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Stability of the Tellurium−Carbon Bond in Vinylic Tellurides toward Commonly Used Reagents in Organic Synthesis

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Several chemical transformations on the side chain of functionalized vinylic tellurides were performed without affecting the tellurium−carbon bond. The stereochemistry of the double bond was maintained in some cases (protection and deprotection of alcohols); in other cases (acetal hydrolysis, oxidation, and reduction) some isomerization of the carbon−carbon double bond was observed.

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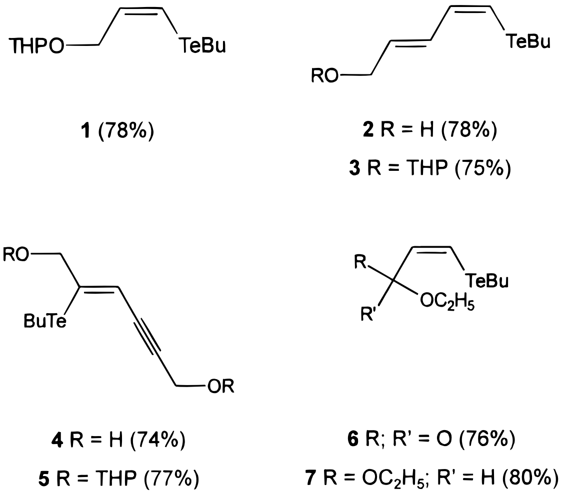
Introduction

In spite of the development of the organic chemistry of tellurium in recent years,[1] the problem of the stability of organic tellurium compounds toward commonly used reagents for synthetic transformations such as acids, bases, oxidizing and reducing agents, and organometallics has not been addressed. On the other hand, several publications dealing with organic derivatives of tellurium emphasize the lability of the tellurium−carbon bond toward some reaction conditions.[1a] In recent years, we[2] and others[3] have shown the applicability of vinylic tellurides as sources of the widely used vinyllithium and vinylcopper reagents. The transformation of vinylic tellurides into vinyl organometallics is unique in the sense that (*Z*)-vinylic derivatives are obtained, while the known methods to access these intermediates through transmetalation reactions lead to the (*E*)-vinyl organometallics.[2g,h] In the course of our recent studies aimed at the application of vinylic tellurides in the synthesis of complex molecules, we faced the problem of performing transformations on specific sites of the molecule without affecting the tellurium−carbon bond. As a more general approach to this problem we undertook a systematic study of the behavior of functionalized vinylic tellurides toward several reagents and reaction conditions.

Chart 1



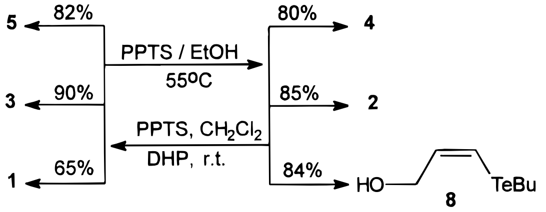
1 (78%)

2 R = H (78%)
3 R = THP (75%)

4 R = H (74%)
5 R = THP (77%)

6 R; R' = O (76%)
7 R = OC_2H_5; R' = H (80%)

Scheme 1



Results

The functionalized vinylic tellurides were prepared by hydrotelluration of the appropriate alkynes[2g,4] and are shown in Chart 1.

We started our investigation with the hydrolysis of tetrahydropyran (THP) ethers **1**, **3**, and **5** to the corresponding alcohols, **8**, **2**, and **4**. The reaction was performed in ethanol under pyridinium *p*−toluenesulfonate (PPTS) catalysis at 55 °C. The products were obtained in high yield with retention of stereochemistry of the double bond (Scheme 1). Compound **8** cannot be obtained by direct hydrotelluration of propargyl alcohol, in view of the reaction conditions employed for such a transformation.[2g,4] Protection of the hydroxy group of

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[⊗] Abstract published in *Advance ACS Abstracts*, January 15, 1997.

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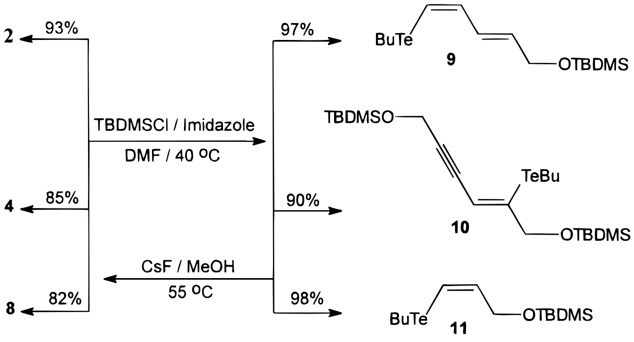
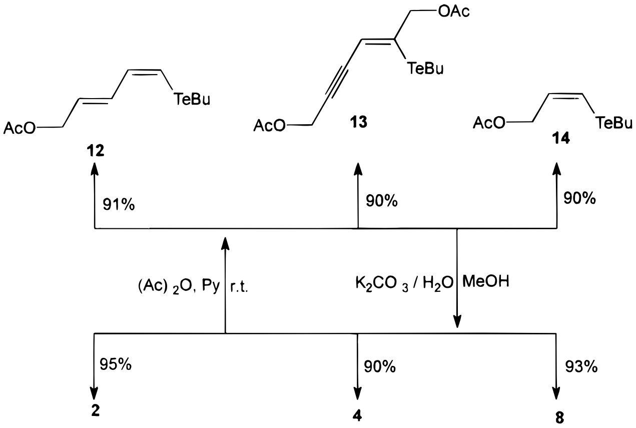
Scheme 2



Scheme 3



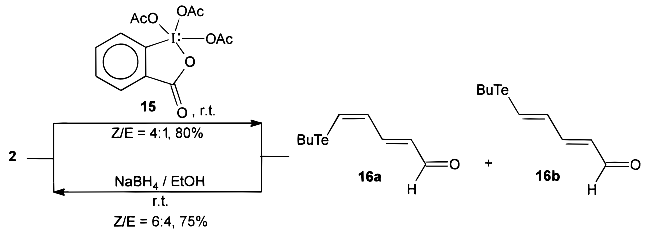
tellurides **2**, **4**, and **8** as the THP ether was initially attempted by employing Amberlyst H 15[5] as the catalyst. However, the formation of a thin layer of telluride on the surface of the Amberlyst pellets, with their consequent aggregation, led to low yields (~40%) of the protected alcohols. Alternatively, PPTS was used as the catalyst. Under these conditions high yields of the THP ethers **1**, **3**, and **5** were obtained (Scheme 1). In the deprotection reaction, dibutyl ditelluride was observed as a byproduct when the reaction temperature was higher than 55 °C.

