Conversion of Tellurol Esters to Enol Silyl Ethers of Acylsilanes

Toru Inoue, Nobuaki Kambe,* Ilhyong Ryu, and Noboru Sonoda*

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

Received July 20, 1994[⊗]

Tellurol esters having an anion stabilizing group at the position α to the carbonyl, such as aryl-, (phenylthio)-, and (benzyloxy)ethanetelluroates, gave enol silyl ethers of the corresponding acylsilanes in good to excellent yields upon treatment with 2 equiv of ^{n}BuLi in the presence of chlorosilanes. This reaction was stereoselective, and *Z*-isomers were obtained as sole or major products from a variety of chlorosilanes, such as trimethyl-, triethyl-, dimethylphenyl-, and *tert*-butyldimethylsilyl chlorides. Control experiments revealed that the reaction comprises the following consecutive processes: (i) α-proton abstraction, (ii) chlorosilane-trapping, (iii) lithium–tellurium exchange, (iv) 1,2-silyl migration, and (v) chlorosilane-trapping. Intramolecular rearrangement of (α-siloxyvinyl)lithiums to lithium enolates (step iv) was very fast even at −105 °C, and the former could not be trapped intermolecularly either with acetic acid or with coexisting trimethylsilyl chloride.

Introduction

Acylsilanes are very useful synthetic intermediates.[1] They can be used, for example, as synthons or precursors of synthetically interesting umpolung species such as β-acyl carbanions[2] and acyl anions.[3] These synthetic applications are based on the unique affinity of silicon for oxide and fluoride anions. In addition, the steric bulkiness of silyl groups enables highly selective transformations such as stereoselective Wittig olefination,[4] synthesis of chiral alcohols by enantioselective reduction or nucleophilic addition,[5] and regioselective allylation or propargylation.[6] Enol silyl ethers of acylsilanes are also attractive compounds not only because they can easily be converted to acylsilanes by hydrolysis[7] or by the reaction with Cl_2,[8] Br_2,[8] PhSCl,[9] or acetals[10] but also because versatile reactivities arising from their unique substructures as enol silyl ethers and/or vinylsilanes can be anticipated.[11,12] Here, we disclose a new transformation of tellurol esters **1** to enol silyl ethers **3** of the corresponding acylsilanes **2** and discuss the mechanism. This reaction provides **3** in good yields with high stereoselectivities. Since **1** can be prepared conveniently by a one-pot reaction from acid halides, metallic tellurium, and butyllithium,[13] this procedure will become a useful addition to the known preparative methods for acylsilanes[14] and/or their enol silyl ethers.[15]

Results and Discussion

We have revealed that tellurol esters **1** react with organolithium reagents at low temperatures to give acyllithiums, which can be trapped with coexisting electrophiles. This reaction could be applied to the synthesis

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1994.

(1) Recent reviews of acylsilanes: Ricci, A.; Degl'Innocenti, A. *Synthesis* **1989**, 647. Page, P. C. B.; Klair, S. S.; Rosenthal, S. *Chem. Soc. Rev.* **1990**, *19*, 147. Cirillo, P. F.; Panek, J. S. *Org. Prep. Proc. Int.* **1992**, *24*, 553.

(2) (a) Kato, M.; Mori, A.; Oshino, H.; Enda, J.; Kobayashi, K.; Kuwajima, I. *J. Am. Chem. Soc.* **1984**, *106*, 1773. (b) Enda, J.; Kuwajima, I. *J. Am. Chem. Soc.* **1985**, *107*, 5495. (c) Reich, H. J.; Eisenhart, E. K.; Olson, R. E.; Kelly, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 7791. (d) Reich, H. J.; Holtan, R. C.; Bolm, C. *J. Am. Chem. Soc.* **1990**, *112*, 5609 and references cited therein.

(3) (a) Degl'Innocenti, A.; Pike, S.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1980**, 1201. (b) Schinzer, D.; Heathcock, C. H. *Tetrahedron Lett.* **1981**, *22*, 1881. (c) DePuy, C. H.; Bierbaum, V. M.; Damrauer, R.; Soderquist, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 3385.

(4) Soderquist, J. A.; Anderson, C. L. *Tetrahedron Lett.* **1988**, *29*, 2425.

(5) (a) Nakada, M.; Urano, Y.; Kobayashi, S.; Ohno, M. *J. Am. Chem. Soc.* **1988**, *110*, 4826. (b) Buynak, J. D.; Strickland, J. B.; Hurd, T.; Phan, A. *J. Chem. Soc., Chem. Commum.* **1989**, 89. (c) Cirillo, P. F.; Panek, J. S. *J. Org. Chem.* **1990**, *55*, 6071. See also: Schinzer, D. *Synthesis* **1989**, 179.

(6) (a) Yanagisawa, A.; Habaue, S.; Yamamoto, H. *J. Org. Chem.* **1989**, *54*, 5198. (b) Suzuki, M.; Morita, Y.; Noyori, R. *J. Org. Chem.* **1990**, *55*, 441. (c) Yanagisawa, A.; Habaue, S.; Yamamoto, H. *Tetrahedron* **1992**, *48*, 1969.

(7) (a) Kuwajima, I.; Arai, M.; Sato, T. *J. Am. Chem. Soc.* **1977**, *99*, 4181. (b) Chatani, N.; Ikeda, S.-i.; Ohe, K.; Murai, S. *J. Am. Chem. Soc.* **1992**, *114*, 9710.

(8) Sato, T.; Abe, T.; Kuwajima, I. *Tetrahedron Lett.* **1978**, 259.

(9) Minami, N.; Abe, T.; Kuwajima, I. *J. Organomet. Chem.* **1978**, *145*, C1.

(10) Sato, T.; Arai, M.; Kuwajima, I. *J. Am. Chem. Soc.* **1977**, *99*, 5827.

(11) (a) Ogoshi, S.; Ohe, K.; Chatani, N.; Kurosawa, H.; Kawasaki, Y.; Murai, S. *Organometallics* **1990**, *9*, 3021. (b) Ogoshi, S.; Ohe, K.; Chatani, N.; Kurosawa, H.; Murai, S. *Organometallics* **1991**, *10*, 3813.

(12) Reviews of organic synthesis using organosilicon compounds: Fleming, I.; Dunogués, J.; Smithers, R. *Org. React.* **1989**, *37*, 57. Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981. Weber W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: New York, 1983. Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988.

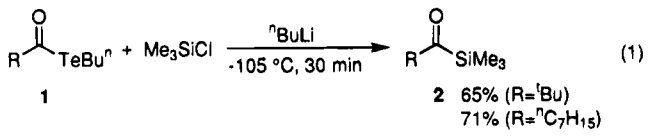
(13) Piette, J. L.; Debergh, D.; Baiwir, M.; Llabres, G. *Spectrochim. Acta, Part A* **1980**, *36A*, 769. For alternative preparative methods of tellurol esters, see: Inoue, T.; Takeda, T.; Kambe, N.; Ogawa, A.; Ryu, I.; Sonoda, N. *J. Org. Chem.* **1994**, *59*, 5824. Inoue, T.; Takeda, T.; Kambe, N.; Ogawa, A.; Ryu, I.; Sonoda, N. *Organometallics*, in press.

