Regioselective Preparation of Allylgermanes

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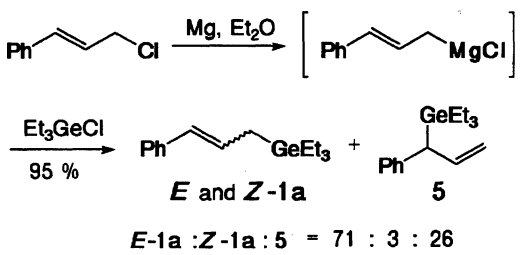
Allylgermanes were obtained by the reaction of allyl acetates with bis(triethylgermyl)cuprate(I) reagent in high yields. It was found that the present reaction proceeded with high regioselectivity, in which a triethylgermyl group was exclusively introduced to the less substituted side of an allylic system regardless of the original location of acetoxyl group. In the case of the allyl acetates possessing two secondary centers at the both ends of the allylic system, the formal S_N2 product was preferentially produced ($S_N2 : S_N2' =$ ca. 9 : 1). The desulfurizative germylation of allyl phenyl sulfides utilizing bis(triethylgermyl)cuprate(I) reagent also proceeded to give allylgermanes in good yields with the same regioselectivity.

In the last decade, many synthetic methods utilizing organometallic compounds containing group 14 elements, such as silicon and tin, have been developed, and they enable us to synthesize various target molecules regio- and stereoselectively. For example, allylsilanes have been employed as reagents for the allylation of a variety of electrophiles, such as aldehydes,[1] acetals,[2] epoxides,[3] and other substrates.[4] Allylstannanes are found to be excellent nucleophiles for the cross-coupling reactions with activated halides,[5] acetals,[6] and thioacetals.[7] The addition of allylstannanes to various carbonyl compounds were also examined,[8] the best known example of which would be the regioselective addition to aldehydes catalyzed by boron trifluoride etherate.[9] Furthermore, the various synthetic reactions utilizing allylstannanes as electrophiles have been developed by us.[10]

In contrast with allylsilanes and stannanes, little has been known about the reactivity and synthetic utility of allylgermanes.[11] Although the reactions of allylmagnesium or allyllithium compounds with trialkylgermyl halides[12,13] and the hydrogermylation of dienes[14] afford allylgermanes, it is apparent that the lack of appropriate preparative methods is one of the obstacles to progress in the chemistry of allylgermanes. Then we have studied the new routes to substituted allylgermanes, and describe here the regioselective preparation of allyltriethylgermanes (**1**) by the reactions of allyl acetates (**2**) and sulfides (**3**) with bis(triethylgermyl)cuprate(I) reagent (**4**).

Results and Discussion

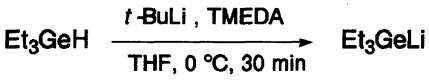
Preparation of Cinnamyltriethylgermane (1a) from Cinnamyl Chloride. It is well-known that the general routes to organogermanium compounds are the reactions of organometallic species with germyl halides and the reactions of anionic complexes of organogermane with alkyl halides.[15] As for the synthesis of allylgermanes, Roberts and Kaissi reported that cinnamylgermane (**1a**) was obtained by the reaction of triethylgermyl chloride with the corresponding Grignard reagent prepared *in situ* from cinnamyl chloride in 30% yield.[12] However, they did not describe the regioselectivity of the reaction in detail. Therefore, we reinvestigated the reaction. As shown in the following scheme, it was found that the allylgermane thus prepared was a mixture of (*E* and *Z*)-**1a** and its regioisomer, 3-phenyl-3-triethylgermyl-1-propene (**5**).



(1)

To the best of our knowledge, the alternative route which consists of the reaction of trialkylgermylmetal species with allylic halides has not yet been investigated. To evaluate the synthetic utility of the process, we examined the reaction of cinnamyl chloride with triethylgermyllithium and bis(triethylgermyl)cuprate(I) reagent (**4**).

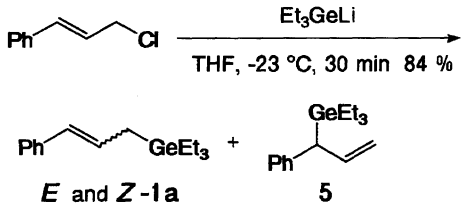
Concerning the preparation of trialkylgermyllithium, the reaction of trimethylgermyl chloride with lithium in the presence of hexamethylphosphoric triamide (HMPA)[16] and the metallation of triethylgermane with phenyllithium or butyllithium in ethereal solvents[17] were reported. Unfortunately, however, we failed to prepare triethylgermyllithium in good yield by all these methods. After several attempts, we found that triethylgermyllithium was prepared quantitatively by the treatment of triethylgermane with *t*-butyllithium in the presence of N,N,N′,N′-tetramethylethylenediamine (TMEDA) in THF (Eq. 2).



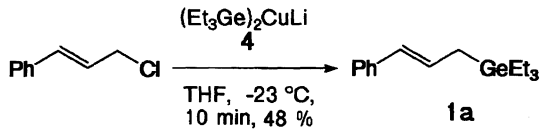
(2)

Although the reaction of cinnamyl chloride with triethylgermyllithium thus prepared gave the substituted product in good yield, the product was also found to

be a mixture of (*E* and *Z*)-**1a** and **5** (Eq. 3). On the other hand, **1a** was obtained with high regioselectivity when cinnamyl chloride was treated with bis(triethylgermyl)cuprate(I) reagent (**4**) prepared by the reaction of copper(I) iodide with twice molar amounts of triethylgermyllithium in THF at 0°C. The yield, however, was insufficient as a preparative method (Eq. 4).



