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Homolytic hydrogermylation of alkenes with dibutylchlorogermane

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Abstract

In the presence of Et_3B-dry air, dibutylchlorogermane (Bu_2GeClH) reacted smoothly with alkenes at room temperature to give hydrogermylation products in high yields. This homolytic hydrogermylation was applicable to various alkenes including electron-deficient, electron-rich, and internal alkenes. Under the same conditions, tributylgermane (Bu_3GeH) showed much lower reactivity than Bu_2GeClH. The Et_3B-initiated reaction of 1,6-dienes with Bu_2GeClH gave germylmethylated cyclopentanes.

Keywords: Hydrogermane; Hydrogermylation; Alkenes; Radical reactions

1. Introduction

Hydrometalation reactions of alkenes with hydrosilanes, -germanes, and -stannanes provide powerful tools for the synthesis of alkylsilanes, -germanes, and -stannanes, respectively [1–3]. Radical initiators and transition metal catalysts are well known to be effective in acceleration of these hydrometalations. The propagation mechanism of the radical-initiated hydrometalations involves reversible addition of a metal radical and hydrogen abstraction of the resultant alkyl radical from a metal hydride (Scheme 1). The radical process is applicable to various alkenes due to high reactivity of the radical species as well as high compatibility with polar functionalities. However, there are some drawbacks such as severe reaction conditions, low reaction efficiency caused by side radical reactions, and low stereoselectivity, particularly, in the reactions using trialkylmetal hydrides (R_3MH, R = alkyl, M = Si, Ge, Sn). Judging from the reaction mechanism, an efficient homolytic hydrometalation under mild conditions can be achieved by low reversibility of the radical addition step and fast hydrogen abstraction of the alkyl radical intermediate. A few kinds of group 14 metal hydrides are known to satisfy these requirements in hydrometalations of both unactivated and activated alkenes. For example, tris(trimethylsilyl)silane ($(Me_3Si)_3SiH$) [4], tri(2-furyl)germane ($(2\text{-furyl})_3GeH$) [5], and dialkylhalostannanes (R_2SnXH) [6] are valuable for efficient, mild homolytic hydrometalations of a wide range of alkenes.

In the course of our studies on highly selective homolytic hydrostannylations of alkenes and alkynes with Lewis acidic hydrostannanes [7], we found that dibutylchlorostannane (Bu_2SnClH) added exclusively to 1-undecen-3-ol in the coexistence of 1-octene (Eq. (1)) [7a]. The high chemoselectivity is attributable to the coordination of the hydroxy group to the Lewis acidic tin nucleus in the β-stannylalkyl radical intermediate (Scheme 2). The Sn–O coordination would retard the decomposition (inverse reaction) of the intermediate to $Bu_2ClSn\cdot$ and the substrate to promote the hydrostannylation process. This chemoselective hydrostannylation with Bu_2SnClH induced us to investigate the reactivity of dibutylchlorogermane (Bu_2GeClH, **1a**), a Lewis acidic hydrogermane, toward homolytic hydrogermylation of alkenes [8]. Herein we describe that **1a** adds smoothly to a variety of alkenes in the presence of Et_3B-dry air.

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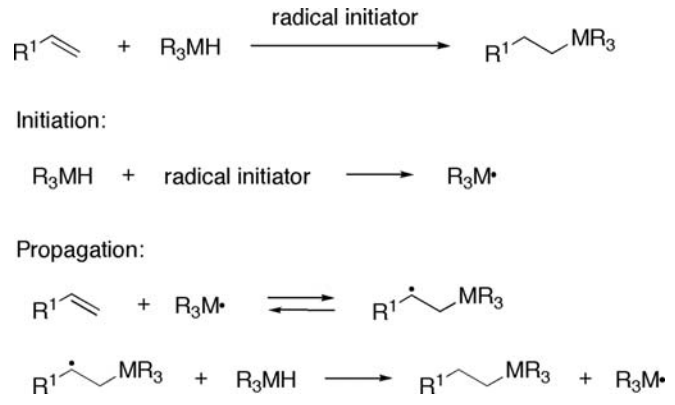
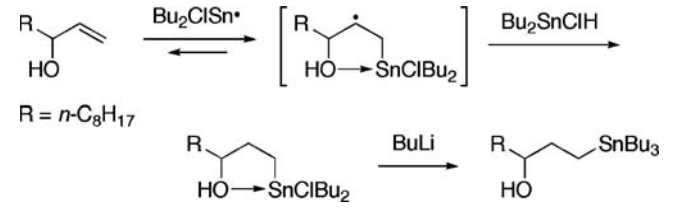
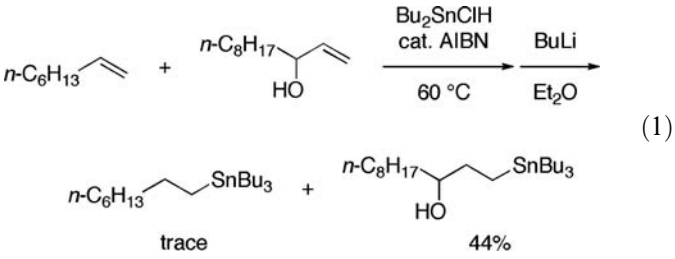


Scheme 1.



