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Acid-dependent selective formation of *trans*-aryl(germyl)ethenes or 1-aryl-1-germylethenes by the protodestannylation of (Z)-germyl(stannyl)ethenes†

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Protodemetallation of (*Z*)-1-aryl-2-germyl-1-stannylethenes using hydrochloric acid in the presence of tetraethylammonium chloride (TEACl) proceeds at 0 °C with retention of configuration to afford *trans*-1-aryl-2-germylethenes with high yields. In contrast, the reaction using hydroiodic acid in the presence of tetrabutylammonium iodide (TBAI) brings about a novel 1,2-germyl migration accompanying the destannylation to form 1-aryl-1-germylethenes. These 1,2-germyl migration products result with especially high selectivity from adducts bearing a substituent at the *ortho*- or *para*-position on the aromatic ring in the adduct. However, the germyl(stannyl)ethenes bearing a substituent at the *meta* position on the ring produce a regioisomeric mixture of a *trans*-germylethene and a 1-aryl-1-germylethene. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: (*Z*)-germyl(stannyl)ethenes; protodestannylation; (*E*)-germylethenes; 1,2-germyl migration; 1-aryl-1-germylethenes

INTRODUCTION

Recently, we reported that a combination of $Pd(dba)_2$ and EPBO (EPBO: 4-ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane) effected the germastannation of arylacetylenes using tributyl(triethylgermyl)stannane.[1,2] The catalysis completes the reaction with a shorter reaction time than the previously reported $Pd(PPh_3)_4$-catalyzed germastannation and gives the (*Z*)-1-aryl-2-germyl-1-stannylethenes **1**[3,4] in much higher yields. The resulting products, **1**, are potentially useful compounds, because they may be transformed into a variety of organogermanium compounds via various reactions of the Migita–Kosugi–Stille type. However, reported examples for the transformation are limited, and little is known about the demetallation of **1**, except for our communication.[1] The germylethenes to be produced are known to serve as important substrates for the synthesis of 5-germyl isoxazolines,[5] which possess antithrombotic activity.[6] As for the germylethenes, several conventional syntheses have been reported: (1) the hydrogermylation of acetylenes using an H_2PtCl_6,[5,7,8] metal complex[9–12] or triethylborane[13–15] as a catalyst; and (2) germacupration of acetylenes with bis(triphenylgermyl)cuprate followed by hydrolysis.[16] Protodemetallation of germyl(stannyl)ethenes has not been reported at all to date. Thus, we report here the alternative stereoselective synthesis of arylgermylethenes via palladium-catalyzed germastannation of arylacetylenes followed by protodestannylation.

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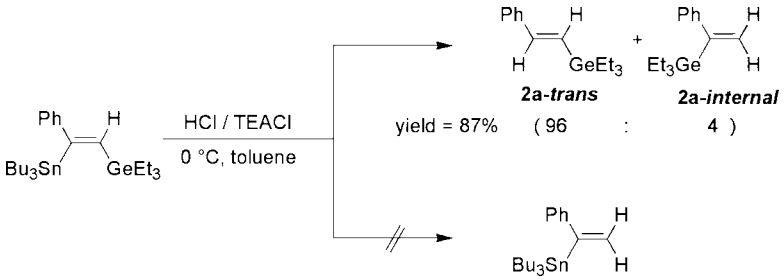
†Dedicated to the memory of Professor Colin Eaborn who made numerous important contributions to the main group chemistry.

RESULTS AND DISCUSSION

(*Z*)-germyl(stannyl)ethenes **1** were prepared by the germastannation of arylacetylenes with tributyl(triethylgermyl)

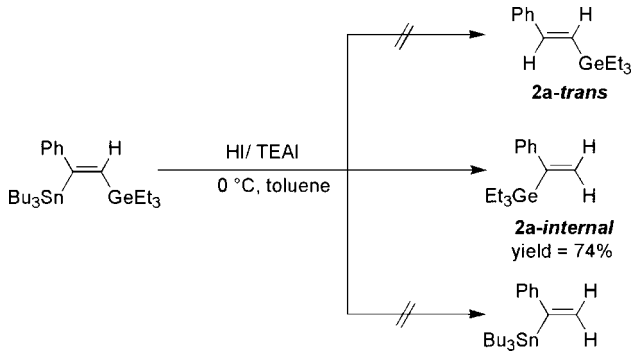


Scheme 1.

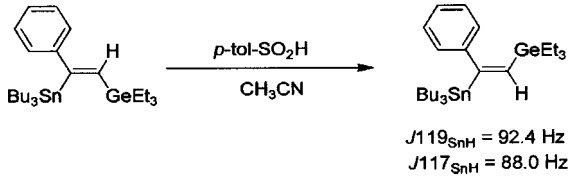
stannane in the presence of a $Pd(dba)_2$–EPBO combination catalyst. Several new adducts of **1** were synthesized in this stage, and their spectral data are shown in the Experimental section. The protodemetallation of (*Z*)-2-germyl-1-stannyl-1-phenylethene, **1a**, was examined under several reaction conditions using hydrochloric acid, hydrobromic acid, hydroiodic acid, acetic acid, benzoic acid or *p*-toluenesulfinic acid. Reactions were carried out at 0 °C except for the reactions with organic acids. While using the inorganic acids, HX (HCl, HBr or HI), a tetralkylammonium halide possessing the corresponding halide (Cl, Br or I) was used as surfactant. The reaction of **1a** using HCl (30%)–TEACl in toluene gave styrylgermane in a high isolated yield of 87%. The product isomer ratio was **2a-*trans*–2a-*internal*** = 96 : 4 (Scheme 1). The formation of another possible product, 1-tributylstannyl-1-phenylethene, was not observed.

