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Et_3B Induced Stereoselective Radical Addition of Ph_3GeH to Carbon-Carbon Multiple Bonds and Its Application to Isomerization of Olefins

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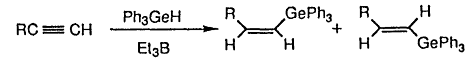
Triphenylgermane easily adds to acetylenes or terminal olefins in the presence of Et_3B to give alkenyltriphenylgermane or alkyltriphenylgermane respectively under excellent control of regio- and stereoselectivities. While Et_3B catalyzed addition of Ph_3GeH to 1-dodecyne at −78 °C affords (*Z*)-1-triphenygermyl-1-dodecene exclusively, the addition of Ph_3GeH at 60 °C provides (*E*)-1-triphenylgermyl-1-dodecene as a single product. The triphenylgermyl radical is also effective to isomerize *Z*-olefins into their thermodynamically more stable *E*-isomers.

Free radical reactions have been used increasingly in recent years for the synthesis of organic molecules.[1] Hydrogermylation[2] and hydrostannation[3] of acetylenes readily take place either in the absence of a catalyst or in the presence of catalytic amount of radical initiator such as azobisisobutyronitrile (AIBN).[4,5] These reactions producing the corresponding alkenyltriphenylgermane[6] or alkenyltriphenylstannane[7] are of particular synthetic interest, however, they have a serious limitation. The reactions are generally not highly stereoselective.[8] Moreover the mechanism of the reactions does not appear to have been well established mainly because the resulting alkenyltriphenylgermane and alkenyltriphenylstannane isomerize under the general reaction conditions of hydrogermylation or hydrostannation.[9] Here we wish to report that trialkylborane facilitates the addition of Ph_3GeH[10] to acetylenes to give(*E*)- or (*Z*)-alkenyltriphenylgermanes with excellent control of regio- and stereoselectivities under equilibrating conditions or non-equilibrating conditions respectively.[11] Reactions of Ph_3GeH with olefins are also described.

Treatment of a toluene solution of 1-dodecyne (1.1 mmol) and Ph_3GeH (1.0 mmol) with Et_3B[12] (1.0 mmol) at −78 °C gave (*Z*)-1-triphenylgermyl-1-dodecene exclusively in 76% yield (*Z*/*E*=>20/1). The representative results are summarized in Table 1. The isomeric ratios of the products heavily depend on the reaction temperature and the ratio [acetylene]/[Ph_3GeH]. The reaction at −78 °C in toluene in the presence of slight excess of the acetylenic compound provides (*Z*)-alkenyltriphenylgermane exclusively, whereas the reaction at 60 °C in benzene with slight excess of Ph_3GeH gives (*E*)-alkenyltriphenylgermane as a single product. Solvent also affects the isomeric ratio of the products. In polar solvents, the (*Z*)-isomer was obtained as major product. For instance, treatment of 1-dodecyne with Ph_3GeH-Et_3B in THF at 0 °C for 2 h gave a mixture of (*Z*)-1-triphenylgermyl-1-dodecene and (*E*)-isomer (*Z*/*E*=8/1) in 84% yield. Addition of methanol (10 mmol per 1.0 mmol of substrate) to toluene is also effective for the selective formation of (*Z*)-isomer (Entry 6 in Table 1).

Table 1. Stereoselective Hydrogermylation of Acetylenes



Entry	Acetylene	Reaction conditions		Y[a]	Product[b]
	R	Temp/°C	Time/h	%	ratio(*Z*/*E*)
1	*n*-$C_{10}H_{21}$	−78[c]	3	76	>20/1
2		−20[d]	2	78	2/1
3		25[d]	2	77	1/9
4		60[d]	2	99	<1/20
5		0(THF)[d]	2	84	8/1
6		0[d] (PhMe-MeOH)	2	80	10/1
7	CH_3[e]	−78[c]	2	65	>20/1
8	$HOCH_2CH_2$	−78[c]	5	80	>20/1
9		60[d]	15	75	<1/20
10	Me_3Si	−78[c]	6	72	56/44
11		60[d]	3	87	0/100
12	$EtOOC(CH_2)_9$	−78[c]	12	64	>10/1
13		60[d]	15	93	<1/20
14	6-Dodecyne	−78[c]	8	65	>20/1

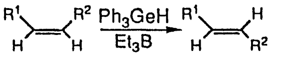
a) Isolated yield. b) Determined by GC and/or NMR. c) Acetylene (1.1 mmol), Ph_3GeH (1.0 mmol), and Et_3B (1.0 mmol) were employed. Toluene was used as solvent. d) Acetylene (1.0 mmol), Ph_3GeH (1.1 mmol), and Et_3B (1.0 mmol) were employed. Benzene was used as solvent unless otherwise stated. e) Propyne (3.0 mmol), Ph_3GeH (1.0 mmol), and Et_3B (1.0 mmol) were employed.