Protection of compounds **2**, **4**, and **8** with *tert*-butyldimethylsilyl chloride (TBDMSCl) catalyzed by imidazole gave the protected alcohols in high yield.[6] Deprotection of the silyl ethers was achieved by reaction with CsF in methanol at 55 °C (Scheme 2).

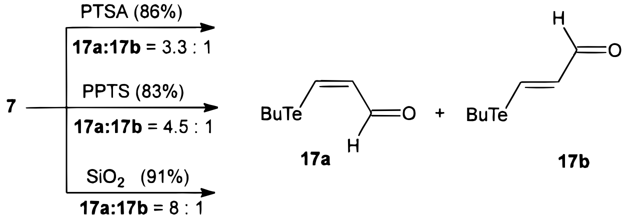
Acetylation of tellurides **2**, **4**, and **8**, was performed by reaction with acetic anhydride in pyridine at room temperature.[7] The yields were high, and the purification of the product was easily accomplished by column chromatography. Hydrolysis of the acetoxy group was performed by reaction of the acetates with potassium carbonate in methanol/water (Scheme 3).

Oxidation of compound **2** to **16** was performed with MnO_2 (20-fold excess) in diethyl ether at room temperature.[8] Aldehyde **16** was obtained in 53% yield as a 10:1 *Z*/*E* mixture at the carbon−carbon double bond of the vinylic telluride. Alternatively, compound **2** was oxidized with 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3-(1*H*)-one (Dess−Martin periodinane 15[9]), leading to compound **16** in 80% yield. With the *Z* isomer **2** as the starting material, compound **16** was obtained as a 5:1 *Z*/*E* mixture at the telluride carbon−carbon double bond (Scheme 4). Oxidation of **2** with pyridinium chlorochromate (PCC) in CH_2Cl_2[10] led to a complex mixture of products. Compound **16** was reduced to **2** with $NaBH_4$ in ethanol at room temperature. With the *Z* isomer of **16** as the starting material, a 6:4 *Z*/*E* mixture of **2** was obtained (Scheme 4).

Scheme 4

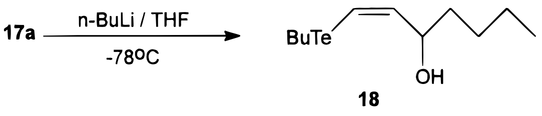


Scheme 5



Hydrolysis of compound **7** was performed under different experimental conditions: with *p*-toluenesulfonic acid (PTSA) in acetone,[11] with PPTS in ethanol,[12] and with a suspension of SiO_2 in hexane. In all cases, aldehyde **17** was obtained in good yield as a mixture of *Z* and *E* isomers. The SiO_2 method was best, giving a *Z*/*E* ratio of 8:1 (Scheme 5). Compound **17a** can be separated from **17b** by chromatography on SiO_2.

Recently, the preparation of compound **17** by hydrotelluration of propargyl aldehyde was described. A Wittig reaction transformed **17** into a tellurium diene, which was transmetalated with *n*-BuLi, and the resulting vinylic lithium was reacted with carbonyl compounds.[13] In this work we tested the selectivity of *n*-BuLi toward aldehyde **17a**. The preferential attack was at the carbonyl group, giving allyl alcohol **18** in 53% yield with retention of the double-bond stereochemistry (eq 1).



(1)

Acetal **7** was transmetalated with $Me_2Cu(CN)Li_2$,[2c,g] and the resulting vinylcuprate was reacted with cyclohexenone, giving the 1,4-addition product **19** in 59% yield after chromatography on SiO_2. Alternatively, compound **7** was transmetalated with *n*-BuLi and the vinylic lithium was reacted with benzaldehyde,[2a] giving **20** in 65% yield (Scheme 6).

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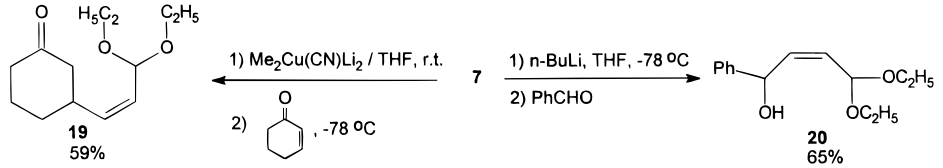
Scheme 6



Finally, the transmetalation reaction of compound **6** was attempted with *n*-BuLi and its reduction was attempted with LiAlH$_4$, leading to undefined products and dibutyl ditelluride. However, **6** reacted with lower order organocuprates, leading to the cross-coupling product in good yields.[14]

Conclusion

Several common synthetic transformations were performed successfully with functionalized vinylic tellurides, demonstrating that these are useful intermediates in multistep syntheses.

Experimental Section

^{1}H (200 MHz) and ^{13}C (50 MHz) NMR spectra were obtained on a Bruker AC-200 spectrometer in CDCl$_3$ with TMS as the internal reference. IR spectra were recorded on a Perkin-Elmer 1600 spectrophotometer. Low-resolution mass spectra were obtained on a Finnigan 4021 spectrometer or on a Hewlett-Packard 5988-8/5890 GC/MS spectrometer, both operating at 70 eV. Elemental analyses were performed at the Microanalytical Laboratory of the Institute of Chemistry-USP. Column chromatography was carried out with Merck silica gel (230−400 mesh) according to the procedure by Still and coworkers.[15] Thin-layer chromatography (TLC) was performed on silica gel 60 F-254 on aluminum. All solvents used were previously dried and distilled according to the usual methods.[16] THF was distilled from sodium/benzophenone under N$_2$, immediately before use. Tellurium (200 mesh) was purchased from Aldrich. Dibutyl ditelluride,[17] (*E*)-2-penten-4-yn-1-ol,[18] and 1,1-diethoxy-2-propyne[19] were prepared by literature procedures. The remaining chemicals were obtained from commercial sources. All operations were carried out in flame-dried glassware, under an inert atmosphere of dry and deoxygenated nitrogen.

