Hydrostannation and Hydrogermylation of Allenes

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Synopsis. Treatment of allenes with Ph_3SnH or Ph_3GeH in the presence of $Pd(PPh_3)_4$ catalyst provides the corresponding allylic stannanes or allylic germanes in good yields. Et_3B induced radical addition of Ph_3SnH or Ph_3GeH to allenes are also described.

Previously reported reaction of Ph_3SnH or Ph_3GeH with acetylenic compounds in the presence of a catalytic amount of palladium[1] or Et_3B[2] affords a simple and general access to the corresponding vinylic triphenylstannanes or vinylic triphenylgermanes. In furhter extension of these techniques, we have examined the reaction of allenic compounds with Ph_3SnH or Ph_3GeH.

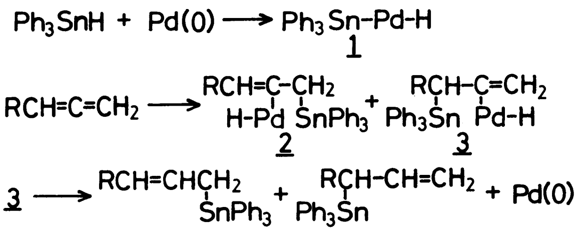
Treatment of allenic compounds with triphenylstannane or triphenylgermane[3] in the presence of a catalytic amount of $Pd(PPh_3)_4$ resulted in exclusive formation of allylic triphenylstannanes or allylic triphenylgermanes. The typical results are summarized in Table 1. We are tempted to assume the following reaction mechanism: (1) Oxidative addition of Ph_3SnH (Ph_3GeH) to Pd(0), (2) stannylpalladation (germylpalladation) to give vinylpalladium, and (3) reductive elimination to produce allylic stannanes (allylic germanes) and regenerate the palladium(0) (Scheme 1). Palladium always attacked the central carbon of allenic linkage and Ph_3Sn (Ph_3Ge) group added to end carbon in the stannylpalladation (germylpalladation) step. The distribution of two regioisomeric products, allylic stannanes or allylic germanes,

Table 1. Hydrostannation and Hydrogermylation of Allenes

Entry	Allene	Ph_3SnH (Ph_3GeH)	Catalyst	Product (Yield/%)
1	CH_2=C=CH_2[a]	Ph_3SnH	$Pd(PPh_3)_4$	CH_2=$CHCH_2SnPh_3$ (40) **5**
2		Ph_3GeH	$Pd(PPh_3)_4$	CH_2=$CHCH_2GePh_3$ (88) **6**
3		Ph_3SnH	Et_3B	**5** (36) CH_2=C(Me)$SnPh_3$ (24)
4		Ph_3GeH	Et_3B	**6** (57)
5	n-$C_{10}H_{21}$CH=C=CH_2	Ph_3GeH	$Pd(PPh_3)_4$	n-$C_{10}H_{21}$CH($GePh_3$)CH=CH_2 (53)
6		Ph_3SnH	Et_3B	n-$C_{10}H_{21}$CH=C(Me)$SnPh_3$ **7** (E/Z=3/2, 51) n-$C_{10}H_{21}CH_2$C($SnPh_3$)=CH_2 **8** (10) n-$C_{10}H_{21}$CH=$CHCH_2SnPh_3$ **9** (5)
7		Ph_3GeH	Et_3B	n-$C_{10}H_{21}$CH=$CHCH_2GePh_3$ (82)
8	PhCH=C=CH_2	Ph_3SnH	$Pd(PPh_3)_4$	$PhCH_2$CH=$CHSnPh_3$ (100)
9	$PhMe_2Si$CH=C=CH_2	Ph_3SnH	$Pd(PPh_3)_4$	$PhMe_2Si$CH=$CHCH_2SnPh_3$ (40)
10		Ph_3GeH	$Pd(PPh_3)_4$	$PhMe_2Si$CH=$CHCH_2GePh_3$ **10** (57) $PhMe_2Si$CH($GePh_3$)CH=CH_2 **11** (38)
11		Ph_3SnH	Et_3B	$PhMe_2SiCH_2$C($SnPh_3$)=CH_2 **12** (62) $PhMe_2Si$CH=C(Me)$SnPh_3$ **13** (33)
12		Ph_3GeH	Et_3B	**10** (69) $PhMe_2Si$CH=C(Me)$GePh_3$ **14** (28)
13	6,7-Tridecadiene	Ph_3GeH	$Pd(PPh_3)_4$	n-C_5H_{11}CH=CHCH($GePh_3$)-C_5H_{11} (79)
14		Ph_3SnH	Et_3B	n-C_5H_{11}CH=C($SnPh_3$)CH_2-C_5H_{11} (E/Z=32/68, 81)
15	1,2-Cyclononadiene	Ph_3SnH	Et_3B	1-(Triphenylstannyl)cyclononene (74)

