Ar). ^{29}Si NMR ($CDCl_3$): δ 16.67. ^{125}Te NMR ($CDCl_3$): δ 214.2. Mass spectrum (*m/e*): 417 (M^+). HRMS (EI) calcd for $C_{16}H_{25}NSi_2Te$ (M^+): 417.05867. Found: 417.05837. Anal. Calcd for $C_{16}H_{25}NSi_2Te$: C, 46.29; H, 6.07. Found: C, 45.64; H, 5.87.

Hydrolysis of *N,N*-Bis(trimethylsilyl)benzenetellurenamide (8c). Water (0.018 mL, 1.0 mmol) was injected via syringe into a chloroform solution (3 mL) of *N,N*-bis(trimethylsilyl)-benzenetellurenamide (**8c**) (0.367 g, 1.0 mmol) at 0 °C under a nitrogen atmosphere. After the temperature was raised to 20 °C and the solution stirred for 15 h, a white precipitate was filtered through a reversed glass filter and dried in vacuo over 4 h. The resulting highly insoluble solid showing the IR spectrum in good agreement with **11a** was recrystallized from a mixed solvent of methanol (5 mL) and chloroform (3 mL) to give white microcrystals (65 mg, 28% as **11a**). The composition of the obtained crystal was further confirmed by elemental analysis. Anal. Calcd for $C_{12}H_{10}O_3Te_2$: C, 31.50; H, 2.20. Found: C, 31.51; H, 2.37. The filtrate was concentrated in vacuo to give 110 mg (53%) of diphenyl ditelluride (**9a**).

Reaction of *N,N*-Diisopropylbenzenetellurenamide (8a) with Terminal Acetylenes. Phenylacetylene (0.2 mL, 2 mmol) or 1-hexyne (0.23 mL, 2 mmol) was injected via syringe into a THF solution of *N,N*-diisopropylbenzenetellurenamide (**8a**) at −70 °C and the resulting solution was stirred for 30 min. After the temperature was raised to room temperature, the reaction mixture was poured onto water, and it was extracted with dichloromethane twice. The organic layer was washed with water and dried over $MgSO_4$, followed by concentration to give acetylenyl tellurides. **15** (R = C_6H_5, 444 mg, 72%): IR (neat) 3000, 2150 (C≡C), 1592, 1570, 1483, 1471, 1430, 1339, 1209, 1040, 990, 886, 750, 725, 682, 517, 437 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.21–7.72 (complex, 10 H, Ph); ^{13}C NMR ($CDCl_3$) δ 47.6, 112.3, 113.0, 122.3, 126.7, 127.2, 127.5, 128.6, 130.6, 133.9; mass spectrum (*m/e*) 309 ($M^+ + 1$). **15** (R = *n*-C_4H_9, 245 mg, 85%): IR (neat) 2950, 2800, 2150 (C≡C), 1620, 1569, 1470, 1428, 1317, 1035, 1009, 990, 880, 720, 679, 638, 439 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, *J* = 7 Hz, 3 H, CH_3), 1.38–1.55 (complex, 4 H, CH_2CH_2), 2.55 (t, *J* = 7 Hz, 2 H, CH_2C), 7.21–7.65 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 13.0, 20.2, 21.2, 24.7, 30.4, 112.6, 115.2, 126.9, 128.9, 133.9; mass spectrum (*m/e*) 289 ($M^+ + 1$).

Reaction of *N,N*-Diisopropylbenzenetellurenamide (8a) with Acetophenone. Acetophenone (0.23 mL, 2 mmol) was injected via syringe into a THF solution (3 mL) of **8a** prepared by the method described above at −70 °C over 1 min. After the temperature was raised to 10 °C over 2 h, the reaction mixture was concentrated in vacuo, and the residue was chromatographed on a silica gel column and eluted with 100 mL of ether/hexane (1/10) to give 121 mg (19%) of α-(phenyltelluro)acetophenone (**16**) as a yellow oil along with 89 mg (19%) of diphenyl ditelluride. IR (neat) 3300, 3070, 1690 (C=O), 1669, 1600, 1580, 1470, 1447, 1430, 1356, 1297, 1260, 1173, 1092, 1069, 1019, 1010, 990, 948, 917, 760, 733, 684, 569, 439 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.28 (s, 2 H, CH_2), 7.2–8.0 (m, 10 H, Ph). Mass spectrum (*m/e*): 326 (M^+).