Scheme 2.



(1)

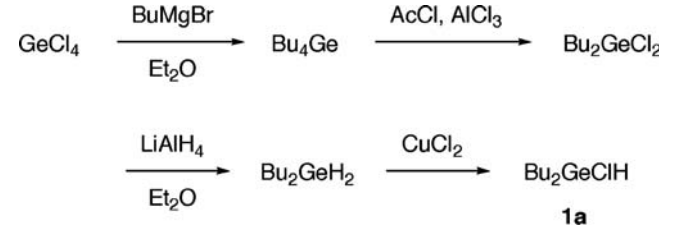
2. Results and discussion

2.1. Synthesis of dibutylchlorogermane (*1a*)

Hydrogermane **1a** was prepared from $GeCl_4$ by four steps without difficulty (Scheme 3) [9]: butylation of $GeCl_4$ with BuMgBr, dealkylative dichlorination of Bu_4Ge with AcCl and $AlCl_3$, reduction of Bu_2GeCl_2 with $LiAlH_4$, and chlorination of Bu_2GeH_2 with $CuCl_2$ [10].

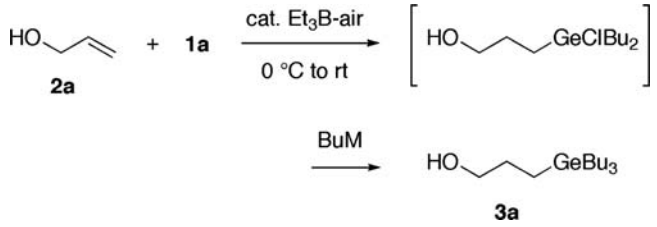
2.2. Optimization of reaction conditions using 2-propen-1-ol (*2a*)

We first examined the radical-initiated hydrogermylation of 2-propen-1-ol (**2a**) with **1a** under various conditions



Scheme 3.

Table 1
Hydrogermylation of allyl alcohol **2a** with **1a**[a]



Entry	Solvent	Time	Isolated yield (%)
1[b]	THF	5 min	99
2	Hexane	10 h	96
3	Toluene	3 h	90
4[b]	Neat[c]	5 min	97
5[d]	Neat[c]	24 h	0
6[e]	THF	1 h	0
7[f]	THF	24 h	37
8[g]	THF	24 h	0

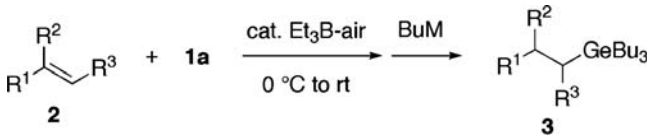
[a] Unless otherwise noted, all reactions were carried out with **2a** (0.50 mmol), **1a** (0.60 mmol), Et_3B (1 M in hexane, 0.025 mmol), dry air (2.5 mL), and solvent (1.0 mL). The mixture was stirred for 10 min at 0 °C and then warmed to rt. The resultant mixture was treated with BuMgBr/Et_2O (1.5 mmol) in entries 1, 4, and 5 or BuLi/hexane (1.2 mmol) in entries 2, 3, and 6.
[b] The reaction was carried out at 0 °C.
[c] The reaction mixture contained a small amount of hexane coming from 1 M solution of Et_3B.
[d] Without Et_3B-dry air.
[e] With galvinoxyl (0.025 mmol).
[f] $Bu_2Ge(OEt)H$ (**1b**) was used instead of Bu_2GeClH.
[g] Bu_3GeH (**1c**) was used instead of Bu_2GeClH.

(Table 1). In the presence of Et_3B-dry air as radical initiator [11], the reaction of **2a** with **1a** in THF at 0 °C reached completion within 5 min. Treatment of the resultant mixture with BuMgBr gave 3-tributylgermyl-1-propanol (**3a**) in a quantitative yield after purification by silica gel column chromatography (entry 1) [12]. Use of hexane and toluene as solvent decreased the reaction rate, although prolonged reaction achieved high yields of **3a** (entries 2 and 3). Without solvent, the hydrogermylation proceeded rapidly and efficiently (entry 4). Hydrogermane **1a** did not add to **2a** in the absence of Et_3B-dry air (entry 5). Addition of galvinoxyl suppressed the Et_3B-initiated reaction completely (entry 6). The results of entries 5 and 6 clearly indicate that the present hydrogermylation involves a radical chain mechanism. The reaction with dibutyl(ethoxy)germane ($Bu_2Ge(OEt)H$, **1b**) was much slower than that with **1a** (entries 1 and 7) [8]. Tributylgermane (Bu_3GeH, **1c**) was insensitive to **2a** even in the presence of Et_3B-dry air (entry 8). Thus, introduction of a chloro group on the germanium atom is very effective in improving the reactivity of hydrogermanes [8].

2.3. Hydrogermylation of various alkenes

The Et_3B-initiated hydrogermylation with **1a** is applicable to various alkenes as shown in Table 2. 1-Undecen-3-ol (**2b**) and 2-methyl-2-propen-1-ol (**2c**) as well as **2a** underwent the hydrogermylation efficiently (entries 1–3).