General Procedure for the Preparation of the Butyl Vinyl Tellurides.[2g] To a solution of the dibutyl ditelluride (1.85 g, 5.0 mmol) and the appropriate acetylene (11.0 mmol) in absolute ethanol (30 mL) under nitrogen (deoxygenated by bubbling through a solution of VCl$_3$ (pH 1) with Zn/Hg amalgam) and magnetic stirring was added NaBH$_4$ (0.48 g, 12.6 mmol) in small portions until the color of the solution turned from dark red to pale yellow. The mixture was then refluxed as indicated below. The mixture was cooled to room temperature and treated with water (4 mL), 10% aqueous NaOH solution (4 mL), and ethyl acetate (200 mL). The organic phase was separated and washed with water (2 × 100 mL) and with saturated NaCl solution (2 × 100 mL). The organic phase was dried over MgSO$_4$, the solvent was evaporated under reduced pressure, and the residue was purified by flash chromatography on silica gel, with petroleum ether/ethyl acetate as eluent.

(*Z*)-3-(Butyltelluro)-2-propenyl tetrahydro-2*H*-2-pyranyl ether (1): yield 2.54 g (78%); reaction time 5 h; ^{1}H NMR δ 6.85 (dt, $J = 9.9$, 1.3 Hz, 1 H), 6.43 (dt, $J = 9.9$, 5.5 Hz, 1 H), 4.69−4.64 (m, 1 H), 4.01 (dd, $J = 5.7$, 1.3 Hz, 2 H), 3.56−3.53 (m, 2 H), 2.63 (t, $J = 7.6$ Hz, 2 H), 1.86−1.50 (m, 8 H), 1.43 (sext, $J = 7.1$ Hz, 2 H), 0.90 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR δ 134.68, 124.10, 122.32, 105.68, 98.03, 97.25, 73.69, 68.53, 61.91, 34.04, 30.42, 25.12, 19.17, 13.34, 6.97; LRMS *m/z* (relative intensity) 328 (13), 326 (12), 244 (39), 242 (31), 240 (18), 187 (12), 185 (13), 170 (13), 168 (12), 85 (100), 67 (21), 57 (77), 55 (33); IR (KBr, film; cm^{-1}) 2953, 2871, 1184, 1133, 1120, 1079, 1026. Anal. Calcd for C$_{12}$H$_{22}$O$_2$Te: C, 44.23; H, 6.80. Found: C, 44.59; H, 6.65.

(2*E*,4*Z*)-5-(Butyltelluro)-2,4-pentadien-1-ol (2): yield 2.10 g (78%); reaction time 5 h; ^{1}H NMR δ 6.73 (ABC system, $J = 10.8$, 9.5 Hz, 2 H), 6.17 (dd, $J = 15.5$, 6.7 Hz, 1H), 5.88 (dt, $J = 15.5$, 5.7 Hz, 1 H), 4.15 (d, $J = 5.6$ Hz, 2 H), 2.70 (t, $J = 7.2$ Hz, 2 H), 2.32 (s, 1H), 1.74 (quart, $J = 7.2$ Hz, 2H), 1.40 (sext, $J = 7.2$ Hz, 2 H), 0.85 (t, $J = 7.3$ Hz, 3 H); ^{13}C NMR δ 136.70, 133.97, 131.62, 106.14, 62.99, 33.97, 24.77, 13.26, 6.93; LRMS *m/z* (relative intensity) 268 (24), 213 (33), 183 (100), 181 (90), 83 (67), 55 (44); IR (KBr, film; cm^{-1}) 3346, 2957. Anal. Calcd for C$_9$H$_{16}$OTe: C, 40.36; H, 6.02. Found: C, 40.62; H, 5.96.

(2*E*,4*Z*)-5-(Butyltelluro)-2,4-pentadienyl tetrahydro-2*H*-2-pyranyl ether (3):[2g] yield 2.64 g (75%); reaction time 5 h; ^{1}H NMR δ 6.84−6.70 (m, 2 H), 6.23 (ddt, J =15.0, 8.9, 1.3 Hz, 1 H), 5.86 (dt, $J = 15.1$, 6.0 Hz, 1 H), 4.66 (t, $J = 3.1$ Hz, 1 H), 4.29 (ddd, $J = 13.2$, 5.6, 1.4 Hz, 1 H), 4.05 (ddd, $J = 13.2$, 6.5, 1.3 Hz, 1 H), 3.93−3.82 (m, 1 H), 3.56−3.46 (m, 1 H), 2.71 (t, $J = 7.5$ Hz, 2 H), 1.85−1.30 (m, 10 H), 0.92 (t, $J = 7.5$ Hz, 3 H); ^{13}C NMR δ 136.93, 133.08, 131.39, 106.07, 97.86, 67.19, 62.10, 34.06, 30.55, 25.39, 24.86, 19.35, 13.34, 6.91; LRMS *m/z* (relative intensity) 354 (20), 352 (18), 350 (12), 195 (42), 193 (38), 191 (23), 86 (10), 85 (100), 67 (55), 66 (50), 65 (20), 57 (55), 55 (35); IR (KBr, film; cm^{-1}) 2953, 2932, 2870, 1076, 1023. Anal. Calcd for C$_{14}$H$_{24}$O$_2$Te: C, 47.78; H, 6.87. Found: C, 48.02; H, 6.71.

(*Z*)-2-(Butyltelluro)-2-hexen-4-yne-1,6-diol (4):[2d] yield 2.18 g (74%); reaction time 2.5 h; ^{1}H NMR δ 6.39 (t, $J = 1.7$ Hz, 1 H), 4.43 (d, $J = 1.7$ Hz, 2 H), 4.30 (s, 2 H), 2.87 (t, $J = 7.5$ Hz, 2 H), 2.80 (s, 2 H), 1.76 (quint, $J = 7.5$ Hz, 2 H), 1.39 (sext, $J = 7.7$ Hz, 2 H), 0.92 (t, $J = 7.3$ Hz, 3 H); ^{13}C NMR δ 134.77, 114.46, 94.13, 84.94, 68.76, 51.49, 34.16, 25.04, 24.99, 13.37, 5.59; LRMS *m/z* (relative intensity) 298 (100), 296 (83), 294 (72), 224 (40), 222 (41), 194 (29), 145 (5), 149 (19), 94 (62), 81 (17), 77 (27), 6 (41); IR (KBr, film; cm^{-1}) 3379, 2948, 2916, 2850, 1461, 1447, 1430, 1414, 1380, 1360, 1015, 993, 965, 814. Anal. Calcd for C$_{10}$H$_{16}$O$_2$Te: C, 40.60; H, 5.45. Found: C, 40.81; H, 5.34.

