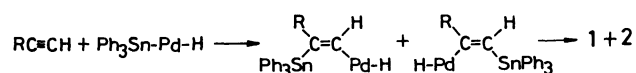
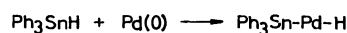
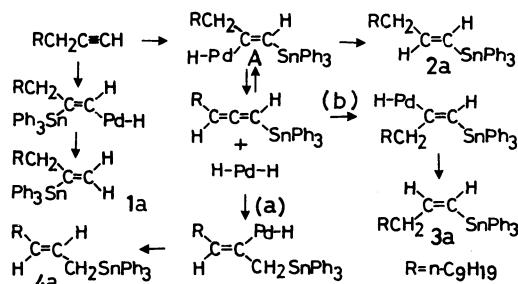


reduce $\text{PdCl}_2(\text{PPh}_3)_2$, $\text{PdCl}_2(\text{CH}_3\text{CN})_2$, and $\text{Pd}(\text{OAc})_2$ to zerovalent palladium which is an active catalyst for the reaction. Thus, these palladium complexes were not effective for the hydrogermylation. In contrast to hydrostannylation, the reaction of terminal acetylenes proceeds stereoselectively⁷ and no (*Z*)-isomers are formed (Table 1). 6-Dodecyne gave a mixture of alkenylgermane **5e** and allylic germane, (*E*)-7-triphenylgermyl-5-dodecene (**8**).

We are tempted to assume following reaction mechanism: (1) Oxidative addition of Ph_3SnH (Ph_3GeH) to $\text{Pd}(0)$, (2) stannylladdation (cis addition),



and (3) reductive elimination to produce alkenylstannanes (alkenylgermanes) and regenerate the palladium(0) complex. The formation of allylic stannane **4a** and allylic germane **8** presumably is explained by elimination of a palladium hydride from vinylpalladium species **A** and subsequent readdition in the opposite end of the 1,2-diene system followed by reductive elimination (path (a) in Scheme 1). The path (b) in Scheme 1 (readdition followed by reductive elimination) may explain the formation of (*Z*)-isomer **3a**.⁸



Scheme 1.

Experimental

General Procedure for the Reaction of Acetylenic Compounds with Triphenylstannane in the Presence of $\text{Pd}(\text{PPh}_3)_4$. The reaction of 1-dodecyne with Ph_3SnH is representative. $\text{Pd}(\text{PPh}_3)_4$ (58 mg, 0.05 mmol) was added to a solution of 1-dodecyne (0.17 g, 1.0 mmol) and Ph_3SnH (0.43 g, 1.2 mmol) in CH_2Cl_2 (10 ml) under an argon atmosphere. The reaction mixture was stirred at 25 °C for 5 h, then poured into water, and extracted with 3 portions of ethyl acetate. The organic extracts were dried (Na_2SO_4) and evaporated. Purification by preparative TLC on silica gel provided a mixture of 2-triphenylstannyl-1-dodecene (**1a**), (*E*)-1-triphenylstannyl-1-dodecene (**2a**), and (*Z*)-isomer **3a** in 77% combined yield (**1a**:**2a**:**3a**=11:82:7, the isomeric ratio was determined by its ^1H NMR spectrum). The spectral data were identical with those reported in the literature.⁹ Phenylacetylene and 4-benzyloxy-1-butyne were treated with Ph_3SnH under the same reaction conditions to give the corresponding mixture of alkenylstannanes whose IR, ^1H NMR, and ^{119}Sn NMR spectra were identical with those reported.⁹

(*E*)-1-Trimethylsilyl-2-triphenylstannylethane: Mp 74 °C (hexane); IR (Nujol) 2950, 1482, 1428, 1246, 1160, 1077, 1016, 861, 838, 724, 696 cm^{-1} ; ^1H NMR (CDCl_3) δ =0.01 (s, 9H), 6.91 (d, J =22.5 Hz, 1H), 7.14 (d, J =22.5 Hz, 1H), 7.30–7.50 (m, 9H), 7.50–7.81 (m, 6H); ^{119}Sn NMR (CDCl_3) δ =-147.0. Found: C, 61.09; H, 5.75%. Calcd for $\text{C}_{23}\text{H}_{26}\text{SiSn}$: C, 61.49; H, 5.83%.

