Reaction of β-Ethoxyvinyl Lithiums Generated from Phenyltellanyl- and Ethyltellanylacetaldehyde Diethyl Acetals with Aldehydes and Ketones and Successive Hydrations

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Reactions of α-tellanyl-β-ethoxyvinyl lithiums of aldehydes and ketones proceeded in good to high yields and the successive treatment with acids gave the α-tellanyl α,β-unsaturated aldehydes. α-Tellanyl α,β-unsaturated aldehydes easily transformed to more useful compounds.

Key words tellanyl propenal; α,β-unsaturated aldehyde; penta-2,4-dienal; electrophile

Wittig type alkenylation of aldehydes and ketones using β-alkoxyvinyl lithiums are novel methods for two-[1] and four-carbon[2] homologation leading to useful polyene compounds.[3] We previously investigated α-sulfanyl[4] or α-selanyl formylations[5] and other useful formylations and acylations using β-alkoxyalkenyl lithiums bearing perfluoroalkyl,[6] cyano groups.[7] Our next attention was on the α-tellanyl alkenylation using α-tellanylalkenyl lithiums. There are some methods for the preparations of the isologues, α-selanyl α,β-unsaturated aldehydes using the selanylating reagents.[8] On the contrary, there are few synthetic methods for α-tellanyl α,β-unsaturated aldehydes and ketones similar to the vinylic selenides except the reaction of the lithiated vinylic tellurides and DMF.[9] It is of great importance to find the new methodology for the preparations of the α-tellanyl α,β-unsaturated aldehydes because the alkenyl tellurides have produced organometal reagents such as organolithium,[10] zinc,[11] copper[12] and magnesium[13] by the Te/metal exchange reactions. Furthermore, the alkenyl tellurides affected the palladium-promoted detellurative coupling reactions to provide the α,β-unsaturated esters[14] and butenolides.[15] Here we report our preliminary studies on the novel α-tellanyl alkenylation of the aldehydes and ketones and the further transformations of the products.

Results and Disccusion

We first attempted the synthesis of the precursor, β-ethoxyvinyl telluride **2**, from phenyltellanylacetaldehyde diethyl acetal[16] according to the preparation of the sulfur and selenium analogs[4]; however, it was difficult to isolate it because of its lability. Therefore, we performed the *in situ* generation of α-tellanyl β-ethoxyvinyl lithium **3** from the acetal **1** *via* the deethoxylation and the subsequent deprotonation (Chart 1). The β-ethoxyvinyl lithium **3** was generated at −70 °C under an Ar atmosphere and the reaction with pivaldehyde gave (*E*)- and (*Z*)-allylic alcohol **4a** in 87% yield (*E*/*Z*=50/50). The stereochemistry of the alcohol was determined by the nuclear Overhauser effect (NOE) experiments as shown in the experimental section. The sulfur or selenium substituted β-ethoxyvinyl lithiums were previously reported to undergo addition with aldehydes and ketones to produce the corresponding alcohols with high stereoselectivity; however, the tellanyl allylic alcohol was obtained as a *Z*/*E* mixture. The treatment of **4a** with trimethylsilyl trifluoromethanesulfonate (TMSOTf) was conducted to give the *Z*-α-tellanyl α,β-unsaturated aldehyde **5a** in 82% yield. The stereochemistry was also determined by the NOE experiments. The reactions with other aldehydes and ketones were performed, and the results are shown in Table 1. The reactions of **1** with aromatic aldehydes produced the α,β-unsaturated aldehydes **5b**, **c** with low stereoselectivity. The reactions with cyclohexanone and cyclopentanone gave the products **5d**, **e** in moderate yields (Entries 4, 5). The ethyltellanylacetaldehyde acetal **6** was also prepared in the same manner as that of the phenyltellanyl acetal **1**. The ethyltellanyl derivative **6** underwent lithiation at −70 °C to react with similar aldehydes or ketones. However, the yields of the addition re-

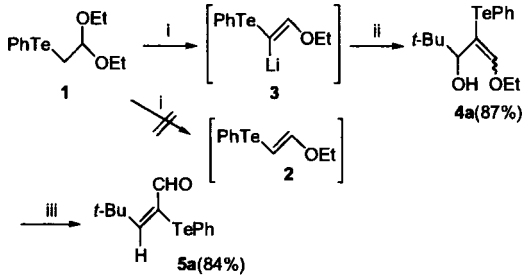
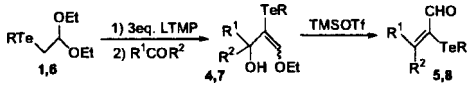


Chart 1

Table 1. α-Tellurenyl Formylation of Aldehydes and Ketones



Entry	R	R^1	R^2	Alcohol (% yield) (*Z*/*E*)	Aldehyde (% yield) (*Z*/*E*)
1	**1**(Ph)	*t*-Bu	H	**4a** (87) (50/50)	**5a** (84) (0/100)
2		Ph	H	**4b** (54) (87/13)	**5b** (57) (32/68)
3		*p*-$MeOC_5H_4$	H	**4c** (80) (51/49)	**5c** (76) (25/75)
4		$(CH_2)_5$		**4d** (47) (40/60)	**5d** (67)
5		$(CH_2)_4$		**4e** (47) (38/62)[a]	**5e** (58)
6	**6** (Et)	Ph	H	**7a** (34) (53/47)	**8a** (54) (10/90)
7		$(CH_2)_5$		—	**8b** (23)[b]
8		$PhCH_2CH_2$	H	—	**8c** (22)[b]

a) 2-Ethoxy-1-phenyltellurenylethene was obtained in 25% yield. *b*) The yield from the acetal **6** is shown.

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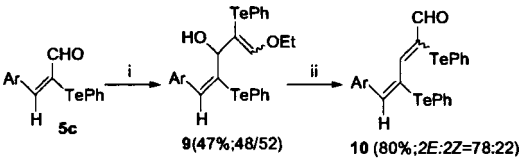

Chart 2

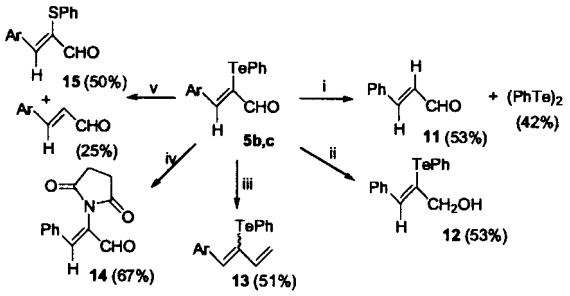

Chart 3

actions were very low (Entries 6—8).

Next, we performed the successive reactions of the aldehydes (*E*)-**5c** with phenyltellanylacetaldehyde diethyl acetal/LTMP (Chart 2). (1*E*,4*Z*)- and (1*E*,4*E*)-5-ethoxy-1-(4-methoxyphenyl)-2,4-bis(phenyltellanyl)penta-1,4-dien-3-ol (**9**) was obtained as a product, which easily converted to the penta-2,4-dienal **10** (2*E*:2*Z*=78:22). However, the conversion of **10** to the corresponding to the hepta-2,4,6-trienal was unsuccessful. In the case of the α-sulfenyl formylation of the aldehydes were successfully provided the (2*Z*,4*Z*,6*Z*)-2,4,6-tris(phenylsulfenyl)hepta-2,4,6-trienals in good yield by the three-times alkenylations.[17]

Next, we performed some transformations of the α-tellanyl alkenylated products (Chart 3). The reaction of **5b** with AIBN gave the detellanylated product **11** accompanied by diphenyl ditelluride. The formyl group on **5b**, **c** was found to easily convert to the corresponding alcohol **12** by the reduction with DIBAH, and the 1,3-butadiene **13** by the Wittig reaction with triphenylphosphonium methylide at −20 °C. Surprisingly, the reaction with *N*-bromosuccinimide provided the 2-succinimidocinnamaldehyde (**14**). The reactions of tellurides with halogenating reagents provide the dihalotellurides, which undergo subsequent hydration to afford the corresponding telluroxides. We attempted the isolation of the intermediates, however, our attempt failed. We also examined the reactions of **5c** with NBS/sodium benzenethiolate to give adduct **15**.