When 20% of HCl was used, the product-yield increased to 98% (**2a-*trans*–2a-*internal*** = 96 : 4). The formation of 2% of **2a-*internal*** is quite interesting. The protodemetallation of **1a** using a combination of HBr and TBABr decreased the *trans*–*internal*. In other words, it increased the proportion of **2a-*internal*** to 11%. Changing HX–R_4NX (X = Cl or Br) to HI and TBAI led to the exclusive formation of **2a-*internal*** in 74% yield (Scheme 2).

The rate of protodemetallation using a weak acid such as acetic acid or benzoic acid was very slow. Therefore, the reaction was heated and gave **2a-*trans*** selectively. In the reaction, HMPA was found to be a more favorable solvent than benzene. Destannylation of **1a** with



Scheme 2.



Scheme 3.

p-toluenesulfinic acid in wet acetonitrile gave germylethenes in 69% yield (*trans*–*internal* = 91 : 9). NMR analysis of recovered substrate disclosed that (*Z*)-germyl(stannyl)ethene isomerized to the (*E*)-isomer under the reaction conditions. Thus, the spectrum showed a singlet at $\delta = 6.17$ ppm for the vinylic proton accompanied by two sets of weak satellite bands. The coupling constants between the Sn and the vinylic proton were 92.4 Hz for ^{119}Sn and 88.0 Hz for ^{117}Sn, suggesting the isomer to be (*E*)-2-germyl-1-phenyl-1-stannylethene (Scheme 3). However, further analysis has not been performed. The results also suggest that acid-catalyzed isomerization of (*Z*)-**1a** to the (*E*)-isomer could be taking place.

Next, we tried to synthesize a variety of *trans*-styrylgermanes from adducts of **1** under similar conditions to run 3, shown in Table 1. The results are shown in Table 2. As is seen from the tables, the selective destannylation occurred in most cases and in short reaction time gave *trans*-germylethenes selectively in high isolated yields. However, in some cases, exceptions were observed. In the demetallation of the *o*-chlorophenyl derivative, **1e**, the reaction required a longer stirring time, and *cis*-1-(*o*-chlorophenyl)-2-germyllethene, **2e-*cis***, and 1-(*o*-chlorophenyl)-1-stannylethene were produced in addition to the corresponding **2e-*trans***, **2e-*internal***. In addition, the reaction of the *p*-nitrophenyl derivative, **1j**, produced *cis*-1-germyl-2-(*p*-nitrophenyl)ethane, **2j-*cis*** (*J* values between vinylic protons were 14 Hz), in addition to *trans*-1-germyl-2-(*p*-nitrophenyl)ethene, **2j-*trans***, and 1-germyl-1-(*p*-nitrophenyl)ethene, **2j-*internal***. The combined yield of the products was 90% and the product ratio (*trans*–*internal*–*cis*) was estimated by NMR to be 77 : 5 : 18. The formation of **2j-*cis*** is a surprising result, because the Newman projection of a carbonium ion produced from the anti-Markovnikoff protonation of the adduct **1j** led us to believe that the

Table 1. Comparison of reaction conditions for the destannylation of **1a** with an acid (HX) in the presence or absence of R_4NX

Run	Acid/ additive	Solvent	Conditions, °C/h	Yield[a] of **2a**, %	Ratio[b] *trans*–*internal*
1	HCl (10%)/TEACl[c]	Toluene	r.t.,/90	97	95 : 5
2	HCl (20%)/c	Toluene	0/12	98	96 : 4
3	HCl (30%)/c	Toluene	0/1	87	96 : 4
4	HCl (30%)/c	Benzene	0/0.5	84	96 : 4
5	HCl (35%)/c	Benzene	0/0.5	76	94 : 6
6	HBr (48%)/TBABr[d]	Toluene	0/4	80	89 : 11
7	HI (57%)/TBAI[e]	Toluene	0/1	74	0 : 100
8	CH_3COOH	Benzene	80/22	37	91 : 9
9	CH_3COOH	HMPA[f]	60/25	75	92 : 8
10	PhCOOH	f	60/25	67	85 : 15
11[h]	*p*-Tol-SO_2H	CH_3CN[g]	Reflux/25	69	91 : 9

[a] Isolated yields by column chromatography. [b] Determined by ^{1}H-NMR. [c] Tetraethylammonium chloride. [d] Tetrabutylammonium bromide. [e] Tetrabutylammonium iodide. [f] Hexamethylphosphoric triamide. [g] Wet acetonitrile was used. [h] (*E*)-2-Germyl-1-phenyl-1-stannylethene was isolated in 20% yield ($J119_{SnH}$ = 92.4 Hz, $J117_{SnH}$ = 88.0 Hz).