(*E*)-6-Triphenylstannyl-6-dodecene: Bp 170 °C (bath temp, 0.3 Torr, 1 Torr=133.322 Pa); IR (neat) 3060, 3012, 2953, 2922, 2852, 1480, 1465, 1458, 1428, 1074, 725, 697 cm^{-1} ; ^1H NMR (CDCl_3) δ =0.72–0.84 (m, 6H), 0.85–1.55 (m, 12H), 2.01 (dt, J =7.2, 7.2 Hz, 2H), 2.28 (t, J =7.1 Hz, 2H), 6.32 (t, J =7.2 Hz, 1H), 7.3–7.8 (m, 15H); ^{119}Sn NMR (CDCl_3) δ =-139.4. Found: C, 69.66; H, 7.51%. Calcd for $\text{C}_{30}\text{H}_{38}\text{Sn}$: C, 69.65; H, 7.40%.

General Procedure for the Hydrogermylation of Acetylenes. 1-Dodecyne (0.17 g, 1.0 mmol) and Ph_3GeH (0.36 g, 1.2 mmol) were combined in THF (10 ml). $\text{Pd}(\text{PPh}_3)_4$ (58 mg, 0.05 mmol) was added to the solution and the resulting mixture was stirred at 25 °C for 5 h under an argon atmosphere. Workup (AcOEt, brine) followed by silica-gel TLC purification gave alkenyltriphenylgermane (0.46 g, 97% combined yield) as a 14:86 (**5a**:**6a**) mixture of regioisomers as determined by the integrations of the olefinic protons in the ^1H NMR spectrum: Bp 120 °C (bath temp, 0.1 Torr); IR (neat) 2880, 2820, 1425, 1085, 730, 695 cm^{-1} ; ^1H NMR (CDCl_3) δ =0.8–0.98 (m, 3H), 1.04–1.51 (bm, 16H), 2.18–2.35 (m, 2H), 5.39 (m, 0.14H), 5.90 (m, 0.14H), 6.12–6.23 (m, 1.72H), 7.32–7.65 (m, 15H). Found: C, 76.23; H, 8.15%. Calcd for $\text{C}_{30}\text{H}_{38}\text{Ge}$: C, 76.47; H, 8.13%.

2-Tripropylgermyl-1-dodecene (5c') and (*E*)-1-Tripropylgermyl-1-dodecene (6c') (**5c'**:**6c'**=20:80): Bp 88 °C (bath temp, 0.08 Torr); IR (neat) 2890, 2820, 1455, 1065, 690 cm^{-1} ; ^1H NMR (CDCl_3) δ =0.67–1.02 (m, 24H), 1.17–1.51 (bm, 16H), 2.03–2.19 (m, 2H), 5.12 (m, 0.2H), 5.54 (m, 0.2H), 5.68. Found: C, 68.46; H, 11.94%. Calcd for $\text{C}_{21}\text{H}_{44}\text{Ge}$: C, 68.32; H, 12.01%.

1-Phenyl-1-triphenylgermylethene (5b) and (*E*)-1-Phenyl-2-triphenylgermylethene (6b) (**5b**:**6b**=9:91): Mp 144–146 °C (benzene-hexane(1:1)); IR (CCl_4) 3020, 1480, 1425, 1085, 985, 710, 695 cm^{-1} ; ^1H NMR (CDCl_3) δ =5.61 (d, J =2.3 Hz, 0.09H), 6.30 (d, J =2.3 Hz, 0.09H), 6.95 (d, J =18.9 Hz, 0.91H), 7.05 (d, J =18.9 Hz, 0.91H), 7.25–7.63 (m, 20H). Found: C, 76.55; H, 5.39%. Calcd for $\text{C}_{26}\text{H}_{22}\text{Ge}$: C, 76.72; H, 5.45%.

2-Triphenylgermyl-4-benzyloxy-1-butene (5c) and (*E*)-1-Triphenylgermyl-4-benzyloxy-1-butene (6c) (**5c**:**6c**:**7c**=7:91:<2): Bp 129 °C (bath temp, 0.08 Torr); IR (neat) 1425, 1090, 735, 695 cm^{-1} ; ^1H NMR (CDCl_3) δ =2.57 (dt, J =6.7, 6.0 Hz, 2H), 3.59 (t, J =6.7 Hz, 2H), 4.52 (s, 2H), 5.50 (bs, 0.07H), 6.01 (bs, 0.07H), 6.14 (dt, J =18.2, 6.0 Hz, 0.91H), 6.31 (d, J =18.2 Hz, 0.91H), 7.28–7.62 (m, 20H). Found: C, 74.40; H, 6.15%. Calcd for $\text{C}_{29}\text{H}_{28}\text{OGe}$: C, 74.89; H, 6.07%.

