Reaction of tetraorganyltelluriums with acetylenes

Li Biao Han, Nobuaki Kambe, Akiya Ogawa, Ilhyong Ryu, and Noboru Sonoda

Organometallics, **1993**, 12 (2), 473-477• DOI: 10.1021/om00026a034 • Publication Date (Web): 01 May 2002

Reaction of Tetraorganyltelluriums with Acetylenes

Li-Biao Han, Nobuaki Kambe,* Akiya Ogawa, Ilhyong Ryu, and Noboru Sonoda*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

Received September 25, 1992

Tetraalkyltelluriums (R_4Te) react with arylacetylenes (ArC≡CH; Ar = Ph, *p*-$MeOC_6H_4$, *p*-FC_6H_4) to afford alkylation products (ArHC=CHR). The alkylation proceeds preferentially in net trans fashion to give a cis-1,2-disubstituted olefin as the major product along with the concomitant formation of a telluride (R_2Te) and an alkene originated from a substituent of R_4Te which plays as a hydrogen source. The reaction of dibutyldidecyltellurium ($^nBu_2Te^nDec_2$) with phenylacetylene yields nearly statistical ratios of products, PhCH=CH^{n}Bu (41%, *E*/*Z* = 10/90), PhCH=CH^{n}Dec (35%, *E*/*Z* = 11/89), $^nBu_2Te$ (20%), ^{n}BuTe^{n}Dec (41%), and $^nDec_2Te$ (18%), indicating a random transfer of primary alkyl substituents. On the contrary, $^nBu_2Te^iPr_2$ reacts with phenylacetylene much faster than $^nBu_4Te$ affording only PhCH=CH^{i}Pr. Under similar conditions Ph_4Te does not react with phenylacetylene and $^nDec_2TePh_2$ decomposes quickly to ^{n}DecTePh (95%), 1-decene (93%), and benzene (99%). The alkylation is proposed to proceed by the radical addition of R_4Te to ArC≡CH to yield (R_3Te)ArC=CHR, which then decomposes to afford an olefin via a β-hydrogen transfer from R on tellurium to the vinyl carbon.

Introduction

Tellurium tetrachloride and organyltellurium halides ($R_{4-n}TeX_n$, $n \leq 4$) afford tetraorganyltelluriums **1** upon treating with a stoichiometric amount of organolithiums or Grignard reagents (eq 1).[1] This reaction provides the most general and the simplest approach to the synthesis of **1**, and several aryl- and alkyl-substituted tetraorganyltellurium compounds have been prepared in this way.[1,2] Tetraorganyltelluriums, thus formed, are expected to possess potentially unique reactivities resulting from the hypervalency of tellurium. Nonetheless, in contrast to the remarkable advances on the chemistry of divalent organotellurium compounds,[1,3] very limited works have been performed on the reaction of tetraorganyltelluriums, partly due to their susceptibility toward air and moisture. Tetraaryltelluriums and tetravinyltelluriums are relatively more stable than tetraalkyltelluriums and, for example, the crystal structure of Ph_4Te has been determined.[2i] As for the tetraalkyltelluriums, only Me_4Te and $(Me_3SiCH_2)_4Te$ have been fully characterized.[2a,d]

$$R_{4-n}TeX_n + n\,RM \longrightarrow R_4Te \quad (1)$$

M = Li or MgX

1

Our research interest has thus focused on the chemical behavior of tetraorganyltelluriums toward a variety of organic compounds. In connection with our recent study on a free-radical carbotelluration of acetylenes with diorganyl tellurides,[4a,b] we have found that the reaction of tetraalkyltelluriums with arylacetylenes leads to regioselective alkylation to give 1,2-disubstituted olefins. Herein we report the details of this reaction.

Results and Discussion

Tetrabutyltellurium (**1a**) was prepared by the reaction of $TeCl_4$ with 4 equiv of ^{n}BuLi in diethyl ether at 0 °C[5] and was allowed to react with 1 equiv of phenylacetylene at room temperature for 8 h. Usual workup followed by separation on a preparative HPLC afforded 1-hexenylbenzene (**2a**, 60%, *E*/*Z* = 8/92) and $^nBu_2Te$ (89%) along with a trace amount of Ph(^{n}BuTe)C=CH^{n}Bu (**3a**, 2%, *E*/*Z* = 51/49). In order to eliminate the effect of LiCl, we examined the reaction of isolated $^nBu_4Te$ with phenylacetylene in a sealed NMR tube using C_6D_6 as a solvent. The ^{1}H NMR measurement revealed the formation of **2a** (66%, *E*/*Z* = 13/87), $^nBu_2Te$ (97%), and 1-butene (61%), which was identical to the result obtained by the reaction using in situ generated $^nBu_4Te$ mentioned above. The formation of 1-butene suggested that one of the ^{n}Bu group on $^nBu_4Te$ acts as a hydrogen source, and the reaction would be presented by eq 2.

In Table I are summarized the results obtained by the reaction of in situ generated $^nBu_4Te$ with some arylacetylenes under various conditions. The reaction of $TeCl_4$ with ^{n}BuLi is a rapid process, and $^nBu_4Te$ has been

(1) Irgolic, K. J. *The Organic Chemistry of Tellurium*; Gorden and Breach Science: New York, 1974.

(2) (a) Gedridge, R. W., Jr.; Higa, K. T.; Nissan, R. A. *Organometallics* **1991**, *10*, 286. (b) Srivastava, P. C.; Trivedi, A. *Indian J. Chem., Sect. A* **1989**, *28A*, 1110. (c) Khandelwal, B. L. *Proc. Indian Natl. Sci. Acad., Part A* **1989**, *55*, 318. (d) Gedridge, R. W., Jr.; Harris, D. C.; Higa, K. T.; Nissan, R. A. *Organometallics* **1989**, *8*, 2817. (e) Jones, C. H. W.; Sharma, R. D. *J. Organomet. Chem.* **1987**, *332*, 115. (f) Khandelwal, B. L.; Singh, A. K.; Bhandari, N. S. *J. Organomet. Chem.* **1987**, *320*, 283. (g) Alam, K.; Janzen, A. F. *J. Fluorine Chem.* **1985**, *27*, 467. (h) Naumann, D.; Wilkes, B. *J. Fluorine Chem.* **1985**, *27*, 115. (i) Smith, C. S.; Lee, J. S.; Titus, D. D.; Ziolo, R. F. *Organometallics* **1982**, *1*, 350. (j) Glover, S. A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1338. (k) Srivastava, T. N.; Srivastava, R. C.; Singh, H. B. *Indian J. Chem., Sect. A* **1979**, *18A*, 71. (l) Barton, D. H. R.; Glover, S. A.; Ley, S. V. *J. Chem. Soc., Chem. Commun.* **1977**, 266.