On the other hand, the α-sulfanyl or α-selanyl α,β-unsaturated aldehydes are easily converted to the corresponding acetals, which are novel precursors for the 2-sulfanyl or 2-selanyl allylic cations.[18] 2-Sulfanyl or selanyl functional groups effectively stabilize the allylic cations and their reactions with various nucleophiles utilize the C–C bond or C–heteroatom bond formation to provide more useful compounds. *p*-Methoxycinnamaldehyde **5c** easily converted to

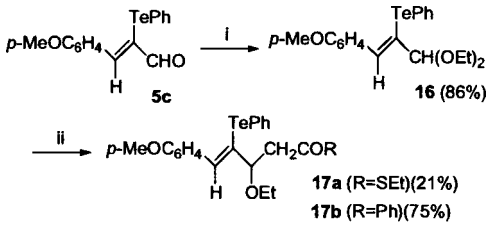

Chart 4

the acetal **16** in good yield (Chart 4). The reactions with the silyl enol ethers gave the alkylated products **17a**, **b** in moderate to good yields.

Summary We successfuly reported the first general synthetic method for α-tellanyl α,β-unstaurated aldehydes using α-tellanylacetaldehyde diethyl acetals with aldehydes and ketones. We showed some transformations of the tellanyl groups to the other useful functional groups. Now we are investigating the synthesis of the α-tellanyl α,β-unsaturated aldehydes bearing no-substituents on the β-position.

Experimental

Melting points were determined by using a Yanagimoto micro-melting point apparatus and uncorrected. Elemental analyses were determined by using Micro Corder (MT-6) of J Science Lob. at the Life Science Research Center, Gifu University. ^{1}H- and ^{13}C-NMR spectra were determined with JEOL ECA500 (500 MHz) spectrometer. IR spectra were determined on JASCO IR A-100 and IRT-30 infraed spectrometer and are expressed in reciprocal centimeter. Electron impact (EI) mass spectra (MS) were obtained using Shimadzu QP-1000 spectrometer with a direct-insertion probe at an ionization voltage of 70 eV. High-resolution mass determination was conducted on the JEOL-GCmate. Analytical and preparative TLC were performed by using Merck silica gel 7749.

Preparation of Phenyltellanylacetaldehyde Diethyl Acetal (1), Typical Procedure $NaBH_4$ (0.36 g, 9.76 mmol) was added in portions to an EtOH (100 ml) solution of diphenyl ditelluride (2.0 g, 4.88 mmol) at room temperature. When the color of the solution changed from red to colorless, bromoacetaldehyde diethyl acetal (1.92 g, 9.76 mmol) was added to the mixture. The whole was refluxed for 1 h, then poured into water (200 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with AcOEt–hexane (1:20) to give the title compound **1** (2.97 g, 94%) as a yellow oil. IR ν 2920, 2860, 1560, 1470, 1430, 1320, 1100, 1040, 720; ^{1}H-NMR δ 1.18 (6H, t, J=7 Hz, Me×2), 3.15 (2H, d, J=6 Hz, CH_2), 3.52—3.54 (1H, m, OCH_2), 3.64—3.68 (1H, m, OCH_2), 4.79 (1H, t, J=6 Hz, CHO), 7.17—7.19 (2H, m, ArH), 7.20—7.26 (1H, m, ArH), 7.74—7.75 (2H, m, ArH); ^{13}C-NMR δ 15.14 (q×2), 61.71 (t×2), 62.36 (t), 101.37 (d), 112.21 (s), 127.45 (d), 129.02 (d×2), 138.18 (d×2); MS *m/z* 307 (M^+−Me). *Anal.* Calcd for $C_{12}H_{18}O_2Te$: C, 44.78; H, 5.64. Found: C, 44.38; 5.35.

Preparation of Ethyltellanylacetaldehyde Diethyl Acetal (6) The reaction of diethyl ditelluride (2.0 g, 6.38 mmol), $NaBH_4$ (0.48 g, 12.8 mmol) and bromoacetaldehyde diethyl acetal (2.51 g, 12.8 mmol) in EtOH (100 ml) gave the title compound (3.35 g, 96%) as a pale red oil. IR ν 3040—2800, 1610, 1440, 1380, 1340, 1200, 1080, 890; ^{1}H-NMR δ 1.21 (6H, t, J=7 Hz, Me×2), 1.62 (3H, t, J=7 Hz, Me), 2.67 (2H, q, J=7 Hz, $TeCH_2$), 2.85 (2H, d, J=6 Hz, CH_2), 3.51—3.57 (2H, m, OCH_2), 3.66—3.69 (2H, m, OCH_2), 4.74 (1H, t, J=6 Hz, CHO); ^{13}C-NMR δ −4.73 (t), 6.17 (q×2), 15.18 (q), 17.54 (t), 61.61 (t×2), 104.57 (d); high-resolution mass calcd for $C_8H_{18}O_2Te$: 276.0369, found *m/z* 276.0334.

Reaction of 2-Ethoxy-1-phenyltellanylvinyl Lithium with Pivaldehyde, Typical Procedure To a THF solution of LTMP (prepared from 2,2,6,6-tetramethylpiperidine (0.57 g, 4.0 mmol) and *n*-BuLi (1.6 M in hexane, 2.0 ml, 3.0 mmol) in THF (5.0 ml)) was added phenyltellanylacetaldehyde diethyl acetal (**1**) (0.32 g, 1.0 mmol) in THF (1.0 ml) at −70 °C under an Ar atmosphere. The reaction mixture was stirred for 10 min. A THF solution of

pivaldehyde (0.43 g, 5.0 mmol) was added dropwise to the mixture. The whole was stirred for 10 min and poured into water (100 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo*. The residue was purified by preparative TLC on silica gel eluting with AcOEt–hexane (1 : 10) to afford (*Z*)-5-ethoxy-2,2-dimethyl-4-(phenyltellanyl)pent-4-en-3-ol (**4a**) (0.16 g, 44%) and (*E*)-isomer **4a** (0.16 g, 44%) as a yellow oil. The stereochemistries were determined by the NOE experiments. Irradiation of the olefinic proton at 6.90 ppm in *Z*-isomer increased the intensities of both the α-proton of the hydroxyl group (18%) and ethoxy methylene protons (24%). Furthermore, irradiation of the ethoxy methylene protons at 3.89 ppm increased the intensity of the *ortho*-aromatic protons (17%). On the other hand, the NOE enhancement of the *E*-isomer was also observed between the olefinic proton and *ortho*-aromatic protons (10%).

(*Z*)-5-Ethoxy-2,2-dimethyl-4-(phenyltellanyl)pent-4-en-3-ol (**4a**): IR ν 3500 (OH), 2950, 1590, 1460, 1420, 1380, 1350, 1230, 1170, 1100, 1060, 990, 720; ^{1}H-NMR δ 0.91 (9H, s, Me×3), 1.25 (3H, t, J=7 Hz, Me), 2.32 (1H, br d, J=9 Hz, OH), 3.89 (2H, q, J=7 Hz, OCH_2), 4.27 (1H, d, J=9 Hz, CHO), 6.90 (1H, s, olefinic H), 7.17—7.18 (3H, m, ArH), 7.62—7.64 (2H, m, ArH); ^{13}C-NMR δ 15.30 (q), 26.36 (q×3), 37.17 (s), 68.53 (t), 76.73 (d), 98.35 (s), 116.86 (s), 126.94 (d), 129.16 (d×2), 134.84 (d×2), 159.45 (d); MS *m*/*z* 360 (M^+). *Anal.* Calcd for $C_{15}H_{22}O_2Te$: C, 49.78; H, 6.13. Found: C, 49.52; H, 5.82.