Et_3B-induced addition of *n*-Pr_3GeH to acetylenes did not proceed with high stereoselectivity as compared to the addition of Ph_3GeH. For instance, the reaction of 1-dodecyne with *n*-Pr_3GeH at 60 °C in the presence of Et_3B gave an isomeric mixture of (*E*)-1-tripropylgermyl-1-dodecene and (*Z*)-isomer in 79% yield (*Z*/*E*=2/1).

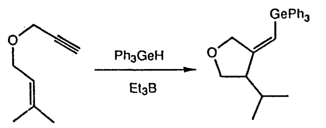
The addition of triphenylgermyl radical to carbon-carbon triple bonds was efficiently applied to the intramolecular cyclization of enynes just like the triphenyltin radical case which we reported previously[10] (Scheme 1).

It was anticipated that the *trans* addition products

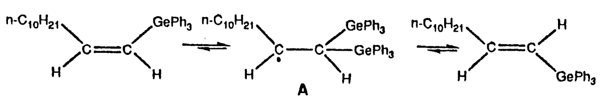
Table 2. Isomerization of Olefins by Means of Ph_3GeH-Et_3B System



Entry	R^1	R^2	Substrate	Reaction	Y	Product
			Z/E	Time/h	%	Z/E
1	$n\text{-C}_5\text{H}_{11}$	$n\text{-C}_5\text{H}_{11}$	>20/1	10	90	15/85
2	t-Bu	$n\text{-C}_8\text{H}_{17}$	>20/1	10	91	0/100
3	$n\text{-C}_6\text{H}_{13}$	Ph	100/0	5	96	0/100
4	Ph	Ph	>20/1	2	81	<1/20
5	$n\text{-C}_6\text{H}_{13}$	$SiPhMe_2$	>20/1	10	84	<1/20
6	$n\text{-C}_{10}\text{H}_{21}$	$GePh_3$	10/1	4	88	<1/20
7	$HO(CH_2)_2$	$GePh_3$	>20/1	10	70	<1/20
8	$EtOOC(CH_2)_9$	$GePh_3$	7/1	10	95	<1/20



Scheme 1.



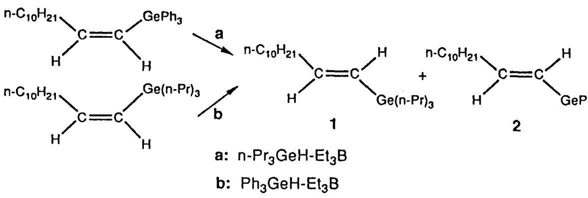
Scheme 2.

(i.e., (Z)-isomers) were kinetically-controlled products and that they isomerized into the (E)-isomers under thermodynamic conditions. This was indeed the case as demonstrated by the isomerization of (Z)-1-triphenylgermyl-1-dodecene into (E)-isomer. Heating a benzene solution of (Z)-1-triphenylgermyl-1-dodecene at 60 °C in the presence of catalytic amount of Ph_3GeH and Et_3B gave (E)-isomer exclusively. This isomerization is explained by addition-elimination sequence of triphenylgermyl radical (Scheme 2).

The germyl radical, $Ph_3Ge\cdot$, attacks the carbon-carbon double bond at the carbon bearing triphenylgermyl group to give a radical intermediate **A**. Free rotation followed by elimination of $Ph_3Ge\cdot$ would induce the stereochemical scrambling of the olefin, so that the composition of the mixture reaches the thermodynamic equilibrium.[13] This mechanism is supported by the following experiment. Treatment of (Z)-1-triphenylgermyl-1-dodecene (1.0 mmol) with n-Pr_3GeH-Et_3B (1.0 mmol each) at 60 °C gave a mixture of (E)-1-tripropylgermyl-1-dodecene (**1**) and (E)-1-triphenylgermyl-1-dodecene (**2**) (**1**/**2**=2/5, path **a** in Scheme 3), while treatment of (Z)-1-tripropylgermyl-1-dodecene with Ph_3GeH-Et_3B also gave the same mixture **1** and **2** (**1**/**2**=2/5, path **b** in Scheme 3).