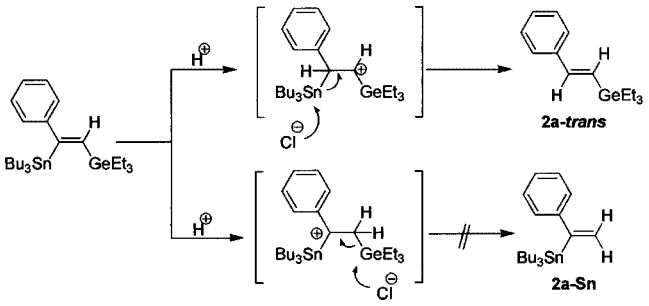
Table 2. Protodemetallation of germyl(stannyl)ethenes **1** with HCl in the presence of TEACl[a]

Run	Ar	Reaction, time (h)	Product	Yield,[b] %	Ratio[c] *trans*–*internal*	*J*, Hz[d]
1	C_6H_5, **1a**	1	**2a**	87	96 : 4	19.2
2	*o*-F C_6H_4, **1b**	10	**2b**	99	95 : 5	19.2
3	*m*-F C_6H_4, **1c**	8	**2c**	97	95 : 5	19.2
4	*p*-F C_6H_4, **1d**	7	**2d**	98	95 : 5	18.8
5	*o*-Cl C_6H_4, **1e**	16	**2e**	52	88 : 3 : 1[e] : 8[f]	18.8
6	*m*-Cl C_6H_4, **1f**	1	**2f**	78	96 : 4	18.8
7	*p*-Cl C_6H_4, **1g**	8	**2g**	96	95 : 5	19.0
8	*m*-$(CF_3)C_6H_4$, **1h**	1	**2h**	97	95 : 5	19.0
9	*p*-CN C_6H_4, **1i**	9	**2i**	94	95 : 5	—[g]
10	*p*-NO_2 C_6H_4, **1j**	15	**2j**	90	77 : 5 : 18[e]	—[g]

[a] The reaction was carried out at 0 °C with 30% HCl. [b] Isolated yields by column chromatography (silica gel, hexane). [c] Determined by ^{1}H NMR. [d] Coupling constant between *vicinal* vinylic protons. [e] *cis*-Isomer. [f] 1-(*o*-Chlorophenyl)-1-stannylethene. [g] Vinylic protons were observed as singlet.

conformation to produce **2j-*cis*** is an unfavorable one due to the steric repulsion between the triethylgermyl group and the *p*-nitrophenyl group. The reason for the formation of such an abundance of **2j-*cis*** is not clear at present. However, it might be conceivable that long-range $\sigma-\pi$ interactions exist between the relatively positive aromatic ring (caused by the inductive and mesomeric effects of the nitro group) and germanium. A plausible mechanism for the formation of **2-*trans*** is drawn in Scheme 4.

A series of (*Z*)-1-aryl-2-germyl-1-stannylethenes **1** were treated with HI in the presence of TBAI in toluene at 0 °C. The reaction rapidly went to completion, forming destannylation products exclusively. (*Z*)-Germyl(stannyl)ethenes **1** bearing a substituent at the *ortho* or *para* positions on the aromatic ring produce 1-aryl-1-germylethenes selectively (Table 3), while the adduct **1** having a *m*-substituted phenyl group gave a near 1 : 1 mixture of **2-*trans*** and **2-*internal*** or an internal-rich product mixture.



Scheme 4. A plausible mechanism for the formation of 2-*trans* from adduct 1 using HCl.

A similar type of protodestannylation has been reported for the demetallation of (*Z*)-silyl(stannyl)ethenes. In those reactions, silyl group migration onto a neighboring carbon

Table 3. Formation of 1-aryl-1-germylethenes from (*Z*)-1-aryl-2-germyl-1-stannylethenes

Run	Ar	Conditions, h	Product	Yield,[b] %	Ratio[c] *trans*–*internal*	J, Hz[d]
1	C_6H_5, **1a**	1	**2a**	74	0 : 100	2.4
2	*o*-FC_6H_4, **1b**	3	**2b**	83	0 : 100	2.8
3	*m*-FC_6H_4, **1c**	3	**2c**	81	37 : 63	2.4
4	*p*-FC_6H_4, **1d**	1	**2d**	78	9 : 91	2.4
5	*o*-ClC_6H_4, **1e**	2	**2e**	74	0 : 100	2.4
6	*m*-ClC_6H_4, **1f**	2	**2f**	87	38 : 62	2.4
7	*p*-ClC_6H_4, **1g**	1	**2g**	85	0 : 100	2.8
8	*m*-$(CF_3)C_6H_4$, **1h**	1	**2h**	94	54 : 46	2.4
9	*p*-PhC_6H_4, **1k**	1.5	**2k**	78	5 : 95	2.8

[a] The reaction was carried out at 0 °C with 57% of HI. [b] Isolated yields by column chromatography (silica gel, hexane). [c] Determined by ^{1}H NMR. [d] Coupling constant between vinylic geminal protons of an internal germylethene.

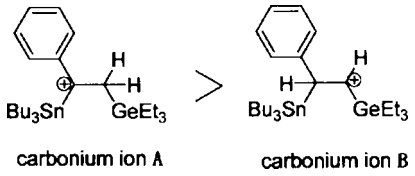


Figure 1. Stability of two-carbonium ion.