(*E*)-Isomer: IR ν 3450 (OH), 2980, 1620, 1450, 1400, 1190, 1150, 1020, 730; ^{1}H-NMR δ 0.89 (9H, s, Me×3), 1.05 (3H, t, J=7 Hz, Me), 2.33 (1H, br s, OH), 3.66 (1H, br s, CHO), 3.72—3.76 (1H, m, OCH_2), 3.82—3.87 (1H, m, OCH_2), 6.46 (1H, s, olefinic H), 7.13—7.22 (3H, m, ArH), 7.67—7.69 (2H, m, ArH); ^{13}C-NMR δ 14.96 (q), 26.46 (q×3), 36.20 (s), 68.16 (t), 80.86 (d), 97.47 (s), 115.54 (s), 127.01 (d), 128.82 (d×2), 136.65 (d×2), 152.35 (d); MS *m*/*z* 360 (M^+). *Anal.* Calcd for $C_{15}H_{22}O_2Te$: C, 49.78; H, 6.13. Found: C, 50.04; H, 6.14.

Reaction of 2-Ethoxy-1-phenyltellanylvinyl Lithium with Benzaldehyde The reaction of phenyltellanylacetaldehyde diethyl acetal (**1**) (0.16 g, 0.5 mmol) and benzaldehyde (0.16 g, 1.5 mmol) was carried out in the presence of LTMP (prepared from 2,2,6,6-tetramethylpiperidine (0.21 g, 1.5 mmol) and *n*-BuLi (0.83 ml, 1.25 mmol) in THF (3 ml)). (*E*)-3-Ethoxy-1-phenyl-2-(phenyltellanyl)prop-2-en-1-ol (**4b**) (90 mg, 47%) and (*Z*)-isomer (**4b**) (14 mg, 7%) were obtained as a yellow oil.

(*Z*)-Isomer **4b**: IR ν 3450 (OH), 3050, 3000, 2900, 1600, 1440, 1380, 1290, 1170, 1100, 720; ^{1}H-NMR δ 1.35 (3H, t, J=7 Hz, Me), 2.47 (1H, d, J=7 Hz, OH), 4.02 (2H, q, J=7 Hz, OCH_2), 5.86 (1H, d, J=7 Hz, CHO), 6.93 (1H, s, olefinic H), 7.08—7.11 (2H, m, ArH), 7.15—7.26 (3H, m, ArH), 7.36—7.38 (2H, m, ArH), 7.47—7.49 (2H, m, ArH); ^{13}C-NMR δ 15.35 (q), 68.86 (t), 70.70 (d), 101.86 (s), 115.00 (s), 125.68 (d×2), 126.91 (d), 126.99 (d), 127.92 (d×2), 128.96 (d×2), 135.54 (d×2), 143.36 (s), 158.09 (d); MS *m*/*z* 382 (M^+). *Anal.* Calcd for $C_{17}H_{18}O_2Te$: C, 53.46; H, 4.75. Found: C, 53.46; H, 4.64.

(*E*)-Isomer **4b**: IR ν 3400 (OH); ^{1}H-NMR δ 1.17 (3H, t, J=7 Hz, Me), 2.39 (1H, d, J=5 Hz, OH), 3.86—3.93 (2H, m, OCH_2), 5.20 (1H, br s, CHO), 6.55 (1H, s, olefinic H), 7.09—7.19 (2H, m, ArH), 7.20—7.35 (6H, m, ArH), 7.60—7.61 (2H, m, ArH); ^{13}C-NMR δ 15.18 (q), 68.49 (t), 76.01 (d), 99.83 (s), 113.29 (s), 126.28 (d×2), 127.31 (d), 128.06 (d×2), 128.89 (d×2), 137.79 (d×2), 142.69 (s), 152.20 (d). A small M^+ was observed at *m*/*z* 382 but was too small for the high-resolution mass spectrum to be measured.

Reaction of 2-Ethoxy-1-phenyltellanylvinyl Lithium with *p*-Methoxybenzaldehyde The reaction of phenyltellanylacetaldehyde diethyl acetal (**1**) (2.0 g, 6.2 mmol) and *p*-methoxybenzaldehyde (2.54 g, 18.6 mmol) was carried out in the presence of LTMP (prepared from 2,2,6,6-tetramethylpiperidine (3.50 g, 24.8 mmol) and *n*-BuLi (12.4 ml, 18.6 mmol) in THF (15 ml)). (*Z*)-3-Ethoxy-1-*p*-methoxyphenyl-2-(phenyltellanyl)prop-2-en-1-ol (**4c**) (1.06 g, 41%) and (*E*)-isomer (**4c**) (0.99 g, 39%) were obtained as a yellow oil.

(*Z*)-Isomer **4c**: IR ν 3530 (OH), 3050, 1610, 1460, 1400, 1260, 1190, 1130, 1050, 840, 750; ^{1}H-NMR δ 1.34 (3H, t, J=7 Hz, Me), 2.47 (1H, d, J=7 Hz, OH), 3.76 (3H, s, OMe), 4.01 (2H, q, J=7 Hz, OCH_2), 5.79 (1H, d, J=7 Hz, CHO), 6.76 (2H, d, J=6 Hz, ArH), 6.90 (1H, s, olefinic H), 7.10—7.18 (3H, m, ArH), 7.26—7.29 (2H, m, ArH), 7.48—7.50 (2H, m, ArH); high-resolution mass calcd for $C_{18}H_{20}O_3Te$: 414.0475, found *m*/*z* 414.0446.

(*E*)-Isomer **4c**: IR ν 3420 (OH), 2950, 1600, 1440, 1240, 1000, 810, 720; ^{1}H-NMR δ 1.19 (3H, t, J=7 Hz, Me), 2.21 (1H, d, J=6 Hz, OH), 3.79 (3H, s, OMe), 3.88—3.94 (2H, m, OCH_2), 5.16 (1H, d, J=6 Hz, CHO), 6.56 (1H, s, olefinic H), 6.82 (2H, d, J=8 Hz, ArH), 7.10—7.13 (2H, m, ArH), 7.20—7.26 (3H, m, ArH), 7.62—7.63 (2H, m, ArH); MS *m*/*z* 410. The molecular ion peak was not observed.

Reaction of 2-Ethoxy-1-(phenyltellanyl)vinyl Lithium with Cyclohexanone The reaction of phenyltellanylacetaldehyde diethyl acetal (**1**) (0.28 g, 0.85 mmol) and cyclohexanone (0.29 g, 3.0 mmol) was carried out in the presence of LTMP (prepared from 2,2,6,6-tetramethylpiperidine (0.42 g, 3.0 mmol) and *n*-BuLi (1.4 ml, 2.1 mmol) in THF (3 ml)). (*E*)- and (*Z*)-1-(2-Ethoxy-1-(phenyltellanyl)ethenyl)cyclohexanol (**4d**) (60 mg, 19%) and (*Z*)-isomer (**4d**) (90 mg, 28%) were obtained as a yellow oil.

(*E*)-**4d**: IR ν 3400 (OH); ^{1}H-NMR δ 1.09—1.14 (1H, m, CH_2), 1.31 (3H, t, J=7 Hz, Me), 1.43—1.45 (2H, m, CH_2), 1.57—1.69 (5H, m, CH_2), 1.79—1.84 (2H, m, CH_2), 3.38 (1H, s, OH), 3.93 (2H, q, J=7 Hz, OCH_2), 6.88 (1H, s, olefinic H), 7.17—7.21 (3H, m, ArH), 7.63—7.65 (2H, m, ArH); high-resolution mass calcd for $C_{16}H_{22}O_2Te$: 376.0682, found *m*/*z* 376.0678. The NOE enhancements were observed between the olefinic H at δ 6.88 ppm and the ortho aromatic H at δ 7.63—7.65 (14%), not between the ethoxy protons at δ 3.93 ppm and the ortho aromatic H.

(*Z*)-**4d**: IR ν 3450 (OH), 2950, 1620, 1440, 1390, 1310, 1190, 1130; ^{1}H-NMR δ 1.10 (3H, t, J=7 Hz, Me), 1.17—1.79 (10H, m, CH_2), 2.46 (1H, br s, OH), 3.84 (2H, q, OCH_2), 6.57 (1H, s, olefinic H), 7.10—7.18 (3H, m, ArH), 7.62 (2H, d, J=7 Hz, ArH); high-resolution mass calcd for $C_{16}H_{22}O_2Te$: 376.0682, found *m*/*z* 376.0664. Irradiation of the ethoxy methylene protons at δ 3.84 ppm increased the intensity of the ortho aromatic protons (11%).

