Alternative Synthesis of (Z)-1-Aryl-1-(tributylstannyl)-2-(triethylgermyl)ethenes and the Unprecedented Germyl 1,2-Migration during the Destannylation of the Adducts

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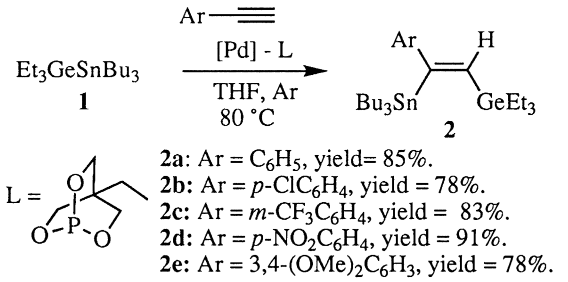
A specific combination catalyst, Pd(dba)$_2$ and 4-ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane, effectively catalyzed the addition of tributyl(triethylgermyl)stannane to arylacetylenes in tetrahydrofuran to give (*Z*)-1-aryl-2-(germyl)-1-(stannyl)ethenes in high yields. The (*Z*)-1-aryl-2-(germyl)-1-(stannyl)ethenes were subject to the unprecedented germyl 1,2-migration during the destannylation using HI / TBAI in toluene to produce 1-aryl-1-(germyl)ethenes in high yields.

Palladium-catalyzed silastannation of acetylenes has been well studied and known to afford vicinal sila(stannyl)ethenes.[1] The addition of a Ge–Sn bond of a (germyl)stannane to a triple bond of nonterminal α,β-acetylenic esters catalyzed by Pd(PPh$_3$)$_4$ forms a mixture of vicinal germa(stannyl)ethenes with (*E*)- and (*Z*)-configrations.[2] In contrast, the addition to terminal alkynes involving phenylacetylene only forms the (*Z*)-germyl(stannyl)ethenes, in which a germyl group is combined with the terminal sp^2 carbon.[3] However, the yields did not exceed 50%. We found that a specific combination catalyst, Pd(dba)$_2$ (dba = dibenzylideneacetone) and P(OCH$_2$)$_3$CEt (4-ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane, L), effectively catalyzed the addition of tributyl(triethylgermyl)stannane **1** to arylacetylenes to produce (*Z*)-1-aryl-1-(tributylstannyl)-2-(triethylgermyl)ethenes in high yields and the unprecedented germyl 1,2-migration occurred during the destannylation of the (*Z*)-1-aryl-2-(triethylgermyl)-1-(stannyl)ethenes to form 1-aryl-1-(triethylgermyl)ethenes. We report these preliminary results.

The germastannation of phenylacetylene using **1** in THF using the Pd(dba)$_2$ and L[4] combination catalyst afforded (*Z*)-1-(tributylstannyl)-2-(triethylgermyl)-1-phenylethenes **2a**[5] in 85% yield. The use of the THF solvent is essential in Scheme 1, in contrast to no reaction in benzene.



2a: Ar = C$_6$H$_5$, yield= 85%.
2b: Ar = *p*-ClC$_6$H$_4$, yield = 78%.
2c: Ar = *m*-CF$_3$C$_6$H$_4$, yield = 83%.
2d: Ar = *p*-NO$_2$C$_6$H$_4$, yield = 91%.
2e: Ar = 3,4-(OMe)$_2$C$_6$H$_3$, yield = 78%.

Scheme 1.

The NMR coupling constants for **2a** between tin and the vinylic proton,$^3J_{\text{Sn-H}}$, were −161.2 and −168.0 Hz for tin-117 and tin-119, respectively. These constants are typical for the structure with tin and the vinylic proton in *trans*-disposition.[3,6]

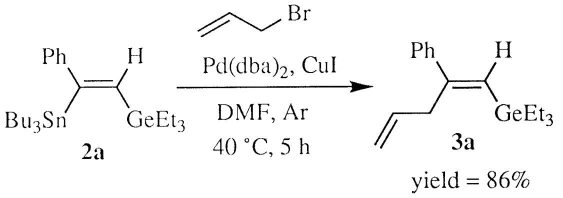
Table 1. Selected NMR data[a] for **2a-e**

product No.	δ(=CH)[b]	δ(C1)[c]	δ(C2)[c]	$^3J_{\text{SnH}}$[d]	
2a	6.63	165.5	151.8	-161.2	-168.4
2b	6.62	164.3	150.3	-157.2	-164.8
2c	6.67	164.3	152.4	-154.8	-162.0
2d	6.69	164.0	158.9	-150.0	-156.8
2e	6.63	164.9	148.2	-162.4	-169.6