does not accompany destannylation, i.e. only *trans*-type silylethenes have been produced.[17,18] In examining the difference between silicon and germanium, it is important to consider the β-cation stabilization effects of a silyl group, a germyl group and a stannyl group. Present results suggest that the carbonium ion **A** arising from Markovnikoff-type protonation of the germyl(stannyl)ethenes **1** seems to be more stable than the carbonium ion **B**. They suggest that the summation of the conjugation effect of an aryl group and the β-ion stabilization effect ($\sigma-\pi$ conjugation effect) of a germyl group is larger than the $\sigma-\pi$ conjugation effect of a stannyl group alone. *Ortho* and *para* substituents on an aromatic ring, in particular, can increase the stability of the carbonium ion **A**. Carbonium ion **B** may produce *trans*-type germylethenes. 1,2-Migration of the germyl group from the **A** type of carbonium ion may be predicted to occur, as shown in Fig. 2. The most important step for the production of the *internal* type of germylethenes seems to be the formation of a complex of the germacyclopropyl cation with iodide ion. Iodide ion seems to stabilize the cation. For bromide and chloride ion, the stabilization effect of the cyclopropyl cation seems to be smaller than the iodide ion, and equilibrium of the protonation may come to favorably produce carbonium ion **B**, which leads to the formation of *trans*-germylethenes. Table 4 shows the effect of halide ion by changing the X in R_4NX.

Table 4. Effect of a halide ion upon isomer ratio [a]

Run	Acid/ additive	Solvent	Reaction time (h)	Yield of **2a**, %	Ratio *trans*–*internal*
1	HCl (30%)/TEACl	toluene	1	87	96 : 4
2	HCl (30%)/TBABr	toluene	1	81	93 : 7
3	HCl (30%)/TBAI	toluene	1	70	46 : 54
4	HBr (48%)/TBABr	toluene	4	80	89 : 11
5	HBr (48%)/TBAI	toluene	2	91	55 : 45
6	HI (57%)/TBACl	toluene	3	90	45 : 55
7	HI (57%)/TBABr	toluene	3	70	0 : 100
8	HI (57%)/TBAI	toluene	2	74	0 : 100

[a] The reaction was carried out at 0 °C.

EXPERIMENT

Method and measurements

The reaction was carried out using a small round-bottomed flask under nitrogen or argon. Gas chromatography was performed using an Ohkura Model 103 gas chromatograph equipped with a thermal conductivity detector connected to a stainless steel column packed with 10 or 20% Silicone KF-96–Celite 545 AW (60–80 mesh, 2 m × 3 mm). IR spectra were measured using a Jasco A-102 spectrophotometer. NMR spectra were recorded at 400 MHz on a Varian UNITY-400 spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as the internal standard. Chemical shifts are expressed as part per million (ppm) with respect to TMS. Splitting patterns were designated as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), ddd (doublet of doublet of doublets), ddt (doublet of doublet of triplets) and m (multiplet). ^{13}C-NMR spectra were measured at 100 MHz on a Varian UNITY-400 spectrometer in $CDCl_3$, and chemical shifts are shown in ppm from that of chloroform-d_1 ($\delta = 77.00$ ppm). Coupling constants are given in Hz.

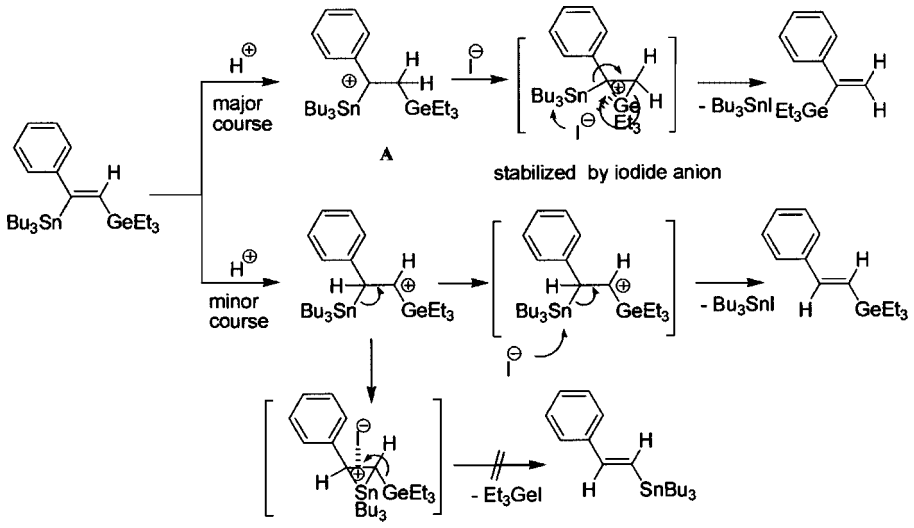


Figure 2. Stability of two-carbonium ion.

^{119}Sn (186.5 MHz)–NMR spectra were recorded on a Jeol JNM-ECA500 spectrometer in $CDCl_3$, and chemical shift was referenced to external Me_4Sn. Mass spectra were obtained at 70 eV using a Jeol JMS-AX-500 with a DA 7000 data system.

Materials

A variety of (*Z*)-1-aryl-2-germyl-1-stannylethenes were prepared by our previously reported method.[1,2] Benzene, toluene, acetic acid, tetraethylammonium chloride, tetrabutylammonium bromide, tetrabutylammonium iodide, hydrochloric acid, hydrobromic acid, hydroiodic acid, hexane and silica gel (Wako gel C-200 or C-300) were purchased from Wako Chemical Co. *o*-F(**1b**), *m*-F(**1c**) and *o*-Cl(**1e**) derivatives of 1-aryl-2-germyl-1-stannylethenes were synthesized by a similar method to that reported previously.[1,2] The data for the new compounds are as follows.