(3) For recent reviews on organotellurium chemistry, see: (a) Petragnani, N.; Comasseto, J. V. *Synthesis* **1991**, 793 and 897. (b) Petragnani, N.; Comasseto, J. V. *Rev. Heteroat. Chem.* **1990**, *2*, 40. (c) Engman, L. *Phosphorus Sulfur* **1988**, *38*, 105. (d) Petragnani, N.; Comasseto, J. V. *Synthesis* **1986**, 1. (e) Engman, L. *Acc. Chem. Res.* **1985**, *18*, 274.

(4) (a) Han, L.-B.; Ishihara, K.-I.; Kambe, N.; Ogawa, A.; Ryu, I.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, *114*, 7591. (b) Han, L.-B.; Ishihara, K.-I.; Kambe, N.; Ogawa, A.; Sonoda, N. *Phosphorus, Sulfur Silicon* **1992**, *67*, 243. For our previous work on the chemistry of diorganyl tellurides, see: (c) Hiiro, T.; Morita, Y.; Inoue, T.; Kambe, N.; Ogawa, A.; Ryu, I.; Sonoda, N. *J. Am. Chem. Soc.* **1990**, *112*, 455. (d) Hiiro, T.; Atarashi, Y.; Kambe, N.; Fujiwara, S.; Ogawa, A.; Ryu, I.; Sonoda, N. *Organometallics* **1990**, *9*, 1355. (e) Hiiro, T.; Kambe, N.; Ogawa, A.; Miyoshi, N.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1187.

(5) No degradation of $^nBu_4Te$ in C_6D_6 was observed by ^{1}H NMR at 0 °C within 4 h, but it gradually decomposed at 25 °C and only 30% of the $^nBu_4Te$ remained after 20 h (62% of $^nBu_2Te$ was detected).

0276-7333/93/2312-0473$04.00/0

Table I. Reaction of ^{n}Bu$_4$Te with Arylacetylenes

$$TeCl_4 \xrightarrow[\text{conditions A}]{^n\text{BuLi (4 eq.)}} {}^n\text{Bu}_4\text{Te} \xrightarrow[\text{conditions B}]{\text{ArC}\equiv\text{CH}} \text{Ar}\!\!\diagup\!\!=\!\!\diagdown{}^n\text{Bu} + {}^n\text{Bu}_2\text{Te}$$

1a

run	conditions A	ArC≡CH (equiv)	conditions B	% yields (E/Z)[a] olefin	% yields (E/Z)[a] ^{n}Bu$_2$Te
1	THF, 0 °C, 0.5 h	PhC≡CH (1)	25 °C, 1 h	**2a**: 16 (17/83)	91
2			8 h	38 (11/89)	90
3			20 h	39 (11/89)	94
4			40 °C, 1 h	30 (10/90)	85
5		(2)		70 (13/87)	87
6		(5)		98 (9/91)	86
7	THF, −78 °C, 0.5 h	(1)	25 °C, 8 h	32 (11/89)	86
8	C_6H_6, 5 °C, 0.5 h	(1)	25 °C, 8 h	63 (11/89)	91
9			40 °C, 1 h	54 (11/89)	89
10	Et_2O, 0 °C, 0.5 h		25 °C, 1 h	16 (14/86)	95
11			8 h	62 (8/92)	93
12			20 h	62 (8/92)	92
13			reflux, 1 h	61 (11/89)	90
14		(2)		92 (12/88)	89
15		p-MeOC$_6$H$_4$C≡CH (1)		**2b**: 50[b] (6/94)	93
16		p-FC$_6$H$_4$C≡CH (1)		**2c**: 80[b] (9/91)	91

[a] Determined by GC. [b] Isolated yield as a mixture of E and Z isomers.

$$^n\text{Bu}_4\text{Te} + \text{PhC}\equiv\text{CH} \longrightarrow$$

1a

$$\text{Ph}\!\!\diagup\!\!=\!\!\diagdown{}^n\text{Bu} + {}^n\text{Bu}_2\text{Te} + \diagup\!\!=\!\!\diagdown \quad (2)$$

2a

prepared only at −70 °C or below in Et_2O.[2a,6] We found that it could be generated more conveniently at 0–5 °C in a solvent such as Et_2O, THF, and benzene and that the temperature of this stage does not affect the yields of the products (runs 2 and 7). On the other hand, the reaction of ^{n}Bu$_4$Te with phenylacetylene was accelerated by raising the temperature. For example, the reaction was complete within 1 h in refluxing ether (run 13), while it required 8 h at 25 °C (run 11). When an excess amount of phenylacetylene was used, the yield of **2a** was significantly improved (runs 5, 6, and 14). This may be explained by the fact that the alkylation competes with the self-degradation of ^{n}Bu$_4$Te to ^{n}Bu$_2$Te, butane, butene, and octane.[7] Benzene and diethyl ether are more suitable solvents than THF. In any runs in Table I, ^{n}Bu$_2$Te was detected in very good yields by GC, even when **2a** was formed in poor yields. This may be due to the thermal decomposition product of ^{n}Bu$_4$Te remaining unreacted to give ^{n}Bu$_2$Te on GC analysis. The fact that the yield of **2a** was not improved in THF even when the reaction time was prolonged (runs 2 and 3) may suggest that the degradation of ^{n}Bu$_4$Te proceeds relatively faster in THF than in Et_2O or benzene.