This concept was successfully applied to the isomerizations of various kinds of olefins and the results are summarized in Table 2.[14] (Z)-6-Dodecene was equilibrated to (E)-isomer after heating a benzene solution of (Z)-6-dodecene (1.0 mmol), Ph_3GeH (0.1 mmol), and Et_3B (0.1 mmol) at 60 °C for 10 h (Entry 1 of Table 2). The product ratio of Z/E=15/85 reflects the thermodynamic stability of (Z)- and (E)-isomer ($H_{\text{trans}}-H_{\text{cis}}=1.0\ \text{kcal mol}^{-1}$).[15]

Triphenylgermane easily added to terminal olefins in contrast to internal olefins. For instance, Ph_3GeH added to 1-dodecene at 25 °C affording dodecyltriphenylgermane in 89% yield.[16]



Scheme 3.

$$n\text{-C}_{10}\text{H}_{21}\text{CH=CH}_2 \xrightarrow[\text{Et}_3\text{B}]{\text{Ph}_3\text{GeH}} n\text{-C}_{10}\text{H}_{21}\text{CH}_2\text{CH}_2\text{GePh}_3$$

Experimental

Distillation of the products was performed by the use of Kugelrohr (Büchi), and boiling points are indicated by an air bath temperature without correction. All melting points were obtained on Yanaco MP-50929 melting points apparatus and are uncorrected. The IR spectra were determined on a JASCO IR-810 spectrometer, the mass spectra on a Hitachi M-80 machine, the ^{1}H and ^{13}C NMR spectra on Varian XL-200 spectrometer. The chemical shifts of the ^{1}H NMR are given in δ with Me_4Si as an internal standard, and those of the ^{13}C NMR are given in δ with $CDCl_3$. The analyses were carried out by the staff at the Elemental Analyses Center of Kyoto University. Tetrahydofuran was freshly distilled from sodium benzophenone ketyl. Purification of products was performed by column chromatography or preparative thin-layer chromatography (tlc) on silica gel.

General Procedure for Triethylborane-Induced Hydrogermylation of Acetylenes and Terminal Olefins. Hydrogermylation of 1-dodecyne is representative. A hexane solution of Et_3B (1.0 M, 1 M=1 mol dm^{-3}, 1.0 ml, 1.0 mmol) was added to a solution of 1-dodecyne (0.18 g, 1.1 mmol) and Ph_3GeH (0.30 g, 1.0 mmol) in toluene (8 ml) at −78 °C under an argon atmosphere. After stirring for 3 h at −78 °C, the reaction mixture was poured into ice-cooled water and extracted with ethyl acetate three times. Combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residual oil was submitted to preparative tlc on silica gel to give (*Z*)-1-triphenylgermyl-1-dodecene exclusively (0.36 g, 76% yield, Z/E=>20/1): ^1H NMR ($CDCl_3$) δ=0.88 (t, J=6.5 Hz, 3H), 0.74—1.49 (m, 16H), 1.95 (dt, J=7.3, 7.3 Hz, 2H), 6.04 (C=CHGe, d, J=12.6 Hz, 1H), 6.67 (C=CHR, dt, J=12.6, 7.3 Hz, 1H), 7.31—7.50 (m, 9H), 7.50—7.76 (m, 6H); ^{13}C NMR ($CDCl_3$) δ=14.12, 22.70, 29.22, 29.31, 29.52, 31.92, 34.65, 123.2, 128.1, 128.9, 134.8, 137.7, 151.2. On the other hand, *E*-isomer was obtained as follows. A hexane solution of Et_3B (1.0 M, 1.0 ml, 1.0 mmol)[17] was added to a solution of 1-dodecyne (0.17 g, 1.0 mmol) and Ph_3GeH (0.33 g, 1.1 mmol) in benzene (8 ml). The mixture was heated at 60 °C for 2 h. Evaporation of the solvent followed by purification provided (*E*)-1-triphenylgermyl-1-dodecene (0.48 g, 99% yield Z/E=<1/20): mp 55—56 °C (toluene); IR (neat) 2880, 2820, 1425, 1085, 730, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.86 (t, J=6.7 Hz, 3H), 1.06—1.66 (m, 16H), 2.14—2.34 (m, 2H), 6.13—6.23 (m, 2H), 7.23—7.45 (m, 9H), 7.45—7.70 (m, 6H); ^{13}C NMR ($CDCl_3$) δ=14,04, 22.70, 28.64, 29.20, 29.36, 29.48, 29.61, 31.92, 36.69, 123.1, 128.1, 128.9, 135.1, 137.0, 151.0. Found C, 76.42; H, 8.16%. Calcd for $C_{30}H_{38}Ge$: C, 76.46; H, 8.13%.