Reaction of 2-Ethoxy-1-(phenyltellanyl)vinyl Lithium with Cyclopentanone The reaction of phenyltellanylacetaldehyde diethyl acetal (**1**) (0.32 g, 1.0 mmol) and cyclopentanone (0.42 g, 5.0 mmol) was carried out in the presence of LTMP (prepared from 2,2,6,6-tetramethylpiperidine (0.42 g, 3.0 mmol) and *n*-BuLi (1.7 ml, 2.5 mmol) in THF (3 ml)). (*Z*)-1-(2-Ethoxy-1-(phenyltellanyl)vinyl)cyclopentanol (**4e**) (64 mg, 18%), (*E*)-isomer (**4e**) (34 mg, 9%) and 2-ethoxy-1-phenyltellanylethene (69 mg, 25%) were obtained as a yellow oil.

(*Z*)-Isomer: IR ν 3600—3100 (OH), 2960, 1600, 1440, 1380, 1300, 1180, 1110, 1000, 910, 740; ^{1}H-NMR δ 1.31 (3H, t, J=7 Hz, Me), 1.58—1.95 (8H, m, CH_2), 3.34 (1H, s, OH), 3.96 (2H, q, J=7 Hz, OCH_2), 6.94 (1H, s, olefinic H), 7.16—7.19 (3H, m, ArH), 7.60—7.62 (2H, m, ArH); ^{13}C-NMR δ 13.36 (q), 21.50 (t×2), 39.60 (t×2), 66.99 (t), 83.01 (s), 101.46 (s), 114.38 (s), 124.97 (d), 127.21 (d×2), 132.98 (d×2), 155.67 (d); high-resolution mass calcd for $C_{15}H_{20}O_2Te$: 362.0533, found *m*/*z* 362.0527. *Anal.* Calcd for $C_{15}H_{20}O_2Te$: C, 50.05; H, 5.60. Found: C, 49.53; H, 5.27.

(*E*)-Isomer: IR ν 3500 (OH); ^{1}H-NMR δ 1.14 (3H, t, J=7 Hz, Me), 1.59—1.89 (8H, m, CH_2), 3.88 (2H, q, J=7 Hz, OCH_2), 6.62 (1H, s, olefinic H), 7.13—7.20 (3H, m, ArH), 7.65—7.67 (2H, m, ArH). A small M^+ was observed at *m*/*z* 362 but was too small for the high-resolution mass spectrum to be measured.

(*Z*)-2-Ethoxy-1-(phenyltellanyl)ethene (**2**): IR ν 3060, 3000, 2900, 1580, 1440, 1380, 1300, 1200, 1080, 890, 680; ^{1}H-NMR δ 1.27 (3H, t, J=7 Hz, Me), 3.91 (2H, q, J=7 Hz, OCH_2), 5.49 (1H, d, J=6 Hz, olefinic H), 6.64 (1H, d, J=6 Hz, olefinic H), 7.16—7.24 (3H, m, ArH), 7.67—7.69 (2H, m, ArH); ^{13}C-NMR δ 15.26 (q), 68.02 (t), 74.77 (d), 113.82 (s), 127.11 (d), 129.06 (d×2), 136.80 (d×2), 150.91 (d); high-resolution mass calcd for $C_{10}H_{12}OTe$: 277.9950, found *m*/*z* 277.9918.

Reaction of 2-Ethoxy-1-(ethyltellanyl)ethenyl Lithium with Benzaldehyde The reaction of ethyltellanylacetaldehyde diethyl acetal (**6**) (0.27 g, 1.0 mmol) and benzaldehyde (0.31 g, 3.0 mmol) was carried out in the presence of LTMP (prepared from 2,2,6,6-tetramethylpiperidine (0.42 g, 3.0 mmol) and *n*-BuLi (1.7 ml, 2.5 mmol) in THF (3 ml)). (*Z*)-3-Ethoxy-2-(ethyltellurenyl)-1-phenylprop-2-en-1-ol (**7a**) (60 mg, 18%) and (*E*)-isomer (53 mg, 16%) were obtained as a yellow oil.

(*Z*)-Isomer: IR ν 3480 (OH), 3000, 2960, 1610, 1450, 1380, 1300, 1190, 1120, 700; ^{1}H-NMR δ 1.33 (6H, t, J=7 Hz, Me×2), 2.15—2.21 (2H, m, CH_2), 2.65 (1H, d, J=9 Hz, OH), 3.964.00 (2H, m, OCH_2), 5.75 (1H, d, J=8 Hz, CHO), 6.78 (1H, s, olefinic H), 7.22—7.30 (3H, m, ArH), 7.40—7.41 (2H, m, ArH); ^{13}C-NMR δ −0.44 (t), 15.38 (q), 16.69 (q), 68.61 (t), 70.12 (d), 98.58 (s), 125.61 (d×2), 126.90 (d), 127.97 (d×2), 143.93 (s), 156.48 (d); MS *m*/*z* 336 (M^+). *Anal.* Calcd for $C_{13}H_{18}O_2Te$: C, 46.77; H, 5.43. Found: C, 47.05; H, 5.37.

(*E*)-Isomer: IR ν 3480 (OH), 3050, 3000, 1650, 1480, 1420, 1330, 1210, 1160, 1050, 770, 720; ^{1}H-NMR δ 1.31 (3H, t, J=7 Hz, Me), 1.47 (3H, t, J=7 Hz, Me), 2.46 (1H, br s, OH), 2.48—2.52 (1H, m, OCH_2), 2.59—2.63 (1H, m, OCH_2), 5.13 (1H, br s, CHO), 6.62 (1H, s, olefinic H), 7.24—7.38 (5H, m, ArH); ^{13}C-NMR δ −1.86 (t), 15.23 (q), 17.14 (q), 68.29 (t), 75.90 (d), 96.73 (s), 126.05 (d×2), 127.11 (d), 127.95 (d×2), 128.38 (s), 151.82 (d); high-resolution mass calcd for $C_{13}H_{18}O_2Te$: 336.0688, found *m*/*z* 336.0648.

Reaction of 2-Ethoxy-1-(ethyltellanyl)vinyl Lithium with Cyclohexanone The reaction of ethyltellanylacetaldehyde diethyl acetal (**6**) (0.27 g, 1.0 mmol) and cyclohexanone (0.20 g, 2.0 mmol) was carried out in the presence of LTMP (prepared from 2,2,6,6-tetramethylpiperidine (0.42 g, 3.0 mmol) and *n*-BuLi (1.7 ml, 2.5 mmol) in THF (3 ml)). The work-up procedure afforded the reaction mixture, which was treated with TMSOTf (0.07 g, 0.32 mmol) at −78 °C without further purification. The work-up procedure gave ethyltellanylformylmethylenecyclohexane (**8b**) (44 mg, 23%) as a yellow oil. IR ν 2980, 2910, 1670 (CO), 1590, 1470, 1210, 1160, 1110, 1020, 880; ^{1}H-NMR δ 1.54 (3H, t, J=7 Hz, Me), 1.69—1.72 (6H, m, CH_2), 2.72—2.78 (4H, m, CH_2 and $TeCH_2$), 2.89—2.91 (2H, m, CH_2), 9.69 (1H, s, CHO); ^{13}C-NMR δ −0.49 (t), 17.36 (q), 26.36 (t), 28.64 (t), 29.08 (t), 32.50 (t), 44.03 (t), 117.18 (s), 173.68 (s), 189.50 (d); high-resolution mass calcd for $C_{10}H_{16}OTe$: 282.0206, found *m*/*z* 282.0263.

