# Stille Coupling Reaction Using 4-(Trimethylsilyl)-2-butenylstannanes To Afford Allylic Silanes

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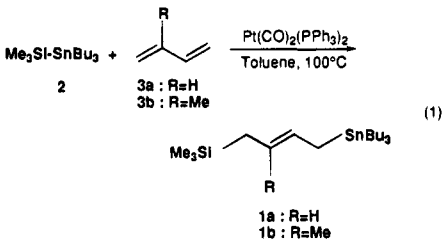
## Introduction

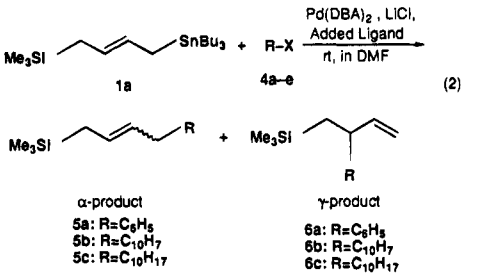
Recently we have reported the first example of 1,4-silastannylation of 1,3-dienes (**3**) with (trimethylsilyl)-tributylstannane (**2**) catalyzed by a platinum complex (eq 1).[1] The reaction is highly regio- and stereoselective and




affords 4-(trimethylsilyl)-2-butenylstannanes (**1**) as products. The products **1** were new compounds and possess both allylic silane[2] and allylic stannane[3] functionalities in the same molecule sharing the same carbon–carbon double bond. Therefore, **1** may be versatile building blocks in organic synthesis.

The palladium-catalyzed coupling of unsaturated halides or triflates with organostannanes is now commonly referred to as the Stille coupling reaction.[4] As the organostannanes, alkyl, aryl, vinyl, and allyl derivatives have been employed.[5] When substituted allylic stannanes are used as the substrates, Stille[6a,b] and other authors[6c,d] reported that extensive allylic rearrangement occurs during the coupling reaction.

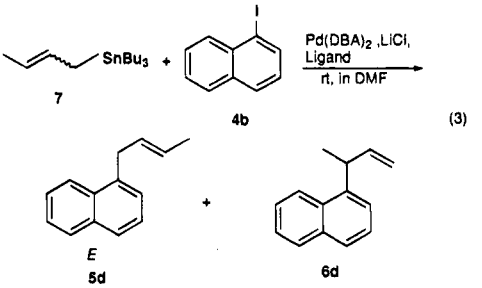
In this paper, **1** is regarded as an allylic stannane derivative and subjected to the Stille coupling reaction (eq 2). If the reaction proceeds without the allylic




rearrangement, synthetically useful *allylic* silanes (**5**: α-product) are obtained.[7] However, the allylic rearrangement may be dominant in a manner similar to that in precedent studies[6] and afford less desirable *homoallylic* silanes (**6**: γ-product). So far, it has not been possible to control the regioselectivity in the Stille coupling reaction using substituted allylic stannanes. However, we recently found that suitable choice of added group 15 ligand to a palladium complex effects the coupling reaction without the allylic rearrangement. Here, we report a new route to allylic silanes via the Stille coupling reaction using **1** (eq 2).

## Results and Discussion

Before the reaction using **1** was explored, the model reaction using crotylstannane (**7**)[6] (used as a mixture of *E* and *Z*; *E*:*Z* = 65:35) was carried out at room temperature (eq 3). Through examining several reaction pa-




rameters, we found that added group 15 ligand to $Pd(DBA)_2$ (DBA = dibenzylideneacetone)[8] has a marked effect on determining the regioselectivity (α- vs γ-product). The results are shown in Table 1. The addition of $AsPh_3$ as the ligand favored formation of the α-product **5d** (entry 1). Lithium chloride[5f–j,6b,7b,11] was indispensable in the catalyst system. The α-product was also obtained as the major product by the addition of $P(OCH_2)_3CEt$,