Table 2
Hydrogermylation of alkenes **2** with **1a**[a]

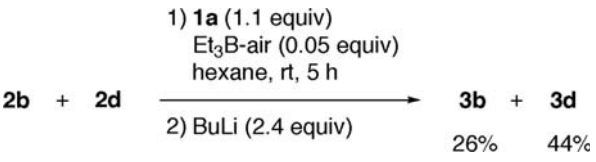


Entry	R^1	R^2	R^3		Time	BuM (equiv)	Isolated yield (%)
1[b]	$HOCH_2$	H	H	**2a**	5 min	BuMgBr (3)	99
2	n-$C_8H_{17}CH(OH)$	H	H	**2b**	30 min	BuLi (2.4)	94
3	$HOCH_2$	Me	H	**2c**	30 min	BuMgBr (3)	99
4	n-C_9H_{19}	H	H	**2d**	30 min	BuLi (1.2)	97
5	BuO	H	H	**2e**	30 min	BuLi (1.2)	82
6	CyO_2C	H	H	**2f**	30 min	BuMgBr (1.2)	59
7[c]	CyO_2C	H	H	**2f**	10 h	BuMgBr (1.2)	86
8[c]	MeO_2C	H	H	**2g**	10 h	BuMgBr (1.2)	82
9[d]	Pr	H	Pr	**2h**	1 h	BuLi (1.3)	92
10[d]	Me_3SiO	$(CH_2)_4$	$(CH_2)_4$	**2i**	1 h	BuLi (1.3)	80

[a] Unless otherwise noted, all reactions were carried out with an alkene **2** (0.50 mmol), **1a** (0.60 mmol), Et_3B (1 M in hexane, 0.025 mmol), and dry air (2.5 mL) in THF (1.0 mL). The mixture was stirred for 10 min at 0 °C and then warmed to rt. The resultant mixture was treated with BuMgBr/Et_2O or BuLi/hexane.
[b] The reaction was carried out at 0 °C.
[c] Instead of THF, hexane was used as solvent.
[d] The reaction was carried out without solvent, although a small amount of hexane coming from 1 M solution of Et_3B was contained.

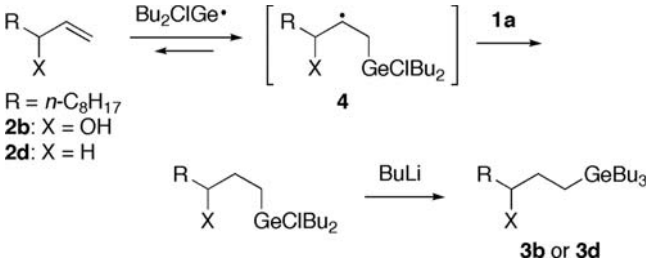
Hydrogermane **1a** reacted smoothly with 1-undecene (**2d**), a non-functionalized alkene, to give the corresponding hydrogermylation product in 97% yield (entry 4). Under the same conditions, **1a** was reactive also to vinyl ether **2e**, an electron-rich alkene (entry 5). Use of electron-deficient alkene **2f** resulted in a low yield of the corresponding adduct **3f** (entry 6). The hydrogermylation of **2f** was not completed, and elongation of the reaction time was not effective in further consumption of **2f**. However, prolonged hydrogermylation of **2f** and methyl acrylate (**2g**) in hexane achieved high efficiency (entries 7 and 8). To our surprise, the present method using **1a** succeeded in efficient hydrogermylation of internal alkenes such as (*E*)-4-octene (**2h**) and 1-(trimethylsiloxy)cyclohexene (**2i**) under solvent-free conditions (entries 9 and 10) [13]. In THF, **1a** did not add to these alkenes at all.

To disclose the chemoselectivity of the present hydrogermylation, we performed competitive reaction of **2b** and **2d** with **1a** (**2b**:**2d**:**1a** = 1:1:1.1, Eq. (2)). Hexane, a non-coordinating solvent, was used in view of the ease of coordination between the hydroxy group and the germanium center. However, the hydrogermylation gave a mixture of **3b** and **3d** with low chemoselectivity. This observation stands in sharp contrast with the previous result shown in Eq. (1). The difference between **1a** and Bu_2SnClH in chemoselectivity may arise from high bond energy of carbon–germanium bond [14], which decelerates the elimination of $Bu_2ClGe^{\bullet}$ from the β-germylalkyl radical intermediates **4** to facilitate the radical chain process irrespective of the presence of the hydroxy group (Scheme 4).