(14) (a) Nakada, M.; Nakamura, S.-i.; Kobayashi, S.; Ohno, M. *Tetrahedron Lett.* **1991**, *32*, 4929. (b) Yoshida, J.-i,; Matsunaga, S.-i.; Ishichi, Y.; Maekawa, T.; Isoe, S. *J. Org. Chem.* **1991**, *56*, 1307 and references cited therein.

(15) Generally synthesized by silylation of corresponding enolates generated by reduction of α,β-unsaturated carboxylic acid halides or esters with Mg or Li, respectively: (a) Dunogués, J.; Bolourtchian, M.; Calas, R.; Duffaut, N.; Picard, J.-P. *J. Organomet. Chem.* **1972**, *43*, 157. (b) Dunogués, J.; Ekouya, A.; Calas, R.; Picard. J.-P.; Duffaut, N. *J. Organomet. Chem.* **1974**, *66*, C39. By reductive lithiation of α-siloxyvinyl sulfides: (c) Kuwajima, I.; Kato, M.; Sato, T. *J. Chem. Soc., Chem. Commun.* **1978**, 478. (d) Kuwajima, I.; Mori, A.; Kato, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2634. By Li–Sn exchange of (α-siloxyvinyl)stannanes: (e) Verlhac, J.-B.; Kwon, H.; Pereyre, M. *J. Organomet. Chem.* **1992**, *437*, C13. By the reaction of silylmethyllithiums with CO: (f) Murai, S.; Ryu, I.; Iriguchi, J.; Sonoda, N. *J. Am. Chem. Soc.* **1984**, *106*, 2440. Alternative preparative methods include photolysis of acylsilanes: (g) Brook, A. G.; Duff, J. M. *Can. J. Chem.* **1973**, *51*, 352. Michael addition to propenoyltrimethylsilane: (h) Ricci, A.; Degl'Innocenti, A.; Borselli, G.; Reginato, G. *Tetrohedron Lett.* **1987**, *28*, 4093. Oxidation of 1,1-bis(trimethylsilyl)alkan-1-ols: ref 7a. Iridium-catalyzed carbonylation of alkenes: ref 7b.

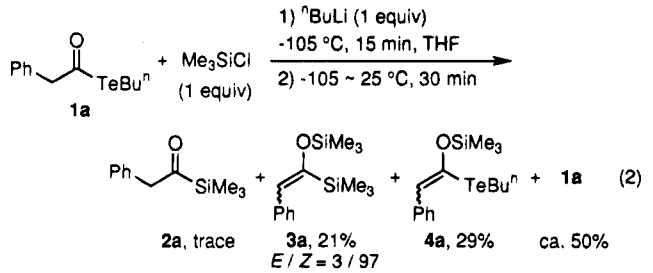
0022-3263/94/1959-8209$04.50/0 © 1994 American Chemical Society

of acylsilanes **2** from tellurol esters as shown by eq 1,[16,17] but some tellurol esters bearing acidic α-hydrogens gave

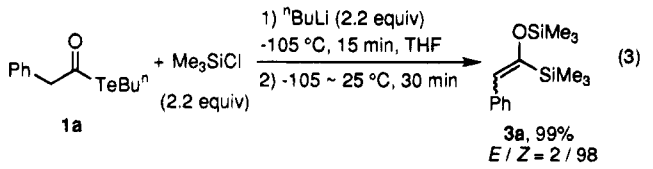


(1)

complex results under similar conditions. For example, reaction of *Te*-butyl phenylethanetelluroate (**1a**) with a stoichiometric amount of butyllithium in the presence of trimethylsilyl chloride afforded a mixture of (α-siloxyvinyl)silane **3a** (an enol silyl ether of the corresponding acylsilane **2a**) in 21% yield, α-siloxyvinyl telluride **4a** in 29% yield, and unchanged **1a** (ca. 50%) (eq 2). Interest-



(2)



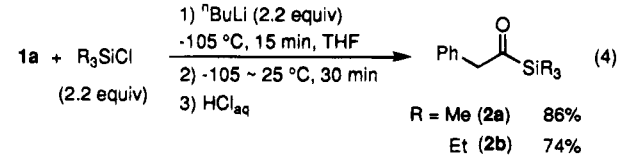
(3)

ingly, however, when **1a** was treated with 2 equiv of butyllithium in the presence of 2 equiv of Me_3SiCl at −105 °C, **3a** was obtained quantitatively with high *Z*-stereoselectivity (eq 3).[18] From a synthetic point of view, this reaction is complementary to a known method that provides the *E*-isomer of **3a** as the major product from benzyltrimethylsilane, CO, and trimethylsilyl chloride.[15f]

Table 1 summarizes the results obtained with different tellurol esters and chlorosilanes.[19] Triethyl- and dimethylphenylsilyl chlorides afforded the corresponding enol silyl ethers in good yields with high stereoselectivities (entries 2 and 3). With ^{t}BuMe$_2$SiCl, no desired product was formed under the same conditions, but a reaction performed at −78 °C using HMPA as a cosolvent gave the desired **3d** in 87% yield (entry 4). Since enol silyl ethers are known to isomerize easily in the presence of LiCl and HMPA, the observed low stereoselectivity of this reaction may be ascribable to the isomerization of the initially formed *Z*-isomer to the *E*-form.[20] Arylethanetelluroates having a *p*-Cl, *p*-Me, or *o*-MeO substituent on the aromatic ring (**1b–d**) could also be converted to the corresponding enol silyl ethers in excellent yields with high *Z*-stereoselectivities (entries 5–7).

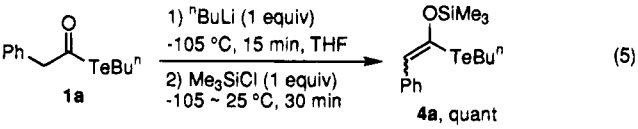
The reaction of phenylthio-substituted ethanetelluroate **1e** with either Me_3SiCl or ^{t}BuMe$_2$SiCl under the same conditions gave only one stereoisomer (entries 8 and 9). The potent synthetic utility of these compounds has been demonstrated by Reich and co-workers, who accomplished regio- and stereoselective syntheses of enol silyl ethers of dialkyl ketones from [(phenylthio)acetyl]silanes, the hydrolyzed forms of **3h** and **3i**.[21] Enol silyl ethers with a benzyloxy group (**3j, k**) could also be obtained in a similar manner (entries 10 and 11).

The direct synthesis of acylsilanes, if desired, can be achieved by treatment of the reaction mixture with aqueous HCl before the usual workup, as shown by eq 4 (see Experimental Section).