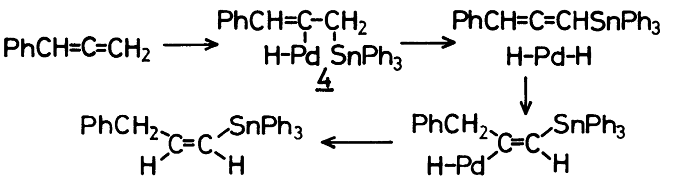
a) Excess (3.0 mmol) of 1,2-propadiene was employed. Yields were based on an amount of Ph_3SnH (or Ph_3GeH) employed.

depended on the nature of the substitution pattern of the starting allenic compounds. For instance, hydrogermylation of 1,2-tridecadiene afforded 3-triphenylgermyl-1-tridecene selectively, while 1-dimethylphenylsilyl-1,2-propadiene gave a mixture of 1-dimethylphenylsilyl-3-triphenylgermyl-1-propene and 3-dimethylphenylsilyl-3-triphenylgermyl-1-propene upon treatment with Ph_3GeH–Pd(0).



Scheme 1.

The formation of (*Z*)-3-phenyl-1-triphenylstannyl-1-propene from 1-phenyl-1,2-propadiene presumably is explained by the following reaction path: Elimination of palladium hydride from vinylpalladium species **4** and subsequent readdition in the opposite end of 1,2-diene, followed by reductive elimination (Scheme 2). The exclusive generation of (*Z*)-olefin as a single stereoisomer may be ascribed to the selective readdition of Pd–H to $PhCH=C=CHSnPh_3$ from less hindered face.



Scheme 2.

On the other hand, triphenylstannyl radical attacked allenes at the center carbon of monosubstituted allenes, $RCH=C=CH_2$, or disubstituted ones, RCH=C=CHR to give vinylic stannanes selectively,[4] in the case of Et_3B induced radical reaction. With unsubstituted 1,2-propadiene, triphenylstannyl radical added to both end and middle carbons to give a mixture of allyltriphenylstannane and 2-triphenylstannyl-1-propene. Triphenylgermyl radical was less reactive than triphenylstannyl radical and disubstituted allenes were reluctant to react with Et_3B–Ph_3GeH system. Reaction of unsubstituted or monosubstituted allenes afforded allylic germanes selectively.

Experimental

The IR spectra were determined on a JASCO IR-810 spectrometer, the ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer. The chemical shifts of the proton NMR are given in δ with TMS as an internal standard. The analyses were performed at the Elemental Analyses Center of Kyoto University. Tetrahydrofuran was dried in benzophenone ketyl and distilled.

General Procedure for the Reaction of Allenic Compounds with Triphenylstannane (or Triphenylgermane) in the Presence of $Pd(PPh_3)_4$. The reaction of 1,2-tridecadiene with Ph_3GeH is representative. $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) was added to a solution of 1,2-tridecadiene (0.18 g, 1.0 mmol) and Ph_3GeH (0.37 g, 1.2 mmol) in tetrahydrofuran (10 ml) under an argon atmosphere. The reaction mixture was stirred at 25 °C for 5 h, then poured into water, and extracted with ethyl acetate (3×20 ml). The combined organic extracts were dried (Na_2SO_4) and concentrated in vacuo. Purification by preparative TLC on silica gel provided 3-triphenylgermyl-1-tridecene (0.26 g) in 53% yield: IR (neat) 3066, 3048, 2994, 2922, 2850, 2034, 1484, 1431, 1091, 998, 732, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (t, *J*=6.5 Hz, 3H), 1.06—1.44 (m, 16H), 1.55—1.83 (m, 2H), 2.60—2.78 (m, 1H), 4.90—5.03 (m, 2H), 5.80 (m, 1H), 7.28—7.43 (m, 9H), 7.43—7.61 (m, 9H); ^{13}C NMR ($CDCl_3$) δ=14.1, 22.7, 29.0, 29.1, 29.3, 29.5, 29.6, 29.9, 31.9, 34.5, 113.6, 128.0, 128.8, 135.5, 136.3, 139.6.