(*Z*)-2-(Butyltelluro)-1,6-bis((tetrahydro-2*H*-2-pyranyl)oxy)-2-hexen-4-yne (5): yield 3.57 g (77%); reaction time 2 h; ^{1}H NMR δ 6.38 (t, $J = 1.4$ Hz, 1 H), 4.92 (t, $J = 3.3$ Hz, 1 H), 4.67 (t, $J = 3.3$ Hz, 1 H), 4.44 (s, 2 H), 4.32−4.11 (m, 2 H), 3.90−3.80 (m, 2 H), 3.59−3.45 (m, 2 H), 2.90 (t, $J = 7.4$ Hz, 2 H), 1.88−1.25 (m, 16 H), 0.92 (t, $J = 7.4$ Hz, 3 H); ^{13}C NMR δ 131.24, 115.15, 96.92, 96.31, 94.29, 91.68, 84.95, 71.96, 63.07, 62.60, 61.88, 54.38, 33.98, 30.24, 25.18, 24.85, 19.50, 18.97, 13.20, 5.14; LRMS *m/z* (relative intensity) 466 (13), 464 (14), 309 (26), 307 (25), 305 (16), 225 (18), 223 (21), 221 (15), 209 (14), 179 (21), 101 (42), 85 (100), 77 (40), 65 (24), 57 (41) 55 (38); IR (KBr, film; cm^{-1}) 2942, 2871, 2852, 1343, 1202, 1183,

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1120. Anal. Calcd for $C_{20}H_{32}O_4Te$: C, 51.76; H, 6.95. Found: C, 52.06; H, 6.80.

Ethyl (*Z*)-3-(butyltelluro)-2-propenoate (6): yield 2.06 g (76%); reaction time 1 h; ^{1}H NMR δ 8.43 (d, $J = 9.6$ Hz, 1 H), 6.90 (d, $J = 9.6$ Hz, 1 H), 4.23 (quart, $J = 7.1$ Hz, 2 H), 2.58 (t, $J = 7.6$ Hz, 2 H), 1.81 (quint, $J = 7.6$ Hz, 2 H), 1.39−1.26 (m, 5 H), 0.93 (t, $J = 7.3$ Hz, 3 H); ^{13}C NMR δ 168.37, 136.12, 123.03, 60.42, 33.87, 24.83, 14.17, 13.20, 7.29; LRMS *m*/*z* (relative intensity) 286 (61), 284 (57), 282 (36), 281 (16), 241 (18), 239 (13), 229 (100), 227 (90), 225 (57), 201 (95), 199 (84), 184 (26), 182 (21), 145 (11), 130 (11), 71 (74), 57 (97), 55 (91); IR (KBr, film; cm^{-1}) 2959, 2927, 1720, 1205, 1145. Anal. Calcd for $C_9H_{16}O_2Te$: C, 38.08; H, 5.68. Found: C, 37.92; H, 5.72.

(*Z*)-1-(Butyltelluro)-3,3-diethoxy-1-propene (7): yield 2.51 g (80%); reaction time 13 h; ^{1}H NMR δ 7.03 (dd, $J = 10.3$, 1.5 Hz, 1 H), 6.36 (dd, $J = 10.3$, 3.7 Hz, 1 H), 4.98 (dd, $J_1 =$ 3.7, 1.5 Hz, 1 H), 3.64−3.51 (m, 4 H), 2.57 (t, $J = 7.4$ Hz, 2 H), 1.77 (quint, $J = 7.6$ Hz, 2 H), 1.38 (sext, $J = 7.6$ Hz, 2 H), 1.23 (t, $J = 7.1$ Hz, 6 H), 0.91 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR δ 134.29, 109.32, 101.08, 60.26, 34.05, 24.95, 15.32, 13.35, 7.16; LRMS *m*/*z* (relative intensity) 316 (5), 314 (5), 269 (10), 185 (14), 183 (12), 129 (22), 103 (12), 101 (13), 85 (13), 75 (21), 73 (28), 71 (34), 64 (16), 57 (100), 55 (78); IR (KBr, film; cm^{-1}) 2974, 2927, 2873, 1458, 1443, 1336, 1164, 1121, 1054, 1005. Anal. Calcd for $C_{11}H_{22}O_2Te$: C, 42.09; H, 7.06. Found: C, 42.27; H, 7.04.

General Procedure for the Deprotection of the THP Ethers. The vinylic telluride (**1**, **3**, or **5**; 2.0 mmol) and PPTS (0.05 g, 0.25 equiv) in ethanol (20 mL) under nitrogen were heated at 55 °C for the time indicated below. Then the mixture was diluted with ethyl acetate (30 mL) and washed with a saturated NaCl solution (20 mL). The organic phase was dried with $MgSO_4$, the solvent was evaporated, and the products were distilled in a Kugelrohr apparatus.

(*Z*)-3-(Butyltelluro)-2-propen-1-ol (8): yield 0.41 g (84%); reaction time 2.3 h; ^{1}H NMR δ 6.81 (dt, $J = 9.8$, 1.2 Hz, 1 H), 6.43 (dt, $J = 9.7$, 5.5 Hz, 1 H), 4.23 (d, $J = 5.4$ Hz, 2 H), 3.00 (s, 1 H), 2.66 (t, $J = 7.4$ Hz, 2 H), 2.18 (m, 1 H), 1.78 (quint, $J = 7.5$ Hz, 2 H), 1.39 (sext, $J = 7.6$ Hz, 2 H), 0.92 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR δ 136.17, 103.13, 63.48, 32.74, 23.61, 12.08, 5.91; LRMS *m*/*z* (relative intensity) 372 (5), 370 (5), 270 (22), 268 (19), 266 (12), 249 (18), 213 (21), 211 (20), 251 (10), 213 (20), 181 (28), 179 (21), 81 (99), 66 (26), 57 (56), 53 (100); IR (KBr, film; cm^{-1}) 3308, 3078, 3011, 2957, 2926, 2870, 1293, 1247, 1182, 1103, 1040. Anal. Calcd for $C_7H_{14}OTe$: C, 34.77; H, 5.84. Found: C, 34.97; H, 5.67. **2**: yield 0.45 g (85%); reaction time 5.5 h. **4**: yield 0.47 g (80%); reaction time 2.3 h. The analytical data for compounds **2** and **4** obtained by this method agree with those of the same compounds obtained by hydrotelluration of the appropriate acetylenes.