(*E*)-2-Triphenylgermyl-1-buten-4-ol (6f): Mp 111–113 °C (hexane- CH_2Cl_2); IR (KBr) 3318, 1638, 1484, 1430, 1091, 1039, 999, 983, 735, 698 cm^{-1} ; ^1H NMR (CDCl_3) δ =1.55 (s, 1H), 2.49 (dt, J =6.3, 6.4 Hz, 2H), 3.69 (dt, J =6.4 Hz, 2H), 6.09 (dt, J =18.3, 6.3 Hz, 1H), 6.35 (d, J =18.3 Hz, 1H), 7.44–7.62 (m, 9H), 7.62–7.87 (m, 6H); ^{13}C NMR (CDCl_3) δ =39.9, 61.4, 127.3, 128.1, 128.9, 134.9, 136.4, 146.1. Found: C, 70.35; H, 5.82%. Calcd for $\text{C}_{22}\text{H}_{22}\text{OGe}$: C, 70.46; H, 5.81%.

(*E*)-1-Trimethylsilyl-2-triphenylgermylethene (6d): Mp 92–94 °C (hexane); IR (KBr) 1430, 1245, 1092, 870, 834, 735, 694 cm^{-1} ; ^1H NMR (CDCl_3) δ =0.14 (s, 9H), 6.78 (d, J =21.8 Hz, 1H), 7.14 (d, J =21.8 Hz, 1H), 7.32–7.47 (m, 9H), 7.47–7.67 (m, 6H); ^{13}C NMR (CDCl_3) δ =-1.5, 128.2, 128.9, 135.4, 136.5, 143.1, 155.2. Found: C, 68.41; H, 6.51%. Calcd for $\text{C}_{23}\text{H}_{26}\text{SiGe}$: C, 68.52; H, 6.50%.

(*E*)-6-Triphenylgermyl-6-dodecene (6d) and (*E*)-7-Tri-

phenylgermyl-5-dodecene (**8**): Bp 165 °C (bath temp, 0.2 Torr); IR (neat) 3048, 2922, 2852, 1430, 1090, 733, 697 cm^{-1} ; ^1H NMR (CDCl_3) δ =0.69–1.01 (m, 6H), 1.01–1.51 (m, 10H), 1.89–2.10 (m, 2H), 2.15–2.37 (m, 2H), 2.58–2.73 (m, 1.33H), 5.24–5.50 (m, 1.33H), 5.80 (t, J =7.0 Hz, 0.33H), 7.05–7.23 (m, 9H), 7.23–7.42 (m, 6H). Found: C, 76.31; H, 8.14%. Calcd for $\text{C}_{30}\text{H}_{38}\text{Ge}$: C, 76.46; H, 8.13%.

Reaction of 1-Dodecyne with Ph_3SnH in the Presence of $\text{PdCl}_2[\text{P}(o\text{-MeC}_6\text{H}_4)_3]_2$. A catalytic amount of $\text{PdCl}_2[\text{P}(o\text{-MeC}_6\text{H}_4)_3]_2$ (35 mg, 0.05 mmol) was added to a solution of 1-dodecyne (0.17 g, 1.0 mmol) and Ph_3SnH (0.42 g, 1.2 mmol) at 25 °C under an argon atmosphere. The resulting mixture was stirred at 25 °C for 6 h. The mixture was poured into water and extracted with ethyl acetate. The organic layers were dried (Na_2SO_4) and concentrated. The residual oil was submitted to preparative TLC (hexane as eluant) gave a mixture of **1a** (15 mg, 3%), **2a** (0.12 g, 24%), **3a**, (10 mg, 2%), and (*E*)-1-triphenylstannyl-2-dodecene (**4a**) (0.22 g, 42%). **4a**: ^1H NMR (CDCl_3) δ =2.38 (d, J =6.0 Hz, 2H), 5.40 (dt, J =15.0, 8.0 Hz, 1H), 5.51 (dt, J =15.0, 7.0 Hz, 1H).

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- 5) $\text{Pd}(\text{OAc})_2$ (0.02 mmol) and (*p*- MeOC_6H_4) $_3\text{P}$ (0.1 mmol) were combined in CH_2Cl_2 and the resulting mixture was stirred for 30 min before the addition of 1-dodecyne (0.5 mmol) and Ph_3SnH (0.6 mmol).
- 6) (*E*)- or (*Z*)-1-Triphenylstannyl-1-dodecene (**2a** or **3a**) was recovered unchanged, respectively, without isomerization into (*E*)-1-triphenylstannyl-2-dodecene (**4a**) on treatment with Ph_3SnH - $\text{PdCl}_2[\text{P}(o\text{-MeC}_6\text{H}_4)_3]_2$.
- 7) Benzyl ether of 3-butyne-1-ol gave trace of (*Z*)-alkenyltriphenylgermane **7c** (<2%).
- 8) The formation of (*Z*)-1-phenyl-2-triphenylstannyl-ethene can not be explained by the above mechanism. Thus, an initial trans-addition of Ph_3Sn -Pd to acetylenic bond can not be excluded.
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