General Procedure for the Et_3B-Induced Radical Reaction of Ph_3SnH (or Ph_3GeH) with Allenes. The reaction of 1,2-tridecadiene with Ph_3GeH is representative. A hexane solution of Et_3B (1.0 M, 1 M=1 mol dm^{-3}, 1.2 ml, 1.2 mmol) was added to a solution of Ph_3GeH (0.37 g, 1.2 mmol) and 1,2-tridecadiene (0.18 g, 1.0 mmol) in benzene (10 ml) at 25 °C. After stirring for 2 h at 25 °C, the reaction mixture was poured into water and extracted with ethyl acetate. Purification by preparative tlc gave (*E*)-1-triphenylgermyl-2-tridecene (0.40 g, 82% yield) as a colorless oil: IR (neat) 3064, 3048, 2920, 2850, 1654, 1484, 1465, 1431, 1091, 1026, 998, 963, 732, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (t, *J*=6.1 Hz, 3H), 1.04—1.45 (m, 16H), 1.79—1.99 (m, 2H), 2.40 (d, *J*=7.4 Hz, 2H), 5.35 (dt, *J*=15.2, 6.4 Hz, 1H), 5.51 (dt, *J*=15.2, 7.4 Hz, 1H), 7.30—7.44 (m, 9H); ^{13}C NMR ($CDCl_3$) δ=13.7, 19.5, 22.7, 29.1, 29.4, 29.6, 29.9, 30.0, 31.9, 32.7, 125.1, 128.1, 128.9, 131.0, 135.0, 136.9. Found: C, 77.12; H, 8.66%. Calcd for $C_{31}H_{40}Ge$: C, 76.73; H, 8.31%.

Allyltriphenylstannane, 2-Triphenylstannyl-1-propene, Allyltriphenylgermane. The reaction of 1,2-propadiene[5] with Ph_3SnH (Ph_3GeH) gave the title compounds whose spectral data were identical with the authentic samples.[6,7]

(*Z*)-2-Triphenylstannyl-2-tridecene (7Z), (*E*)-2-Triphenylstannyl-2-tridecene (7E), and 2-Triphenylstannyl-1-tridecene (8) (a 35:50:15 Mixture): IR (neat) 3062, 3046, 2922, 2850, 1637, 1480, 1458, 1429, 1074, 1022, 997, 726, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.89 (t, *J*=6.0 Hz, 3H), 1.06—1.50 (m, 16.3H), 1.86—2.08 (m, 2.5H, $=CCH_3$ (**7E**) and $=CCH_2$ (**7E**)), 2.13—2.31 (m, 1.75H, $=CCH_3$ (**7Z**) and $=CCH_2$ (**7Z**)), 2.36—2.48 (m, 0.3H, $=CCH_2$ (**8**)), 5.08—5.12 (m, 0.15H, $=CH_2$ (**8**)), 5.78—5.89 (m, 0.5H, =CH (**7E**)), 5.94—5.99 (m, 0.15H, $=CH_2$ (**8**)), 6.33—6.43 (m, 0.35H, =CH (**7Z**)), 7.31—7.52 (m, 9H), 7.52—7.77 (m, 6H); ^{13}C NMR ($CDCl_3$) δ=14.2, 22.7, 28.6, 29.4, 29.6, 29.7, 32.0, 33.3, 116.9, 128.5, 128.6, 128.8, 128.89, 128.93, 136.8, 137.1, 137.2, 138.8, 143.1. Found: C, 70.09; H, 7.68%. Calcd for $C_{31}H_{40}Sn$: C, 70.07; H, 7.59%.