Reaction of 2-Ethoxy-1-(ethyltellanyl)ethenyl Lithium with Hydrocinnamaldehyde The reaction of ethyltellanylacetaldehyde diethyl acetal (**6**) (0.27 g, 1.0 mmol) and hydrocinnamaldehyde (0.42 g, 3.0 mmol) was carried out in the presence of LTMP (prepared from 2,2,6,6-tetramethylpiperidine (0.42 g, 3.0 mmol) and *n*-BuLi (1.7 ml, 2.5 mmol) in THF (3 ml)). The work-up procedure provided a yellow residue. The mixture was not further purified and used to the hydrolysis process. Me_3SiOTf (64 mg, 0.29 mmol) was added to the mixture in dry CH_2Cl_2 (2.0 ml) at −78 °C. The almost same work-up provided (*E*)-2-ethyltellanyl-5-phenylpent-2-enal (**8c**) (24 mg, 22%). IR ν 3010, 2910, 2850, 2700, 1660, 1570, 1420, 1170, 1100, 1060, 710; ^{1}H-NMR δ 1.52 (3H, t, J=7 Hz, Me), 2.80 (2H, q, J=7 Hz, CH_2), 2.85—2.94 (4H, m, CH_2), 7.09—7.12 (1H, m, ArH), 7.20—7.23 (2H, m, ArH), 7.29—7.32 (2H, m, ArH), 9.08 (1H, s, CHO); ^{13}C-NMR δ −0.93 (t), 17.61 (q), 34.28 (t), 38.08 (t), 125.03 (s), 126.37 (d), 128.41 (d×2), 128.56 (d×2), 140.12 (s), 164.72 (d), 193.36 (d); high-resolution mass calcd for $C_{13}H_{16}OTe$: 318.0223, found *m*/*z* 318.0263.

Treatment of (*Z*)-5-Ethoxy-2,2-dimethyl-4-(phenyltellanyl)pent-4-en-3-ol (4a) with TMSOTf, Typical Procedure To a CH_2Cl_2 (3.0 ml) solution of (*Z*)- and (*E*)-**4a** (0.22 g, 0.61 mmol) was added dropwise *O*-trimethylsilyl trifluoromethanesulfonate (0.14 g, 0.11 ml, 0.61 mmol) at −78 °C under an Ar atmosphere. The reaction mixture was stirred for 10 min and then poured into a $NaHCO_3$ (100 ml) solution. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$. The combined organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt–hexane (1 : 40) to give (*E*)-4,4-dimethyl-2-(phenyltellanyl)pent-2-enal (**5a**) (0.16 g, 84%) as a yellow oil, accompanied by diphenyl ditelluride (11 mg, 4%). The stereochemistry was determined by the NOE experiments as *E*. Irradiation of the *t*-butyl group at δ 1.33 ppm increased the intensity of the formyl proton (5%), not that of the olefinic proton. IR ν 2950, 1680 (CO), 1570, 1460, 1330, 1200, 1080, 1020, 720; ^{1}H-NMR δ 1.33 (9H, s, Me×3), 7.16—7.17 (2H, m, ArH), 7.45 (1H, s, olefinic H), 7.67 (2H, d, J=8 Hz, ArH), 8.91 (1H, s, CHO); ^{13}C-NMR δ 30.07 (q×3), 35.61 (s), 113.50 (s), 122.22 (s), 127.72 (d), 129.14 (d×2), 137.85 (d×2), 174.56 (d), 193.51 (d); MS *m*/*z* 318 (M^+). *Anal.* Calcd for $C_{13}H_{16}OTe$: C, 49.43; H, 5.11. Found: C, 49.18; H, 5.05.

Treatment of (*Z*)- and (*E*)-3-Ethoxy-1-phenyl-4-(phenyltellanyl)prop-2-en-1-ol (4b) with TMSOTf The reaction of **4b** (0.54 g, 1.42 mmol) and TMSOTf (0.32 g, 0.26 ml, 1.42 mmol) in CH_2Cl_2 (10.0 ml) at −78 °C provided (*E*)-2-(phenyltellanyl)cinnamaldehyde (**5b**) (0.128 g, 27%) and (*Z*)-isomer (0.27 g, 57%).

(*E*)-Isomer: IR ν 1660 (CO); ^{1}H-NMR δ 7.19—7.26 (2H, m, ArH), 7.32—7.38 (7H, m, olefinic and ArH), 7.91 (2H, d, J=7 Hz, ArH), 9.63 (1H, s, CHO); MS *m*/*z* 338 (M^+). *Anal.* Calcd for $C_{15}H_{12}OTe$: C, 53.64; H, 3.60. Found: C, 52.66; H, 3.54.

(*Z*)-Isomer: IR ν 3050, 2800, 1660, 1560, 1340, 1170, 1080, 1020, 720; ^{1}H-NMR δ 7.07—7.19 (2H, m, ArH), 7.34—7.35 (3H, m, ArH), 7.58—7.60 (5H, m, ArH), 8.13 (1H, s, olefinic H), 9.28 (1H, s, CHO); ^{13}C-NMR δ 112.74 (s), 124.29 (s), 127.91 (d), 128.20 (d×2), 129.16 (d×2), 130.33 (d×2), 130.43 (d), 135.17 (s), 138.14 (d×2), 157.02 (d), 193.42 (d); MS *m*/*z* 338 (M^+). *Anal.* Calcd for $C_{15}H_{12}OTe$: C, 53.64; H, 3.60. Found: C, 53.77; H, 3.59.

Treatment of (*Z*)- and (*E*)-3-Ethoxy-1-*p*-methoxyphenyl-4-(phenyltellanyl)prop-2-en-1-ol (4c) with TMSOTf The reaction of **4c** (0.80 g, 1.95 mmol) and TMSOTf (0.43 g, 0.35 ml, 1.95 mmol) in CH_2Cl_2 (15.0 ml) at −78 °C provided (*E*)-2-(phenyltellanyl)-*p*-methoxycinnamaldehyde (**5c**) (0.135 g, 19%) and (*Z*)-isomer (0.41 g, 57%).

(*E*)-Isomer: IR ν 2950, 2850, 1650 (CO), 1600, 1510, 1440, 1290, 1260, 1170, 1060, 1020, 890, 830, 720; ^{1}H-NMR δ 3.78 (3H, s, OMe), 6.86 (2H, d, J=9 Hz, ArH), 7.15 (2H, d, J=9 Hz, ArH), 7.25—7.32 (2H, m, ArH), 7.36 (1H, s, olefinic H), 7.39—7.40 (1H, m, ArH), 7.88—7.89 (2H, m, ArH), 9.62 (1H, s, CHO); ^{13}C-NMR δ 55.32 (q), 111.85 (s), 113.94 (d×2), 125.27 (s), 128.91 (d), 129.78 (d×2), 131.20 (d×2), 141.13 (d×2), 150.86 (d), 160.76 (s), 190.36 (d); high-resolution mass calcd for $C_{16}H_{14}O_2Te$: 368.0063, found *m*/*z* 368.0074. *Anal.* Calcd for $C_{16}H_{14}O_2Te$:C, 52.52; H, 3.86. Found: C, 53.07; H, 4.23. The NOE enhancement between the formyl proton at δ 9.62 ppm and the ortho aromatic protons at δ 7.88—7.89 ppm was observed as 7.5%.

(*Z*)-Isomer: IR ν 3080, 2950, 2850, 2710, 1670 (CO), 1570, 1430, 1250, 1180, 1100, 1020, 880, 820, 730; ^{1}H-NMR δ 3.81 (3H, s, OMe), 6.87 (2H, d, J=8 Hz, ArH), 6.88—7.17 (3H, m, ArH), 7.57 (2H, d, J=8 Hz, ArH), 7.70 (2H, m, ArH), 8.05 (1H, s, olefinic H), 9.21 (1H, s, CHO); ^{13}C-NMR δ 55.35 (q), 113.04 (s), 113.71 (d×2), 120.46 (s), 127.55 (s), 127.68 (d×2), 129.16 (d×2), 133.03 (d×2), 137.47 (d), 157.60 (d), 161.80 (s), 193.52 (d); high-resolution mass calcd for $C_{16}H_{14}O_2Te$: 368.0063, found *m*/*z* 368.0085. *Anal.* Calcd for $C_{16}H_{14}O_2Te$:C, 52.52; H, 3.86. Found: C, 53.03; H, 4.03. The NOE enhacement between the olefinic proton at δ 8.05 ppm and the formyl proton at δ 9.21 ppm was observed as 19%.