General Procedure for the Tetrahydropyranylation Reaction. The vinylic telluride (**2**, **4**, or **8**, 1 mmol) and pyridinium *p*-toluenesulfonate (PPTS; 0.025 g, 0.1 equiv) in dry CH_2Cl_2 (10 mL) were stirred at room temperature for 10 h; then the mixture was diluted with ethyl acetate (15 mL) and washed with a saturated NaCl solution (15 mL). The organic phase was dried over $MgSO_4$, the solvents were evaporated, and the residue was chromatographed on silica gel with hexane/ethyl acetate (9:1) as eluent. **1**: yield 0.21 g (65%). **3**: yield 0.32 g (90%). **5**: yield 0.38 g (82%). The analytical data for compounds **1**, **3**, and **5** obtained by this method agree with those of the same compounds prepared by hydrotelluration of the corresponding acetylenes.

General Procedure for the Silylation Reaction. To a solution of *tert*-butyldimethylsilyl chloride (TBDMSCl; 0.1 g, 1.2 equiv) and imidazole (0.85 g, 2.5 equiv) in DMF (2 mL/g of the telluride) was added the vinylic telluride (**2**, **4**, and **8**; 2.0 mmol). After 3 h of stirring the mixture was diluted with ethyl acetate (15 mL) and washed with ice−water. The organic phase was dried over $MgSO_4$, the solvent was evaporated, and the residue was chromatographed on silica gel with hexane/ethyl acetate (9.5:0.5) as eluent.

(2*E*,4*Z*)-5-(Butyltelluro)-2,4-pentadienyl *tert*-butyldimethylsilyl ether (9): yield 0.74 g (97%); reaction time 1.5 h; ^{1}H NMR δ 6.76−6.74 (m, 2 H), 6.24−6.20 (m, 1 H), 5.85 (dt, $J = 14.9$, 4.8 Hz, 1 H), 4.24 (dd, $J = 4.8$, 1.6 Hz, 2 H), 2.72 (t, $J = 7.4$ Hz, 2 H), 1.78 (quint, $J = 7.5$ Hz, 2 H), 1.39 (sext, $J =$ 7.5 Hz, 2 H), 0.95−0.88 (m, 12 H), 0.09 (s, 6 H); ^{13}C NMR δ 136.98, 134.53, 130.31, 104.95, 63.25, 34.05, 25.88, 24.84, 18.28, 13.33, 6.68, 5.25; LRMS *m*/*z* (relative intensity) 386 (1), 385 (5), 384 (20), 382 (18), 380 (11), 327 (20), 325 (18), 323 (11), 197 (27), 187 (10), 145 (18), 139 (41), 115 (23), 89 (72), 73 (100), 67 (22), 66 (48), 57 (55); IR (KBr, film; cm^{-1}) 2956, 2928, 2884, 2856, 1254, 1131, 1082, 1043. Anal. Calcd for $C_{15}H_{30}OSiTe$: C, 47.15; H, 7.91. Found: C, 46.91; H, 7.66.

(*Z*)-2-(Butyltelluro)-1,6-bis(*tert*-butyldimethylsiloxy)-2-hexen-4-yne (10): yield 0.94 g (90%); reaction time 5 h; ^{1}H NMR δ 6.40 (t, $J = 1.93$ Hz, 1 H), 4.48 (d, $J = 1.7$ Hz, 2 H), 4.31 (d, $J = 1.8$ Hz, 2 H), 2.84 (t, $J = 7.4$ Hz, 2 H), 1.74 (quint, $J = 7.3$ Hz, 2 H), 1.36 (sext, $J = 7.4$ Hz), 0.93−0.82 (m, 21 H), 0.12 (s, 6H), 0.06 (s, 6 H); ^{13}C NMR δ 132.87, 113.90, 93.95, 84.28, 69.62, 52.32, 34.27, 25.83, 25.06, 18.31, 13.39, 5.08, −5.04, −5.31; LRMS *m*/*z* (relative intensity) 469 (30), 467 (29), 465 (44), 411 (12), 282 (17), 225 (34), 282 (17), 225 (34), 151 (11), 147 (51), 133 (16), 89 (17), 73 (100), 57 (38); IR (KBr, film; cm^{-1}) 2956, 2931, 2891, 2858, 1255, 1113, 1004. Anal. Calcd for $C_{22}H_{44}O_2Si_2Te$: C, 50.39; H, 8.46. Found: C, 50.59; H, 8.37.

(*Z*)-3-(Butyltelluro)-2-propenyl *tert*-butyldimethylsilyl ether (11): yield 0.70 g (98%); reaction time 2 h; ^{1}H NMR δ 6.69 (dt, $J = 9.9$, 1.5 Hz, 1 H), 6.34 (dt, $J = 9.8$, 4.9 Hz, 1 H), 4.16 (dd, $J = 4.9$, 1.4 Hz, 2 H), 2.60 (t, $J = 7.6$ Hz, 2 H), 1.75 (quint, $J = 7.5$ Hz, 2 H), 1.37 (sext, $J = 7.8$ Hz, 2 H), 0.91 (s, 9 H), 0.90 (t, $J = 7.8$ Hz, 3 H), 0.10 (s, 6 H); ^{13}C NMR δ 137.69, 102.53, 65.56, 33.69, 26.02, 25.88, 24.95, 18.40, 13.38, 7.12, 5.98, −5.09, −5.24; LRMS *m*/*z* (relative intensity) 358 (6), 354 (4), 241 (4), 189 (11), 171 (77), 169 (21), 167 (13), 115 (34), 99 (22), 75 (40), 73 (100), 59 (14), 57 (30), 55 (15); IR (KBr, film; cm^{-1}) 2956, 2929, 2885, 2856, 1253, 1088. Anal. Calcd for $C_{13}H_{28}OSiTe$: C, 43.85; H, 7.93. Found: C, 44.02; H, 7.48.

General Procedure for the Desilylation Reaction. The tellurides **9**, **10**, and **11** (2 mmol) and CsF (0.453 g, 3 mmol) in dry methanol (20 mL) were heated at 55 °C for 24 h; then water (10 mL) was added, the mixture was diluted with ethyl acetate (30 mL), and the organic phase was washed with saturated NaCl solution (2 × 20 mL), dried with $MgSO_4$, and evaporated. The residue was chromatographed on SiO_2, with hexane/ethyl acetate (9:1) as eluent. **2**: yield 0.51 g (95%). **4**: yield 0.50 g (85%). **8**: yield 0.40 g (82%). The analytical data for compounds **2** and **4** obtained by this method agree with those of the same compounds prepared by hydrotelluration of the corresponding acetylenes, and compound **8** presented analytical data identical with those of the same compound obtained by deprotection of **1**.