Substrate **1b**—yield: 87%. IR(neat): 3060, 3015, 2950, 2925, 2860, 1570, 1475, 1460, 1375, 1220, 1095, 1020, 750, 695 cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 7.27 (m, 1H), 7.03 (m, 1H), 6.94 (m, 2H), 6.67 (s, 1H, $^3J_{119Sn-H}$ = 162.0 Hz, $^3J_{117Sn-H}$ = 154.8 Hz), 1.39 (m, 6H), 1.224(sext, 6H, J = 7.6 Hz), 1.08 (t, 6H, J = 7.6 Hz), 0.88 (m, 15H), 0.84 (t, 9H, J = 7.6 Hz) ppm. ^{13}C-NMR ($CDCl_3$): δ 159, 158.1 (d, $^1J_{CF}$ = 241.2 Hz), 148.3, 139.5 (d, $^2J_{CF}$ = 16.0 Hz), 128.5, 127.1, 124.1, 114.6 (d, $^2J_{CF}$ = 22.7 Hz), 28.9, 27.4, 13.6, 11.5, 9.1, 5.4 ppm. ^{119}Sn-NMR ($CDCl_3$): δ −67.1 ppm. LRMS (EI): 515($M^+ - 57$).

Substrate **1c**—yield: 89%. IR(neat): 3050, 2950, 2920, 2860, 1600, 1575, 1480, 1460, 1255, 1135, 1015, 960, 940, 870, 840, 770, 714, 680 cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 7.2 (m, 1H), 6.82 (m, 1H), 6.74 (m, 1H), 6.68 (m, 1H), 6.64 (s, 1H, $^3J_{119SnH}$ = 163.2 Hz, $^3J_{117SnH}$ = 156.0 Hz), 1.39 (m, 6H), 1.24 (sext, 6H, J = 7.6 Hz), 1.08 (t, 6H, J = 7.6 Hz), 0.88 (m, 15H), 0.84 (t, 9H, J = 7.6 Hz) ppm. ^{13}C-NMR ($CDCl_3$): δ 164.3, 162.5 (d, $^1J_{CF}$ = 244.3 Hz), 154.2, 147.5, 129.2, 121.8, 112.8 (d, $^2J_{CF}$ = 20.5 Hz), 112.0 (d, $^2J_{CF}$ = 21.3 Hz), 29.0, 27.3, 13.6, 11.6, 9.1, 5.5 ppm. ^{119}Sn-NMR ($CDCl_3$): δ −53.23 ppm. LRMS (EI, 70 eV): 572 (M^+), 543($M^+ - 29$), 515($M^+ - 57$). HRMS (EI, 70 eV): calc. for $C_{26}H_{47}FGeSn$, 572.1896; found, 572.1890.

Substrate **1e**—yield: 89%. IR(neat): 3050, 2975, 2865, 1460, 1050, 1020, 770, 740, 700, 670 cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 7.27 (dd, 1H, J = 7.5, 1.2 Hz), 7.16 (dt, 1H, J = 7.5, 1.2 Hz), 7.06 (dt, 1H, J = 7.5, 1.8 Hz), 6.93 (dd, 1H, J = 7.5, 1.8 Hz), 6.51 (s, 1H, $^3J_{119SnH}$ = 162.4 Hz, $^3J_{117SnH}$ = 155.6 Hz), 1.36 (m, 6H), 1.23 (sext, 6H, J = 7.6 Hz), 1.08 (t, 6H, J = 7.6 Hz), 0.88 (m, 15H), 0.83 (t, 9H, J = 7.6 Hz) ppm. ^{13}C-NMR ($CDCl_3$): δ 163.9, 150.3, 146.2, 130.5, 128.6, 128.1, 126.8, 126.5, 29.0, 27.4, 13.6, 11.9, 9.1, 5.3 ppm. ^{119}Sn-NMR ($CDCl_3$): δ −57.1 ppm. LRMS (EI, 70 eV): 530 ($M^+ - 58$).

Protodestannylation of 1a with HCl in the presence of TEACl

To a stirred toluene (1 ml) suspension of TEACl (0.038 g, 0.23 mmol) and germyl(stannyl)ethene **1a** (0.124 g, 0.22 mmol), hydrochloric acid (30%, 0.08 ml) was slowly added with a syringe at 0 °C. After 12 h, TLC of the resulting mixture showed that **1a** was consumed completely. Then the mixture was neutralized with saturated aqueous sodium bicarbonate, and then the organic layer was extracted with ether. The combined ether solution was concentrated to 10 ml. The resulting concentrate was stirred with saturated aqueous KF overnight. Then, filtration of tin fluoride, extraction of the organic layer with ether, drying over magnesium sulfate, concentration and column chromatography (silica gel, hexane) gave 0.058 g (98%) of analytically pure **2a-*trans***[2,3] as a colorless oil (*trans–internal* = 95 : 5 by ^{1}H-NMR). IR (neat): 3050, 2950, 2900, 2875, 1600, 1575, 1495, 1460, 1445, 1430, 1020, 985, 735, 720, 685 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.42 (m, 2H), 7.32 (m, 2H), 7.22 (m, 1H), 6.82 (d, 1H, J = 19.2 Hz), 6.61 (d, 1H, J = 19.2 Hz), 1.07 (t, 9H, J = 7.2 Hz), 0.87 (q, 6H, J = 7.2 Hz) ppm. ^{13}C NMR ($CDCl_3$): δ 143.3, 138.4, 128.5, 127.8, 127.6, 126.1, 8.9, 4.4 ppm. LRMS (EI, 70 eV): 264 (M^+).