Treatment of (*E*)- and (*Z*)-1-(2-Ethoxy-1-(phenyltellanyl)ethenyl)cyclohexanol (4d) with TMSOTf The reaction of **4d** (0.10 g, 0.27 mmol) and TMSOTf (0.06 g, 0.05 ml, 0.27 mmol) in CH_2Cl_2 (2.0 ml) at −78 °C provided [(phenyltellanyl)formylmethylene]cyclohexane (**5d**) (0.06 g, 67%).

5d: IR ν 3070, 2950, 2840, 1660 (CO), 1570, 1440, 1370, 1240, 1060, 1000, 860, 730; ^{1}H-NMR δ 1.56—1.71 (6H, m, CH_2), 2.73—2.76 (2H, m, CH_2), 2.92—2.94 (2H, m, CH_2), 7.16—7.23 (3H, m, ArH), 7.61—7.63 (2H, m, ArH), 9.71 (1H, s, CHO); ^{13}C-NMR δ 26.28 (t), 28.43 (t), 29.04 (t), 32.87 (t), 44.14 (t), 114.52 (s), 121.44 (s), 127.39 (d), 129.22 (d×2), 137.22 (d×2), 174.53 (s), 189.39 (d); high-resolution mass calcd for $C_{14}H_{16}OTe$: 330.0263, found *m*/*z* 330.0276.

Treatment of (*E*)- and (*Z*)-1-(2-Ethoxy-1-(phenyltellanyl)vinyl)cyclopentanol (4e) with TMSOTf The reaction of **4e** (40 mg, 0.11 mmol) and TMSOTf (0.02 g, 0.02 ml, 0.11 mmol) in CH_2Cl_2 (2.0 ml) at −78 °C provided [(phenyltellanyl)formylmethylene]cyclopentane (**5e**) (35 mg, 58%).

5e: IR ν 1630 (CO); ^{1}H-NMR δ 1.67—1.72 (2H, m, CH_2), 1.89—1.95 (2H, m, CH_2), 2.60—2.63 (2H, m, CH_2), 3.03—3.05 (2H, m, CH_2), 7.15—7.26 (3H, m, ArH), 7.63—7.65 (2H, m, ArH), 9.58 (1H, s, CHO); ^{13}C-NMR δ 24.39 (t), 27.28 (t), 33.47 (t), 42.61 (t), 98.03 (s), 113.67 (s), 127.54 (d), 129.27 (d×2), 137.60 (d×2), 190.33 (d); MS *m*/*z* 284, 251. The molecular ion peak was not observed.

Treatmwnt of (*Z*)- and (*E*)-3-Ethoxy-4-(ethyltellanyl)-1-phenylprop-2-en-1-ol (7a) with TMSOTf The reaction of **7a** (47 mg, 0.14 mmol) and TMSOTf (31 mg, 0.03 ml, 0.14 mmol) in CH_2Cl_2 (2.0 ml) at −78 °C provided (*Z*)-2-(ethyltellanyl)cinnamaldehyde (**8a**) (23 mg, 54%) as a yellow oil. IR ν 3110, 3000, 2750, 1680 (CO), 1610, 1590, 1460, 1300, 1210, 1110, 940, 770, 700; ^{1}H-NMR δ 1.49 (3H, t, J=7 Hz, Me), 2.89 (2H, t, J=7 Hz, CH_2), 7.42—7.48 (3H, m, ArH), 7.64—7.66 (2H, m, ArH), 8.07 (1H, s, olefinic H), 9.31 (1H, s, CHO); ^{13}C-NMR δ 0.39 (t), 17.19 (q), 121.67 (s), 128.43 (d×2), 130.13 (d×2), 130.38 (d), 135.86 (s), 158.01 (d), 194.13 (d); MS *m*/*z* 254. *Anal.* Calcd for $C_{11}H_{12}OTe$: C, 45.90; H, 4.20. Found: C, 45.54; H, 4.19. The olefinic and formyl protons of the *E*-isomer were observed at δ 7.91 (s), 9.50 (s) in the ^{1}H-NMR spectrum.

Tandem α-Tellanyl Alkenylation of 5c Reaction of 2-phenyltellanyl-4-methoxycinnamaldehyde (**9**) (0.50 g, 1.37 mmol) with 2-ethoxy-1-phenyltellanylvinyl lithium (generated from phenyltellanylacetaldehyde diethyl acetal (**1**) (0.66 g, 2.1 mmol), 2,2,6,6-tetramethylpiperidine (1.16 g, 8.2 mmol) and *n*-BuLi (4.1 ml, 1.6 M in hexane, 6.2 mmol) in THF (10 ml)) afforded (1*E*,4*Z*)- and (1*E*,4*E*)-5-ethoxy-1-(4-methoxyphenyl)-2,4-bis(phenyltellanyl)penta-1,4-dien-3-ol (**9**) (0.53 g, 60%) as a pale red oil.

(1*E*,4*E*)-**9**: IR ν 3440 (OH), 1590, 1230, 1160, 1000, 720; ^{1}H-NMR δ 1.17 (3H, t, J=7 Hz, Me), 2.49 (1H, d, J=6 Hz, OH), 3.77 (3H, s, OMe), 3.79—3.91 (2H, m, OCH_2), 4.62 (1H, br s, CHO), 6.37 (1H, s, olefinic H), 6.78 (2H, d, J=9 Hz, ArH), 7.07—7.23 (8H, m, ArH), 7.33 (1H, s, olefinic H), 7.57 (2H, d, J=7 Hz, ArH), 7.64 (2H, d, J=7 Hz, ArH); ^{13}C-NMR δ 15.22 (q), 55.13 (q), 68.49 (t), 79.78 (d), 98.16 (s), 113.22 (d×2), 113.31 (s), 114.13 (s), 114.22 (s), 125.83 (s), 127.12 (d), 127.61 (d), 128.91 (d×2), 129.12 (d×2), 130.05 (d×2), 131.02 (s), 136.90 (d), 137.31 (d×2), 138.14 (d×2), 153.87 (d), 159.07 (s); MS *m*/*z* 640 (M^+). *Anal.* Calcd for $C_{26}H_{26}O_3Te_2$: C, 48.67; H, 4.08. Found: C, 48.49; H, 4.03.

(1*E*,4*Z*)- and (1*Z*,4*Z*)-**9**: IR ν 3500 (OH), 3040, 1620, 1430, 1400, 1260, 1200, 1130, 1040, 890, 840, 750; ^{1}H-NMR δ 1.20 (t, J=7 Hz, 1*Z*-Me), 1.24 (t, J=7 Hz, 1*E*-Me), 2.71 (d, J=5 Hz, 1*Z*-OH), 2.77 (d, J=8 Hz, 1*E*-OH), 3.77 (s, 1*Z*-OMe), 3.78 (s, 1*E*-OMe), 3.88—3.93 (m, 1*Z*- and 1*E*-OCH_2), 5.00 (d, J=4 Hz, 1*Z*-CHO), 5.27 (d, J=8 Hz, 1*E*-CHO), 6.70 (d, J=9 Hz, 1*Z*-ArH), 6.74 (d, J=8 Hz, 1*E*-ArH), 6.93 (s, 1*E*-olefinic H), 7.01—7.26

(olefinic and ArH), 7.29 (s, 1*E*-olefinic H), 7.54 (d, *J*=8 Hz, 1*E*-ArH), 7.63 (d, *J*=8 Hz, 1*E*-ArH), 7.75 (d, *J*=8 Hz, 1*Z*-ArH), 7.85 (d, *J*=8 Hz, 1*Z*-ArH); MS *m/z* 596 ($M^+-OMe+1$), 519, 410; *Anal.* Calcd for $C_{26}H_{26}O_3Te_2$: C, 48.67; H, 4.08. Found: C, 48.67; H, 4.20.