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**Table 1. Reaction of Crotylstannane (7) with 4b: The Model Reaction[a]**

| entry | ligand | yield,[b] % | ratio of 5d[c]:6d |
|---|---|---|---|
| 1 | $AsPh_3$ | 61 | 91:9 |
| 2 | $P(OCH_2)_3CEt$ | 14 | 79:21 |
| 3 | $P(2\text{-furyl})_3$ | 71 | 15:85 |
| 4 | $PPh_3$ | 23 | 0:100 |

[a] A mixture of **7** (0.20 mmol), 1-iodonaphthalene (**4b**) (0.60 mmol), $Pd(DBA)_2$ (0.010 mmol), ligand (0.020 mmol), LiCl (0.60 mmol), and DMF (0.80 mL) was stirred at room temperature for 48 h. [b] Isolated yields. [c] Only *E* isomer.

**Table 2. Reaction of 1a with Iodides or Triflates[a]**

| entry | R–X | ligand | yield,[b] % | ratio of 5[c]:6 |
|---|---|---|---|---|
| 5 | $C_6H_5I$ | $AsPh_3$ | 36 | 97(86):3 |
| 6 | $C_6H_5I$ | $SbPh_3$ | 62 (51) | 97(87):3 |
| 7 | $C_6H_5I$ | $P(OCH_2)_3CEt$ | 52 | 86(60):14 |
| 8 | $C_6H_5I$ | $P(2\text{-furyl})_3$ | 72 | 17(76):83 |
| 9 | $C_6H_5I$ | $PPh_3$ | 52 | 0:100 |
| 10 | $C_6H_5I$ | $P(OPh)_3$ | 51 | 0:100 |
| 11 | $C_6H_5I$ | $PBu_3$ | 0 | |
| 12 | $C_{10}H_7I$ | $AsPh_3$ | (67) | 97(80):3 |
| 13 | $C_6H_5OTf$ | $AsPh_3$ | 87 | 91(84):9 |
| 14 | $C_6H_5OTf$ | $P(OCH_2)_3CEt$ | 58 | 86(78):14 |
| 15 | $C_6H_5OTf$ | $P(2\text{-Furyl})_3$ | 83 | 83(57):17 |
| 16 | $C_6H_5OTf$ | $PPh_3$ | 66 | 61(15):39 |
| 17 | $C_6H_5OTf$ | $P(OPh)_3$ | 51 | 45(40):55 |
| 18 | $C_{10}H_7OTf$ | $AsPh_3$ | (64) | 92(90):8 |
| 19 | $C_{10}H_{17}OTf$ | $AsPh_3$ | 64 | 46(80):54 |
| 20 | $C_{10}H_{17}OTf$ | $P(OCH_2)_3CEt$ | 23 | 39(67):61 |
| 21 | $C_{10}H_{17}OTf$ | $P(2\text{-furyl})_3$ | 65 | 8(63):92 |
| 22 | $C_{10}H_{17}OTf$ | $PPh_3$ | 13 | 8(0):92 |

[a] A mixture of **1a** (0.20 mmol), triflates or iodides **4a–e** (0.20 mmol), $Pd(DBA)_2$ (0.010 mmol), ligand (0.020 mmol), LiCl (0.60 mmol), and DMF (0.80 mL) was stirred at room temperature for 48 h. [b] GLC yields. The numbers in parentheses show isolated yields. [c] Percentages of *E* isomers are shown in parentheses.

albeit in low yield (entry 2). In contrast, the use of tri(2-furyl)phosphine [$P(2\text{-furyl})_3$] or $PPh_3$ as the ligand afforded the γ-product (**6d**) with predominant allylic rearrangement (entries 3 and 4). Particularly with $PPh_3$, although conversion of the substrates was low, only the γ-product was obtained with complete allylic rearrangement (entry 4). This observation is consistent with the precedent studies[6] in which $PPh_3$ was adopted as the ligand.