(*Z*)-1-Triphenylgermyl-1-propene: Mp 35—37 °C (toluene); IR (KBr) 3044, 2982, 1609, 1483, 1429, 1090, 1020, 1004, 734, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.68 (d, J=7.0 Hz, 3H), 6.10 (C=CHGe, d, J=13.0 Hz, 1H), 6.80 (C=CHMe, dq, J=13.0, 7.0 Hz, 1H), 7.33—7.48 (m, 9H), 7.48—7.65 (m, 6H); ^{13}C NMR ($CDCl_3$) δ=21.2, 125.6, 129.1, 129.7, 135.7, 138.4, 146.1. Found: C, 73.25; H, 5.69%. Calcd for $C_{21}H_{20}Ge$: C, 73.11; H, 5.84%.

(*E*)-4-Triphenylgermyl-3-buten-1-ol; IR (KBr) 3350, 3060, 2973, 1618, 1484, 1430, 1091, 1039, 999, 982, 735, 698, 671 cm^{-1}; ^1H NMR ($CDCl_3$)δ=1.25 (bs, 1H), 2.54 (dt, J=6.3, 6.4 Hz, 2H), 3.69 (t, J=6.4 Hz, 2H), 6.18 (C=CHR, dt, J=18.3, 6.3 Hz, 1H), 6.35 (C=CHGe, d, J=18.3 Hz, 1H), 7.44—7.62 (m, 9H), 7.62—7.87 (m, 6H); ^{13}C NMR ($CDCl_3$) δ=40.00, 61.45, 127.3, 128.2, 129.0, 135.0, 136.4, 141.6. Found: C, 70.35; H, 5.82%. Calcd for $C_{22}H_{22}OGe$: C, 70.46; H, 5.91%.

(*Z*)-4-Triphenylgermyl-3-buten-1-ol: Bp 170 °C (bath temp, 0.3 Torr, 1 Torr=133.322 Pa); ^1H NMR ($CDCl_3$) δ=1.22 (bs, 1H), 2.28 (dt, J=7.5, 6.8 Hz, 2H), 3.49 (t, J=6.8 Hz, 2H), 6.18 (C=CHGe, d J=12.5 Hz, 1H), 6.76 (C=CHR dt, J=18.3, 6.3 Hz, 1H), 7.36—7.51 (m, 9H), 7.56—7.69 (m, 6H).

(*Z*)-6-Triphenylgermyl-6-dodecene: Bp 170 °C (bath temp, 0.3 Torr); IR (neat) 3066, 2924, 2854, 1730, 1432, 1090 cm^{-1}; ^1H NMR($CDCl_3$) δ=0.71 (t, J=6.7 Hz, 3H), 0.73 (t, J=6.8 Hz, 3H), 0.84—1.43 (m, 12H), 1.81 (dt, J=7.4, 7.4 Hz, 2H), 2.09 (t, J=7.4 Hz, 2H), 6.24 (t,J=7.4 Hz, 1H), 7.35—7.67 (m, 15H); ^{13}C NMR ($CDCl_3$) δ=13.95, 14.00, 22.22, 22.38, 29.14, 30.17, 31.35, 31.42, 33.60, 38.81, 128.0, 128.6, 135.1,135.9, 137.7, 143.3. Found: C, 76.66; H, 8.34%. Calcd for $C_{30}H_{38}Ge$: C, 76.47; H, 8.13 %.

(*E*)-6-Triphenylgermyl-6-dodecene: ^1H NMR ($CDCl_3$) δ= 0.71 (t, J=6.7 Hz, 3H), 0.73 (t, J=6.8 Hz, 3H), 0.84—1.43 (m, 12H), 2.17—2.33 (m, 4H), 5.83 (t, J=7.4 Hz, 1H), 7.35—7.67 (m, 15H).