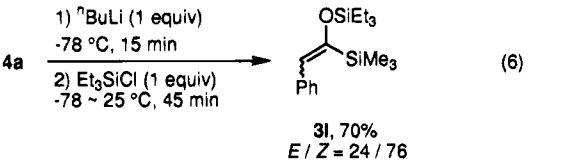
(4)

In order to probe the reaction pathway, we carried out several control experiments. When **1a** was allowed to react with an equimolar amount of butyllithium at −105 °C for 15 min and the reaction was quenched with trimethylsilyl chloride, α-siloxyvinyl telluride **4a** was formed quantitatively (eq 5), indicating that **1a** was



(5)

deprotonated efficiently by ^{n}BuLi. The intermediacy of **4a** in (α-siloxyvinyl)silane formation was proven by the successful conversion of **4a** to **3l** by the reaction with butyllithium and subsequent quenching with triethylsilyl chloride (eq 6).[22] What should be noted here is that



(6)

trimethylsilyl group migrated from oxygen to the adjacent vinylic carbon. These results indicate that (α-siloxyvinyl)silanes **3** were formed via the following five consecutive reactions (Scheme 1): (i) α-proton abstraction to give enolate **5**, (ii) chlorosilane-trapping of **5** to give **4**, (iii) lithium−tellurium exchange of **4** to form (α-siloxyvinyl)lithium **6**, (iv) 1,2-silicon shift, and (v) chlorosilane-trapping of the resulting acylsilane enolate. The fact that the reaction of **1a** with equimolar amounts of butyllithium and trimethylsilyl chloride gave a mixture of **4a**

(16) Hiiro, T.; Morita, Y.; Inoue, T.; Kambe, N.; Ogawa, A.; Ryu, I.; Sonoda, N. *J. Am. Chem. Soc.* **1990**, *112*, 455. Additional examples will be reported in due course.

(17) Acyllithiums generated in situ by the reaction of alkyllithiums with CO could also be trapped efficiently with trimethylsilyl chloride to give acylsilanes: Seyferth, D.; Weinstein, R. M. *J. Am. Chem. Soc.* **1982**, *104*, 5534.

(18) This product could be isolated in pure form by flash column chromatography on silica gel after treatment of the reaction mixture with MeI, which reacts with ^{n}Bu$_2$Te generated by Li−Te exchange reaction to form a easily separable telluronium salt (^{n}Bu$_2$MeTeI) (see Experimental Section). For the formation of telluronium salts, see: Balfe, M. P.; Chaplin, C. A.; Phillips, H. *J. Chem. Soc.* **1938**, 341. Zhou, Z.-L.; Huang, Y.-Z.; Tang, Y.; Chen, Z.-H.; Shi, L.-P.; Jin, X.-L.; Yang, Q.-C. *Organometallics* **1994**, *13*, 1575.

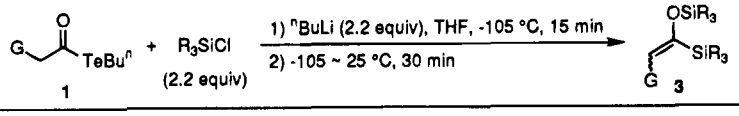
(19) For determination of the stereochemistry, see Experimental Section.

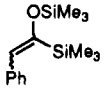
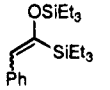
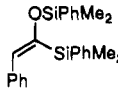
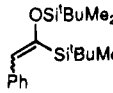
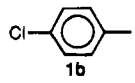
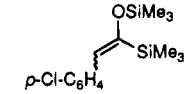
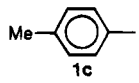
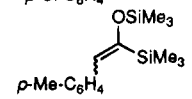
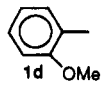
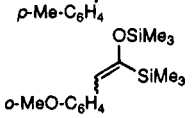
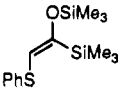
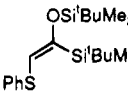
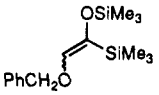
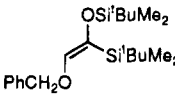
(20) It is reported that the *E*-enol silyl ether of methyl phenylacetate isomerizes to the *Z*-isomer in the presence of LiCl and HMPA at 20 °C in THF; see: Tanaka, F.; Fuji, K. *Tetrahedron Lett.* **1992**, *33*, 7885.

(21) Reich, H. J.; Holtan, R. C.; Borkowsky, S. L. *J. Org. Chem.* **1987**, *52*, 312.

(22) The structure of **3l** was determined by its hydrolysis to give only **2a**.

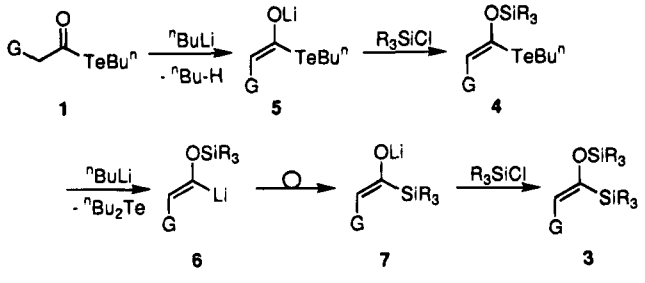
Table 1. Synthesis of (α-Siloxyvinyl)silanes from Tellurol Esters



entry	tellurol ester, G	R_3	product	isolated yield (%)	E/Z[a]
1	**1a**, Ph	Me_3		**3a** 99	2 / 98
2	**1a**, Ph	Et_3		**3b** 87	4 / 96
3	**1a**, Ph	$PhMe_2$		**3c** 74	only *Z*-isomer
4[b]	**1a**, Ph	$^tBuMe_2$		**3d** 87	20 / 80
5	 **1b**	Me_3		**3e** 99	4 / 96
6	 **1c**	Me_3		**3f** 96	2 / 98
7	 **1d**	Me_3		**3g** 92	<1 / 99
8	**1e**, PhS	Me_3		**3h** 100	only *Z*-isomer
9[b]	**1e**, PhS	$^tBuMe_2$		**3i** 89	only *Z*-isomer
10	**1f**, $PhCH_2O$	Me_3		**3j** 79	7 / 93
11[b]	**1f**, $PhCH_2O$	$^tBuMe_2$		**3k** 54	only *Z*-isomer

Reaction conditions: tellurol ester (1 mmol), chlorosilane (2.2 mmol), ^{n}BuLi (2.2 mmol), THF (10 mL). [a] Determined by GLC and/or ^{1}H NMR of a crude mixture. For details of stereochemical assignment, see Experimental Section. [b] After ^{n}BuLi was added at −105 °C in the presence of HMPA (1 mL), the reaction temperature was raised and maintained at −78 °C for 1 h.

Scheme 1. Reaction Pathway



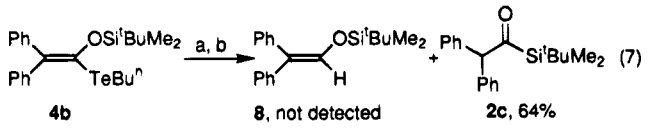
and **3a** (eq 2) suggests that the first three steps (i–iii) are all fast, even at −105 °C.

It is noteworthy that α-siloxyvinyl tellurides **4** exclusively underwent Li–Te exchange to give **6** although Li–Si exchange can regenerate thermodynamically more stable anions **5**. This result indicates that the former is kinetically more favored than the latter.