Treatment of 9 with TMSOTf TMSOTf (0.18 g, 0.82 mmol) was added dropwise to a CH_2Cl_2 (6 ml) solution of (1*E*,4*Z*)- and (1*E*,4*E*)-5-ethoxy-1-(4-methoxyphenyl)-2,4-bis(phenyltellanyl)penta-1,4-dien-3-ol (**9**) (0.66 g, 2.05 mmol) at −78 °C under an Ar atmosphere. The reaction mixture was stirred for 10 min. The work-up procedure afforded (2*E*,4*E*)- and (2*Z*,4*E*)-2,4-bis(phenyltellanyl)-5-(4-methoxyphenyl)penta-2,4-dienal (**10**) (0.39 g, 80%) as a yellow oil. The isomer ratio was determined by the intensity of the formyl group as 2*E*:2*Z*=78:22. IR *ν* 3050, 3000, 2910, 2800, 1660 (CO), 1590, 1560, 1240, 1160, 1100, 1010, 810, 720; ^{1}H-NMR *δ* 3.79 (s, 2*E*-OMe), 3.83 (s, 2*Z*-OMe), 6.81 (d, *J*=6 Hz, 2*E*-ArH), 6.89—7.35 (m, ArH), 7.57—7.63 (m, ArH), 7.70—7.42 (m, 2*Z*-ArH), 7.81 (d, *J*=7 Hz, 2*E*-ArH), 8.10 (d, *J*=1 Hz, 2*E*-olefinic H), 8.88 (s, 2*Z*-CHO), 9.15 (2*E*-CHO); ^{13}C-NMR of 2*E*-**10**: *δ* 55.27 (q), 114.02 (d×2), 116.82 (s), 128.06 (d), 128.21 (d), 128.55 (s), 129.07 (d×2), 129.48 (d×2), 129.85 (s), 130.61 (d×2), 138.66 (d×2), 138.69 (d×2), 139.62 (d), 147.18 (s), 159.93 (d), 159.96 (d), 191.78 (d); MS *m/z* 284, 207 (PhTe), 202. *Anal.* Calcd for $C_{24}H_{20}O_2Te_2$: C, 48.40; H, 3.38. Found: C, 47.92; H, 3.42.

Reaction of 2-(Phenyltellanyl)cinnamaldehyde with AIBN A benzene solution of the aldehyde **5a** (0.10 g, 0.30 mmol) and AIBN (98 mg, 0.60 mmol) was refluxed for 10 min. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt–*n*-hexane (1:20) afforded cinnamaldehyde (21 mg, 53%) and diphenyl ditelluride (26 mg, 42%).

Reduction of 5a with DIBAH A hexane solution of DIBAH (1.0 M, 0.30 ml, 0.30 mmol) was added dropwise to a toluene (1.0 ml) solution of 2-(phenyltellanyl)cinnamaldehyde (**5a**) (0.10 g, 0.30 mmol) at −78 °C under an Ar atmosphere. The mixture was stirred for 10 min and poured into water (100 ml). The work-up procedure afforded 2-(phenyltellanyl)cinnamyl alcohol (**12**) (54 mg, 53%) as a yellow oil. IR *ν* 3400 (OH), 3040, 2940, 1600, 1580, 1440, 1220, 1010, 740, 690; ^{1}H-NMR *δ* 2.22 (1H, br s, OH), 4.20 (2H, s, CH_2O), 6.88 (1H, s, olefinic H), 7.12 (2H, d, *J*=8 Hz, ArH), 7.21—7.35 (6H, m, ArH), 7.85 (2H, d, *J*=8 Hz, ArH); ^{13}C-NMR *δ* 64.24 (t), 113.55 (s), 127.22 (d), 127.73 (s), 128.30 (d×2), 128.35 (d×2), 128.39 (d×2), 129.59 (d×2), 137.49 (s), 138.48 (d), 139.63 (d); MS *m/z* 340 (M^+). *Anal.* Calcd for $C_{15}H_{14}OTe$: C, 53.32; H, 4.18. Found: C, 52.97; H, 4.14.

Reaction of 5c with Triphenylphosphonium Methylide *n*-BuLi (3.0 ml, 4.50 mmol) was added to methyltriphenylphosphonium bromide (0.71 g, 2.0 mmol) in THF (10 ml) at −20 °C under an Ar atmosphere. The reaction mixture was stirred for 30 min. (*Z*)-2-Phenyltellanyl-3-(4-methoxyphenyl)cinnamaldehyde (**5c**) (0.10 g, 0.27 mmol) in THF (2 ml) was added dropwise to the reaction mixture. The whole was stirred for 10 min and poured into water (50 ml). The work-up procedure afforded (*Z*)- and (*E*)-1-(4-methoxyphenyl)-2-(phenyltellanyl)buta-1,3-diene (**13**) (50 mg, 51%) as a colorless oil. IR *ν* 3080, 2950, 1610, 1590, 1510, 1450, 1260, 1180, 1030, 830, 740; ^{1}H-NMR *δ* 3.80 (s, *E*-, *Z*-Me), 5.13 (d, *J*=6 Hz, *E*-olefinic H), 5.35 (d, *J*=10 Hz, *Z*-olefinic H), 5.57 (d, *J*=16 Hz, *E*-olefinic H), 5.65 (d, *J*=16 Hz, *Z*-olefinic H), 6.34 (dd, *J*=10, 16 Hz, *E*-olefinic H), 6.65 (dd, *J*=10, 16 Hz, *Z*-olefinic H), 6.86 (d, *J*=9 Hz, ArH), 7.12—7.26 (m, *E*-, *Z*-ArH), 7.36 (d, *J*=8 Hz, ArH), 7.53 (d, *J*=8 Hz, *E*-ArH), 7.71 (d, *J*=8 Hz, *Z*-ArH); MS *m/z* 289 (M^+-Ph); *Anal.* Calcd for $C_{17}H_{16}OTe$: C, 56.11; H, 4.43. Found: C, 55.79; H, 4.65.

Reaction of 5b with *N*-Bromosuccinimide *N*-Bromosuccinimide (0.133 g, 0.75 mmol) was added to a $ClCH_2CH_2Cl$ (1 ml) solution of (*E*)-2-(phenyltellanyl)cinnamaldehyde (0.10 g, 0.30 mmol) at 0 °C. The mixture was stirred for 1 h. The work-up procedure provided 2-succinimidocinnamaldehyde (**14**) (46 mg, 67%). IR *ν* 3040, 2960, 1780 (CO), 1710 (CO), 1360, 1170, 1090, 750; ^{1}H-NMR *δ* 2.78 (4H, s, NCH_2×2), 6.00 (1H, s, olefinic H), 7.27—7.41 (3H, m, ArH), 7.60 (2H, d, *J*=7 Hz, ArH), 9.08 (1H, s, CHO); ^{13}C-NMR *δ* 27.93 (t×2), 65.47 (d), 72.56 (s), 128.73 (d×2), 129.68 (d), 130.79 (d×2), 132.46 (s), 176.38 (s×2), 179.67 (d); MS *m/z* 228 (M^+-1). The molecular ion peak was not observed.

Reaction of 5c with *N*-Bromosuccinimide/PhSNa NBS (58 mg, 0.32 mmol) was added to a CH_2Cl_2 (2.0 ml) solution of (*Z*)-**5c** (0.10 g, 0.27 mmol) at 0 °C. After 10 min stirring, PhSNa (prepared from thiophenol (59 mg, 0.54 mmol and NaH (60%, 22 mg, 0.54 mmol) in THF (2 ml)) was added to the reaction mixture. The whole was stirred for 30 min. The work-up procedure provided a mixture of 3-(4-methoxyphenyl)-2-(phenylsulfanyl)prop-2-enal (**15**) and *p*-methoxycinnamaldehyde (55 mg, 75%), accompanied by diphenyl ditelluride (31 mg, 56%). The compound **15** was determined by comparing with the authentic sample prepared by another method from *β*-ethoxyvinyl phenyl sulfide and *p*-methoxybenzaldehyde.[5)]

15: Yellow needles, mp 67—68 °C, IR *ν* 1682 (CO), 1600, 1589, 1508, 1308, 1251, 1180, 1110, 1026, 747, 540; ^{1}H-NMR *δ* 3.83 (3H, s, OMe), 6.93 (2H, d, *J*=9 Hz, ArH), 7.14—7.25 (5H, m, ArH), 7.85 (1H, s, olefinic H), 8.03 (2H, d, *J*=9 Hz, ArH), 9.54 (1H, s, CHO); ^{13}C-NMR *δ* 55.37 (q), 114.12 (d×2), 126.25 (d), 126.34 (s), 128.22 (d×2), 129.01 (d×2), 129.68 (s), 133.76 (d×2), 134.19 (s), 152.65 (d), 162.16 (s), 191.06 (d); MS *m/z* 270 (M^+). *Anal.* Calcd for $C_{16}H_{14}O_2S$: C, 71.08; H, 5.22. Found: C, 70.96; H, 5.22.