(*E*)-1-Trimethylsilyl-2-(triphenylgermyl)ethene: Mp 92—94 °C (hexane); IR (KBr) 2310, 1484, 1410, 1245, 1169, 1092, 1005, 834, 735, 616 cm^{-1}; ^1H 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= −1.51, 128.2, 128.9, 135.1, 136.5, 143.1, 155.1. Found: C, 68.41; H, 6.51%. Calcd for $C_{23}H_{26}GeSi$: C, 68.52; H, 6.50%.

(*E*)-Ethyl 11-Triphenylgermyl-10-undecenoate: Bp 200 °C (bath temp, 1.0 Torr); IR (neat) 2924, 2850, 1735, 1613, 1484, 1431, 1183, 1092, 734, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.09—1.29 (m, 10H), 1.25 (t, J=7.1 Hz, 3H), 1.29—1.78 (m, 2H), 2.19—2.43 (m, 2H), 2.28 (t, J=7.5 Hz, 2H), 4.12 (q, J=7.1 Hz, 2H), 6.11—6.24 (m, 2H), 7.31—7.48 (m, 9H), 7.48—7.65 (m, 6H); ^{13}C NMR ($CDCl_3$) J=14.27, 25.00, 28.57, 29.11, 29.95, 34.37, 36.65, 60.14, 123.1, 127.9, 128.9, 135.0, 136.9, 150.9. Found: C, 72.33; H, 7.55%. Calcd for $C_{31}H_{38}O_2Ge$: C, 72.27; H, 7.43%.

(*Z*)-Ethyl 11-Triphenylgermyl-10-undecenoate: Bp 200 °C (bath temp, 1.0 Torr); ^1H NMR ($CDCl_3$) δ=0.85—1.45 (m, 10H), 1.24 (t, J=7.2 Hz, 3H), 1.48—1.73 (m, 2H), 1.95 (dt, J=7.4, 7.0 Hz, 2H), 2.26 (t, J=7.5 Hz, 2H), 4.12 (q, J=7.2 Hz, 2H), 6.04 (C=CHGe, d, J=12.6 Hz, 1H), 6.67 (C=CHR, dt, J=12.6, 7.4 Hz, 1H), 7.31—7.45 (m, 9H), 7.45—7.73 (m, 6H); ^{13}C NMR ($CDCl_3$) δ=14.24, 24.91, 29.06, 34.35, 34.58, 60.09, 123.3, 128.1, 128.8, 134.8, 135.0, 137.7, 151.0, 173.8.

Dodecyltriphenylgermane: Mp 63—64 °C (methanol); IR (CH_2Cl_2) 3050, 2926, 2854, 1432, 1278, 1092 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.87 (t, J=6.4 Hz, 3H), 1.22 (bs, 20H), 1.45—1.60 (m, 2H), 7.33—7.45 (m, 9H), 7.45—7.58 (m, 6H); ^{13}C NMR ($CDCl_3$) δ=14.00, 14.13, 22.69, 25.01, 29.12, 29.58, 29.64, 31.92, 34.46, 128.1, 128.8, 134.9, 137.4. Found: C, 76.07; H, 8.46%. Calcd for $C_{30}H_{40}Ge$: C, 76.14; H, 8.52%.

Radical Cyclization of 3-Methyl-2-butenyl 2-Propynyl Ether. A hexane solution of triethylborane (1.0 M, 0.2 ml, 0.2 mmol) was added to a solution of Ph_3GeH (0.37 g, 1.2 mmol) and 3-methyl-2-butenyl 2-propynyl ether (0.12 g, 1.0 mmol) in benzene (100 ml) at 25 °C under an argon atmosphere. After stirring for 3 h at 25 °C, the reaction mixture was poured into water and extracted with ethyl acetate. Purification by preparative tlc on silica gel gave the cyclized compound, (*Z*)-4-isopropyl-3-(triphenylgermylmethylene)oxolane (0.29 g, 68%) as a single product: mp 101—102 °C (methanol); IR (neat, before crystallization) 3062, 2954, 1729, 1632, 1432, 1090, 1062, 737, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.94 (d, J=6.8 Hz, 3H), 1.01 (d, J=6.9 Hz, 3H), 1.92—2.15 (m, 1H), 2.66—2.80 (m, 1H), 3.70—3.95 (m, 4H), 6.05 (bs, 1H), 7.32—7.48 (m, 9H), 7.49—7.65 (m, 6H); ^{13}C NMR ($CDCl_3$) δ=17.96, 21.27, 30.52, 52.88, 69.78, 71.88, 112.8, 128.3, 129.1, 134.8, 136.6, 162.4. Found: C, 72.49; H, 6.71%. Calcd for $C_{26}H_{28}OGe$: C, 72.78; H, 6.58%.