Arylacetylenes having either an electron-donating (MeO) or an electron-withdrawing substituent (F) on the benzene ring reacted with **1a** in a similar manner to afford corresponding alkylation products in good yields. However, alkyl-substituted acetylenes such as 1-octyne did not react with **1a** at all. The reaction of tetradecyltellurium (^{n}Dec$_4$Te, **1b**) with 2 equiv of phenylacetylene in refluxing Et_2O afforded PhCH=CH^{n}Dec (**2d**, 86%, E/Z = 14/86), ^{n}Dec$_2$Te (92%), and 1-decene (91%).

(6) Hellwinkel, D.; Fahrbach, G. *Chem. Ber.* **1968**, *101*, 574.

(7) Formation of 1-butene has not been confirmed in the pyrolysis of ^{n}Bu$_4$Te reported in ref 6. But we believe it should be formed as suggested by the following reaction: ^{n}Dec$_4$Te (1.0 mmol), generated by the reaction of ^{n}DecLi with $TeCl_4$ in THF at 0 °C, gave a mixture of ^{n}Dec$_2$Te (0.891 mmol, 89%), eicosane (0.408 mmol, 41%), 1-decene (0.277 mmol, 28%), and 1-decane (0.455 mmol, 46%) on heating at 40 °C for 1 h.

Dibutyldidecyltellurium (**1c**), generated in situ by the reaction of ^{n}Dec$_2$TeCl$_2$ with 2 equiv of ^{n}BuLi, reacted with phenylacetylene to afford PhCH=CH^{n}Bu (**2a**), PhCH=CH^{n}Dec (**2d**), and three kinds of tellurides, as shown in eq 3. The facts that almost equimolar amounts of **2a** and

$$^n\text{Dec}_2\text{TeCl}_2 \xrightarrow[\text{Et}_2\text{O, 0 °C, 0.5 h}]{^n\text{BuLi (2.0 eq.)}} {}^n\text{Dec}_2\text{Te}^n\text{Bu}_2 \xrightarrow[\text{reflux, 1 h}]{\text{PhC}\equiv\text{CH (2.0 eq.)}}$$

1c

$$\text{Ph}\!\!\diagup\!\!=\!\!\diagdown{}^n\text{Bu} + \text{Ph}\!\!\diagup\!\!=\!\!\diagdown{}^n\text{Dec} +$$

2a, 41% (E/Z = 10/90) **2d**, 35% (E/Z = 11/89)

$$^n\text{Bu}_2\text{Te} + {}^n\text{BuTe}^n\text{Dec} + {}^n\text{Dec}_2\text{Te} \quad (3)$$

20% 41% 18%

$$^i\text{Pr}_2\text{TeCl}_2 \xrightarrow[\text{Et}_2\text{O, -78 °C, 0.5 h}]{^n\text{BuLi (2.0 eq.)}} {}^i\text{Pr}_2\text{Te}^n\text{Bu}_2 \xrightarrow[\text{-78 °C~0 °C, 0.5 h}]{\text{PhC}\equiv\text{CH (2.0 eq.)}}$$

1d

$$\text{Ph}\!\!\diagup\!\!=\!\!\diagdown{}^i\text{Pr} + {}^n\text{Bu}_2\text{Te} +$$

2e, 35% (E/Z = 11/89) 57%

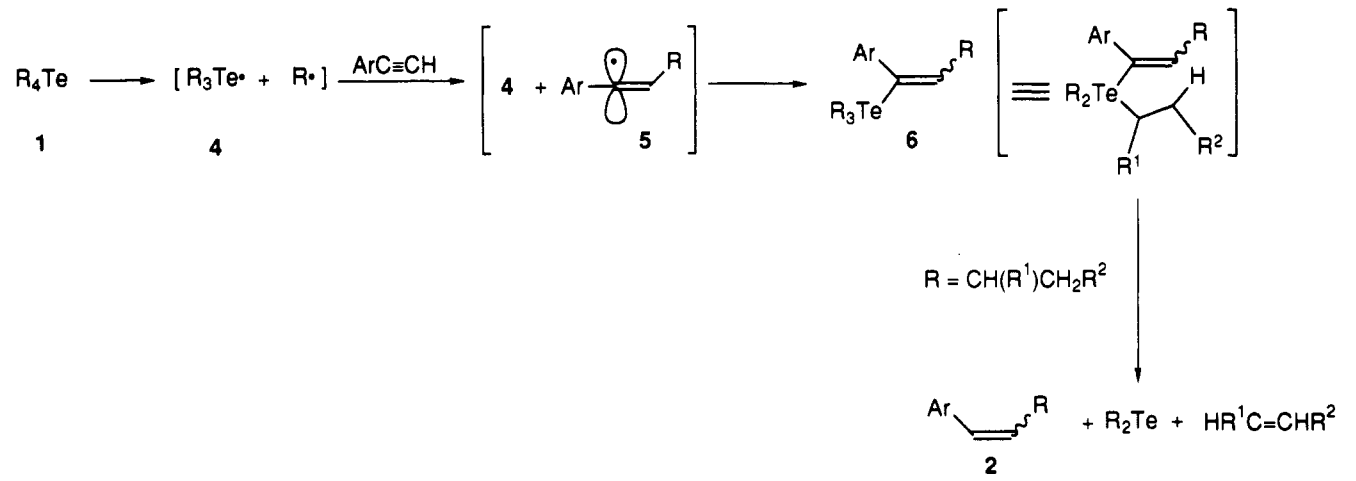
$$\text{Ph}(\text{}^n\text{BuTe})\text{C}=\text{CH}\,{}^n\text{Bu} + \text{Ph}(\text{}^n\text{BuTe})\text{C}=\text{CH}\,{}^i\text{Pr} \quad (4)$$

3a, 12% (E/Z = 47/53) **3b**, 32% (E/Z = 47/53)