With these introductory findings, we next carried out the Stille coupling reaction using tributyl[(*E*)-4-(trimethylsilyl)-2-butenyl]stannane (**1a**) (eq 2; Table 2). At room temperature, **1a** smoothly reacted with iodobenzene (**4a**)[4e] to afford cross-coupling products (**5a** and **6a**) in the presence of a palladium catalyst. As the catalyst precursor, $Pd(DBA)_2$ combined with 2 equiv of group 15 ligand was employed in the presence of excess LiCl. When $Pd(DBA)_2$ with $AsPh_3$ (As/Pd = 2) was employed as a catalyst precursor, the reaction afforded predominantly the α-product **5a** without the allylic rearrangement (entry 5). The addition of $SbPh_3$ in place of the $AsPh_3$ increased the yield considerably, maintaining the high α-product selectivity (entry 6). We believe that this regioselectivity is important, since the reaction affords synthetically useful allylic silanes[2] as the products. Sterically less demanding $P(OCH_2)_3CEt$ also provided the α-product (**5a**) as the major product (entry 7). In contrast, the formation of the γ-adducts (**6a**) increased exceedingly when $P(2\text{-furyl})_3$ was added as the ligand (entry 8). Furthermore, with $PPh_3$ as the added ligand, the γ-product was obtained exclusively (entry 9), reminiscent of the model reaction (eq 3; entry 4 in Table 1). Triphenylphosphite [$P(OPh)_3$] also afforded the γ-product exclusively (entry 10). The addition of an alkylphosphine such as $PBu_3$ totally suppressed the catalytic activity (entry 11). Thus, by suitable choice of the group 15 ligands, the regioselectivity can be controlled almost completely. A soft and highly dissociating ligand such as $AsPh_3$ might be favorable for the α-product. A similar remarkable effect of the added $AsPh_3$ ligand was observed in the Stille reaction by Farina and co-workers.[9] Lithium chloride[5f–j,6b,7b,11] was indispensable in the reaction. After the reaction, $Bu_3SnCl$ and $Bu_3SnI$ (ca. 1:1) were detected in the reaction mixture by GLC analysis (OV-17; programmed from 120 to 250 °C at 10 °C/min). When LiCl was removed from the catalyst system of entry 5, the yield of the coupling products decreased to 3%. Tetrabutylammonium chloride could replace LiCl and gave the products in 44% yield. Ligand exchange with chloride ion in the catalytic cycle seems to facilitate the coupling reaction.[4c] Other salts such as $ZnCl_2$,[5c,5j] CsCl, NaCl,[5j] CuI,[9b] and $CuCl_2$ were not effective (yield < 5%). Other catalyst precursors such as $PdCl(PhCH_2)(PPh_3)_2$[5b,c,6a] and $RhCl(PPh_3)_3$[5a] are totally inert for the present reaction. As the solvent, DMF[5h,i,6b] was most favorable, presumably due to suitable coordination ability and good solubility for LiCl. Other solvents such as THF, dioxane, toluene, HMPA, DMSO, 1,3-dimethyl-2-imidazolidinone (DMI), and 1-methyl-2-pyrrolidinone (NMP) lowered the yield considerably. 1-Iodonaphthalene (**4b**) also reacted with **1a** to provide the α-products (**5b**) selectively in good yield by employing $Pd(DBA)_2$–$AsPh_3$ catalyst system (entry 12). However, other halide substrates such as chlorobenzene, bromobenzene,[5a] and benzoyl chloride[5k] did not provide the corresponding coupling product under the present reaction conditions.