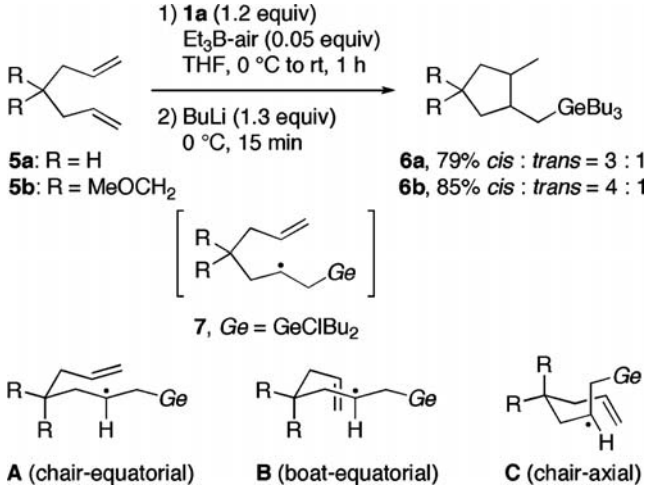


(2)

We next tried radical cyclization of dienes with **1a**. Use of 1,6-heptadiene (**5a**) afforded the cyclized product **6a** in good yield with moderate *cis*-selectivity (Scheme 5). Introduction of methoxymethyl groups slightly improved the yield and the stereoselectivity. This radical cyclization proceeds via radical intermediate **7**. The observed *cis*-selectivity can be



Scheme 4.



Scheme 5.

rationalized by cyclization through chair-equatorial conformation **A** of **7**, which is energetically more favored than boat-equatorial and chair-axial conformations, **B** and **C**, leading to *trans*-**6** [15].

Previously we have reported that **1a** acts as a good radical reducing agent and has higher hydrogen-donating ability to an alkyl radical than **1b** and **1c** [8]. Judging from this observation, the high reactivity of **1a** toward homolytic hydrogermylation is attributable to its high hydrogen-donating ability, which promotes the latter step of the propagation process (Schemes 1 and 4). Additionally, in the hydrogermylation of unactivated and electron-rich alkenes, the relatively electrophilic character of $Bu_2ClGe^{\bullet}$ would facilitate its addition to these alkenes.

3. Conclusion

We have demonstrated that Bu_2GeClH (**1a**) acts as an efficient hydrogermylating agent. With this reagent, a variety of alkenes can be converted into the corresponding alkylgermanes in good to high yields. The present study has disclosed also that a proper change of the substituent on germanium makes hydrogermanes synthetically more useful.

4. Experimental

Unless otherwise noted, all reactions and distillations were carried out under N_2. Solvents were dried by distillation from sodium metal/benzophenone ketyl (THF, Et_2O, toluene) and CaH_2 (hexane). All other commercially obtained reagents were used as received. Infrared spectra were measured on a JASCO FT/IR-230 spectrophotometer. ^1H NMR spectra at 270 MHz and ^{13}C NMR spectra at 67.7 MHz were recorded on a JEOL JNM-EX-270 spectrometer. The chemical shifts (δ) are reported with reference at 0.00 ppm (Me_4Si) or 7.26 ppm ($CHCl_3$) for the proton and at 77.00 ppm (centered on the signal of $CDCl_3$) for the carbon. Mass spectra were measured (by EI method) on a Shimadzu GCMS-QP5050 instrument. Elemental analyses were performed by the Analysis Center of the University of Tsukuba.

4.1. Synthesis of dibutylchlorogermane

As shown in Scheme 3, the title compound was prepared from tetrachlorogermane by four steps. See the references for the steps from tetrachlorogermane to dibutylgermane [9]. The last step, chlorination of dibutylgermane, was performed by the method reported by Kunai and co-workers [10] as follows: under a nitrogen atmosphere, dibutylgermane (12.5 g, 66.2 mmol) was added to a mixture of $CuCl_2$ (19.5 g, 145 mmol), CuI (0.42 g, 2.2 mmol), and Et_2O (260 mL) at 0 °C. After being stirred for an hour, the reaction mixture was warmed to room temperature and stirred for 3 h. The resultant mixture was filtered through celite®. After evaporation of the filtrate, the residual oil was diluted with dry pentane (50 mL) again, filtered through celite®, and evaporated. Purification of the crude product by distillation gave the title compound (13.6 g, 60.9 mmol) in 92% yield. Bp 114 °C (2.3 Torr). IR (neat) 2958, 2929, 2860, 2058, 1464 cm^{-1}; ^1H NMR (C_6D_6) δ 0.85 (t, $J = 7.3$ Hz, 6H), 0.91–1.10 (m, 4H), 1.81–1.31 (m, 4H), 1.37–1.48 (m, 4H), 5.50 (tt, $J = 2.7$, 1.9 Hz, 1H); ^{13}C NMR (C_6D_6) δ 13.73 ($CH_3 \times 2$), 18.67 ($CH_2 \times 2$), 25.58 ($CH_2 \times 2$), 26.79 ($CH_2 \times 2$); MS *m*/*z* (relative intensity) 224 (M^+, 1.3), 222 ($M^+ - 2$, 1.5), 220 ($M^+ - 4$, 1.3), 57 (100). Anal. Calc. for $C_8H_{19}GeCl$: C, 43.03; H, 8.59. Found: C, 42.90; H, 8.45%.