Similar (siloxyvinyl)lithiums have been generated from α-siloxy sulfides[15c,d,23] or -stannanes[15e] by reductive metalation or Li–Sn exchange reactions, respectively, and are known to undergo similar rearrangement.[24] Verlhac and co-workers reported that the rearrangement was a fast process and was complete within 10 min at −78 °C.[15e]

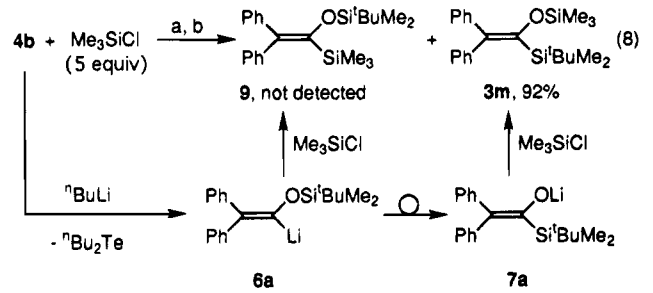
In order to reveal how fast the rearrangement is, and to examine the possibility of intermolecular trapping of (α-siloxyvinyl)lithiums, **4b** was treated with ^{n}BuLi at −105 °C for 5 min, and the products were quenched with AcOH at that temperature (eq 7). From the resulting

(23) Cohen, T.; Matz, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 6900.
(24) (a) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77. (b) Wright, A.; West, R. *J. Am. Chem. Soc.* **1974**, *96*, 3214, 3227. (c) Linderman, R. J.; Ghannam, A. *J. Am. Chem. Soc.* **1990**, *112*, 2392. (d) Nakahira, H.; Ryu, I.; Ogawa, A.; Kambe, N.; Sonoda, N. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3361. (e) Antoniotti, P.; Tonachini, G. *J. Org. Chem.* **1993**, *58*, 3622. (f) Hwu, J. R.; Tsay, S.-C.; Wang, N.; Hakimelahi, G. H. *Organometallics* **1994**, *13*, 2461.



a) ^{n}BuLi, THF, -105 °C, 5 min. b) AcOH/Et_2O.

mixture, only **2c** was isolated in 64% yield, but **8** could not be detected by NMR or GLC analysis. A similar reaction of **4b** with ^{n}BuLi in the presence of a large excess of trimethylsilyl chloride gave only **3m** without formation of **9** (eq 8). These results indicate that rearrangement



a) ^{n}BuLi, THF, -105 °C, 15 min. b) -105~25 °C, 30 min.

from **6a** to **7a** is extremely rapid even at −105 °C and that vinyllithium **6a** cannot be trapped by acetic acid or coexisting Me_3SiCl. The results of eqs 6 and 8 may also suggest that silyl migration from oxygen to sp^2 carbon proceeds intramolecularly like the usual reverse Brook rearrangements from oxygen to sp^3 carbon.

The high stereoselectivities of the present reaction might be attributable to stereoselective proton abstraction from tellurol esters. This hypothesis is supported by the following evidence. First, kinetic α-proton abstraction from methyl phenylacetate, an analogue of **1a**, preferentially affords the corresponding lithium enolate with the same configuration as that of the present cases.[20,25] Second, lower selectivities resulted when stereoisomerization was promoted by additives[20] or accelerated by elevating the reaction temperature to −78 °C (entry 4 in Table 1 and eq 6).

In conclusion, we have developed a new and convenient method for the preparation of acylsilanes **2** and their enol silyl ethers **3** from tellurol esters **1** bearing an anion stabilizing substituent at the position α to the carbonyl. The synthetic utility of this method was demonstrated by high yields and stereoselectivities, simplicity in operation, and easy availability of tellurol esters. Several control experiments revealed that the reaction was triggered by proton abstraction from tellurol esters with ^{n}BuLi to give lithium enolates **5**, which were trapped with chlorosilanes to form α-siloxyvinyl tellurides **4** as intermediates. Li−Te exchange to form (α-siloxyvinyl)lithiums **6** and subsequent 1,2-silicon shift leading to (α-lithioxyvinyl)silanes **7** followed by trapping with chlorosilanes afford (α-siloxyvinyl)silanes **3** or acylsilanes **2** after hydrolysis.

Experimental Section

General Procedure. All reactions were conducted under a nitrogen atmosphere. THF was distilled from sodium benzophenone ketyl. Commercially unavailable acid chlorides were prepared by the reaction of corresponding carboxylic acids with thionyl chloride. HMPA was dried over CaH_2 and fractionally distilled. Chlorosilanes and methyl iodide were used as purchased. Tellurium pieces were ground with a mortar and pestle just before use. ^1H and ^{13}C NMR spectra were recorded using $CDCl_3$ as a solvent with dioxane as an internal standard except for the measurement of tellurol esters (Me_4Si).

Synthesis of Tellurol Esters. *Te*-Butyl Phenylethanetelluroate (1a) as a Typical Example. Finely ground elemental tellurium (30 mmol, 3.83 g) and 60 mL of THF were placed under nitrogen in a flame-dried, round-bottom flask equipped with a N_2 inlet and a rubber septum. To the mixture was added ca. 18.8 mL of ^{n}BuLi (1.6 N in hexane, 30 mmol) at 25 °C until the mixture turned to a pale yellow homogeneous solution. The solution was stirred for 10 min and then cooled to −78 °C, and 30 mmol (4.84 g, 3.97 mL) of phenylacetyl chloride was injected. After the solution was warmed to rt in 30 min, it was poured into aqueous NH_4Cl (100 mL) and extracted with Et_2O (30 mL × 3). The combined organic layer was dried over $MgSO_4$ and concentrated. The residue was subjected to column chromatography (silica gel, i.d. 50 mm × 25 cm). After elution of byproducts (Bu_2Te_2, Bu_2Te, etc.) with hexane (ca. 500 mL), **1a** was obtained (hexane/Et_2O = 10/1, 200 mL), 7.05 g (23.2 mmol, 77%): ^1H NMR (270 MHz, $CDCl_3$) δ 0.88 (t, J = 7.32 Hz, 3 H), 1.32 (sextet, J = 7.32 Hz, 2 H), 1.72 (quint, J = 7.32 Hz, 2 H), 2.79 (t, J = 7.32 Hz, 2 H), 3.67 (s, 2 H), 7.22−7.35 (m, 5 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.2 ($^1J_{CTe}$ = 76.3 Hz), 13.4, 25.3, 33.9, 60.5, 128.1, 128.6, 130.8, 132.6, 203.1; IR (neat) 2956, 2927, 1686, 1010, 999, 699 cm^{-1}; MS m/z (relative intensity) 306 (M^+, 1.9), 119 (23), 91 (100). Anal. Calcd for $C_{12}H_{16}OTe$: C, 47.43; H, 5.31. Found: C, 47.60; H, 5.35.

***Te*-Butyl (*p*-chlorophenyl)ethanetelluroate (1b):** ^1H NMR (270 MHz, $CDCl_3$) δ 0.89 (t, J = 7.32 Hz, 3 H), 1.32 (sextet, J = 7.32 Hz, 2 H), 1.73 (quint, J = 7.32 Hz, 2 H), 2.82 (t, J = 7.32 Hz, 2 H), 3.67 (s, 2 H), 7.20 (d, J = 8.30 Hz, 2 H), 7.32 (d, J = 8.30 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.6 ($^1J_{CTe}$ = 75.8 Hz), 13.4, 25.3, 33.8, 59.9, 128.9, 131.1, 132.0, 134.2, 202.1; IR (neat) 2957, 2927, 1689, 1492, 1007 cm^{-1}; MS m/z (relative intensity) 340 (M^+, 8.6), 153 (22), 127 (39), 125 (100). Anal. Calcd for $C_{12}H_{15}ClOTe$: C, 42.60; H, 4.47. Found: C, 42.36; H, 4.48.