General Procedure for the Acetylation Reaction. The vinylic tellurides **2**, **4**, and **9** (2 mmol) and acetic anhydride (4 mmol) in anhydrous pyridine (10 mL) were stirred at room temperature for the time indicated below; then the mixture was diluted with ethyl acetate (20 mL) and washed with saturated NaCl solution (2 × 20 mL). The organic phase was dried over $MgSO_4$ and evaporated. The residue was purified by column chromatography on SiO_2, with hexane/ethyl acetate (9.5:0.5) as eluent.

(2*E*,4*Z*)-5-(Butyltelluro)-2,4-pentadienyl acetate (12): yield 0.56 g (91%); reaction time 45 min; ^{1}H NMR δ 6.90 (d, $J = 9.7$ Hz, 1 H), 6.74 (t, $J = 9.8$ Hz, 1 H), 6.27 (dd, $J = 14.9$, 9.7 Hz, 1 H), 5.84 (dt, $J = 15.0$, 6.4 Hz, 1H), 4.54 (d, $J = 6.3$ Hz, 2 H), 2.75 (t, $J = 7.4$ Hz, 2 H), 2.00 (s, 3 H), 1.71 (quint, $J = 7.4$ Hz, 2 H), 1.32 (sext, $J = 7.4$ Hz, 2 H), 0.84 (t, $J = 7.4$ Hz, 3 H); ^{13}C NMR δ 170.49, 136.26, 134.52, 128.16, 107.85, 64.46, 33.97, 24.76, 20.80, 13.27, 7.06; LRMS *m*/*z* (relative intensity) 256 (2), 255 (2), 253 (3), 213 (5), 195 (100), 193 (84), 187 (11), 183 (5), 130 (4), 83 (5), 66 (20), 57 (9); IR (KBr, film;

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cm^{-1}) 2958, 2928, 1742, 1457, 1378, 1360, 1326, 1228, 1024, 969. Anal. Calcd for $C_{11}H_{18}O_2Te$: C, 42.64; H, 5.86. Found: C, 42.84; H, 5.97.

(*Z*)-2-(Butyltelluro)-6-((methylcarbonyl)oxy)-2-hexen-4-ynyl acetate (13): yield 0.68 g (90%); reaction time 2 h; ^{1}H NMR δ 6.32 (m, 1 H), 4.85 (d, J = 1.9 Hz, 2 H), 4.77 (d, J = 1.2 Hz, 2 H), 2.88 (t, J = 7.6 Hz, 2 H), 2.10 (s, 3 H), 1.78 (quint, J = 7.7 Hz, 2 H), 1.40 (sext, J = 7.5 Hz, 2 H), 0.93 (t, J = 7.3 Hz, 3 H); ^{13}C NMR δ 169.96, 128.87, 116.50, 90.39, 85.33, 69.28, 67.34, 52.69, 34.03, 24.98, 20.77, 13.32, 5.98; LRMS *m*/*z* (relative intensity) 382 (15), 380 (14), 283 (12), 281 (12), 224 (14), 195 (21), 153 (17), 135 (18), 111 (100), 94 (49), 93 (19), 77 (29), 65 (24), 57 (29), 55 (24), 51 (18); IR (KBr, film; cm^{-1}) 2958, 2932, 1746, 1220, 1027. Anal. Calcd for $C_{14}H_{20}O_4Te$: C, 44.26; H, 5.31. Found: C, 44.04; H, 4.98.

(*Z*)-3-(Butyltelluro)-2-propenyl acetate (14): yield 0.51 g (90%); reaction time 12 h; ^{1}H NMR δ 6.98 (dt, J = 9.9, 1.1 Hz, 1 H), 6.37 (dt, J = 9.9, 5.9 Hz, 1 H), 4.56 (dd, J = 5.9, 1.1 Hz, 2 H), 2.70 (t, J = 7.6 Hz, 2 H), 2.08 (s, 3 H), 1.78 (quint, J = 7.3 Hz, 2 H), 1.39 (sext, J = 7.2 Hz, 2 H), 0.92 (t, J = 7.2 Hz, 3 H); ^{13}C NMR δ 170.43, 132.92, 125.46, 107.97, 70.84, 66.08, 33.92, 24.76, 20.71, 13.25, 7.22; LRMS *m*/*z* (relative intensity) 286 (10), 284 (10), 282 (5), 170 (16), 168 (16), 130 (4), 57 (28), 43 (100), 41 (27), 39 (16); IR (KBr, film; cm^{-1}) 2958, 2929, 2872, 1742, 1229, 1029. Anal. Calcd for $C_9H_{16}O_2Te$: C, 38.09; H, 5.68. Found: C, 38.30; H, 5.59.

General Procedure for the Deacetylation Reaction. The vinylic tellurides **12**, **13**, and **14** (2 mmol) and K_2CO_3 (0.440 g, 3.2 mmol) in methanol (40 mL) and water (13 mL) were stirred for the time indicated below at room temperature. Then the mixture was diluted with ethyl acetate (20 mL) and washed with saturated NaCl solution (2 × 20 mL). The organic phase was dried over $MgSO_4$, and the solvent was evaporated. The residue was chromatographed on SiO_2, with hexane/ethyl acetate (9:1) as eluent. **2**: yield 0.51 g (95%); reaction time 2 h. **4**: yield 0.53 g (90%); reaction time 1 h. **8**: yield 0.45 g (93%); reaction time 40 min. The analytical data agree with those of the same compounds obtained by desilylation of **9**, **10**, and **11**, respectively.

Oxidation of Compound 2 with the Periodinane 15.[9] The vinylic telluride **2** (1.34 g, 5 mmol) and the periodinane **15** (2.55 g, 6 mmol) in CH_2Cl_2 (10 mL) were stirred at room temperature for 30 min. Then the mixture was diluted with diethyl ether (20 mL) and poured into a saturated NaHCO3 solution (20 mL) containing 1.0 g of $Na_2S_2O_3$. The mixture was stirred for 10 min; the organic phase was washed with a saturated solution of $NaHCO_3$ (20 mL) and then with water. After drying with $MgSO_4$ and evaporation of the solvent the residue was chromatographed on SiO_2, with hexane/ethyl acetate (6:1) as eluent.