(*E*)-1-Triphenylstannyl-2-tridecene (9). The compound was separated from other three isomers (**7E**, **7Z**, **8**) by preparative thin layer chromatography in pure form. ^{1}H NMR ($CDCl_3$) δ=0.89 (t, *J*=6.0 Hz, 3H), 1.06—1.50 (m, 16H), 1.85—2.04 (m, 2H), 2.41 (d, *J*=8.0 Hz, 2H), 5.31—5.58 (m, 1H), 5.58—5.80 (m, 1H), 7.31—7.52 (m, 9H), 7.52—7.77 (m, 6H).

(*Z*)-1-Triphenylstannyl-3-phenyl-1-propene: Mp 69 °C; IR (KBr) 3060, 3014, 2986, 1636, 1494, 1481, 1429, 1075, 1045, 1022, 997, 959, 749, 727, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.62 (d, *J*=7.9 Hz, 2H), 6.33 (d, *J*=15.7 Hz, 1H), 6.49 (dt, *J*=15.7, 7.9 Hz, 1H), 7.09—7.34 (m, 5H), 7.34—7.51 (m, 9H), 7.51—7.78 (m, 6H); ^{13}C NMR ($CDCl_3$) δ=17.6, 125.5, 126.2, 127.7, 128.1, 128.4, 128.6, 129.1, 137.1, 138.2, 138.3. Found: C, 69.14; H, 5.01%. Calcd for $C_{27}H_{24}Sn$: C, 69.41; H, 5.18%.

1-Dimethylphenylsilyl-3-triphenylstannyl-1-propene: IR (neat) 3062, 2950, 1597, 1429, 1247, 1111, 1075, 997, 843, 822, 726, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.20 (s, 6H), 2.59 (dd, *J*=8.2, 1.1 Hz, 2H), 5.66 (dt, *J*=18.2, 1.1 Hz, 1H), 6.34 (dt, *J*=18.2, 8.2 Hz, 1H), 7.20—7.46 (m, 12H), 7.46—7.95 (m, 8H); ^{13}C NMR ($CDCl_3$) δ=−2.4, 21.7, 124.8, 127.6, 128.5, 128.6, 129.0, 129.1, 133.8, 137.1, 137.2, 138.2. Found: C, 66.09; H, 5.60%. Calcd for $C_{29}H_{30}SiSn$: C, 66.30; H, 5.76%.

A Mixture of 1-Dimethylphenylsilyl-3-triphenylgermyl-1-propene (10) and 3-Dimethylphenylsilyl-3-triphenylgermyl-1-propene (11) (a 61:39 Mixture): IR (neat) 3064, 3044, 2952, 1604, 1485, 1430, 1248, 1113, 1091, 827, 732, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=−0.01 (s, 3.66H, Me_2Si (**10**)), 0.18 (s, 2.34H, Me_2Si (**11**)), 0.98 (d, *J*=12 Hz, 0.39H, CH (**11**)), 2.58 (dd, *J*=1.2, 8.0 Hz, 1.22H, CH_2 (**10**)), 4.82 (dd, *J*=2.0, 16.5 Hz, 0.39H, =CH_2 (**11**)), 4.86 (dd, *J*=2.0, 10.0 Hz, 0.39H, =CH_2 (**11**)), 5.65 (dt, *J*=18.4, 1.3 Hz, 0.61H, =CHSi (**10**)), 5.88 (ddd, *J*=10.0, 12.0, 16.5 Hz, 0.39H, =CH (**11**)), 6.20 (dt, *J*=18.4, 8.0 Hz, 0.61H, =CH (**10**)), 5.68—6.08 (m, 20H); ^{13}C NMR ($CDCl_3$) δ=−2.0, 24.6, 25.0, 114.3, 127.5, 127.6, 127.9, 128.2, 128.3, 128.65, 128.72, 128.9, 129.0, 133.8, 134.1, 135.0, 135.4, 136.4, 136.5, 137.2, 138.7, 143.1, 144.9. Found: C, 72.63; H, 6.25%. Calcd for $C_{29}H_{30}GeSi$: C, 72.68; H, 6.31%.