2d were formed and that the ratio of ^{n}Bu$_2$Te/^{n}BuTe^{n}Dec/^{n}Dec$_2$Te was ca. 1/2/1 suggest that there is essentially no difference in reactivity between ^{n}Bu and ^{n}Dec in this reaction. In contrast to this random addition of primary alkyl groups in the reaction of **1c**, ^{i}Pr$_2$Te^{n}Bu$_2$ (**1d**), generated in situ from ^{i}Pr$_2$TeCl$_2$ and ^{n}BuLi at −78 °C,[8] transferred an ^{i}Pr group exclusively to afford only PhCH=CH^{i}Pr (**2e**) as a sole alkylation product. This reaction was quite rapid and was complete on raising the temperature from −78 to 0 °C in 30 min. A careful

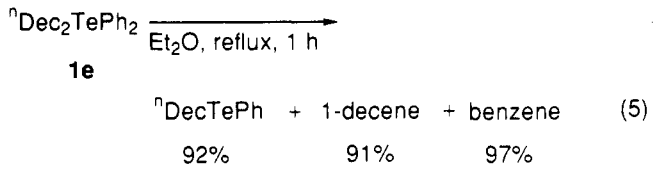
(8) Decomposition of **1d** is rapid at 0 °C, so it should be prepared at low temperatures.

Scheme I



examination of the resulting mixture by GC showed the presence of $^{n}Bu_2Te$ in 57% yield, but neither $^{n}BuTe^{i}Pr$ nor $^{i}Pr_2Te$ was detected. It should be noted that two other products, **3a** and **3b**, were formed in 12% and 32% yields, respectively, and this accounts for the low yield of **2e** (vide infra).

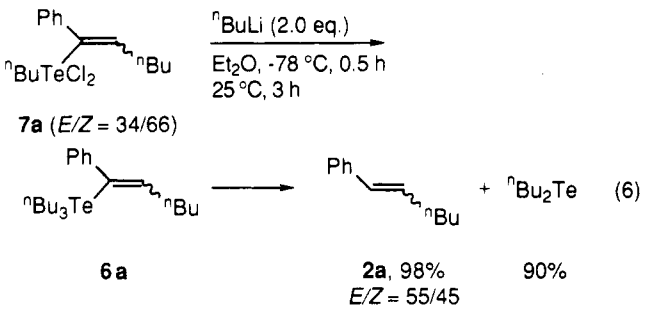
When a mixture of didecyldiphenyltellurium ($^{n}Dec_2TePh_2$, **1e**), generated from $^{n}Dec_2TeCl_2$ and PhLi, and phenylacetylene in Et_2O was refluxed for 1 h, phenylacetylene remained unreacted, resulting in the formation of ^{n}DecTePh, 1-decene, and benzene in 95%, 93%, and 99% yields, respectively.[9] A similar result was obtained in the absence of phenylacetylene, as shown in eq 5. The



(5)

stoichiometry of this reaction may indicate that the decomposition of **1e** involves the transfer of a hydrogen on a β-carbon of a ^{n}Dec group onto the vinyl carbon to which tellurium was attached.[10,11]

Although the reaction mechanism of the formation of **2** has not yet been confirmed in detail, a plausible pathway is shown in Scheme I. The intermediacy of **6**[12] was strongly supported by the evidence that tributylvinyltellurium (**6a**), generated from **7a** and ^{n}BuLi at −78 °C in Et_2O, afforded **2a** and $^{n}Bu_2Te$ almost quantitatively on standing at 25 °C for 3 h (eq 6), in which the $^{n}Bu_3Te$ moiety in **6a** was replaced with a hydrogen. Although no effort was made for the detection of butene in this experiment, the origin of the



(6)

hydrogen is likely to be the one on the β-carbon of ^{n}Bu of **6a**. This is supported by the reactions mentioned above (eqs 2 and 5), and the possibility of some other hydrogen sources could be excluded by the facts that a deuterated product PhCD=CH^{n}Bu (**2f**) was not formed when the reaction of $^{n}Bu_4Te$ with phenylacetylene was conducted in THF-d_8 or when the reaction was quenched with D_2O and that no deuterium was incorporated on the internal vinyl carbon of the product when PhC≡CD was used. Although the mechanism from **6a** to **2a** is still in question, it may not be a concerted mechanism since the *E*/*Z* ratio of **7a** was not fully retained in **2a**. A similar β-hydrogen transfer was observed in the thermolysis of $(CH_2{=}CH)_4Te$ at 75 °C to $(CH_2{=}CH)_2Te$, acetylene, and ethylene.[2a] As for the formation of the intermediate **6**, a radical addition mechanism of **1** to arylacetylenes initiated by the homolytic cleavage of a R_3Te—R bond was supported by the following evidence. In the reaction of $^{n}Bu_2Te^{i}Pr_2$ (**1d**) with phenylacetylene (eq 4), only an ^{i}Pr group transferred to give PhCH=CH^{i}Pr (**2e**) as a sole alkylation product. This can be explained by the selective bond scission on ^{i}Pr—Te$^{n}Bu_2{}^{i}$Pr rather than on ^{n}Bu—Te^{n}Bu$^{i}Pr_2$ due to the difference of thermodynamic stability between ^{i}Pr• and ^{n}Bu•. Secondly, the yields of the alkylation products **2**, which may reflect the rate of their formation since the reaction competes with a self-degradation of **1**, increased as the electron density of the arylacetylene decreased. This is in accord with the nucleophilic nature of the alkyl radicals.[13] Thirdly, the generation of the methyl radical was confirmed in the thermolysis of tetramethyltellurium.[2d] Fourthly, the reaction of **1d** with phenylacetylene afforded alkenyl tellurides (**3a** and **3b**) as the byproducts. It is likely that **3a** is formed by the carbotelluration reaction of pheny-