(2*E*,4*Z*)-5-(Butyltelluro)-2,4-pentadienal (16a): yield 0.79 g (60%); ^{1}H NMR (360 MHz) δ 9.60 (d, J = 8.0 Hz, 1 H), 7.70 (d, J = 8.8 Hz, 1 H), 7.03 (m, 2 H), 6.20 (m, 1 H), 2.83 (t, J = 7.5 Hz, 2 H), 1.82 (quint, J = 7.5 Hz, 2 H), 1.41 (sext, J = 7.4 Hz, 2 H), 0.92 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (90 MHz) δ 193.88, 150.93, 134.92, 132.05, 123.74, 34.27, 25.07, 13.59, 8.92; LRMS *m*/*z* (relative intensity) 268 (4.3), 183 (10.9), 84 (24.3), 81 (100), 53 (33.7), 49 (13.5), 41 (17.2); IR (KBr, film; cm^{-1}) 2957, 2926, 1676, 1608, 1322, 1246, 665; exact mass calcd for $C_9H_{14}OTe$ (**16a**) 268.0107, found 268.0095.

(2*E*,4*E*)-5-(Butyltelluro)-2,4-pentadienal (16b): yield 0.27 g (20%); ^{1}H NMR (360 MHz) δ 9.54 (d, J = 8.0 Hz, 1 H), 7.81 (d, J = 16.0 Hz, 1 H), 7.03 (dd, J = 15.0, 10.8 Hz, 1 H), 6.85 (dd, J = 16.0, 10.8 Hz, 1 H), 5.96 (dd, J = 15.0, 7.8 Hz, 1 H), 2.87 (t, J = 7.5 Hz, 2 H), 1.83 (quint, J =7.5 Hz, 2 H), 1.43 (sext, J = 7.4 Hz, 2 H), 0.94 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (90 MHz) δ 194.08, 151.58, 137.06, 128.01, 122.23, 33.79, 25.23, 13.60, 8.02; LRMS *m*/*z* (relative intensity) 268 (10.3), 183 (9.4), 82 (13.5), 81 (100), 53 (36.3), 41 (18.8); IR (KBr, film; cm^{-1}) 2957, 2868, 1672, 1602, 1170, 1120, 979, 849; exact mass calcd for $C_9H_{14}OTe$ (**16b**) 268.0107, found 268.0110.

Reaction of Compound 16 with Sodium Borohydride. To a solution of telluride **16** (0.26 g, 1.0 mmol) in ethanol (10 mL) was added dropwise a solution of $NaBH_4$ (0.057 g, 1.5 mmol) in ethanol (2 mL). After 1 h at room temperature the mixture was treated with a saturated solution of NH_4Cl and extracted with ethyl acetate (2 × 20 mL). The organic phase was dried with $MgSO_4$, and the solvent was evaporated. The residue was chromatographed on SiO_2, with hexane/ethyl acetate (9:1) as eluent. **2**: yield 0.20 g (75%).

Hydrolysis of Compound 7 with SiO_2. The telluride **7** (0.63 g, 2.0 mmol) was added to a slurry of SiO_2 (2.5 g/mmol of **7**) in hexane (7 mL/mmol of **7**). The mixture was stirred for 4 h at room temperature and filtered, and the residue was washed with ethyl acetate (20 mL). The solvents were evaporated, giving a mixture of *Z* and *E* isomers, which were separated by silica gel column chromatography with hexane/ethyl acetate (9:1) as eluent.

(*Z*)-3-(Butyltelluro)-2-propenal (17a): yield 0.35 g (73%); ^{1}H NMR δ 9.98 (s, 1 H), 9.03 (d, J = 9.2 Hz, 1 H), 7.62 (d, J = 9.2 Hz, 1 H), 2.57 (t, J = 7.7 Hz, 2 H), 1.81 (quint, J = 7.6 Hz, 2 H), 1.41 (sext, J = 7.6 Hz, 2 H), 0.93 (t, J = 7.2 Hz, 3 H); ^{13}C NMR δ 189.26, 142.04, 128.78, 33.64, 24.92, 13.37, 11.50; LRMS *m*/*z* (relative intensity) 242 (27), 240 (25), 238 (16), 185 (91), 183 (90), 181 (58), 180 (23), 157 (9), 131 (16), 130 (15), 129 (15), 57 (30), 55 (100); IR (KBr, film; cm^{-1}) 2958, 2923, 1692. Anal. Calcd for $C_7H_{12}OTe$: C, 35.07; H, 5.04. Found: C, 35.38; H, 5.01.

(*E*)-3-(Butyltelluro)-2-propenal (17b): yield 0.08 g (18%); ^{1}H NMR δ 9.40 (d, J = 7.5 Hz, 1 H), 8.71 (d, J = 16.5 Hz, 1H), 6.70 (dd, J = 16.5, 7.5 Hz, 1 H), 2.90 (t, J = 7.6 Hz, 2 H), 1.85 (quint, J = 7.5 Hz, 2 H), 1.43 (sext, J = 7.6 Hz, 2 H), 0.95 (t, J = 7.2 Hz, 3 H); ^{13}C NMR δ 190.00, 139.29, 138.57, 33.05, 24.88, 13.22, 8.64; LRMS *m*/*z* (relative intensity) *m*/*z* 242 (32), 240 (30), 238 (19), 185 (69), 183 (67), 181 (43), 180 (18), 155 (9), 131 (15), 130 (18), 126 (13), 57 (55), 55 (100); IR (KBr, film; cm−1) 2958, 1673. Anal. Calcd for $C_7H_{12}OTe$: C, 35.07; H, 5.04. Found: C, 35.37; H, 5.05.

Hydrolysis of Compound 7 with *p*-Toluenesulfonic Acid (PTSA). The telluride **7** (1.88 g, 6 mmol) was added dropwise to a solution of PTSA monohydrate (0.23 g, 1.19 mmol) in acetone (10 mL). After 30 min at room temperature the mixture was treated with 10% $NaHCO_3$ solution (20 mL) and extracted with ethyl acetate (2 × 20 mL). The organic phase was dried over $MgSO_4$, the solvent was evaporated, and the residue was chromatographed on silica gel, with hexane/ethyl acetate (9.5:0.5) as eluent. **17a**: yield 1.00 g (70%). **17b**: yield 0.23 g (16%). The analytical data agree with those of the same compound obtained in the preceeding experiment.