***Te*-Butyl (*p*-methylphenyl)ethanetelluroate (1c):** ^1H NMR (270 MHz, $CDCl_3$) δ 0.88 (t, J = 7.32 Hz, 3 H), 1.31 (sextet, J = 7.32 Hz, 2 H), 1.72 (quint, J = 7.32 Hz, 2 H), 2.36 (s, 3 H), 2.78 (t, J = 7.32 Hz, 2 H), 3.62 (s, 2 H), 7.15 (s, 4 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.1 ($^1J_{CTe}$ = 75.8 Hz), 13.4, 21.2, 25.4, 33.9, 60.0, 129.4, 129.5, 130.8, 138.0, 203.9; IR (neat) 2956, 2926, 1689, 1513, 1008 cm^{-1}; MS (CI) m/z (relative intensity) 321 (M^+ + 1, 100), 319 (92), 317 (58), 133 (34), 105 (69). Anal. Calcd for $C_{13}H_{18}OTe$: C, 49.12; H, 5.71. Found: C, 49.42; H, 5.74.

***Te*-Butyl (*o*-methoxyphenyl)ethanetelluroate (1d):** ^1H NMR (270 MHz, $CDCl_3$) δ 0.88 (t, J = 7.32 Hz, 3 H), 1.31 (sextet, J = 7.32 Hz, 2 H), 1.71 (quint, J = 7.32 Hz, 2 H), 2.77 (t, J = 7.32 Hz, 2 H), 3.67 (s, 2 H), 3.80 (s, 3 H), 6.88 (d, J = 7.81 Hz, 1 H), 6.94 (t, J = 7.81 Hz, 1 H), 7.20 (d, J = 7.81 Hz, 1 H), 7.35 (t, J = 7.81 Hz, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 10.3 ($^1J_{CTe}$ = 76.3 Hz), 13.5, 25.3, 34.0, 55.0, 55.4, 110.7, 120.5, 121.5, 129.9, 132.7, 158.5, 203.7; IR (neat) 2955, 2927, 1691, 1494, 1249, 1008, 753 cm^{-1}; MS m/z (relative intensity) 336 (M^+, 3.2), 149, (50), 121 (100), 91 (46); HRMS calcd for $C_{13}H_{18}O_2Te$ 336.0369, found 336.0377.

***Te*-Butyl (phenylthio)ethanetelluroate (1e):** ^1H NMR (270 MHz, $CDCl_3$) δ 0.90 (t, J = 7.32 Hz, 3 H), 1.35 (sextet, J = 7.32 Hz, 2 H), 1.73 (quint, J = 7.32 Hz, 2 H), 2.78 (t, J = 7.32 Hz, 2 H), 3.65 (s, 2 H), 7.21−7.38 (m, 5 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.0 ($^1J_{CTe}$ = 77.9 Hz), 13.5, 25.4, 33.7, 55.7, 127.1, 129.2, 129.5, 134.4, 205.8; IR (neat) 2955, 2926, 1682, 998, 737, 688 cm^{-1}; MS m/z (relative intensity) 338 (M^+, 12), 296 (10), 151 (12), 123 (100). Anal. Calcd for $C_{12}H_{16}OSTe$: C, 42.90; H, 4.80. Found: C, 43.01; H, 4.88.

***Te*-Butyl (benzyloxy)ethanetelluroate (1f):** ^1H NMR (270 MHz, $CDCl_3$) δ 0.91 (t, J = 7.52 Hz, 3 H), 1.37 (sextet, J = 7.52 Hz, 2 H), 1.75 (quint, J = 7.52 Hz, 2 H), 2.81 (t, J =

(25) Corset, J.; Froment, F.; Lautié, M.-F.; Ratovelomanana, N.; Seyden-Penne, J.; Strzalko, T.; Roux-Schmitt, M.-C. *J. Am. Chem. Soc.* **1993**, *115*, 1684.

7.52 Hz, 2 H), 3.74 (s, 2 H), 4.68 (s, 2 H), 7.30–7.38 (m, 5 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 8.1 ($^1J_{CTe}$ = 75.3 Hz), 13.5, 25.4, 33.9, 74.4, 80.5, 127.8, 128.1, 128.5, 136.7, 209.1; IR (neat) 2955, 2927, 1696, 1117, 736, 697 cm^{-1}; MS *m/z* (relative intensity) 336 (M^+, 5.6), 278 (10), 91 (100). Anal. Calcd for $C_{13}H_{18}O_2Te$: C, 46.76; H, 5.43. Found: C, 47.06; H, 5.53.

***Te*-Butyl diphenylethanetelluroate (1g):** ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.42 Hz, 3 H), 1.33 (sextet, *J* = 7.42 Hz, 2 H), 1.75 (quint, *J* = 7.42 Hz, 2 H), 2.85 (t, *J* = 7.42 Hz, 2 H), 4.98 (s, 1 H), 7.31 (s, 10 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 12.1 ($^1J_{CTe}$ = 76.8 Hz), 13.4, 25.4, 33.9, 74.4, 127.8, 128.6, 129.6, 137.5, 204.5; IR (neat) 2956, 2927, 1689, 1494, 969, 727, 699 cm^{-1}; MS *m/z* (relative intensity) 382 (M^+, 2.0), 168 (19), 167 (100), 165 (22), 152 (11). Anal. Calcd for $C_{18}H_{20}$-OTe: C, 56.90; H, 5.31. Found: C, 57.17; H, 5.40.

General Procedure for Conversion of Tellurol Esters to Enol Silyl Ethers of Acylsilanes. To 10 mL of a THF solution of the tellurol ester (1 mmol) at −78 °C was added 2.2 mmol of chlorosilane. The solution was cooled to −105 °C, and 2.2 mmol of ^{n}BuLi (1.6 N in hexane) was added. After 10 min, the solution was slowly warmed to rt over 1 h, and 4 mmol of MeI was added. The solution was stirred for 2 h at rt, poured into aqueous $NaHCO_3$, and extracted with Et_2O (20 mL × 3). The combined organic layer was dried over $MgSO_4$ and concentrated. Flash column chromatography of the residue on silica gel using Et_2O/hexane (1/100) gave the (α-siloxyvinyl)silanes. Quick operation is recommended in order to avoid hydrolysis of the products.

***(Z)*-β-(Trimethylsiloxy)-β-(trimethylsilyl)styrene (3a):** [15f] ^{1}H NMR (270 MHz, $CDCl_3$) δ −0.04 (s, 9 H), 0.25 (s, 9 H), 6.72 (s, 1 H), 7.14–7.29 (m, 5 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ −0.9, 0.8, 126.3, 126.5, 127.8, 129.3, 137.0, 160.7; IR (neat) 2958, 1251, 1124, 890, 840 cm^{-1}; MS *m/z* (relative intensity) 264 (M^+, 18), 149 (73), 73 (100); HRMS calcd for $C_{14}H_{24}OSi_2$ 264.1372, found 264.1369.