Preparation of the (*Z*)-2-(Phenyltellanyl)-*p*-methoxycinnamaldehyde Diethyl Acetal (16) A EtOH (3 ml) solution of the aldehyde **5c** (0.26 g, 0.70 mmol) and triethyl orthoformate (0.52 g, 3.5 mmol) in the presence of *p*-toluenesulfonic acid (27 mg, 0.14 mmol) at 0 °C. The reaction mixture was stirred for 30 min. The work-up procedure and the purification by preparative TLC on silica gel eluting with AcOEt–hexane (1:40) gave the title compound **16** (0.27 g, 86%).

(*Z*)-Isomer: IR *ν* 3060, 3000—2850, 1600, 1440, 1290, 1250, 1030, 820, 730; ^{1}H-NMR *δ* 1.25 (3H, t, *J*=7 Hz, Me), 3.58—3.65 (2H, m, OCH_2), 3.70—3.75 (2H, m, OCH_2), 3.78 (3H, s, OMe), 5.05 (1H, s, acetal H), 6.53 (1H, s, olefinic H), 6.81 (2H, d, *J*=8 Hz, ArH), 7.18 (2H, d, *J*=8 Hz, ArH), 7.25—7.34 (3H, m, ArH), 7.91 (2H, d, *J*=9 Hz, ArH); ^{13}C-NMR *δ* 15.20 (q×2), 55.20 (q), 61.95 (t×2), 99.83 (d), 113.52 (d×2), 114.13 (s), 124.55 (s), 128.32 (d), 129.43 (d×2), 129.84 (d×2), 130.60 (s), 136.57 (d), 136.57 (d), 140.83 (d×2), 158.70 (s); MS *m/z* 442 (M^+). *Anal.* Calcd for $C_{20}H_{24}O_3Te$: C, 54.59; H, 5.50. Found: C, 54.60; H, 5.54.

The other condition provided the *E*- and *Z*-isomers, respectively. The spectral data of the *E*-isomer was described as follows.

(*E*)-Isomer: IR *ν* 3000, 2890, 1600, 1570, 1510, 1440, 1250, 1100, 1040, 860, 820, 730; ^{1}H-NMR *δ* 1.18 (3H, t, *J*=7 Hz, Me), 3.37—3.43 (1H, m, OCH_2), 3.58—3.64 (1H, m, OCH_2), 3.79 (3H, s, OMe), 4.78 (1H, s, acetal H), 6.81 (2H, d, *J*=8 Hz, ArH), 7.10—7.25 (3H, m, ArH), 7.33 (2H, d, *J*=8 Hz, ArH), 7.42 (1H, s, olefinic H), 7.68—7.70 (2H, m, ArH); ^{13}C-NMR *δ* 15.10 (q×2), 55.20 (q), 62.15 (t×2), 99.88 (s), 105.42 (d), 113.31 (d×2), 119.06 (s), 127.67 (d), 128.86 (d×2), 129.43 (s), 130.35 (d×2), 137.14 (d), 138.90 (d×2), 159.27 (s); MS *m/z* 442 (M^+). *Anal.* Calcd $C_{20}H_{24}OTe$: C, 54.59; H, 5.50. Found: C, 54.32; H, 5.44.

The Reaction of Acetal 16 with Nucleophile, Typical Procedure $Sc(OTf)_3$ (10 mg, 0.02 mmol) was added to a CH_2Cl_2 (2.0 ml) solution of (*Z*)-2-(phenyltellanyl)-*p*-methoxycinnamaldehyde diethyl acetal (**16**) (93 mg, 0.21 mmol) and *S*-ethyl *O*-trimethylsilyloxyethylene (0.11 g, 0.63 mmol) at 0 °C. The reaction mixture was stirred for 30 min and poured into a sat. $NaHCO_3$ (50 ml). The organic layer was separated and aqueous layer was extracted with $CHCl_3$. The combined organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt–hexane (1:20) to give *S*-ethyl 3-ethoxy-5-*p*-methoxyphenyl-4-(phenyltellanyl)pent-4-enoate (**17a**) (28 mg, 27%) and 2-(phenyltellanyl)-*p*-methoxycinnamaldehyde (**5c**) (39 mg, 51%). IR *ν* 3030, 2990, 1700, 1630, 1600, 1520, 1460, 1270, 1200, 1080, 900, 840; ^{1}H-NMR *δ* 1.06 (3H, t, *J*=7 Hz, Me), 1.20 (3H, t, *J*=7 Hz, Me), 2.83—2.89 (4H, m, CH_2), 3.02 (1H, dd, *J*=4, 15 Hz, CH_2), 2.89—3.04 (1H, m, OCH_2), 3.05—3.51 (1H, m, OCH_2), 3.80 (3H, s, OMe), 4.27 (1H, dd, *J*=4, 9 Hz, 3-H), 6.83 (2H, d, *J*=9 Hz, ArH), 7.04—7.16 (3H, m, ArH), 7.24—7.31 (8H, m, olefinic and ArH), 7.63—7.67 (2H, m, ArH); ^{13}C-NMR *δ* 14.71 (q), 15.02 (q), 23.29 (t), 50.68 (t), 55.22 (q), 64.49 (t), 82.37 (d), 112.77 (s), 113.36 (d×2), 121.92 (s), 128.04 (d), 129.21 (d×2), 130.21 (d×2), 130.59 (s), 136.77 (d), 138.96 (d×2), 159.24 (s), 196.62 (s); MS *m/z* 500 (M^+). *Anal.* Calcd $C_{22}H_{26}O_3STe$: C, 53.05; H, 5.26. Found: C, 53.04; H, 5.48.

Reaction of 16 with 1-Phenyl-1-trimethylsilyloxyethylene The reaction of the acetal **16** (0.10 g, 0.23 mmol), 1-phenyl-1-trimethylsilyloxyethylene (0.13 g, 0.68 mmol) and TMSOTf (50 mg, 0.04 ml, 0.23 mmol) at −78 °C provided (*Z*)-3-ethoxy-5-*p*-methoxyphenyl-4-phenyltellanyl-pent-4-enophenone (**17b**) (90 mg, 75%) as a yellow oil. IR *ν* 3010, 1690 (CO), 1620, 1420, 1460, 1255, 1200, 1100, 1050, 840, 760; ^{1}H-NMR *δ* 1.03 (3H, t, *J*=7 Hz, Me), 3.23—3.28 (1H, m, OCH_2), 3.31—3.36 (2H, m, CH_2), 3.50—3.57 (1H, m, OCH_2), 3.77 (3H, s, OMe), 4.49 (1H, dd, *J*=4, 7 Hz, 3-H), 6.82 (2H, d, *J*=8 Hz, ArH), 6.98—7.19 (3H, m, ArH), 7.34 (2H, d, *J*=8 Hz, ArH), 7.36—7.49 (3H, m, ArH), 7.62 (2H, d, *J*=8 Hz, ArH), 7.83 (2H, d, *J*=8 Hz, ArH); ^{13}C-NMR *δ* 15.03 (q), 45.62 (t), 55.12 (q), 64.30 (t), 82.21 (d), 112.91 (s), 113.28 (d×2), 123.04 (s), 127.82 (d), 128.09 (d×2), 128.30 (d×2), 129.12 (d×2), 130.20 (d×2), 130.53 (s), 132.72 (d), 136.92 (d), 137.18 (s), 138.54 (d×2), 159.16 (s), 197.55 (s). The small M^+ was observed at *m/z* 516 but was too small for the high-resolution mass spectrum to be measured.

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