Hydrolysis of Compound 7 with Pyridinium *p*-Toluenesulfonate (PPTS). The telluride **7** (0.63 g, 2.0 mmol) was added dropwise to a solution of PPTS (0.13 g, 0.52 mmol) in ethanol (30 mL). After 4 h at room temperature the mixture was diluted with ethyl acetate (30 mL) and washed with a saturated solution of NaCl (20 mL). The organic phase was dried with $MgSO_4$, the solvents were evaporated, and the residue was chromatographed on silica gel, with hexane/ethyl acetate (9:1) as eluent. **17a**: yield 0.30 g (63%). **17b**: yield: 0.10 g (20%).

Reaction of Compound 17a with *n*-Butyllithium. *n*-Butyllithium (0.91 mL, 2.0 mmol of a 2.2 M solution in hexane) was added to **17a** (0.48 g, 2 mmol) in THF at −78 °C. After 20 min at room temperature the mixture was treated with saturated NH_4Cl solution (20 mL) and extracted with ethyl acetate (2 × 20 mL). The organic phase was dried with $MgSO_4$, and the solvents were evaporated. The residue was chromatographed on silica gel, with hexane/ethyl acetate (9:1) as eluent.

(*Z*)-1-(Butyltelluro)-1-hepten-3-ol (18): yield 0.32 g (53%); ^{1}H NMR δ 6.75 (dd, J = 9.7, 1.02 Hz, 1 H), 6.26 (dd, J = 9.7, 6.9 Hz, 1 H), 4.18−4.10 (m, 1 H), 2.65 (t, J = 7.65 Hz, 3 H), 1.80−1.25 (m, 10 H), 0.95−0.88 (m, 6 H); ^{13}C NMR δ 140.96, 104.33, 74.46, 36.21, 34.07, 27.32, 24.94, 22.63, 13.99, 13.37, 7.17; LRMS *m/z* (relative intensity) 300 (31), 299 (11), 298 (25), 283 (4), 243 (8), 225 (5), 185 (10), 128 (4), 114 (13), 95 (34), 85 (8), 67 (21), 58 (50), 57 (100); IR (KBr, film; cm^{-1}) 3338, 2957, 1464. Anal. Calcd for $C_{11}H_{22}OTe$: C, 44.35; H, 7.44. Found: C, 45.68; H, 7.46.

Reaction of Compound 7 with Dilithium Dimethylcyanocuprate and Capture with Cyclohexenone. Methyllithium (3.64 mL of a 1.10 M solution in diethyl ether, 4.0 mmol) was added to a suspension of CuCN (0.18 g, 2.0 mmol) in THF (5 mL) under nitrogen at −78 °C. The colorless solution was stirred for 30 min at −78 °C and then heated to room temperature. A solution of the vinylic telluride **7** (0.63 g, 2 mmol) in THF (3 mL) was added, and the mixture was stirred at room temperature for 1 h. To this solution, cooled to −78 °C, was added cyclohexenone (0.20 g, 2.1 mmol) via syringe. The cooling bath was removed, and the mixture was then stirred for 20 min at room temperature, treated with a mixture of saturated solutions of NH_4Cl and NH_4OH (4:1), and extracted with ethyl acetate (30 mL). The organic phase was separated, washed with a saturated solution of NaCl (2 × 50 mL), and dried with $MgSO_4$. The solvents were evaporated, and the residue was chromatographed on a silica gel column, first with hexane as eluent to remove the diorgano telluride and then with a mixture of hexane/ethyl acetate (5:1).

3-((*Z*)-3,3-Diethoxy-1-propenyl)-1-cyclohexanone (19): yield 0.27 g (59%); ^{1}H NMR δ 5.48 (m, 2 H), 5.07 (d, $J = 5.07$ Hz, 1 H), 3.67−3.44 (m, 4 H), 2.80−2.70 (m, 1 H), 2.0−2.4 (m, 5 H), 1.40−1.90 (m, 3 H), 1.20 (t, $J = 6.9$ Hz, 6 H); ^{13}C NMR δ 210.11, 136.56, 127.22, 97.30, 60.10, 47.26, 40.89, 37.82, 31.20, 24.96, 15.09; LRMS *m/z* (relative intensity) 225 (0.06), 181 (14), 180 (90), 151 (14), 135 (10), 124 (37), 123 (32), 106 (31), 105 (17), 96 (41), 95 (100), 91 (30), 67 (77), 57 (15), 55 (76); IR (KBr, film; cm^{-1}) 2974, 2932, 2873, 1713, 1121, 1054. Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.80; H, 9.69.

Transmetalation of Compound 7 with *n*-Butyllithium and Capture with Benzaldehyde. *n*-Butyllithium (0.91 mL, 2.0 mmol of a 2.2 M solution in hexane) was added to the vinylic telluride **7** (0.63 g, 2.0 mmol) at −78 °C. After 15 min at this temperature benzaldehyde (0.233 g, 2.2 mmol) was added and the mixture was warmed to room temperature, and after 30 min it was diluted with ethyl acetate (20 mL) and washed with a saturated solution of NaCl (3 × 20 mL). The organic phase was dried over $MgSO_4$, and the solvents were evaporated. The residue was purified by column chromatography on silica gel, first with hexane as eluent to remove dibutyl telluride and then with hexane/ethyl acetate (9:1) to remove the product.

(*Z*)-4,4-Diethoxy-1-phenyl-2-buten-1-ol (20): yield 0.31 g (65%); ^{1}H NMR δ 7.26−7.42 (m, 5 H), 5.85 (dd, $J = 10.7$, 8.5 Hz, 1 H), 5.66−5.50 (m, 2 H), 5.41 (d, $J = 5.3$ Hz, 1 H), 3.45−3.75 (m, 4 H), 2.84 (s, 1 H), 1.24 (t, $J = 7.0$ Hz, 3 H), 1.18 (t, $J = 7.02$ Hz, 3 H); ^{13}C NMR δ 142.75, 136.36, 128.77, 128.41, 127.47, 126.00, 97.58, 69.99, 60.73, 60.17, 15.16, 15.11; LRMS *m/z* (relative intensity) 191 (5), 189 (3), 174 (1), 161 (6), 145 (100), 133 (2), 115 (47), 105 (8), 85 (5), 77 (2), 63 (3), 51 (4); IR (KBr, film; cm^{-1}) 3428, 2976, 1455, 1390, 1004. Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.27; H, 8.51.

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