The Isomerization of (*Z*)-1-Triphenylgermyl-1-dodecene into (E)-1-Triphenylgermyl-1-dodecene. Heating a benzene solution (5 ml) of (*Z*)-1-triphenylgermyl-1-dodecene (0.47 g, 1.0 mmol) at 60 °C for 4 h in the presence of Ph_3GeH (30 mg, 0.1 mmol) and Et_3B (1.0 M in hexane, 0.1 ml, 0.1 mmol) gave (*E*)-triphenylgermyl-1-dodecene (0.41 g, 88% yield) exclusively.

The Reactions of (*Z*)-1-Triphenylgermyl-1-dodecene with Tripropylgermane in the Presence of Triethylborane. Treatment of (*Z*)-1-triphenylgermyl-1-dodecene (1.0 mmol) with *n*-Pr_3GeH–Et_3B (1.0 mmol each) at 60 °C for 4 h gave a mixture of (*E*)-1-tripropylgermyl-1-dodecene (**1**) and (*E*)-1-triphenylgermyl-1-dodecene (**2**) (**1**/**2**=2/5) in 88% combined yield. **1**: ^{1}H NMR ($CDCl_3$) δ=0.65—1.00 (m, 18H), 1.15—1.52 (m, 22H), 2.00—2.18 (m, 2H), 5.70 (C=CHGe, d, J=18.4 Hz, 1H), 5.87 (C=CHR, dt, J=18.4, 6.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=14.13, 16.00, 18.20, 18.69, 22.72, 28.64, 29.39, 29.53, 29.66, 31.96, 36.82, 127.3.

1-Tripropylgermyl-1-dodecyne: To a solution of 1-dodecyne (830 mg, 5.0 mmol) in THF (10 ml) was added n-BuLi (1.60 M in hexane, 3.13 ml, 5.0 mmol) at 0 °C under an argon atmosphere. After stirring for 15 min at 0 °C, tripropylgermyl chloride (1.33 g, 5.5 mmol) was added slowly to this mixture. After 15 min at 0 °C, the ice bath was removed and the resulting mixture was stirred for another 30 min at 25 °C. The reaction mixture was quenched with ice-aqueous HCl (1 M) and extracted with ethyl acetate three times. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The product was purified by silica-gel column chromatography to give 1-tripropylgermyl-1-dodecyne in 60% yield: bp 120 °C (bath temp, 1.0 Torr); IR (neat) 2952, 2924, 2856, 2166, 1730, 1462, 1072 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.73—1.10 (m, 18H), 1.15—1.65 (m, 22H), 2.22 (t, J=6.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=14.10 17.18, 17.79, 18.72, 19.89, 22.70, 28.74, 28.99, 29.13, 29.36, 29.58, 31.92, 81.62, 107.6; Found: C, 68.81; H, 11.79%. Calcd for $C_{21}H_{42}Ge$: C, 68.70; H, 11.53%.

(Z)-1-Tripropylgermyl-1-dodecene:[18] A hexane solution of diisobutylaluminium hydride (1.0 M, 2.5 ml, 2.5 mmol) was added to a solution of 1-tripropylgermyl-1-dodecyne (0.74 g, 2.0 mmol) in hexane (2.0 ml)-ether (1.5 ml) at 0 °C under an argon atmosphere. After 15 min at 0 °C, the mixture was allowed to come to room temperature and then stirred for 3 h at 25 °C. To this mixture were added KF (0.15 g, 2.6 mmol), water (0.10 ml) and then hexane (10 ml). Filtration, condensation, and purification by silica-gel column chromatography gave (Z)-1-tripropylgermyl-1-dodecene (0.64 g) in 86% yield: bp 123 °C (bath temp, 1.0 Torr); IR (neat) 2952, 2922, 2854, 1608, 1459, 1075 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.75—1.05 (m, 18H), 1.20—1.55 (m, 22H), 2.00—2.15 (m, 2H), 5.55 (C=CHGe, d, J=12.9 Hz, 1H), 6.33 (C=CHR, dt, J=12.9, 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=14.12, 17.28, 18.25, 18.82, 22.70, 29.38, 29.47, 29.63, 29.85, 31.94, 34.29, 127.2, 147.4. Found: C, 68.17; H, 12.05%. Calcd for $C_{21}H_{44}Ge$: C, 68.32; H, 12.01%.