Aryl trifluoromethanesulfonates (triflates) also can be employed in the present coupling reaction (Table 2). When the reaction of phenyl triflate[5h,i, 6b] (**4c**) with **1a** was carried out in the presence of a palladium complex, the added ligand, and LiCl, the coupling products (**5a**, **6a**) were obtained. With $AsPh_3$, the α-product (**5a**) was obtained in high yield with high selectivity (entry 13). The ratio of the γ-product (**6a**) increased with $P(OCH_2)_3CEt$, $P(2\text{-furyl})_3$, $PPh_3$, and $P(OPh)_3$ in this order, as was observed with aryl iodides in Table 2. However, with the triflates the α-product (**5a**) still formed even when $PPh_3$ or $P(OPh)_3$ was used as the additive (entries 16 and 17; cf. entries 9 and 10 in Table 2). After the reaction, $Bu_3SnCl$ was found in the reaction mixture.[5h,i, 6b] 1-Naphthyl triflates (**4d**) also afforded the α-product (**5b**) selectively (entry 18). However, with other esters such as phenyl *p*-toluenesulfonate (Ph-OTs) and diethyl phenyl phosphate [$PhOP(=O)(OEt_2)_2$], no cross-coupling products were obtained under the present reaction conditions. With a vinyl triflate, 4-*tert*-butyl-1-cyclohexenyl triflate (**4e**),[5j,11] the corresponding cross-coupling products (**5c**, **6c**) were afforded under the standard reaction conditions (entries 19 and 20). Unlike the aryl iodides and aryl triflates, selectivity to the α-product (**5c**) was not satisfactory; even with $AsPh_3$ as the ligand, the allylic rearrangement took place considerably (entry 19). Note that the yield of the γ-adduct was increased with $P(OCH_2)_3CEt$, $P(2\text{-furyl})_3$, and $PPh_3$ in this order as observed with aryl iodides and aryl triflates (entries 13–18). Other vinyl substrates such as 1-hexylvinyl triflate, (*E*)-1-octenyl triflate, and (*E*)-1-iodo-1-cyclohexene afforded the coupling products only in low yields (<10%).

Tributyl[(*E*)-4-(trimethylsilyl)-3-methyl-2-butenyl]stannane (**1b**)[1] is also obtained selectively in high yield

by the 1,4-silastannylation of isoprene with **2** (eq 1). We attempted to utilize **1b** in the coupling reactions. However, the reaction was sluggish with **1b**, and no selective cross-coupling reactions took place under the standard reaction conditions.

## Experimental Section

**Material.** The reagents and the solvents were dried and purified before use.[11] The substrates, **1a** and **1b**, were prepared according to the reported procedure.[1] Phenyl triflate (**4c**),[12a] 1-naphthyl triflate (**4d**),[12a] diethyl phenyl phosphate,[12b] 4-*tert*-butyl-1-cyclohexenyl triflates (**6**),[12c] 1-hexylvinyl triflate,[12d] (*E*)-1-octenyl triflates,[12e] (*E*)-1-iodo-1-cyclohexene,[12f] (*E*)-1-iodo-1-octene,[12g] and tri(2-furyl)phosphine[12h] were prepared by using known methods. Crotylstannane (**7**) was prepared by following a published method.[13] Other iodides and ligands were commercial products. The following catalyst precursors were prepared according to literature methods: $Pd(dba)_2$,[8] $Pt(CO)_2(PPh_3)_2$,[14a] $Pd(PPh_3)_4$,[14b] $PdCl(PhCH_2)(PPh_3)_2$,[14c] and $RhCl(PPh_3)_3$.[14d]

**General Procedure.** A typical reaction procedure is described for the reaction with **1a** (entry 5, Table 2). A mixture of **1a** (0.20 mmol, 84 mg), **4a** (0.20 mmol, 41 mg), $Pd(DBA)_2$ (0.01 mmol, 6 mg), $AsPh_3$ (0.02 mmol, 6 mg), LiCl (0.60 mmol, 25 mg), and DMF (0.80 mL) was stirred at room temperature for 48 h under an argon atmosphere. After the reaction, the reaction mixture was treated with saturated ammonium fluoride aqueous solution and filtered to remove tributyltin halides as insoluble tributyltin fluoride. The product was isolated by medium-pressure chromatography (silica gel: Wakogel 300, 45–75 μm; hexane as an eluent) followed by Kugelrohr distillation in 51% yield (21 mg, pot temperature 80 °C/0.3 mmHg). The identification of the products was made by $^1$H NMR, $^{13}$C NMR, and GC/MS. The NMR spectra (in $CDCl_3$) were recorded with a JEOL α-400 or GX-270 spectrometer. The mass spectra were measured on a Shimadzu QP-1000 (GC/MS) equipped with a PAC 1100S computer system. GLC analyses were made using a column (3 mm i.d. × 3 m) packed with Apiezon Grease L (5% on Uniport HP, 60/80 mesh) or Silicon OV-17 (2% on Uniport HP, 60/80 mesh). Elemental analyses were performed at the Microanalytical Center of Kyoto University. The analytical data for the products are as follows.