4.2. Et_3B-Initiated hydrogermylation of alkenes followed by butylation

Under a nitrogen atmosphere, Et_3B (1.0 M in hexane, 0.025 mL, 0.025 mmol) and dry air (2.5 mL) were added to a solution of Bu_2GeClH (**1a**, 134 mg, 0.60 mmol) and allyl alcohol **2a** (30 mg, 0.50 mmol) in THF (1 mL) at 0 °C. After being stirred for 5 min, the resultant mixture was treated with BuLi (1.60 M in hexane, 0.93 mL, 1.5 mmol) and stirred for 10 min. The mixture was poured into saturated aqueous NH_4Cl (10 mL). The extract with *t*-BuOMe (3×10 mL) was dried over Na_2SO_4 and evaporated. Purification of the crude product by silica gel column chromatography gave 3-tributylgermyl-1-propanol (**3a**, 150 mg, 0.495 mmol) in 99% yield.

4.2.1. 3-Tributylgermyl-1-propanol (*3a*)

Bp 150 °C (0.45 Torr, bath temp.). IR (neat) 3323 (br s, OH), 2956, 2923, 1463, 1053 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.64–0.74 (m, 8H), 0.88 (t, $J = 7.0$ Hz, 9H), 1.25–1.37 (m, 12H), 1.54–1.66 (m, 3H), 3.59 (t, $J = 6.8$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 8.15 (CH_2), 12.40 ($CH_2 \times 3$), 13.76 ($CH_3 \times 3$), 26.61 ($CH_2 \times 3$), 27.45 ($CH_2 \times 3$), 28.48 (CH_2), 65.94 (CH_2); MS *m*/*z* (relative intensity) 247 ($M^+ - Bu$, 100), 245 ($M^+ - 2 - Bu$, 78), 243 ($M^+ - 4 - Bu$, 56); Anal. Calc. for $C_{15}H_{34}GeO$: C, 59.45; H, 11.31. Found: C, 59.76; H, 11.02%.

4.2.2. 1-Tributylgermyl-3-undecanol (*3b*)

IR (neat) 3354 (br s, OH), 2956, 2924, 2854, 1464 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.60–0.80 (m, 8H), 0.89 (t, $J = 6.8$ Hz, 12H), 1.28–1.54 (m, 29H), 3.44–3.54 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 7.90 (CH_2), 12.33 ($CH_2 \times 3$), 13.73 ($CH_3 \times 3$), 14.06 (CH_3), 22.65 (CH_2), 25.69 (CH_2), 26.60 ($CH_2 \times 3$), 27.44 ($CH_2 \times 3$), 29.27 (CH_2), 29.60 (CH_2), 29.74 (CH_2), 31.87 (CH_2), 32.70 (CH_2), 36.61 (CH_2), 74.31 (CH); MS *m*/*z* (relative intensity) 359 ($M^+ - Bu$, 24), 357 ($M^+ - 2 - Bu$, 30), 355 ($M^+ - 4 - Bu$, 21), 205 (100). Anal. Calc. for $C_{23}H_{50}GeO$: C, 66.52; H, 12.14. Found: C, 66.29; H, 12.17%.

4.2.3. 2-Methyl-3-tributylgermyl-1-propanol (*3c*)

IR (neat) 3327 (br s, OH), 2956, 2924, 1464, 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.52 (dd, $J = 13.8$, 9.6 Hz, 1H), 0.70–0.76 (m, 6H), 0.82 (dd, $J = 13.8$, 4.8 Hz, 1H), 0.89 (t,

$J = 7.0$ Hz, 9H), 0.95 (d, $J = 6.6$ Hz, 3H), 1.28–1.35 (m, 12H), 1.53 (br s, 1H), 1.71–1.83 (m, 1H), 3.35 (dd, $J = 10.3$, 6.9 Hz, 1H), 3.44 (dd, $J = 10.3$, 5.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.20 ($CH_2 \times 3$), 13.75 ($CH_3 \times 3$), 16.86 (CH_2), 19.46 (CH_3), 26.65 ($CH_2 \times 3$), 27.44 ($CH_2 \times 3$), 33.17 (CH), 70.79 (CH_2). Anal. Calc. for $C_{16}H_{36}GeO$: C, 60.61; H, 11.44. Found: C, 60.31; H, 11.37%.

4.2.4. 1-(Tributylgermyl)undecane (**3d**)

Bp 180 °C (1.3 Torr, bath temp.). IR (neat) 2956, 2924, 2854, 1464 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.65–0.71 (m, 8H), 0.86–0.94 (m, 12H), 1.12–1.52 (m, 30H); ^{13}C NMR ($CDCl_3$) δ 11.86 (CH_2), 12.49 ($CH_2 \times 3$), 13.79 ($CH_3 \times 3$), 14.12 (CH_3), 22.71 (CH_2), 25.23 (CH_2), 26.67 ($CH_2 \times 3$), 27.54 ($CH_2 \times 3$), 29.32 (CH_2), 29.38 (CH_2), 29.67 (CH_2), 29.68 (CH_2), 29.74 (CH_2), 31.95 (CH_2), 33.71 (CH_2); MS *m*/*z* (relative intensity) 343 (M^+ – Bu, 33), 341 (M^+ – 2 – Bu, 21), 339 (M^+ – 4 – Bu, 17), 57 (100). Anal. Calc. for $C_{23}H_{50}Ge$: C, 69.19; H, 12.62. Found: C, 69.29; H, 12.71%.