(9) An attempt for the preparation of dialkyldiphenyltellurium by the reaction of Ph_2TeCl_2 with RLi resulted in somewhat complex results. For example, when Ph_2TeCl_2 was allowed to react with 2 equiv of ^{n}BuLi at −78 °C in Et_2O and the resulting mixture was warmed and refluxed for 1 h, ^{n}BuTePh was formed in 70% yield along with $^{n}Bu_2Te$ (22%) and Ph_2Te (12%). These symmetrical tellurides arose probably from the decomposition of $^{n}Bu_3TePh$ (and partly $^{n}Bu_4Te$) and $^{n}BuTePh_3$ (and partly Ph_4Te), respectively, which would be formed by the disproportionation of tetravalent telluriums via exchange reactions as exemplified by $^{n}Bu_2TePh_2 + {}^{n}BuLi \rightarrow {}^{n}Bu_3TePh + PhLi$.[6]

(10) Under similar conditions, 2,2′-biphenylylenedimethyltellurium has been reported to decompose in a different manner to give bis(2,2′-biphenylylene)tellurium.[6]

(11) It is reported that the thermal decomposition of tetravinyltellurium proceeds in a similar manner to give divinyl telluride, acetylene, and ethylene, and the process was called a noncoupling reductive elimination.[2a]

(12) A direct abstraction of a β-hydrogen of **4** by **5** might not yet be ruled out.

(13) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 969.

lacetylene with in situ generated $^nBu_2Te$, which takes place only in the presence of a radical source.[4a,b,14] Finally, the preferred formation of *cis*-**2** is explained by assuming that a vinyl radical, **5**, which has a π-radical structure,[13] reacts with **4** to give the trans form of **6** as the major isomer due to the steric repulsion between the R and R_3Te moieties, which then produces *cis*-**2** predominantly with retention of the stereochemistry (see eq 6).

Experimental Section

General Procedures. All reactions were carried out under Ar atmosphere. Tetrahydrofuran (THF) and Et_2O were distilled under N_2 from sodium/benzophenone, and benzene was distilled from CaH_2. Phenylacetylene was purchased from Aldrich Chemical Co. and distilled under a reduced pressure prior to use. *p*-MeO- and *p*-F-phenylacetylenes were prepared according to the literature.[15] Diorganyl tellurides and diorganyltellurium dichlorides were synthesized by the reported procedures.[1] ^{n}BuLi and PhLi were purchased from Kanto Chemical Co., Japan. ^{n}DecLi was prepared from Li and ^{n}DecCl according to the literature[16] and was titrated using $(PhTe)_2$.[17]

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM270-GSX spectrometer operating at 270 and 68 MHz, respectively, using Me_4Si as an internal standard. IR spectrum were obtained with a Perkin-Elmer Model 1600 spectrometer. GC–mass spectra were obtained with a Shimazu GC-MS-QP2000 or a JEOL JMS-DX303. GC analyses were performed with a Shimazu GC-8A instrument fitted with a flame ionization detector using a capillary column (Hicap-CBP1-S25-050). GC yields of the products were obtained by using the response factors of the standard samples. HPLC separations were performed on a recycling preparative HPLC (Japan Analytical Industry Co. Ltd., Model LC-908), equipped with JAIGEL-1H and -2H columns (GPC) using $CHCl_3$ as an eluent.

Reaction of $^nBu_4Te$ with Phenylacetylene (Typical Procedure for the Reaction of R_4Te with Acetylenes). To a stirred suspension of $TeCl_4$ (323 mg, 1.2 mmol) in 6 mL of Et_2O at 0 °C was added ^{n}BuLi (4.8 mmol, 3.1 mL, 1.58 M in hexane) dropwise. The suspension turned brown initially and then yellowish orange as the addition came to completion. The mixture was stirred for 0.5 h at 0 °C and phenylacetylene (123 mg, 1.2 mmol) was added to it. The mixture was then warmed to room temperature and stirred until no more increase of **2a** was observed by GC (8 h). GC analysis of the mixture using dodecane as an internal standard showed that $^nBu_2Te$, **2a**, and **3a** were formed in 93%, 62% (*E*/*Z* = 8/92), and 4% (*E*/*Z* = 50/50) yields, respectively. The reaction mixture was then poured into water (5 mL), and the products were extracted with ether (20 mL × 2) and dried over $MgSO_4$. After removal of the solvent under a reduced pressure, a yellow oil was obtained. By separation on a recycling preparative HPLC, $^nBu_2Te$, **2a**, and **3a** were obtained in 89% (258 mg, 1.07 mmol), 60% (115 mg, 0.72 mmol, *E*/*Z* = 8/92), and 2% (8.3 mg, 0.02 mmol, *E*/*Z* = 51/49) yields, respectively. The *E*/*Z* ratio was determined by GC. Spectral and analytical data of products **2** and **3** are listed below.

1-Hexenylbenzene (2a):[18] 60% (115 mg, 0.72 mmol, *E*/*Z* = 8/92). IR (neat): 3019, 2950, 2939, 2846, 1587, 1489, 1460, 1442, 1067, 755, 687 cm^{-1}. *E* isomer: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.14–7.34 (m, 5 H), 6.37 (d, 1 H, *J* = 15.9 Hz), 6.22 (dt, 1 H, *J* = 6.7, 15.9 Hz), 2.20 (dt, 2 H, *J* = 6.7, 7.0 Hz), 1.26–1.51 (m, 4 H), 0.90 (t, 3 H, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 137.99, 131.19, 129.73, 128.46, 126.74, 125.91, 32.72, 31.55, 22.28, 13.95; GC–MS (EI) *m*/*e* (relative intensity) 160 (M^+, 29), 118 (14), 117 (100), 115 (42), 104 (64), 91 (34), 51 (11). *Z* isomer: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.20–7.34 (m, 5 H), 6.40 (d, 1 H, *J* = 11.6 Hz), 5.66 (dt, 1 H, *J* = 7.8, 11.6 Hz), 2.32 (dt, 2 H, *J* = 7.0, 7.8 Hz), 1.33–1.45 (m, 4 H), 0.89 (t, 3 H, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 137.87, 133.21, 128.76, 128.73, 128.09, 126.40, 32.18, 28.36, 22.43, 13.96; GC–MS (EI) *m*/*e* (relative intensity) 160 (M^+, 36), 118 (17), 117 (100), 115 (50), 104 (78), 91 (39), 51 (11).