**(*E*)-5a**: $^1$H NMR δ 0.01 (s, 9H), 1.45 (d, $J$ = 7 Hz, 2H), 3.32 (d, $J$ = 7 Hz, 2H), 5.34–5.55 (m, 2H), 7.14–7.30 (m, 5H); NOE difference measurement, irradiation at the methylene proton resonances at δ 3.32 ($-CH_2C_6H_5$) caused enhancement of olefin proton resonance at δ 5.34–5.55, while almost no NOE was observed at methylene proton resonance at δ 1.45 ($-CH_2SiMe_3$); $^{13}$C NMR δ −1.87 (q), 22.73 (t), 39.32 (t), 125.8 (d), 127.4 (d), 128.0 (d), 128.3 (d), 128.5 (d), 141.6 (s); MS, *m/e* 204 ($M^+$). Anal. Calcd for $C_{13}H_{20}Si$: C, 76.40; H, 9.86. Found: C, 76.23; H, 9.93.

**(*Z*)-5a**: $^1$H NMR δ 0.16 (s, 9H), 1.70 (d, $J$ = 7 Hz, 2H), 3.47 (d, $J$ = 7 Hz, 2H), 5.35–5.65 (m, 2H), 7.17–7.38 (m, 5H); $^{13}$C NMR δ −1.66 (q), 18.57 (t), 33.34 (t), 125.8 (d), 127.5 (d), 128.3 (d), 128.4 (d), 128.7 (d), 141.6 (s); MS, *m/e* 204 ($M^+$).

**(*E*)-5b**: $^1$H NMR δ 0.01 (s, 9H), 1.49 (d, $J$ = 7 Hz, 2H), 3.82 (d, $J$ = 7 Hz, 2H), 5.53–5.65 (m, 2H), 7.41–8.20 (m, 7H); $^{13}$C NMR δ −1.85 (q), 22.73 (t), 36.38 (t), 124.3 (d), 125.4 (d), 125.6 (d, 2C), 125.9 (d), 126.5 (d), 126.7 (d), 128.2 (d), 128.6 (d), 132.1 (s), 133.9 (s), 137.5 (s); MS, *m/e* 254 ($M^+$). Anal. Calcd for $C_{17}H_{22}Si$: C, 80.25; H, 8.71. Found: C, 80.18; H, 8.71.

**(*Z*)-5b**: $^1$H NMR δ 0.02 (s, 9H), 1.73 (d, $J$ = 7 Hz, 2H), 3.88 (d, $J$ = 7 Hz, 2H), 5.47–5.65 (m, 2H), 7.41–8.20 (m, 7H); MS, *m/e* 254 ($M^+$).

**(*E*)-5c**: $^1$H NMR δ −0.02 (s, 9H), 0.86 (s, 9H), 1.02–1.32 (m, 1H), 1.42 (d, $J$ = 7 Hz, 2H), 1.70–2.12 (m, 6H), 2.60 (d, $J$ = 7 Hz, 2H), 5.15–5.54 (m, 3H); $^{13}$C NMR δ −1.83 (q), 19.8 (t), 22.74 (t), 24.47 (t), 26.98 (t), 27.35 (q), 29.95 (s), 41.09 (t), 44.39 (d), 121.03 (d), 126.89 (d), 127.39 (d), 141.0 (s); MS, *m/e* 264 ($M^+$).