By a procedure similar to that for **2a-*trans***, other germylethenes were obtained from the corresponding (*Z*)-germyl(stannyl)ethenes **1**. Analytical data of the **2-*trans*** adducts isolated by column chromatography are shown below.

2b-*trans* (*o*-fluorophenyl)—IR (neat): 3070, 3010, 2950, 2900, 2870, 1600, 1480, 1455, 1420, 1223, 1200, 1090, 1020, 985, 755, 710 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.54 (dt, 1H, $J = 8.0$, 1.6 Hz), 7.2 (m, 1H), 7.09 (t, 1H, $J = 8.0$ Hz), 7.02 (ddd, 1H, $J = 10.4$, 8.0, 0.8 Hz), 7.03 (d, 0.95H, $J = 19.2$ Hz), 6.68 (d, 0.95H, $J = 19.2$ Hz), 5.86 (d, 0.05H, $J = 2.8$ Hz), 5.56 (d, 0.05H, $J = 2.8$ Hz), 1.07 (t, 9H, $J = 7.6$ Hz), 0.88 (d, 6H, $J = 7.6$ Hz) ppm. ^{13}C NMR ($CDCl_3$): δ 160 (d, $J = 247.3$ Hz), 135.1, 135.0 (d, $J = 5.3$ Hz), 131.0 (d, $J = 3.8$ Hz), 128.8, 126.7 (d, $J = 3.8$ Hz), 124.0 (d, $J = 3.8$ Hz), 115.7 (d, $J = 22.8$ Hz), 8.9, 4.4 ppm. LRMS (EI, 70 eV): 282(M^+). HRMS (EI, 70 eV): calcd for $C_{14}H_{21}FGe$, 282.0839; found, 282.0842.

2c-*trans* (*m*-fluorophenyl)—IR (neat): 3050, 2950, 2900, 1870, 1825, 1610, 1580, 1485, 1480, 1455, 1440, 1425, 1265, 1255, 1250, 1135, 1020, 980, 765 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.28 (dt, 1H, $J = 8.0$, 6.0 Hz), 7.17 (d, 1H, $J = 7.6$ Hz), 7.13 (m, 1H), 6.92 (ddt, 1H, $J = 8.4$, 2.4, 0.8 Hz), 6.78 (d, 0.95H, $J = 19.2$ Hz), 6.63 (d, 0.95H, $J = 19.2$ Hz), 5.89 (d, 0.05H, $J = 2.8$ Hz), 5.45 (d, 0.05H, $J = 2.8$ Hz), 1.07 (t, 9H, $J = 8.0$ Hz), 0.87 (q, 6H, $J = 8.0$ Hz) ppm. ^{13}C NMR ($CDCl_3$): δ 163.2 (d, $J = 243.5$ Hz), 142.1 (d, $J = 3$ Hz), 140.8 (d, $J = 7.6$ Hz), 129.8 (d, $J = 2.3$ Hz), 122.1 (d, $J = 3$ Hz), 114.3 (d, $J = 21.2$ Hz), 112.6, 112.4, 8.9, 4.4 ppm. LRMS (EI, 70 eV): 282(M^+). HRMS(EI, 70 eV): calcd for $C_{14}H_{21}FGe$, 282.0839; found, 282.0820.

2d-*trans* (*p*-fluorophenyl)—IR (neat): 3025, 1600, 1510, 1420, 1235, 785, 710 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.39 (dd, 2H, $J = 8.6$, 5.4 Hz), 7.01 (dd, 2H, $J = 8.6$, 5.4 Hz), 6.77 (d, 1H, $J = 18.8$ Hz), 6.51 (d, 1H, $J = 18.8$ Hz), 5.85 (d, 0.05H, $J = 2.8$ Hz), 5.41 (d, 0.05H, $J = 2.4$ Hz), 1.07 (t, 9H, $J = 7.8$ Hz), 0.86 (q, 6H, $J = 7.8$ Hz) ppm. ^{13}C NMR ($CDCl_3$): δ 162.4 (d, $J = 245.0$ Hz), 142.0, 134.7 (d, $J = 3$ Hz), 127.6 (d, $J = 7.6$ Hz), 127.5 (d, $J = 2.3$ Hz), 115.3 (d, $J = 21.2$ Hz), 8.9, 4.4 ppm. LRMS (EI, 70 eV): 282(M^+). HRMS(EI, 70 eV): calcd for $C_{14}H_{21}FGe$, 282.0839; found, 282.0842.

2e-*trans* (*o*-chlorophenyl)—IR (neat): 3060, 3015, 1590, 1465, 1440, 985, 750, 700, 680 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.59 (dd, 1H, $J = 7.6$, 1.6 Hz), 7.34 (dd, 1H, $J = 7.6$, 1.6 Hz), 7.22 (d, 1H, $J = 18.8$ Hz), 7.2 (m, 1H), 7.16 (dt, 1H, $J = 7.6$, 1.6 Hz), 6.62 (d, 1H, $J = 18.8$ Hz), 1.09 (t, 9H, $J = 7.6$ Hz), 0.89 (q, 6H, $J = 7.6$ Hz) ppm. ^{13}C NMR ($CDCl_3$): δ 139.4, 136.5, 132.8, 131.6, 129.6, 128.5, 126.7, 126.6, 8.9, 4.4 ppm. LRMS (EI, 70 eV): 298 (M^+). HRMS (EI, 70 eV): calcd for $C_{14}H_{21}ClGe$, 298.0544; found, 298.0526.