1-(1-Hexenyl)-4-methoxybenzene (2b): 50% (98 mg, 0.52 mmol, *E*/*Z* = 6/94). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 82.23; H, 9.23. IR (neat): 3010, 2958, 1610, 1512, 1246, 1174, 1069, 837 cm^{-1}. *E* isomer:[19] ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.25 (d, 2 H, *J* = 8.8 Hz), 6.80 (d, 2 H, *J* = 8.8 Hz), 6.32 (d, 1 H, *J* = 15.6 Hz), 6.08 (dt, 1 H, *J* = 6.8, 15.6 Hz), 3.79 (s, 3 H), 2.18 (dt, 2 H, *J* = 6.8, 7.2 Hz), 1.20–1.46 (m, 4 H), 0.90 (t, 3 H, *J* = 6.8 Hz); GC–MS (EI) *m*/*e* (relative intensity) 190 (M^+, 46), 147 (100), 134 (10), 91 (16); HRMS for $C_{13}H_{18}O$ calcd 190.1358, found 190.1341. *Z* isomer: ^{1}H NMR $CDCl_3$, 270 MHz) δ 7.21 (d, 2 H, *J* = 8.8 Hz), 6.85 (d, 2 H, *J* = 8.8 Hz), 6.35 (d, 1 H, *J* = 11.2 Hz), 5.56 (dt, 1 H, *J* = 7.3, 11.2 Hz), 3.80 (s, 3 H), 2.31 (ddt, 2 H, *J* = 2.0, 7.0, 7.3 Hz), 1.25–1.48 (m, 4 H), 0.89 (t, 3 H, *J* = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 158.15, 131.65, 130.55, 129.93, 128.09, 113.53, 55.22, 32.24, 28.38, 22.46, 13.98; GC–MS (EI) *m*/*e* (relative intensity) 190 (M^+, 39), 147 (100), 134 (12), 91 (23); HRMS for $C_{13}H_{18}O$ calcd 190.1358, found 190.1353.

1-Fluoro-4-(1-hexenyl)benzene (2c): 80% (124 mg, 0.70 mmol, *E*/*Z* = 9/91). Anal. Calcd for $C_{12}H_{15}F$: C, 80.86; H, 8.48. Found: C, 80.82; H, 8.53. IR (neat): 3010, 2958, 1603, 1509, 1398, 1225, 1157, 1093, 966, 841, 743, 615 cm^{-1}. The stereochemistry was determined by the coupling constants of vinyl protons. *E* isomer: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.28–7.31 (m, 2 H), 6.93–6.97 (m, 2 H), 6.31 (d, 1 H, *J* = 15.6 Hz), 6.13 (dt, 1 H, *J* = 6.8, 15.6 Hz), 2.18 (dt, 2 H, *J* = 6.8, 7.3 Hz), 1.27–1.42 (m, 4 H), 0.91 (t, 3 H, *J* = 7.8 Hz); GC–MS (EI) *m*/*e* (relative intensity) 178 (M^+, 28), 136 (12), 135 (100), 122 (57), 109 (26); HRMS for $C_{12}H_{15}F$ calcd 178.1158, found 178.1165. *Z* isomer: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.21 (dd, 2 H, *J* = 5.4, 8.3 Hz), 7.00 (t, 2 H, *J* = 8.3 Hz), 6.34 (d, 1 H, *J* = 11.2 Hz), 5.64 (dt, 1 H, *J* = 7.3, 11.2 Hz), 2.29 (ddt, 2 H, *J* = 1.5, 6.8, 7.3 Hz), 1.33–1.48 (m, 4 H), 0.89 (t, 3 H, *J* = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 161.42 ($^1J_{C-F}$ = 245 Hz), 133.10, 130.95, 130.31 ($^3J_{C-F}$ = 7.3 Hz), 127.60, 114.80 ($^2J_{C-F}$ = 20.8 Hz), 32.09, 28.22, 22.40, 13.95; GC–MS (EI) *m*/*e* (relative intensity) 178 (M^+, 24), 136 (13), 135 (100), 122 (60), 109 (33); HRMS for $C_{12}H_{15}F$ calcd 178.1158, found 178.1145.

1-Dodecenylbenzene (2d):[20] 86% (195 mg, 0.80 mmol, *E*/*Z* = 14/86). IR (neat): 2924, 2853, 1598, 1493, 1466, 744, 698 cm^{-1}. *E* isomer: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.18–7.35 (m, 5 H), 6.37 (d, 1 H, *J* = 14.2 Hz), 6.23 (dt, 1 H, *J* = 6.8, 14.2 Hz), 2.19 (dt, 2 H, *J* = 6.8, 7.2 Hz), 1.25–1.44 (m, 16 H), 0.88 (t, 3 H, *J* = 6.8 Hz); GC–MS (EI) *m*/*e* (relative intensity) 244 (M^+, 11), 117 (49), 105 (10), 104 (100), 91 (16); HRMS for $C_{18}H_{28}$ calcd 244.2191, found 244.2180. *Z* isomer: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.22–7.40 (m, 5 H), 6.40 (d, 1 H, *J* = 11.7 Hz), 5.66 (dt, 1 H, *J* = 7.4, 11.7 Hz), 2.32 (ddt, 2 H, *J* = 1.5, 6.8, 7.4 Hz), 1.25–1.45 (m, 16 H), 0.88 (t, 3 H, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 137.84, 133.30, 128.75, 128.66, 128.08, 126.38, 31.92, 29.99, 29.61, 29.52, 29.37, 28.65, 22.69, 14.12; GC–MS (EI) *m*/*e* (relative intensity) 244 (M^+, 10), 117 (44), 105 (11), 104 (100), 91 (18); HRMS for $C_{18}H_{28}$ calcd 244.2191, found 244.2181.