***(Z)*-β-(Triethylsiloxy)-β-(triethylsilyl)styrene (3b):** ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.46 (q, *J* = 7.81 Hz, 6 H), 0.74 (q, *J* = 7.30 Hz, 6 H), 0.84 (t, *J* = 7.81 Hz, 9 H), 1.02 (t, *J* = 7.30 Hz, 9 H), 6.67 (s, 1 H), 7.13–7.28 (m, 5 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 3.6, 5.6, 6.9, 7.4, 124.0, 126.3, 127.7, 129.3, 137.2, 159.5; IR (neat) 2954, 2910, 1131, 882, 781 cm^{-1}; MS *m/z* (relative intensity) 348 (M^+, 28), 217 (46), 189 (100), 161 (53), 59 (58). Anal. Calcd for $C_{20}H_{36}OSi_2$: C, 68.89; H, 10.41. Found: C, 69.02; H, 10.69.

***(Z)*-β-(Dimethylphenylsiloxy)-β-(dimethylphenylsilyl)-styrene (3c):** ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.16 (s, 6 H), 0.46 (s, 6 H), 6.73 (s, 1 H), 6.99–7.59 (m, 15 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ −2.3, −0.8, 126.5, 126.9, 127.5, 127.6, 127.8, 128.8, 129.3, 129.5, 133.4, 133.9, 136.4, 138.0, 138.1, 158.8; IR (neat) 2959, 1118, 814, 783, 698 cm^{-1}; MS *m/z* (relative intensity) 388 (M^+, 16), 209 (43), 193 (44), 135 (100). Anal. Calcd for $C_{24}H_{28}OSi_2$: C, 74.17; H, 7.26. Found: C, 74.29; H, 7.45.

***β*-(*tert*-Butyldimethylsiloxy)-β-(*tert*-butyldimethylsilyl)-styrene (3d). *Z*-Isomer:** ^{1}H NMR (270 MHz, $CDCl_3$) δ −0.23 (s, 6 H), 0.26 (s, 6 H), 0.90–1.04 (m, 18 H), 6.74 (s, 1 H), 7.17–7.42 (m, 5 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ −4.6, −3.8, 17.1, 18.4, 26.0, 27.3, 124.7, 126.3, 127.4, 129.8, 137.0, 159.6; MS *m/z* (relative intensity) 348 (M^+, 3.9), 189 (26), 147 (100); HRMS calcd for $C_{20}H_{36}OSi_2$ 348.2305, found 348.2334.

***E*-Isomer:** ^{1}H NMR (270 MHz, $CDCl_3$) δ −0.25 (s, 6 H), 0.16 (s, 6 H), 0.90–1.04 (m, 18 H), 6.00 (s, 1 H), 7.17–7.42 (m, 5 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ −5.0, −3.4, 17.3, 18.3, 26.1, 26.9, 124.8, 126.2, 127.8, 129.4, 136.7, 158.0; MS *m/z* (relative intensity) 348 (M^+, 3.6), 189 (25), 147 (100); HRMS calcd for $C_{20}H_{36}OSi_2$ 348.2305, found 348.2303.

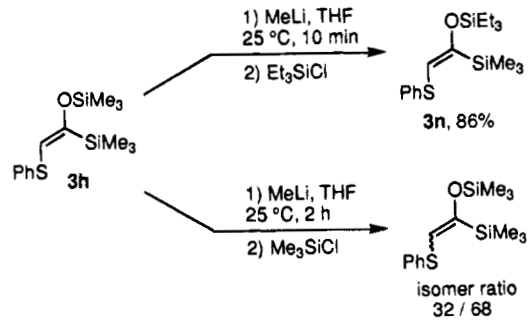
***E*/*Z* mixture:** IR (neat) 2955, 2929, 2857, 1257, 1122, 837, 822, 810, 777 cm^{-1}. Anal. Calcd for $C_{20}H_{36}OSi_2$: C, 68.89; H, 10.41. Found: C, 68.82; H, 10.65.

***(Z)*-β-(Trimethylsiloxy)-β-(trimethylsilyl)-*p*-chlorostyrene (3e):** ^{1}H NMR (270 MHz, $CDCl_3$) δ −0.02 (s, 9 H), 0.25 (s, 9 H), 6.63 (s, 1 H), 7.09 (d, *J* = 8.30 Hz, 2 H), 7.24 (d, *J* = 8.30 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ −0.9, 0.7, 124.7, 127.9, 130.5, 132.3, 135.5, 161.6; IR (neat) 2959, 1251, 1125, 898, 842 cm^{-1}; MS *m/z* (relative intensity) 298 (M^+, 10), 149 (49), 73 (100); HRMS calcd for $C_{14}H_{23}ClOSi_2$ 298.0976, found 298.0964.

***(Z)*-β-(Trimethylsiloxy)-β-(trimethylsilyl)-*p*-methylstyrene (3f):** ^{1}H NMR (270 MHz, $CDCl_3$) δ −0.02 (s, 9 H), 0.26 (s, 9 H), 2.33 (s, 3 H), 6.70 (s, 1 H), 7.06 (s, 4 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ −0.8, 0.8, 21.1, 126.4, 128.5, 129.2, 134.0, 136.1, 160.2; IR (neat) 2959, 1252, 1122, 900, 843 cm^{-1}; MS *m/z* (relative intensity) 278 (M^+, 26), 162 (18), 147 (80), 73 (100); HRMS calcd for $C_{15}H_{26}OSi_2$ 278.1522, found 278.1534.

***(Z)*-β-(Trimethylsiloxy)-β-(trimethylsilyl)-*o*-methoxystyrene (3g):** ^{1}H NMR (270 MHz, $CDCl_3$) δ −0.05 (s, 9 H), 0.26 (s, 9 H), 3.80 (s, 3 H), 6.62 (s, 1 H), 6.81 (d, *J* = 7.32 Hz, 1 H), 6.88 (t, *J* = 7.32 Hz, 1 H), 7.13 (d, *J* = 7.32 Hz, 1 H), 7.24 (t, *J* = 7.32 Hz, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ −1.0, 0.8, 55.3, 109.9, 119.7, 122.4, 126.1, 128.3, 131.1, 157.3, 160.1; IR (neat) 2958, 1247, 1128, 1100, 899, 841, 752 cm^{-1}; MS *m/z* (relative intensity) 294 (M^+, 21), 150 (11), 149 (58), 73 (100). Anal. Calcd for $C_{15}H_{26}O_2Si_2$: C, 61.17; H, 8.90. Found: C, 61.12; H, 8.96.