The Reaction of (Z)-1-Tripropylgermyl-1-dodecene with Triphenylgermane in the Presence of Triethylborane. Treatment of (Z)-1-tripropylgermyl-1-dodecene (1.0 mmol) with Ph_3GeH-Et_3B (1.0 mmol each) at 60 °C for 4 h gave a mixture of (E)-1-tripropylgermyl-1-dodecene (**1**) and (E)-1-triphenylgermyl-1-dodecene (**2**) (**1**/**2**=2/5) in 92% combined yield.

The Isomerization Reactions of General Olefins with Triphenylgermane–Triethylborane System. (Table 2) Typical procedure is as follows. Triethylborane (1.0 M hexane solution, 0.1 ml, 0.1 mmol) and triphenylgermane (0.03 g, 0.1 mmol) were added to a solution of (Z)-6-dodecene (Z/E=>20/1, 0.17 g, 1.0 mmol) in benzene (5 ml). The mixture was heated at 60 °C for 10 h. Evaporation of the solvent and purification gave 6-dodecene (Z/E=15/85) in 90% yield.

(Z)-1-Phenyldimethylsilyl-1-octene: Bp 120 °C (bath temp, 1.0 Torr); IR (neat) 3064, 3048, 2996, 2954, 2922, 1605, 1466, 1428, 1248, 1112, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.36 (s, 6H), 0.85 (t, J=6.3 Hz, 3H), 1.13—1.40 (m, 8H), 1.97—2.09 (m, 2H), 5.61 (C=CHSi, dt, J=14.0, 1.2 Hz, 1H), 6.43 (C=CHR, dt, J=14.0, 7.4 Hz, 1H), 7.35—7.47 (m, 3H), 7.55—7.69 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=0.69, 14.07, 22.58, 28.96, 29.48, 31.71, 33.79, 126.4, 127.7, 128.3, 128.7, 133.7, 139.8, 151.1. Found: C, 78.11; H, 10.91%. Calcd for $C_{16}H_{26}Si$: C, 77.97; H, 10.63%.

(E)-1-Phenyldimethylsilyl-1-octene: Bp 120 °C (bath temp, 1.0 Torr); IR (neat) 3066, 3046, 2954, 2924, 2852, 1617, 1428, 1248, 1114 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.31 (s, 6H), 0.88 (t, J=6.5 Hz, 3H), 1.15—1.50 (m, 8H), 2.10—2.22 (m, 2H), 5.74 (C=CHSi, dt, J=18.6, 1.4 Hz, 1H), 6.13 (C=CHR, dt, J=18.6, 6.2 Hz, 1H), 7.30—7.47 (m, 3H), 7.50—7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−2.41, 14.09, 22.63, 28.59, 29.74, 31.73, 36.83, 127.2, 127.7, 128.8, 133.8, 139.4, 149.5; Found: C, 78.23; H, 10.86%. Calcd for $C_{16}H_{26}Si$: C, 77.97; H, 10.63%.

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References

1) a) G. Stork; "Selectivity—A Goal for Synthetic Efficiency," ed by W. Bartmann and B. M. Trost, Verlag Chemie, Weinheim (1984), pp. 281—298. b) D. H. R. Barton, D. Crich, and W. B. Motherwell, *Tetrahedron,* **41**, 3901 (1985). c) B. Giese and H. Horler, *ibid.*, **41**, 4025 (1985). d) D. J. Hart, *Science,* **223**, 883 (1984). e) G. A. Kraus and K. Landgrebe, *Tetrahedron,* **41**, 4039 (1985). f) D. P. Curran, *Synthesis,* **1988**, 417, 489.

2) a) R. J. P. Corriu and J. J. E. Moreau, *J. Organomet. Chem.*, **40**, 73 (1972). b) K. I. Cherkezishvili, K. Sh. Gelashvili, and R. I. Kublashvili, *Soobshch. Akad. Nauk. Cruz. SSSR.*, **109**, 297 (1983). c) H. Oda, Y. Morizawa, K. Oshima, and H. Nozaki, *Tetrahedron Lett.*, **25**, 3221 (1984).