Reaction of *N,N*-Diisopropylbenzenetellurenamide (8a) with Dimethyl Acetylenedicarboxylate (DMAD). DMAD (1.0 mL, 10 mmol) was injected via syringe into a THF solution (15 mL) of **8a** prepared by the method described above at −70 °C over 1 min. After stirring for 2 h at −70 °C, the reaction mixture was concentrated in vacuo. To the residue was added chloroform (100 mL), and then the solution was washed with aqueous sodium bicarbonate. The organic layer was dried over $MgSO_4$. The solvent was evaporated by a rotary evaporator, and the residue was chromatographed on Sephadex LH-20, eluting with chloroform/*n*-hexane (1/10) to give 103 mg (13%) of **17a** as a stereoisomeric mixture. IR (neat): 3000, 2900, 1728 (C=O), 1588, 1486, 1245, 1103, 1006, 956, 728, 703, 688, 660, 456 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.30 (d, *J* = 7 Hz, 12 H, CH_3), 3.5–4.0 (complex, 7 H, CH_3O, CH), 7.15–7.86 (m, 5 H, Ar). HRMS (EI) calcd for $C_{18}H_{25}NO_4Te$ (M^+): 449.0845. Found: 449.08254.

Reaction of *N,N*-Bis(trimethylsilyl)benzenetellurenamide (8c) with DMAD. DMAD (0.2 mL, 2 mmol) was injected via syringe into a THF solution (5 mL) of **8c** at 0 °C over 1 min. After stirring for 2 h at 0 °C, the resulting dark red reaction mixture was concentrated in vacuo, and the residue was distilled by kugelrohr to give 136 mg (10%) of **17b** as a yellow oil. Bp: 170 °C/13 Torr. IR (neat): 3000, 1732 (C=O), 1620, 1430, 1323, 1252, 1248 (s), 1136, 1020, 910 (s), 860 (s), 801, 722, 680 cm^{-1}. ^1H NMR: δ 0.08 (s, 18 H, Me_3Si), 3.71 (s, 3 H, OCH_3), 3.84 (s, 3 H, OCH_3), 7.26–7.91 (m, 5 H, Ph) HRMS (EI) calcd for $C_{18}H_{29}NO_4Si_2Te$ (M^+): 509.0693. Found: 509.06685.

Reaction of *N,N*-Bis(trimethylsilyl)-4-methoxybenzenetellurenamide (8e) with DMAD. DMAD was injected via syringe into a THF solution (5 mL) of *N,N*-bis(trimethylsilyl)-4-methoxybenzenetellurenamide (**8e**), prepared by the reaction of **6c** and **7e** at 0 °C, and stirred for 30 min. The reaction mixture was concentrated, and the residue was chromatographed through silica gel by using 100 mL of chloroform/*n*-hexane (1/1) as an eluent to give **17c** in 81% yield. IR (neat): 2950, 1725 (C=O), 1590, 1495, 1435, 1250 (s), 1140, 1040, 910, 820, 765 (s), 740, 650, 590, 525 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.26 (s, 18 H, CH_3), 3.15 (s, H, ArO–CH_3), 3.65 (s, 3 H, $COOCH_3$), 3.76 (s, 3 H, $COOCH_3$), 6.73 (d, *J* = 8.53 Hz, 2 H, Ar–H), 7.71 (d, *J* = 8.53 Hz, 2 H, Ar–H). ^{13}C NMR ($CDCl_3$): δ 2.4, 51.4, 51.8, 55.1, 103.0, 115.0, 143.5, 160.8, 163.8, 165.9. HRMS (EI) calcd for $C_{19}H_{31}NO_5Si_2Te$ (M^+): 539.08019. Found: 539.08117. The product was further distilled by kugelrohr to give an isomeric mixture. ^1H NMR ($CDCl_3$): δ 0.26 (s, 18 H, CH_3), 3.15 (s, 3 H, ArO–CH_3), 3.65, (s, 1.5 H, $COOCH_3$ of *cis*-**17c**), 3.73 (s, 1.5 H, $COOCH_3$ of *trans*-**17c**), 3.76 (s, 1.5 H, $COOCH_3$ of *cis*-**17c**), 3.79 (s, 1.5 H, $COOCH_3$ of *trans*-**17c**), 6.70 (d, *J* = 8.53 Hz, Ar–H of *trans*-**17c**), 6.73 (d, *J* = 8.53 Hz, Ar–H of *cis*-**17c**), 7.58 (d, *J* = 8.53 Hz, Ar–H of *trans*-**17c**), 7.71 (d, *J* = 8.53 Hz, *cis*-**17c**). the stereochemistry of the product obtained by silica gel column purification was identified by the NOE experiment: the irradiation of the Me_3Si of **17c** at δ 0.26 enhanced the intensity of Ar–H by 30% at δ 7.71, whereas no effect was observed for that at δ 7.58.

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