2f-*trans* (*m*-chlorophenyl)—IR (neat): 3060, 1590, 1560, 1465, 985, 765 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.42 (m, 1H), 7.21 (m, 3H), 6.75 (d, 1H, $J = 18.8$ Hz), 6.64 (d, 1H, $J = 18.8$ Hz), 1.07 (t, 9H, $J = 7.6$ Hz), 0.87 (q, 6H, $J = 7.6$ Hz) ppm. ^{13}C NMR ($CDCl_3$): δ 141.8, 140.2, 134.5, 130.0, 129.7, 127.5, 126.0, 124.4, 8.9, 4.3 ppm. LRMS (EI, 70 eV): 298 (M^+). HRMS (EI, 70 eV): calcd for $C_{14}H_{21}ClGe$, 298.0544; found, 298.0580.

2g-*trans* (*p*-chlorophenyl)—IR (neat): 3050, 2950, 2925, 2910, 2875, 1600, 1490, 1095, 1010, 990, 780 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.35(dt, 2H, $J = 8.4$ Hz), 7.28 (d, 2H, $J = 8.4$ Hz), 6.76 (d, 1H, $J = 19$ Hz), 6.59 (d, 1H, $J = 19$ Hz), 1.06 (t, 9H, $J = 8$ Hz), 9.87 (q, 6H, $J = 8$ Hz) ppm. ^{13}C NMR ($CDCl_3$): δ 142, 136.9, 133.2, 128.9, 128.6, 127.3, 8.9, 4.4 ppm. LRMS (EI, 70 eV): 298 (M^+). HRMS (EI, 70 eV): calcd for $C_{14}H_{21}ClGe$, 298.0544; found, 298.0540.

2h-*trans* (*m*-trifluoromethylphenyl)—IR (neat): 3060, 3015, 1590, 1465, 1440, 985, 750, 700, 680 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.66 (s, 1H), 7.58 (d, 1H, $J = 7.6$ Hz), 7.48 (t, 1H, $J = 7.6$ Hz), 6.84 (d, 1H, $J = 19$ Hz), 6.71 (d, 1H, $J = 19$ Hz), 1.08 (t, 9H, $J = 8$ Hz), 0.89 (q, 6H, $J = 8$ Hz) ppm. ^{13}C NMR ($CDCl_3$): δ 141.8, 139.1, 130.9 (q, $J = 31.8$ Hz), 130.7, 129.3, 128.9, 126.3 (q, $J = 152.5$ Hz), 124.1 (q, $J = 3.8$ Hz), 122.8 (q, $J = 3.8$ Hz), 8.9, 4.4 ppm. LRMS (EI, 70 eV): 332 (M^+). HRMS (EI, 70 eV): calcd for $C_{15}H_{21}F_3Ge$, 332.0810; found, 332.0815.

2i-*trans* (*p*-cyanophenyl)—IR (neat): 2945, 2870, 2225, 1600, 1460, 1020, 980, 860, 785, 710, 680 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.61 (dt, 2H, $J = 8.8$, 1.6 Hz), 7.49 (dt, 2H, $J = 8.4$, 1.6 Hz), 6.82 (s, 2H), 1.07 (t, 9H, $J = 8$ Hz), 0.89 (q, 6H, $J = 8$ Hz) ppm. ^{13}C NMR ($CDCl_3$): δ 142.4, 141.5, 133.8, 132.3, 126.6, 119.0, 110.7, 8.9, 4.3 ppm. LRMS (EI, 70 eV): 289 (M^+). HRMS (EI, 70 eV): calcd for $C_{15}H_{21}NGe$, 289.0888; found, 289.0886.

2j-*trans* (*p*-nitrophenyl)—IR (neat): 2950, 2870, 1590, 1520, 1490, 1460, 1420, 1380, 1340, 1110, 990, 860, 740 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.19 (dt, 2H, $J = 9.0$, 2 Hz), 7.54 (dt, 2H, $J = 9.0$, 2 Hz), 6.88 (s, 2H), 1.08 (t, 9H, $J = 7.6$ Hz), 0.91 (q, 6H, $J = 7.6$ Hz) ppm. ^{13}C NMR ($CDCl_3$): δ 144.3, 141.1, 135.3, 126.7, 124, 123.4, 8.9, 4.3 ppm. LRMS (EI, 70 eV): 309 (M^+). HRMS (EI, 70 eV): calcd for $C_{14}H_{21}NO_2Ge$, 309.0787; found, 309.0785.

Protodestannylation of 1a with HI in the presence of TBAI

To a toluene (1 ml) suspension of TBAI (0.085 g, 0.23 mmol) and germyl(stannyl)ethene **1a** (0.131 g, 0.237 mmol), hydroiodic acid (57%, 0.3 ml) was slowly added with a syringe at 0 °C. TLC after addition of the HI showed that **1a** was consumed completely. The resulting mixture was neutralized with saturated aqueous sodium bicarbonate, and then the organic layer was extracted with ether. The combined ether solution was concentrated to 10 ml. The concentrated ether solution was stirred with saturated aqueous KF overnight. Then, filtration of tin fluoride, extraction of the organic layer with ether, drying over magnesium sulfate, concentration, and column chromatography (silica gel, hexane) gave 0.045 g (72%) of analytically pure **2a-*internal***[5,16] as a colorless oil (*internal* only). IR (neat): 3050, 3010, 2865, 2850, 2845, 2830, 1485, 1455, 1425, 1375, 1015, 920, 765, 705 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.29 (m, 2H), 7.19 (m, 3H), 5.89 (d, 1H, $J = 2.4$ Hz), 5.42 (d, 1H, $J = 2.4$ Hz), 1.01 (t, 9H, $J = 8$ Hz), 0.88 (q, 6H, $J = 8$ Hz). ^{13}C NMR ($CDCl_3$): δ 151.5, 145.3, 128.1, 126.4, 126.2, 125.7, 8.8, 4.6 ppm. LRMS (EI, 70 eV): 264 (M^+).