3-Methyl-1-phenyl-1-butene (2e):[21] 32% (52 mg, 0.36 mmol, *E*/*Z* = 16/84). IR (neat): 3025, 2960, 2866, 1651, 1598, 1493, 1464, 1448, 1362, 966, 746, 692 cm^{-1}. *E* isomer: ^{1}H NMR ($CDCl_3$,

(14) The formation of **3b** might also be explained by the carbotelluration of phenylacetylene with ^{n}BuTe^{i}Pr which proceeds by a radical chain mechanism, but it would more likely be formed by the S_H2 reaction of $^nBu_2Te$ with **5** (Ar = Ph, R = ^{i}Pr), since it was confirmed that the carbotelluration of phenylacetylene with ^{n}BuTe^{i}Pr afforded not only **3b** but also **3a**, **3c** (Ph(^{i}PrTe)C=CH^{n}Bu), and **3d** (Ph(^{i}PrTe)C=CH^{i}Pr); the last two were not detected, however, in the reaction of **1d** with phenylacetylene (eq 4).

(15) Chatani, N.; Takeyasu, T.; Horiuchi, N.; Hanafusa, T. *J. Org. Chem.* **1988**, *53*, 3539.

(16) Bryce, S. D.; Turner, E. E. *J. Chem. Soc.* **1953**, 861.

(17) Aso, Y.; Yamashita, H.; Otsubo, T.; Ogura, F. *J. Org. Chem.* **1989**, *54*, 5627.

(18) Brown, H. C.; Basavaiah, D.; Kulkarni, S. U.; Bhat, N. G.; Prasad, J. V. N. V. *J. Org. Chem.* **1988**, *53*, 239.

(19) Negishi, E.-i.; Takahashi, T.; Baba, S.; Horn, D. E. V.; Okukado, N. *J. Am. Chem. Soc.* **1987**, *109*, 2393.

(20) Branchaud, B. P.; Choi, Y. L. *Tetrahedron Lett.* **1988**, *29*, 6037.

(21) Buss, A. D.; Warren, S. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2307.

270 MHz) δ 7.15–7.37 (m, 5 H), 6.34 (d, 1 H, J = 16.1 Hz), 6.19 (dd, 1 H, J = 6.8, 16.1 Hz), 2.40–2.56 (m, 1 H), 1.09 (d, 6 H, J = 6.8 Hz); ^{13}C NMR $CDCl_3$, 68 MHz) δ 138.00, 137.96, 128.45, 126.86, 126.74, 125.96, 31.51, 22.44; GC–MS (EI) m/e (relative intensity) 146 (M^+, 48), 131 (100), 91 (36). Z isomer: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.14–7.37 (m, 5 H), 6.30 (d, 1 H, J = 11.7 Hz), 5.47 (dd, 1 H, J = 10.3, 11.7 Hz), 2.83–2.97 (m, 1 H), 1.04 (d, 6 H, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 140.5, 137.91, 128.63, 128.14, 126.41, 126.38, 27.12, 23.18; GC–MS (EI) m/e (relative intensity) 146 (M^+, 50), 131 (100), 91 (40).

1-Phenyl-1-(butyltelluro)-1-hexane (3a): E/Z = 51/49. Anal. Calcd for $C_{16}H_{24}Te$: C, 55.87; H. 7.03. Found: C, 55.99; H, 7.12. IR (neat): 2957, 2925, 1595, 1486, 1463, 1182, 755, 697 cm^{-1}. The NMR assignment of E and Z isomers was determined by comparing the spectra of their mixture with those of the pure Z form obtained by carbotelluration of phenylacetylene with ^{n}Bu$_2$Te, and the details will be presented in due course.[4a] E isomer: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.19–7.29 (m, 5 H), 6.24 (t, 1 H, J = 7.3 Hz), 2.49 (t, 2 H, J = 7.4 Hz), 2.01 (dt, 2 H, J = 7.3, 7.4 Hz), 1.12–1.73 (m, 8 H), 0.82 (t, 3 H, J = 7.4 Hz), 0.83 (t, 3 H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 142.24, 142.02, 128.73, 128.03, 126.64, 113.92, 33.86, 31.81, 31.12, 25.09, 22.16, 13.87, 13.37, 7.71; GC–MS (EI) m/e (relative intensity) 346 (M^+, 17), 117 (100), 91 (95). Z isomer: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.38–7.41 (m, 2 H), 7.16–7.30 (m, 3 H), 5.85 (t, 1 H, J = 7.1 Hz), 2.25–2.46 (m, 4 H), 1.13–1.99 (m, 8 H), 0.93 (t, 3 H, J = 7.1 Hz), 0.76 (t, 3 H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 144.14, 140.56, 128.82, 128.04, 126.82, 120.70, 36.57, 33.93, 31.46, 24.89, 22.39, 14.06, 13.27, 7.23; GC-MS (EI) m/e (relative intensity) 346 (M^+, 16), 117 (100), 91 (90). NOE experiment for the Z isomer: irradiation on the signals at δ 7.38–7.41 (o-Ph) resulted in a 9% enhancement of the vinyl triplet at δ 5.85.

3-Methyl-1-phenyl-1-(butyltelluro)-1-butene (3b): 28% (103 mg, 0.31 mmol, E/Z = 46/54). Anal. Calcd for $C_{15}H_{22}Te$: C, 54.61; H, 6.72. Found: C, 54.08; H, 6.71. HRMS for $C_{15}H_{22}$-Te: calcd 332.0784; found 332.0790. IR (neat): 2957, 2925, 2865, 1594, 1488, 1463, 1182, 758, 700 cm^{-1}. E isomer: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.19–7.39 (m, 5 H), 6.04 (d, 1 H, J = 9.8 Hz), 2.49 (t, 2 H, J = 7.4 Hz), 2.31–2.42 (m, 1 H), 1.64 (quint, 2 H, J = 7.4 Hz), 1.26 (sext, 2 H, J = 7.4 Hz), 0.93 (d, 6 H, J = 6.4 Hz), 0.83 (t, 3 H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 148.78, 142.48, 128.49, 128.03, 126.63, 111.60, 33.77, 30.61, 25.07, 22.98, 13.37, 7.74; GC–MS (EI) m/e (relative intensity) 332 (M^+, 11), 145 (100), 129 (24), 117 (38), 91 (33). Z isomer: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.16–7.41 (m, 5 H), 5.67 (d, 1 H, J = 8.8 Hz), 2.64–2.77 (m, 1 H), 2.33 (t, 2 H, J = 7.4 Hz), 1.55 (quint, 2 H, J = 7.4 Hz), 1.21 (sext, 2 H, J = 7.4 Hz), 1.06 (d, 6 H, J = 6.3 Hz), 0.76 (t, 3 H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 147.51, 143.94, 128.86, 128.02, 126.82, 117.74, 36.43, 33.92, 24.86, 22.54, 13.28, 7.14; GC–MS (EI) m/e (relative intensity) 332 (M^+, 25), 145 (100), 129 (38), 117 (59), 91 (47).