Stereochemistry of Enol Silyl Ethers 3. The stereochemistry of **3a** was confirmed by comparison of its NMR data with reported values.[15f] Configurations of **3b–g** were determined by comparing chemical shifts of the vinylic hydrogens of stereoisomers, assigning isomers having a vinylic hydrogen at lower fields as *Z*-isomers.[15f] To determine the stereochemistry of **3h**, the isolated **3h** was treated with MeLi at 25 °C to generate the corresponding lithium enolate.[26] Although quenching of the enolate with Et_3SiCl after 10 min afforded **3n** as almost a single isomer, a mixture of stereoisomers having vinylic hydrogens at δ 5.80 and δ 6.09 with 32/68 ratio was obtained when the reaction was quenched after 2 h (eq 9),



(9)

indicating that the lithium enolate did isomerize but very slowly under these conditions. Since the major isomer (vinylic hydrogen at δ 6.09) showed the same spectra as the starting **3h**, its configuration was assigned as the *Z*-form. Compound **3i**, which had NMR spectra quite similar to those of **3h**, was assigned also as the *Z*-isomer. Products **3k** and the major isomer of **3j** showed similar chemical shifts of vinylic hydrogens at δ 6.62 and δ 6.64, respectively. Since comparison of these values with reported NMR data of similar compounds[15d] revealed that these compounds are stereoisomers having vinylic hydrogens at lower fields, they were determined to be *Z*-isomers. All attempts to determine the configuration of **3** by NOE experiments were unsuccessful.

2-(Phenylthio)-1-(trimethylsiloxy)-1-(trimethylsilyl)-ethylene (3h). *Z*-Isomer: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.21 (s, 9 H), 0.25 (s, 9 H), 6.09 (s, 1 H), 7.12–7.30 (m, 5 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ −0.9, 0.7, 112.5, 125.1, 126.4, 128.8, 138.7, 169.8; IR (neat) 2958, 1252, 1138, 907, 840, 737 cm^{-1}; MS *m/z* (relative intensity) 296 (M^+, 64), 147 (50), 99 (30), 73 (100). Anal. Calcd for $C_{14}H_{24}OSSi_2$: C, 56.69; H, 8.16. Found: C, 56.25; H, 8.24.

***E*-Isomer:** ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.16 (s, 9 H), 0.28 (s, 9 H), 5.80 (s, 1 H), 7.12–7.37 (m, 5 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ −1.9, 0.9, 116.1, 126.1, 126.4, 128.9, 136.6, 160.0.

(Z)-2-(Phenylthio)-1-(triethylsiloxy)-1-(trimethylsilyl)-ethylene (3n): ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.22 (s, 9 H), 0.74 (q, *J* = 7.82 Hz, 6 H), 1.02 (t, *J* = 7.82 Hz, 9 H), 6.03 (s, 1 H), 7.11–7.29 (m, 5 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ −0.8, 5.3, 6.8, 110.2, 125.0, 126.2, 128.7, 139.0, 160.5; IR (neat) 2956, 2877, 1246, 842, 776, 737 cm^{-1}; MS *m/z* (relative intensity)

(26) Stork, G.; Hudrlik, P. F. *J. Am. Chem. Soc.* **1968**, *90*, 4464.

338 (M^+, 95), 309 (100), 195 (38), 147 (40), 115 (69), 87 (40), 73 (25). Anal. Calcd for $C_{17}H_{30}OSSi_2$: C, 60.29; H, 8.93. Found: C, 60.56; H, 9.10.

(*Z*)-2-(Phenylthio)-1-(*tert*-butyldimethylsiloxy)-1-(*tert*-butyldimethylsilyl)ethylene (3i): ^1H NMR (270 MHz, $CDCl_3$) δ 0.21 (s, 6 H), 0.25 (s, 6 H), 0.95 (s, 18 H), 6.07 (s, 1 H), 7.05–7.15 (m, 1 H), 7.18–7.28 (m, 4 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ −4.2, −3.9, 17.5, 18.2, 25.8, 27.0, 111.0, 124.9, 126.2, 128.7, 139.2, 167.5; IR (neat) 2955, 2929, 1136, 838, 809, 736 cm^{-1}; MS *m*/*z* (relative intensity) 380 (M^+, 4.5), 323 (31), 147 (100), 73 (69); HRMS calcd for $C_{20}H_{36}OSSi_2$ 380.2026, found 380.2023.

(*Z*)-2-(Benzyloxy)-1-(trimethylsiloxy)-1-(trimethylsilyl)ethylene (3j): ^1H NMR (270 MHz, $CDCl_3$) δ 0.12 (s, 9 H × 2), 4.65 (s, 2 H), 6.62 (s, 1 H), 7.33 (brs, 5 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ −1.7, 0.4, 74.3, 127.6, 127.7, 128.3, 137.2, 143.7, 147.4; IR (neat) 2958, 1250, 1142, 876, 844 cm^{-1}; MS *m*/*z* (relative intensity) 294 (M^+, 24), 147 (100), 91 (32), 73 (39); HRMS calcd for $C_{15}H_{26}O_2Si_2$ 294.1471, found 294.1443.

(*Z*)-2-(Benzyloxy)-1-(*tert*-butyldimethylsiloxy)-1-(*tert*-butyldimethylsilyl)ethylene (3k): ^1H NMR (270 MHz, $CDCl_3$) δ 0.09 (s, 6 H × 2), 0.91 (s, 9 H), 0.92 (s, 9 H), 4.62 (s, 2 H), 6.64 (s, 1 H), 7.33 (s, 5 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ −5.6, −4.0, 17.3, 18.2, 25.9, 26.8, 74.3, 127.3, 127.7, 128.3, 137.4, 143.0, 146.0; IR (neat) 2956, 2929, 1255, 1139, 839, 824 cm^{-1}; MS *m*/*z* (relative intensity) 378 (M^+, 22), 147 (100), 91 (36), 73 (69); HRMS calcd for $C_{21}H_{38}O_2Si_2$ 378.2411, found 378.2417.

One Pot Conversion of 1a to (Phenylacetyl)trimethylsilane (2a). To a mixture of **1a** (1 mmol) and Me_3SiCl (2.2 mmol) in THF (10 mL) at −105 °C was added 2.2 mmol of ^{n}BuLi (1.6 N in hexane). After 15 min, the solution was gradually warmed to rt over 30 min. Then 10 mL of 1 N HCl solution was added. Monitoring of **3a** by GLC showed that **3a** disappeared within 1 h. Then the solution was poured into a saturated solution of NH_4Cl, extracted with Et_2O (20 mL × 3), dried over $MgSO_4$, and evaporated. Chromatography of the residue on silica gel gave 165 mg (86%) of **2a**.

(Phenylacetyl)triethylsilane (2b): ^1H NMR (270 MHz, $CDCl_3$) δ 0.67 (q, J = 7.81 Hz, 6 H), 0.91 (t, J = 7.81 Hz, 9 H), 3.83 (s, 2 H), 7.11 (d, J = 7.32 Hz, 2 H), 7.23 (t, J = 7.32 Hz, 1 H), 7.31 (t, J = 7.32 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 2.4, 7.2, 56.6, 126.8, 128.5, 129.9, 132.9, 243.7; IR (neat) 2955, 2876, 1649, 1636, 722, 700 cm^{-1}; MS *m*/*z* (relative intensity) 234 (M^+, 0.6), 143 (14), 115 (100), 87 (85), 59 (33); HRMS calcd for $C_{14}H_{22}OSi$ 234.1440, found 234.1429.