Protodestannylation with HI was carried out similarly and analytical data for the other products are shown below.

2b-*internal* (*o*-fluorophenyl)—IR (neat): 3050, 3020, 2950, 2900, 2850, 1480, 1460, 1420, 1375, 1235, 1200, 1020, 920, 750 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.18 (m, 1H), 7.06 (m, 2H), 7.0 (m, 1H), 5.86 (d, 1H, $J = 2.8$ Hz), 5.56 (d, 1H, $J = 2.8$ Hz), 1.00 (t, 9H, $J = 7.6$ Hz), 0.85 (q, 6H, $J = 7.6$ Hz) ppm. ^{13}C NMR ($CDCl_3$): δ 159.0 (d, $J_{C-F} = 243.5$ Hz), 146.9, 133.4, 129.2, 128.0, 127.7 (d, $J = 8.4$ Hz), 123.9, 115.1 (d, $J = 22.0$ Hz), 8.5, 4.4 ppm. LRMS (EI, 70 eV): 282(M^+). HRMS(EI, 70 eV): calcd for $C_{14}H_{21}FGe$, 282.0839; found, 282.0873.

2d-*internal* (*p*-fluorophenyl)—IR (neat): 3030, 1600, 1500, 1460, 1230, 840, 705 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.13 (m, 2H), 6.98 (m, 2H), 5.85 (d, 1H, $J = 2.4$ Hz), 5.41 (d, 1H, $J = 2.4$ Hz), 1.01 (t, 9H, $J = 7.6$ Hz), 0.87 (q, 6H, $J = 7.6$ Hz) ppm. ^{13}C NMR ($CDCl_3$): δ 161.7 (d, $J = 243.5$ Hz), 150.5, 141.3, 127.8 (d, $J = 7.6$ Hz), 125.8, 114.9 (d, $J = 21.3$ Hz), 8.8, 4.5 ppm. LRMS (EI, 70 eV): 282(M^+), HRMS(EI, 70 eV): calcd for $C_{14}H_{21}FGe$, 282.0839; found, 282.0802.

2e-*internal* (*o*-chlorophenyl)—IR (neat): 3045, 1460, 1425, 1375, 1040, 1020, 925, 760, 700 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.33 (m, 1H), 7.15 (m, 2H), 6.99 (m, 1H), 5.73 (d, 1H, $J = 2.4$ Hz), 5.56 (d, 1H, $J = 2.4$ Hz), 1.00 (t, 9H, $J = 7.6$ Hz), 0.85 (q, 6H, $J = 7.6$ Hz) ppm. ^{13}C NMR ($CDCl_3$): δ 151.4, 144.8, 131.4, 129.1, 128.9, 127.2, 127.0, 126.4, 8.7, 4.7 ppm. LRMS (EI, 70 eV): 298 (M^+). HRMS (EI, 70 eV): calcd for $C_{14}H_{21}ClGe$, 298.0544; found, 298.0525.

2g-*internal* (*p*-chlorophenyl)—IR (neat): 3050, 1485, 1460, 1450, 1090, 1010, 835, 700 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.26 (dt, 2H, $J = 8.8$ Hz), 7.09 (dt, 2H, $J = 8.8$ Hz), 5.49 (d, 1H, $J = 2.8$ Hz), 5.43 (d, 1H, $J = 2.8$ Hz), 1.01 (t, 9H, $J = 7.6$ Hz), 0.87 (q, 6H, $J = 7.6$ Hz) ppm. ^{13}C NMR ($CDCl_3$): δ 150.5, 143.9, 132.1, 128.3, 127.7, 126.2, 8.8, 4.5 ppm. LRMS (EI, 70 eV): 298 (M^+). HRMS (EI, 70 eV): calcd for $C_{14}H_{21}ClGe$, 298.0544; found, 298.0579.

2k-*internal* (*p*-phenylphenyl)—IR (neat): 3070, 3050, 3010, 1600, 1505, 1380, 1455, 1425, 1005, 840, 770, 740, 695 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.61 (m, 2H), 7.54 (m, 2H), 7.44 (m, 2H), 7.33 (m, 1H), 7.26 (m, 2H), 5.95 (d, 1H, $J = 2.8$ Hz), 5.45 (d, 1H, $J = 2.8$ Hz), 1.04 (t, 9H, $J = 7.4$ Hz), 0.92 (q, 6H, $J = 7.4$ Hz) ppm. ^{13}C NMR ($CDCl_3$): δ 151.0, 144.3, 140.9, 139.1, 128.7, 127.1, 126.9, 126.8, 125.71, 125.68, 8.8, 4.6 ppm. LRMS (EI, 70 eV): 340 (M^+), 311, 283, 255. HRMS (EI, 70 eV): calcd for $C_{20}H_{26}Ge$, 340.1246; found, 340.1279.

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