4.2.5. 1-Butoxy-2-(tributylgermyl)ethane (**3e**)

Bp 130 °C (2 Torr, bath temp.). IR (neat) 2956, 2925, 2854, 1107 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.68–0.74 (m, 6 H), 0.85–0.94 (m, 12H), 1.05–1.12 (m, 2H), 1.28–1.44 (m, 14H), 1.50–1.60 (m, 2H), 3.39 (t, $J = 6.6$ Hz, 2H), 3.45–3.51 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 12.67 ($CH_2 \times 3$), 13.74 ($CH_3 \times 3$), 13.94 (CH_3), 14.21 (CH_2), 19.46 (CH_2), 26.56 ($CH_2 \times 3$), 27.41 ($CH_2 \times 3$), 32.03 (CH_2), 68.65 (CH_2), 70.07 (CH_2); MS *m*/*z* (relative intensity) 289 (M^+ – Bu, 13), 287 (M^+ – 2 – Bu, 9.5), 285 (M^+ – 4 – Bu, 6.9), 261 (100). Anal. Calc. for $C_{18}H_{40}GeO$: C, 62.64; H, 11.68. Found: C, 62.52; H, 11.76%.

4.2.6. Cyclohexyl 3-(tributylgermyl)propanoate (**3f**)

Bp 230 °C (1 Torr, bath temp.). IR (neat) 2927, 2858, 1732 (C=O), 1454, 1200 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.69–0.75 (m, 6H), 0.89 (t, $J = 7.0$ Hz, 9H), 0.96–1.02 (m, 2H), 1.23–1.50 (m, 18H), 1.69–1.90 (m, 4H), 2.26–2.32 (m, 2H), 4.71–4.78 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 7.71 (CH_2), 12.25 ($CH_2 \times 3$), 13.72 ($CH_3 \times 3$), 23.79 ($CH_2 \times 2$), 25.41 (CH_2), 26.57 ($CH_2 \times 3$), 27.35 ($CH_2 \times 3$), 30.47 (CH_2), 31.66 ($CH_2 \times 2$), 72.43 (CH), 174.66 (C); MS *m*/*z* (relative intensity) 261 (M^+ – Bu –C_6H_{10}, 54), 259 (M^+ – 2 – Bu – C_6H_{10}, 44), 257 (M^+ – 4 – Bu – C_6H_{10}, 32). Anal. Calc. for $C_{21}H_{42}GeO_2$: C, 63.19; H, 10.61. Found: C, 63.18; H, 10.76%.

4.2.7. Methyl 3-(tributylgermyl)propanoate (**3g**)

Bp 130 °C (2 Torr, bath temp.). IR (neat) 2956, 2923, 2856, 1741 (C=O), 1464, 1205 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.68–0.76 (m, 6H), 0.89 (t, $J = 6.8$ Hz, 9H), 0.97–1.04 (m, 2H), 1.32 (br s, 12H), 2.32–2.49 (m, 2H), 3.67 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 7.68 (CH_2), 12.22 ($CH_2 \times 3$), 13.72 ($CH_3 \times 3$), 26.56 ($CH_2 \times 3$), 27.33 ($CH_2 \times 3$), 29.92 (CH_2), 51.54 (CH_3), 175.62 (C); MS *m*/*z* (relative intensity) 275 (M^+ – Bu, 100), 273 (M^+ – 2 – Bu, 78), 271 (M^+ – 4 – Bu, 44). Anal. Calc. for $C_{16}H_{34}GeO_2$: C, 58.05; H, 10.35. Found: C, 58.10; H, 10.39%.

4.2.8. 4-(Tributylgermyl)octane (**3h**)

Bp 200 °C (1 Torr, bath temp.). IR (neat) 2956, 2924, 2856, 1464 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.67–0.73 (m, 6H), 0.85–0.91 (m, 15H), 0.97–1.06 (m, 1H), 1.20–1.42 (m, 22H); ^{13}C NMR ($CDCl_3$) δ 12.16 ($CH_2 \times 3$), 13.76 ($CH_3 \times 3$), 14.12 (CH_3), 14.48 (CH_3), 22.22 (CH_2), 23.08 (CH_2), 25.67 (CH), 26.85($CH_2 \times 3$), 27.67 ($CH_2 \times 3$), 30.71 (CH_2), 31.41 (CH_2), 33.51 (CH_2); MS *m*/*z* (relative intensity) 301 (M^+ – Bu, 5.4), 299 (M^+ – Bu – 2, 4.0), 297 (M^+ – Bu – 4, 2.9), 189 (100). Anal. Calc. for $C_{20}H_{44}Ge$: C, 67.25; H, 12.42. Found: C, 67.16; H, 12.79%.