[a] Chemical shifts referenced to TMS in ppm in chloroform-*d*. [b] Vinyl proton. [c] C1 is the tin-bearing vinyl carbon, C2 bears germanium. [d] Measured three times in CDCl3 and its mean is described in Hz. The former is for tin-117, the latter for 119.

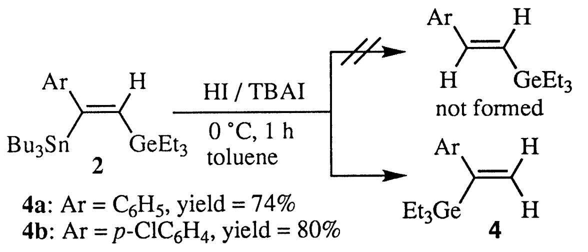
Other reaction examples are summarized in Scheme 1 and selected NMR data for **2a**–**e** in Table 1.

Next, we examined the Kosugi•Migita-Stille coupling[7] of **2a** with allyl bromide in order to obtain chemical confirmation for the structure. Thus, a DMF (*N,N*-dimethylformamide, 5 mL) solution of **2a** (1 mmol), the bromide (5.5 mmol), Pd(dba)$_2$ (0.01 mmol) and CuI (0.018 mmol) was stirred at 40 °C. The reaction smoothly proceeded and went to completion in 5 h to produce (*E*)-1-(triethylgermyl)-2-phenylpenta-1,4-diene **3a**[8] in 86% yield (Scheme 2). The reaction also proceeded at room temperature to yield **3a** in 85% yield, although a longer reaction time (20 h) was needed.



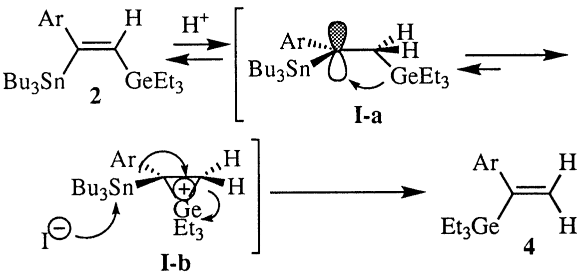
Scheme 2.

The NMR spectrum of the **3a** clearly showed that vinyl proton on the sp^2 carbon bearing the germyl group appeared as a singlet (δ = 6.02 ppm), and supported the fact that the allyl group did combine with the sp^2 carbon bearing the phenyl group, not another sp^2 carbon. Results from Scheme 2 again showed that **2a** had the (*Z*)-configuration with the stannyl group connected to the sp^2-carbon bearing an aryl group. We next examined a preliminary experiment for the destannylation of **2a**, aimed at the synthesis of a series of *trans*-1-aryl-2-(triethylgermyl)ethenes using HI / TBAI (tetrabutylammonium iodide). The method has been reported by Mori et al. as a selective substitution of the stannyl moiety in (*Z*)-1-(silyl)-2-(stannyl)alk-1-enes by hydrogen with retention of the configuration.[1g]



Scheme 3.

However, strikingly enough, the destannylation of **2a** did not form the expected product, but only 1-(triethylgermyl)-1-phenylethene **4a**[9] {chemical shifts of vinyl protons; δ 5.89 ppm (d, 1H, J = 2.4 Hz), 5.43 ppm (d, 1H, J = 2.4 Hz)} in an isolated yield of 74%, as shown in Scheme 3. The reaction was very clean, and no other products were formed except for tributylstannyl iodide. Under similar reaction conditions, **2b** also underwent a migration to form 1-(*p*-chlorophenyl)-1-(triethylgermyl)ethene **4b**[10] in 80% yield. The **4a** and **4b** possibly form through the Markownikov addition followed by the formation of a transient cyclic cation, **I-b**, followed by destannylation forming a double bond (the unprecedented germyl 1,2-migration), as shown in Scheme 4.