Synthesis of β-(trimethylsiloxy)-β-(butyltelluro)styrene (4a). To a solution of **1a** (1 mmol) in THF (10 mL) at −105 °C was added 1 mmol of ^{n}BuLi (1.6 N in hexane), and the mixture was stirred for 15 min. After 1.1 mmol of Me_3SiCl was added, the solution was gradually warmed to rt over 30 min, poured into aqueous $NaHCO_3$, and extracted with Et_2O (30 mL × 2). The combined organic layer was dried over $MgSO_4$ and evaporated to give **4a** quantitatively: ^1H NMR (270 MHz, $CDCl_3$) δ 0.35 (s, 9 H), 0.90 (t, J = 7.32 Hz, 3 H), 1.36 (sextet, J = 7.32 Hz, 2 H), 1.77 (quint, J = 7.32 Hz, 2 H), 2.74 (t, J = 7.32 Hz, 2 H), 6.41 (s, 1 H), 7.20–7.29 (m, 5 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 0.0, 7.4, 13.3, 25.1, 34.2, 119.3, 126.3, 128.0, 128.1, 130.7, 137.3; IR (neat) 2957, 2927, 1592, 1252, 1120, 880, 847 cm^{-1}; MS *m*/*z* (relative intensity) 378 (M^+, 12), 309 (47), 307 (26), 163 (21), 118 (24), 90 (21), 73 (100); HRMS calcd for $C_{15}H_{24}OSiTe$ 378.0658, found 378.0645.

β-(Triethylsiloxy)-β-(trimethylsilyl)styrene (3l). *Z*-Isomer: ^1H NMR (270 MHz, $CDCl_3$) δ −0.03 (s, 9 H), 0.75 (q, J = 7.81 Hz, 6 H), 1.04 (t, J = 7.81 Hz, 9 H), 6.68 (s, 1 H), 7.14–7.26 (m, 5 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ −0.8, 5.5, 6.9, 124.6, 126.4, 127.7, 129.3, 137.2, 161.0; MS *m*/*z* (relative intensity) 306 (M^+, 21), 175 (51), 147 (100), 119 (60), 59 (56); HRMS calcd for $C_{17}H_{30}OSi_2$ 306.1835, found 306.1812.

***E*-Isomer:** ^1H NMR (270 MHz, $CDCl_3$) δ 0.19 (s, 9 H), 0.55 (q, J = 7.81 Hz, 6 H), 0.87 (t, J = 7.81 Hz, 9 H), 5.88 (s, 1 H), 7.22–7.58 (m, 5 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ −1.3, 5.6, 6.8, 122.9, 126.2, 127.9, 128.9, 136.4, 160.1; MS *m*/*z* (relative intensity) 306 (M^+, 19), 175 (46), 147 (100), 119 (61), 59 (69); HRMS calcd for $C_{17}H_{30}OSi_2$ 306.1835, found 306.1817.

***E*/*Z* mixture:** IR (neat) 2956, 2877, 1128, 840, 750 cm^{-1}. Anal. Calcd for $C_{17}H_{30}OSi_2$: C, 66.59; H, 9.86. Found: C, 66.95; H, 10.10.

Synthesis of 1-(*tert*-Butyldimethylsiloxy)-1-(butyltelluro)-2,2-diphenylethylene (4b). To 20 mL of a THF solution of LDA (7 mmol), prepared from $^iPr_2NH$ and ^{n}BuLi (1.6 N in hexane), at −78 °C was added **1g** (6 mmol). The mixture was stirred for 30 min. After ^{t}BuMe$_2$SiCl (7 mmol) and HMPA (6 mL) were added at −78 °C, the solution was warmed to rt over 1 h and then poured into aqueous $NaHCO_3$ and extracted with Et_2O (30 mL × 2). After the combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure, column chromatography on silica gel gave 3.97 mmol (66%) of **4b** in an Et_2O/hexane (1/10) eluent: ^1H NMR (270 MHz, $CDCl_3$) δ −0.02 (s, 6 H), 0.84–0.91 (m, 12 H), 1.35 (sextet, J = 7.33 Hz, 2 H), 1.78 (quint, J = 7.33 Hz, 2 H), 2.71 (t, J = 7.33 Hz, 2 H), 7.14–7.29 (m, 10 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ −4.9, 8.5 ($^1J_{CTe}$ = 78.4 Hz), 13.4, 18.1, 25.0, 25.7, 33.7, 126.1, 127.4, 127.5, 128.1, 128.5, 130.3, 130.4, 135.3, 139.6, 143.8; IR (neat) 2956, 2928, 1094, 830, 699 cm^{-1}; MS *m*/*z* (relative intensity) 496 (M^+, 27), 494 (24), 309 (44), 253 (53), 115 (28), 73 (100). Anal. Calcd for $C_{24}H_{34}OSiTe$: C, 58.33; H 6.93. Found: C, 58.54; H, 6.93.

An Attempt for Trapping of 6a with Acetic Acid. To a solution of **4b** (200 mg, 0.40 mmol) in THF (10 mL) at −105 °C was added 0.31 mL of ^{n}BuLi (1.6 N in THF, 0.50 mmol). The solution was stirred for 5 min, and acetic acid (0.5 mL in Et_2O (5 mL)) was injected by syringe. The solution was warmed to rt, poured into aqueous $NaHCO_3$, and extracted with Et_2O (30 mL × 2). The combined organic layer was dried over $MgSO_4$ and concentrated. Short column chromatography on silica gel using hexane and Et_2O to remove ^{n}Bu$_2$Te and subsequent PTLC (hexane/Et_2O = 20/1) gave 79 mg (64%) of pure **2c**.

(Diphenylacetyl)-*tert*-butyldimethylsilane (2c): ^1H NMR (270 MHz, $CDCl_3$) δ 0.02 (s, 6 H), 0.91 (s, 9 H), 5.51 (s, 1 H), 7.12–7.31 (m, 10 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ −6.5, 16.9, 26.4, 69.5, 126.9, 128.5, 129.4, 137.1, 241.7; IR (neat) 2953, 2929, 2857, 1646, 839, 702 cm^{-1}; MS *m*/*z* (relative intensity) 310 (M^+, 4.6), 253 (17), 115 (31), 75 (16), 73 (100); HRMS calcd for $C_{20}H_{26}OSi$ 310.1753, found 310.1730.

1-(*tert*-Butyldimethylsilyl)-2,2-diphenyl-1-(trimethylsiloxy)ethylene (3m): ^1H NMR (270 MHz, $CDCl_3$) δ −0.31 (s, 6 H), −0.16 (s, 9 H), 0.96 (s, 9 H), 7.12–7.22 (m, 10 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ −4.6, 0.8, 18.1, 27.5, 126.4, 126.9, 127.7, 127.9, 130.6, 131.3, 141.0, 141.7, 142.2, 154.9; IR (neat) 2955, 2928, 1250, 1112, 957, 862, 844, 778 cm^{-1}; MS *m*/*z* (relative intensity) 382 (M^+, 2.4), 148 (17), 147 (100), 73 (28). Anal. Calcd for $C_{23}H_{34}OSi_2$: C, 72.18; H, 8.96. Found: C, 72.25; H, 9.15.

Acknowledgment. This work was supported in part by a Grant-in-Aid from the Ministry of Education, Science and Culture, Japan. T.I. is grateful to the JSPS Fellowship for Japanese Junior Scientists. Thanks are due to the Instrumental Analysis Center, Faculty of Engineering, Osaka University.

Supplementary Material Available: Copies of ^1H and ^{13}C NMR spectra for those compounds which do not have elemental analysis data (23 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.