4.2.9. 1-Tributylgermyl-2-(trimethylsiloxy)cyclohexane (**3i**, single isomer)

Bp 230 °C (1 Torr, bath temp.). IR (neat) 2956, 2925, 2871, 1738, 1252 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 9H), 0.65–0.75 (m, 6H), 0.89 (t, $J = 6.9$ Hz, 9H), 1.13–1.81 (m, 21H), 4.03–4.06 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 0.68 ($CH_3 \times 3$), 12.13 ($CH_2 \times 3$), 13.80 ($CH_3 \times 3$), 20.94 (CH_2), 23.78 (CH_2), 26.93 ($CH_2 \times 3$), 27.64 (CH_2), 27.71 ($CH_2 \times 3$), 33.28 (CH), 35.05 (CH_2), 70.31 (CH); MS *m*/*z* (relative intensity) 277 (M^+ – Bu – C_6H_{10}, 47), 275 (M^+ – 2 – Bu – C_6H_{10}, 32), 273 (M^+ – 4 – Bu – C_6H_{10}, 25), 73 (100). Anal. Calc. for $C_{21}H_{46}GeOSi$: C, 60.74; H, 11.16. Found: C, 60.68; H, 11.10%.

4.2.10. 1-Methyl-2-(tributylgermylmethyl)cyclopentane (**6a**, cis:trans = 3:1)

Bp 220 °C (1 Torr, bath temp.). IR (neat) 2954, 2924, 2870, 1462 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.62–0.95 (m, 20H) including 0.80 (d, $J = 9.2$ Hz), 0.88 (t, $J = 7.0$ Hz), and 0.94 (d, $J = 6.1$ Hz), 1.01–1.36 (m, 16H), 1.45–1.95 (m, 4H); ^{13}C NMR ($CDCl_3$) for the major isomer δ 13.09 ($CH_3 \times 3$), 13.51 (CH_2), 13.80 ($CH_2 \times 3$), 14.85 (CH_3), 22.63 (CH_2), 26.77 ($CH_2 \times 3$), 27.57 ($CH_2 \times 3$), 32.33 (CH_2), 33.07 (CH_2), 38.39 (CH), 40.25 (CH), for the minor isomer δ 13.13 ($CH_3 \times 3$), 13.80 ($CH_2 \times 3$), 17.59 (CH_2), 18.72 (CH_3), 23.13 (CH_2), 26.77 ($CH_2 \times 3$), 27.57 ($CH_2 \times 3$), 34.22 (CH_2), 34.92 (CH_2), 44.38 (CH), 45.09 (CH); MS *m*/*z* (relative intensity) for the major isomer 285 (M^+ – Bu, 23), 283 (M^+ – Bu – 2, 15), 281 (M^+ – Bu – 4, 14), 55 (100), for the minor isomer 285 (M^+ – Bu, 17), 283 (M^+ – Bu – 2, 10), 281 (M^+ – Bu – 4, 12), 55 (100). Anal. Calc. for $C_{19}H_{40}Ge$: C, 66.89; H, 11.82. Found: C, 66.59; H, 11.90%.

4.2.11. 1,1-Bis(methoxymethyl)-3-methyl-4-(tributylgermylmethyl)cyclopentane (**6b**, cis:trans = 4:1)

Bp 250 °C (1 Torr, bath temp.). IR (neat) 2954, 2924, 2871, 1458, 1113 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.35–0.95 (m, 20H), 1.15–1.34 (m, 14H), 1.53–1.78 (m, 2.4H), 1.89–2.08 (m, 1.6H), 3.17 (s, 2.4H), 3.24 (br s, 1.6H), 3.33 (s, 6H); ^{13}C NMR ($CDCl_3$) for the major isomer δ 13.00 ($CH_2 \times 3$), 13.41 (CH_2), 13.76 ($CH_3 \times 3$), 15.81 (CH_3),

26.68 ($CH_2 \times 3$), 27.49 ($CH_2 \times 3$), 37.79 (CH), 39.09 (CH), 39.28 (CH_2), 39.79 (CH_2), 46.33 (C), 59.16 ($CH_3 \times 2$), 77.46 (CH_2), 78.79 (CH_2), for the minor isomer δ 13.07 ($CH_2 \times 3$), 13.76 ($CH_3 \times 3$), 16.51 (CH_2), 17.78 (CH_3), 26.68 ($CH_2 \times 3$), 27.49 ($CH_2 \times 3$), 41.34 (CH_2), 41.94 (CH_2), 43.16 (CH), 43.97 (CH), 45.06 (C), 59.16 ($CH_3 \times 2$), 78.05 ($CH_2 \times 2$); MS *m/z* (relative intensity) for the major isomer 373 (M^+ – Bu, 59), 371 (M^+ – Bu – 2, 48), 369 (M^+ – Bu – 4, 37), 45 (100), for the minor isomer 373 (M^+ – Bu, 36), 371 (M^+ – Bu – 2, 25), 369 (M^+ – Bu – 4, 20), 45 (100). Anal. Calc. for $C_{23}H_{48}GeO_2$: C, 64.36; H, 11.27. Found: C, 64.54; H, 11.27%.