A Mixture of 3-Dimethylphenylsilyl-2-triphenylstannyl-1-propene (12) and 1-Dimethylphenylsilyl-2-triphenylstannyl-1-propene (13) (a 68:32 Mixture): IR (neat) 3060, 2950, 1480, 1428, 1247, 1112, 1074, 997, 833, 808, 726, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.14 (s, 4.08H, Me_2Si (**12**)), 0.41 (s. 1.92H, Me_2Si (**13**)), 2.13—2.25 (m, 2.32H, CH_2 (**12**) and =CCH_3 (**13**)), 5.30—5.41 (m, 0.68H, =CH_2 (**12**)), 5.78—5.84 (m, 0.68H, =CH_2 (**12**)), 6.31—6.38 (m, 0.32H, =CH (**13**)), 7.20—7.48 (m, 14H), 7.48—7.73 (m, 6H); ^{13}C NMR ($CDCl_3$) δ=−2.8, 29.2, 127.7, 127.8, 128.0, 128.1, 128.5, 128.6, 128.8, 128.9, 133.6, 133.7, 136.8, 137.2, 138.7, 143.1. Found: C, 66.11; H, 6.06%. Calcd for $C_{29}H_{30}SiSn$: C, 66.30; H, 5.76%.

8-Triphenylgermyl-6-tridecene: IR (neat) 2952, 2922, 2852, 1654, 1485, 1458, 1431, 1090, 969, 732, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.85 (t, *J*=5.5 Hz, 6H), 0.99—1.34 (m, 14H), 1.81—1.99 (m, 2H), 2.50—2.68 (m, 1H), 5.125—5.39 (m, 2H), 7.26—7.41 (m, 9H), 7.41—7.58 (m, 6H); ^{13}C NMR ($CDCl_3$) δ=13.3, 22.5, 22.6, 25.6, 28.7, 29.4, 30.5, 31.2, 31.4, 32.6, 33.1, 127.9, 128.7, 130.2, 130.7, 135.5, 136.7. Found: C, 76.73; H, 8.34%. Calcd for $C_{31}H_{40}Ge$: C, 76.73; H, 8.31%.

A Mixture of (*Z*)-7-Triphenylstannyl-6-tridecene and (*E*)-Isomer (a 65:35 Mixture): IR (neat) 3062, 2952, 2922, 2850, 1618, 1578, 1480, 1458, 1428, 1377, 1074, 1022, 997, 725, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.65—0.82 (m, 6H), 0.82—1.51 (m, 14H), 1.89—2.08 (m, 1.3H, =$C(SnPh_3)CH_2$ (*Z*)), 2.12—2.33 (m, 2H, =CCH_2 (*E* and *Z*)), 2.39 (t, *J*=7.3 Hz, 0.7H, =$C(SnPh_3)CH_2$ (*E*)), 5.80 (t, *J*=7.1 Hz, 0.35H, =CH (*E*)), 6.29 (t, *J*=7.3 Hz, 0.65H, =CH (*Z*)), 7.47—7.51 (m, 9H), 7.51—7.76 (m, 6H); ^{13}C NMR ($CDCl_3$) δ=13.9, 14.0, 22.4, 22.5, 22.6, 28.6, 28.7, 29.0, 29.6, 30.3, 30.7, 31.3, 31.5, 31.6, 32.9, 35.7, 40.3, 127.9, 128.4, 128.6, 128.7, 128.8, 136.4, 137.0, 137.2, 137.4, 139.7, 140.2, 143.5. Found: C, 70.17; H, 7.64%. Calcd for $C_{31}H_{40}Sn$: C, 70.07; H, 7.59%.

1-(Triphenylstannyl)cyclononene: Mp 88—89 °C; IR (KBr) 3060, 3012, 2984, 2922, 2850, 1480, 1074, 726, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.20—1.65 (m, 10H), 2.06—2.40 (m, 2H), 2.45—2.65 (m, 2H), 6.03 (t, *J*=8.0 Hz, 1H), 7.20—7.75 (m, 15H); ^{13}C NMR ($CDCl_3$) δ=24.6, 25.46, 25.52, 25.8, 26.0, 27.7, 31.3, 128.4, 128.7, 128.9, 137.2, 137.5, 139.1, 145.0. Found: C, 68.43; H, 6.39%. Calcd for $C_{27}H_{30}Sn$: C, 68.53; H, 6.39%.

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