Palladium Catalyzed Hydrostannylation and Hydrogermylation of Acetylenes

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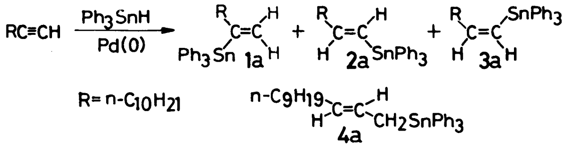
Synopsis. Treatment of acetylenes with Ph_3SnH or Ph_3GeH in the presence of a catalytic amount of $Pd(PPh_3)_4$ provides the corresponding alkenyltriphenylstannanes or alkenyltriphenylgermanes in good yields.

Transition-metal-catalyzed hydrosilylation reaction has been extensively developed.[1] On the other hand, hydrostannylation[2] and hydrogermylation[3] have not been well-established. Here we wish to disclose the hydrostannylation and hydrogermylation of acetylenic compounds in the presence of a palladium catalyst to give the corresponding alkenyltriphenylstannanes and alkenyltriphenylgermanes.

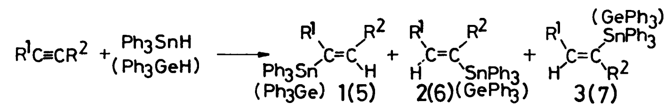
The hydrostannylation or hydrogermylation of acetylenes takes place readily in the presence of a catalytic amount of free radical initiator such as azobisisobutyronitrile (AIBN) to give the corresponding alkenylstannanes or alkenylgermanes in good yields.[4] The reaction is regioselective but nonstereoselective. Thus, terminal acetylenes give 1-stannyl-1-alkenes or 1-germyl-1-alkenes as stereoisomeric mixtures (E and Z) upon treatment with R_3SnH or R_3GeH.

On the other hand, triphenylstannane adds to acetylenes in the presence of a catalytic amount of $Pd(PPh_3)_4$ to give a mixture of three isomeric alkenyltriphenylstannanes. The representative results are summarized in Table 1. (E)-Isomer **2** (cis addition products) predominates and (Z)-isomers **3** and its regio isomers **1** are obtained as minor products. Solvents (CH_2Cl_2, THF, and benzene) did not affect the isomeric ratios of the products. Palladium complexes such as $PdCl_2(PPh_3)_2$, $PdCl_2(CH_3CN)_2$, and $Pd(OAc)_2$ are equally effective as $Pd(PPh_3)_4$. Distribution of the isomeric products depends on the ligand on palladium. For instance, the reaction of 1-dodecyne with Ph_3SnH in the presence of $PdCl_2(n\text{-}Bu_3P)_2$ or $Pd(OAc)_2$-$(p\text{-}MeOC_6H_4)_3P$ combination[5] provided a mixture of **1a**, **2a**, and **3a** (**1a**:**2a**:**3a**=10:80:10) as $Pd(PPh_3)_4$. Meanwhile, $PdCl_2[P(o\text{-}MeC_6H_4)_3]_2$-catalyzed reaction gave (*E*)-1-triphenylstannyl-2-dodecene (**4a**) in 42% yield along with **1a** (3%), **2a** (24%), and **3a** (2%).[6] Catalysts such as $Pd(OAc)_2$ and $PdCl_2(CH_3CN)_2$ without phosphine compounds were also effective for the addition of Ph_3SnH to acetylenes to give allylic stannane as a major product. For instance, 1-dodecyne gave a mixture of **4a** and **2a** (**4a**:**2a**=7:3, combined yield 65—75%) upon treatment with Ph_3SnH in the presence of these palladium salts.



Hydrogermylation reaction could also be catalyzed by $Pd(PPh_3)_4$. The use of $Pd(PPh_3)_4$ was essential for the successful reaction. Triphenylgermane is less reactive hydrogen donor than Ph_3SnH and can not

Table 1. $Pd(PPh_3)_4$-Catalyzed Hydrostannation and Hydrogermylation of Acetylenes