Scheme 4.

Under similar conditions, (*Z*)-1-(tributylstannyl)-2-(trimethylsilyl)-1-phenylethene prepared by the palladium-catalyzed addition of tributyl(trimethylsilyl)stannane to phenylacetylene did not produce a similar type of silyl 1,2-migration. The reaction gave 1-phenyl-2-(silyl)ethene. A full study for the present reactions is now underway.

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4 $P(OCH_2)_3CEt$: For the use of the particular ligand in the Pd-catalyzed addition of Si–Si and Ge–Ge bonds to acetylenes in benzene solvent, see: (the former); H. Yamashita, M. Catellani, and M. Tanaka, *Chem. Lett.*, **1991**, 241. (the latter); a) T. Hayashi, H. Yamashita, T. Sakakura, Y. Uchimaru, and M. Tanaka, *Chem. Lett.*, **1991**, 245. b) K. Mochida, C. Hodota, H. Yamashita, and M. Tanaka, *Chem. Lett.*, **1992**, 1635.

5 A THF (5 mL) solution of 1 mmol, 4 mmol, 0.05 mmol and 0.1 mmol of **1**, phenylacetylene, $Pd(dba)_2$ and L was stirred at 80 °C for 50h. Treating the resulting mixture with aqueous KF followed by purification by column chromatography (silica gel, hexane) gave spectroscopically pure **2a** in 85% yield. ^{1}H-NMR ($CDCl_3$) δ 7.24 (m, 2H), 7.13 (m, 2H), 6.98 (m, 1H), 6.63 (s, 1H), 1.4 (m, 6H), 1.26 (sep, 6H, J = 7.2 Hz), 1.07 (t, 9H, J = 7.6 Hz), 0.87 (m, 21H) ppm. Other reactions were carried out similar to the synthesis of **2a**. Reaction time; 19 h for **2b**, 30 h for **2c**, 40 h for **2d**, and 35 h for **2e**.

6 a) T. N. Mitchell, A. Amamria, H. Killing, and D. Rutschow, *J. Organomet. Chem.*, **241**, C45 (1983). b) T. N. Mitchell, A. Amamria, H. Killing, and D. Rutschow, *J. Organomet. Chem.*, **304**, 257 (1986).

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8 Treating the resulting mixture with aqueous KF followed by purification by column chromatography (silica gel, hexane) gave spectroscopically pure **3a** in 86% yield. ^{1}H-NMR ($CDCl_3$) δ 7.41 (m, 2H), 7.29 (m, 2H), 7.22 (m, 1H), 6.02 (s, 1H), 5.77 (m, 1H), 5.01 (m, 2H), 3.33 (m, 2H), 1.07 (t, 9H, J = 7.6 Hz), 0.91 (q, 6H, J = 7.6 Hz) ppm.

9 To a mixture of **2a** (0.23 mmol), TBAI (0.23 mmol) and toluene (1 mL) was added dropwise hydroiodic acid (0.35 mL, 57%) at 0 °C, then stirred for 1 h. The resulting mixture was washed with aqueous sodium bicarbonate. Treating the organic layer with aqueous KF followed by purification by column chromatography (silica gel, hexane) gave spectroscopically pure **4a** in 74% yield. ^{1}H NMR ($CDCl_3$) δ 7.28 (m, 2H), 7.19 (m, 3H), 5.89 (d, 1H, J = 2.4 Hz), 5.43 (d, 1H, J = 2.4 Hz), 1.01 (t, 9H, J = 7.6 Hz), 0.88 (q, 6H, J = 7.6 Hz) ppm.

10 By a procedure similar to that for **4a**, spectroscopically pure **4b** was isolated in 80% yield. ^{1}H-NMR ($CDCl_3$) δ 7.26 (dd, 2H, J = 6.4, 2.2 Hz), 7.09 (dd, 2H, J = 6.4, 2.2 Hz), 5.86 (d, 1H, J = 2.8 Hz), 5.43 (d, 1H, J = 2.8 Hz), 1.00 (t, 9H, J = 8.4 Hz), 0.87 (q, 6H, J = 8.4 Hz) ppm.