3) a) A. J. Leusink, H. A. Budding, and J. W. Marsman, *J. Organomet. Chem.*, **9**, 285 (1967). b) A. J. Leusink, H. A. Budding, and W. Drenth, *ibid.*, **9**, 295 (1967).

4) E. J. Corey, P. Ulrich, and J. M. Fitzpatrick, *J. Am. Chem. Soc.*, **98**, 222 (1976); E. J. Corey and R. H. Wollenberg, *J. Org. Chem.*, **40**, 2265 (1975); H. Sano, Y. Miyazaki, M. Okawara, and Y. Ueno, *Synthesis*, **1986**, 776.

5) Transition metals also catalyze both hydrogermylation and hydrostannation. a) Y. Ichinose, K. Oshima, and K. Utimoto, *Bull. Chem. Soc. Jpn.*, **60**, 3468 (1987). b) K. Kikukawa, H. Umekawa, T. Idemoto, and T. Matsuda, 33rd Symposium on Organometallic Chemistry, Tokyo, 1986, Abstr., A223. See also Ref. 2.

6) For general preparation and reaction of organogermanium compound, a) D. Barton and W. D. Ollis, "Comprehensive Organic Chemistry," Pergamon Press, Oxford (1979), Vol, 3, pp. 1061—1073, b) H. Oda, K. Oshima, and H. Nozaki, *Tetrahedron Lett.*, **25**, 3217 (1984).

7) For the utility of alkenyltriphenylstannane, see e.g., H. Pereyre, J. -P. Quintard, and A. Rahm, "Tin in Organic Synthesis," Butterworth & Co. Ltd. (1987), pp. 127—243.

8) E. Negishi, "Organometallic in Organic Synthesis,"John Wiley & Sons, New York (1980), Chap. 6

9) a) R. Fosty, M. Gielen, M. Pereyre, and J. P. Quintard, *Bull. Soc. Chim. Belg.*, **85**, 523 (1976). b) M. E. Jung and L. A. Light, *Tetrahedron Lett.*, **23**, 3851 (1982).

10) We have reported that Ph_3SnH easily adds to acetylenes in the presence of Et_3B (K. Nozaki, K. Oshima, and K. Utimoto, *J. Am. Chem. Soc.*, **109**, 2547 (1987); *idem.*, *Tetrahedron*,**45**, 923 (1989)). In contrast to the reaction of Ph_3GeH, the ratios of the products, (*E*)-alkenyltriphenylstannane and (*Z*)-isomer were always 8/2—7/3 and not affected by the reaction temperature or the ratio of [acetylene]/[Ph_3SnH]. See Ref 9.

11) A part of this work was published in a communication form: Y. Ichinose, K. Nozaki, K. Wakamatsu, K. Oshima, and K. Utimoto, *Tetrahedron Lett.*, **28**, 3709 (1987).

12) *i*-Pr_3B and (*n*-$C_8H_{17})_3B$ were as effective as Et_3B. We thank Tosoh Akzo Co. for a gift of a hexane solution of Et_3B (1.0 M).

13) Same mechanism has been proposed for the partial isomerization of (*Z*)-1-tributylgermyl-2-phenylethene into (*E*)-isomer. See Ref 2a.

14) Benzenethiyl radical-initiated isomerizations of double bonds have been reported. C. Moussebois and J. Dale, *J. Chem. Soc. C.* **1966**, 260; E. J. Corey and E. Hamanaka, *J. Am. Chem. Soc.*, **89**, 2758 (1967).

15) F. D. Rossini, K. S. Pitzer, R. L. Arnitt, R. M. Braun, and G. C. Pimentel,"Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsbourgh, PA (1953), p. 475.

16) Triphenystannane added neither to terminal olefins nor to internal olefins.

17) The amount of Et_3B could be reduced to 0.1 mol per 1.0 mol of acetylene without decrease of the yield and reaction rate above 0 °C.

18) a) J. J. Eisch and M. W. Foxon, *J. Org. Chem.*, **36**, 3520 (1971). b) J. J. Eisch, H. Gopal, and S. -G. Rhee *ibid.*, **40**, 2064 (1975).