Preparation of 7a and Its Reaction with ^{n}BuLi. To a benzene solution (10 mL) of phenylacetylene (1.02 g, 10 mmol) were added ^{n}Bu$_2$Te (2.42 g, 10 mmol) and AIBN (0.16 g, 1 mmol). The solution was refluxed for 5 h, the solvent was evaporated, and the residues were distilled by Kugelrohr distillation to give **3a** as a pale yellow oil, 2.17 g (6.3 mmol, E/Z = 34/66), 63%.

To a solution of **3a** (1.72 g, 5 mmol, E/Z = 34/66) in CH_2Cl_2 (10 mL) was added dropwise SO_2Cl_2 (0.68 g, 5 mmol) at 0 °C, and the solution was stirred for 0.5 h. The solvent was removed under a reduced pressure, and the residue was subjected to column chromatography (silica gel; eluent, CH_2Cl_2) to give **7a** as a colorless oil in 95% yield (1.97 g, 4.5 mmol, E/Z = 34/66). Anal. Calcd for $C_{16}H_{24}Cl_2Te$: C, 46.32; H, 5.83. Found: C, 46.75; H, 5.78. IR (neat): 2955, 2929, 2872, 1488, 1464, 1442, 1380, 1178, 761, 701 cm^{-1}. Mass (EI): m/e (relative intensity) 381 (M^+ – Cl, 15), 346 (M^+ – 2 Cl, 20), 222 (54), 194 (45), 159 (60), 117 (100), 91 (89), 81 (38), 57 (38). E isomer: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.39–7.45 (m, 5 H), 6.53 (t, 1 H, J = 7.3 Hz), 3.02 (t, 2 H, J = 7.3 Hz), 2.12 (q, 2 H, J = 7.3 Hz), 2.02 (q, 2 H, J = 7.3 Hz), 1.27–1.48 (m, 6 H), 0.89 (t, 3 H, J = 7.3 Hz), 0.84 (t, 3 H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 147.31, 137.03, 134.40, 129.42, 129.46, 128.49, 52.09, 30.74, 30.53, 26.67, 24.57, 22.08, 13.81, 13.48. Z isomer: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.39–7.47 (m, 5 H), 5.98 (t, 1 H, J = 7.3 Hz), 2.88 (t, 2 H, J = 7.3 Hz), 2.62 (q, 2 H, J = 7.3 Hz), 1.94 (q, 2 H, J = 7.3 Hz), 1.64 (quint, 2 H, J = 7.3 Hz), 1.27–1.55 (m, 4 H), 0.97 (t, 3 H, J = 7.3 Hz), 0.89 (t, 3 H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 142.69, 139.06, 137.15, 129.74, 129.59, 128.18, 49.75, 34.70, 30.74, 26.66, 24.45, 22.43, 13.89, 13.45.

To a solution of **7a** (415 mg, 1.0 mmol) containing an internal standard (dodecane) in 5 mL of Et_2O was added ^{n}BuLi (2.0 mmol, 1.3 mL, 1.58 M in hexane) dropwise at –78 °C. The solution was kept at –78 °C for 0.5 h and then warmed to 25 °C. Every 0.5 h, an aliquot portion of the solution was taken out by a syringe, quenched with water, and analyzed by GC. After 3 h at 25 °C, no more increase of the products was observed, showing the formation of ^{n}Bu$_2$Te and **2a** in 90% and 98% (E/Z = 55/45) yields, respectively.

^{1}H NMR Experiment of the Reaction of ^{n}Bu$_4$Te with Phenylacetylene. To a vigorously stirred suspension of $TeCl_4$ (2.7 g, 10 mmol) in 25 mL of Et_2O was added dropwise ^{n}BuLi (40 mmol, 25.3 mL, 1.58 M in hexane) at 0 °C. The suspension turned brown initially and then yellowish orange. It was stirred for 1 h at 0 °C, and the white precipitate was filtered off and washed with ether (20 mL × 2). The combined solution was concentrated under vacuum at 0 °C to give a yellowish orange oil. The ^{1}H and ^{13}C NMR analyses showed the formation of ^{n}Bu$_4$Te (**1a**) in pure form (2.8 g, 7.9 mmol, 79%) contaminated by less than 2% with ^{n}Bu$_2$Te. ^{1}H NMR (C_6D_6, 270 MHz): δ 1.59–1.70 (m, 16 H), 1.33–1.41 (m, 8 H), 0.91–0.96 (m, 12 H). ^{13}C NMR (C_6D_6, 68 MHz): δ 34.38, 30.31, 26.48, 14.06.

A solution of ^{n}Bu$_4$Te (80 mg) and phenylacetylene in 0.5 mL of C_6D_6 was kept at 25 °C in a sealed NMR tube under Ar, and the reaction was monitored by ^{1}H NMR using dioxane as an internal standard. Signals of ^{n}Bu$_4$Te gradually decreased and those of **2a**, 1-butene, and ^{n}Bu$_2$Te increased. The reaction was complete in 8 h.

Acknowledgment. This work was supported in part by a Grant in Aid for Scientific Research on Priority Areas (No. 04217101) from the Ministry of Education, Science, and Culture, Japan. Thanks are due to the Instrumental Analysis Center, Faculty of Engineering, Osaka University, for assistance in obtaining MS and elemental analyses.

OM920584G