4.3. Competitive reaction of alkenes **2b** and **2d**

Under a nitrogen atmosphere, Et_3B (1.0 M in hexane, 0.025 mL, 0.025 mmol) and dry air (2.5 mL) were added to a solution of 1-undecen-3-ol (**2b**, 86 mg, 0.51 mmol), 1-undecene (**2d**, 76 mg, 0.49 mmol) and Bu_2GeClH (**1a**, 129 mg, 0.58 mmol) in hexane (1 mL) at 0 °C. After being stirred for 5 min, the resultant mixture was warmed to room temperature and stirred for 5 h. After then, the mixture was treated with BuLi (1.60 M in hexane, 0.75 mL, 1.2 mmol) and stirred for 10 min. The mixture was poured into saturated aqueous NH_4Cl (10 mL). The extract with *t*-BuOMe (3×10 mL) was dried over Na_2SO_4 and evaporated. Purification of the crude product by silica gel column chromatography gave 1-tributylgermyl-3-undecanol (**3b**, 54 mg, 0.13 mmol, 26%) and 1-(tributylgermyl)undecane (**3d**, 87 mg, 0.22 mmol, 44%).

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References

[1] (a) G. Wilkinson, G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry I, vol. 2, Pergamon, Oxford, 1982 (Chapters 9.1, 10, and 11);
(b) G. Wilkinson, G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry II, vol. 2, Pergamon, Oxford, 1995 (Chapters 1, 5, and 6).

[2] (a) J. Pietruszka, in: I. Fleming (Ed.), Science of Synthesis, vol. 4, Thieme, Stuttgart, Germany, 2001, p. 159 (Chapter 4.4.4);
(b) K. Oshima, in: M. Moloney (Ed.), Science of Synthesis, vol. 5, Thieme, Stuttgart, Germany, 2002, p. 9 (Chapter 5.1.1);
(c) A.J. Clark, in: M. Moloney (Ed.), Science of Synthesis, vol. 5, Thieme, Stuttgart, Germany, 2002, p. 205 (Chapter 5.2.1).

[3] (a) M.A. Brook, Silicon in Organic, Organometallic, and Polymer Chemistry, Wiley Interscience, New York, 2000, p. 401;
(b) A.G. Davies, Organotin Chemistry, Wiley-VCH, Weinheim, 2004, p. 54.

[4] (a) B. Kopping, C. Chatgilialoglu, M. Zehnder, B. Giese, J. Org. Chem. 57 (1992) 3994;
(b) C. Chatgilialoglu, Acc. Chem. Res. 25 (1992) 188;
(c) . A related work:C. Chatgilialoglu, M. Guerra, A. Guerrini, G. Seconi, J. Org. Chem. 57 (1992) 2427.

[5] (a) S. Tanaka, T. Nakamura, H. Yorimitsu, H. Shinokubo, K. Oshima, Org. Lett. 2 (2000) 1991;
(b) T. Nakamura, S. Tanaka, H. Yorimitsu, H. Shinokubo, K. Oshima, C.R. Acad. Sci. Paris, Chimie 4 (2001) 461.

[6] W.P. Neumann, J. Pedain, Tetrahedron Lett. (1964) 2461.

[7] (a) K. Miura, H. Saito, S. Uchinokura, A. Hosomi, Chem. Lett. (1999) 659;
(b) K. Miura, D. Wang, Y. Matsumoto, N. Fujisawa, A. Hosomi, J. Org. Chem. 68 (2003) 8730;
(c) K. Miura, D. Wang, Y. Matsumoto, A. Hosomi, Org. Lett. 7 (2005) 503;
(d) K. Miura, D. Wang, A. Hosomi, Synlett (2005) 406;
(e) K. Miura, D. Wang, A. Hosomi, J. Am. Chem. Soc. 127 (2005) 9366.

[8] For radical reduction and addition of haloalkanes using **1a** and **1b**, see: K. Miura, K. Ootsuka, A. Hosomi, Synlett (2005) 3151.

[9] (a) J. Satge, Ann. Chim. 6 (1961) 519;
(b) K. Mochida, I. Miyagawa, Bull. Chem. Soc. Jpn. 56 (1983) 1875.

[10] For the last step, see: J. Ohshita, Y. Toyoshima, A. Iwata, H. Tang, A. Kunai, Chem. Lett. (2001) 886.

[11] It is known that Et_3B-dry air effectively initiates homolytic hydrogermylation and hydrostannylation under mild conditions. See Ref. [5] and references therein. For this reason, we selected Et_3B-dry air as radical initiator.

[12] The butylation was performed only for the ease of isolation and characterization of the hydrogermylation products in the atmosphere.

[13] The successful addition to less reactive internal alkenes under solvent-free conditions seems only due to rate-acceleration of the intermolecular reaction by increased concentration of the reactants.

[14] Bond dissociation enthalpies of C–M bond in Me_4M are *ca.* 340 (M = Ge) and 300 (M = Sn) kJ/mol J.A.M. Simões, J.F. Liebman, S.W. Sladen, in: S. Patai (Ed.), The Chemistry of Organic Germanium, Tin, and Lead Compounds, Wiley, Chichester, 1995, p. 245 (Chapter 4).

[15] D.P. Curran, N.A. Porter, B. Giese, Stereochemistry of Radical Reactions, VCH, Weinheim, 1995, p. 38.