**(*Z*)-5c**: $^1$H NMR δ 0.01 (s, 9H), 0.86 (s, 9H), 1.02–1.32 (m, 1H), 1.47 (d, $J$ = 7 Hz, 2H), 1.70–2.12 (m, 6H), 2.71 (d, $J$ = 7 Hz, 2H), 5.15–5.45 (m, 3H); $^{13}$C NMR δ −1.6 (q), 18.4 (t), 22.7 (t), 24.5 (t), 27.1 (t), 27.4 (q), 30.5 (s), 35.0 (t), 44.3 (d), 121.6 (d), 125.5 (d), 126.3 (d), 140.9 (s); MS, *m/e* 264 ($M^+$).

**5d**: $^1$H NMR δ 1.73 (dq, $J$ = 7 Hz, 1 Hz, 3 H), 3.82 (d, $J$ = 7 Hz, 2H), 5.59 (dqt, $J$ = 15 Hz, 7 Hz, 1 Hz, 1H), 5.79 (dtq, $J$ = 15 Hz, 7 Hz, 1 Hz, 1H), 7.37–8.20 (m, 7H); $^{13}$C NMR δ 17.98 (q), 36.13 (t), 124.12 (d), 125.37 (d), 125.65 (d), 126.05 (d), 126.70 (d), 126.77 (d), 128.67 (d), 129.35 (d), 132.01 (s), 133.87 (s), 137.13 (s).

**6a:** $^1$H NMR δ 0.01 (s, 9H), 1.17 (d, $J$ = 7 Hz, 2H), 3.52 (q, $J$ = 7 Hz, 1H), 5.03 (d, $J$ = 10 Hz, 1H), 5.11 (d, $J$ = 17 Hz, 1H), 6.08 (ddd, $J$ = 17 Hz, 10 Hz, 7 Hz, 1H), 7.27–7.39 (m, 5H); $^{13}$C NMR δ −0.94 (q), 23.78 (t), 46.01 (d), 112.4 (t), 126.1 (d), 127.4 (d), 128.4 (d), 145.0 (d), 146.5 (s); MS, *m/e* 204 ($M^+$).

**6b**: $^1$H NMR δ 0.05 (s, 9H), 1.45 (d, $J$ = 7 Hz, 2H), 3.59 (q, $J$ = 7 Hz, 1H), 5.30 (d, $J$ = 10 Hz, 1H), 5.60–5.85 (m, 1H), 6.25–6.45 (m, 1H), 7.41–8.20 (m, 7H); MS, *m/e* 254 ($M^+$).

**6c**: $^1$H NMR δ −0.01 (s, 9H), 0.86 (s, 9H), 1.02–1.32 (m, 3H), 1.70–2.12 (m, 6H), 2.74 (q, 1H), 4.83–5.02 (m, 2H), 5.13–5.30 (m, 1H), 5.62–5.82 (m, 1H); $^{13}$C-NMR δ −0.68 (q), 20.8 (t), 22.74 (t), 24.42 (t), 27.04 (t), 27.33 (q), 29.95 (s), 44.47 (d), 47.09 (d), 112.42 (t), 121.35 (d), 137.4 (s), 144.3 (d); MS, *m/e* 264 ($M^+$).

**6d**: $^1$H NMR δ 1.51 (d, $J$ = 7 Hz, 3H), 4.29 (quin, $J$ = 6 Hz, 1H), 5.17 (dt, $J$ = 10 Hz, 1 Hz, 1H), 5.18 (dt, $J$ = 17 Hz, 1Hz, 1H), 6.21 (ddd, $J$ = 17 Hz, 10 Hz, 6 Hz, 1H), 7.35–7.57 (m, 7H); $^{13}$C NMR δ 20.20 (q), 37.84 (d), 113.65 (t), 123.48 (d), 123.65 (d), 125.33 (d), 125.59 (d), 125.74 (d), 126.77 (d), 128.88 (d), 131.42 (s), 133.95 (s), 141.42 (s), 142.86 (d).

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