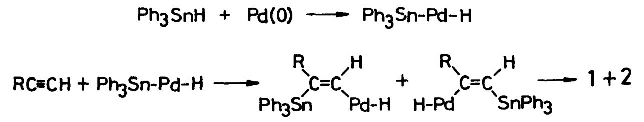


Run		Acetylene R^1	Acetylene R^2	Ph_3SnH (Ph_3GeH)	Yield %	Ratio of **1(5)**:**2(6)**:**3(7)**
1	**a**	$C_{10}H_{21}$	H	Ph_3SnH	77	11:82:7
2	**b**	Ph	H	Ph_3SnH	61	12:71:17
3	**c**	$PhCH_2OCH_2CH_2$	H	Ph_3SnH	82	25:65:10
4	**d**	Me_3Si	H	Ph_3SnH	69	0:100:0
5	**e**	C_5H_{11}	C_5H_{11}	Ph_3SnH	53	0:100:0
6	**a**	$C_{10}H_{21}$	H	Ph_3GeH	97	14:86:0
7	**a**	$C_{10}H_{21}$	H	$n\text{Pr}_3GeH$	83	20:80:0
8	**b**	Ph	H	Ph_3GeH	89	9:91:0
9	**c**	$PhCH_2OCH_2CH_2$	H	Ph_3GeH	52	7:91:<2
10	**f**	$HOCH_2CH_2$	H	Ph_3GeH	57	0:100:0
11	**d**	Me_3Si	H	Ph_3GeH	98	0:100:0
12	**e**	C_5H_{11}	C_5H_{11}	Ph_3GeH	80	a)

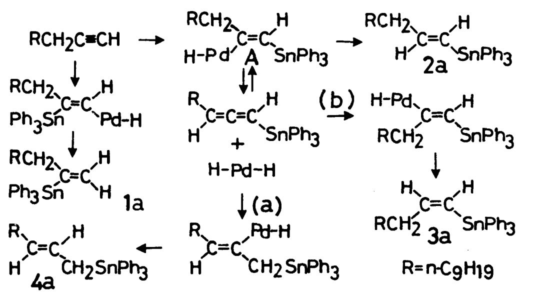
a) (*E*)-6-Triphenylgermyl-6-dodecene (**5a**) and (*E*)-7-triphenylgermyl-5-dodecene (**8**) were obtained (**5a**:**8**=1:2).

reduce $PdCl_2(PPh_3)_2$, $PdCl_2(CH_3CN)_2$, and $Pd(OAc)_2$ 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 stereoselectively[7] 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 Pd(0), (2) stannylpalladation (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 **3**.[8]



Scheme 1.

Experimental

General Procedure for the Reaction of Acetylenic Compounds with Triphenylstannane in the Presence of $Pd(PPh_3)_4$. The reaction of 1-dodecyne with Ph_3SnH is representative. $Pd(PPh_3)_4$ (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 ^{1}H 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, ^{1}H 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}; ^{1}H 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 $C_{23}H_{26}SiSn$: 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}; ^{1}H 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 $C_{30}H_{38}Sn$: 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). $Pd(PPh_3)_4$ (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 ^{1}H NMR spectrum: Bp 120 °C (bath temp, 0.1 Torr); IR (neat) 2880, 2820, 1425, 1085, 730, 695 cm^{-1}; ^{1}H 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 $C_{30}H_{38}Ge$: 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}; ^{1}H 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 $C_{21}H_{44}Ge$: 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}: ^{1}H NMR ($CDCl_3$) δ=5.61 (d, J=2.3 Hz, 0.09 H), 6.30 (d, J=2.3 Hz, 0.09 H), 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 $C_{26}H_{22}Ge$: 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}; ^{1}H 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 $C_{29}H_{28}OGe$: 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}; ^{1}H 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 $C_{22}H_{22}OGe$: 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}; ^{1}H 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 $C_{23}H_{26}SiGe$: 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}; ^{1}H 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 $C_{30}H_{38}Ge$: C, 76.46; H, 8.13%.

Reaction of 1-Dodecyne with Ph_3SnH in the Presence of $PdCl_2[P(o\text{-}MeC_6H_4)_3]_2$. A catalytic amount of $PdCl_2[P(o\text{-}MeC_6H_4)_3]_2$ (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**: ^{1}H 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) $Pd(OAc)_2$ (0.02 mmol) and $(p\text{-}MeOC_6H_4)_3P$ (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 revovered unchanged, respectively, without isomerization into (*E*)-1-triphenylstannyl-2-dodecene (**4a**) on treatment with $Ph_3SnH\text{-}PdCl_2[P(o\text{-}MeC_6H_4)_3]_2$.

7) Benzyl ether of 3-butyn-1-ol gave trace of (*Z*)-alkenyltriphenylgermane **7c** (<2%).

8) The formation of (*Z*)-1-phenyl-2-triphenylstannylethene can not be explained by the above mechanism. Thus, an initial trans-addition of $Ph_3Sn\text{–}Pd$ to acetylenic bond can not be excluded.

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