(3)

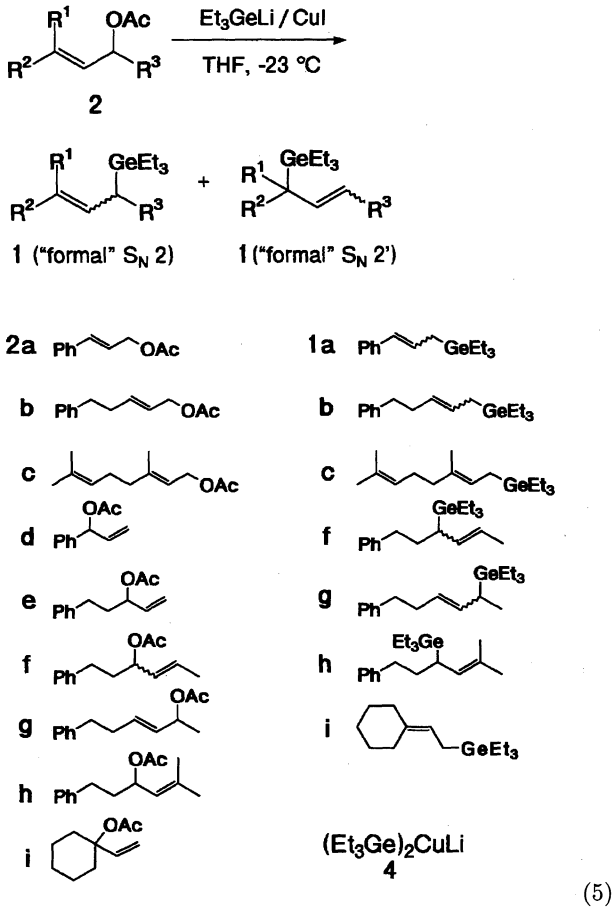


(4)

Since conversion of allylic alcohols to the corresponding halides is sometimes complicated by allylic rearrangement and the stereochemical relationship of the alcohol to the halide is frequently uncertain, we did not examined the preparation of allylgermanes (**1**) utilizing allylic halides further. Then the preparation of **1** by the treatment of allylic acetates, which were easily prepared by acetylation of alcohols with retention of configuration, with the germylcopper species was examined.

Preparation of 1 Using Allyl Acetates (2). Previously, we showed that allylstannanes were obtained by the reaction of allyl sulfides with tributylstannyllithium in the presence of copper(I) bromide in good yields.[18] In this reaction, a tributylstannyl group is introduced with excellent regioselectivity except for the reaction of α,γ-disubstituted allyl sulfides. Then we first examined the preparation of allylgermanes (**1**) by the treatment of **2** with triethylgermyllithium in the presence of copper(I) salt (Eq. 5).

When 3-acetoxy-5-phenyl-1-pentene (**2e**) was treated with 1.1 equivalents of triethylgermyllithium in the presence of a catalytic amount of copper(I) iodide in THF at −23°C, the corresponding allylgermane (**1b**) was selectively produced in 56% yield without formation of the corresponding regioisomer (Run 2 in Table 1). As shown in Table 1, the optimum amounts of copper(I) iodide and triethylgermyllithium were found to be 1 equivalent and 2 equivalents, respectively (Run 5). These results suggested that the active species formed in the present reaction would be bis(triethylgermyl)cuprate(I) reagent (**4**), similarly to the preparation of allylsilanes by the reaction of allyl acetates with bis(dimethylphenylsilyl)cuprate(I) reagent reported by Fleming et al.[19] In fact, the allylgermane (**1a**) was obtained in a similar yield when **2a** was treated with preformed **4** (Run 8).



(5)

In a similar manner, various allylgermanes (**1**) were prepared by the reaction of substituted allyl acetates (**2**) with the cuprate (**4**) in high yields (Table 2). In the reactions of primary allyl acetates (**2a**, **b**, and **c**), allyl-

Table 1. The Effect of Amounts of Copper(I) Iodide in the Reaction of Triethylgermyllithium with 3-Acetoxy-5-phenyl-1-pentene (**2e**)

Run	CuI equiv	Et_3GeLi equiv	Time h	Procedure[a]	Yield of **1b** % (Recovered **2e**)
1	0	1.1	Overnight	—	0 (53)[b]
2	0.1	1.1	Overnight	A	56 (37)
3	0.2	1.2	5.5	A	52 (44)
4	0.5	1.5	Overnight	A	76 (17)
5	0.8	1.8	Overnight	A	91
6	1.0	2.0	1.0	A	92
7	1.0	1.0	2.5	B	48 (51)
8	1.0	2.0	0.5	B	94

a) See experimental section. b) The allyl alcohol was obtained in 41% yield.

Table 2. The Reaction of Allyl Acetates (**2**) with Bis-(triethylgermyl)cuprate(I) Reagent (**4**)[a]

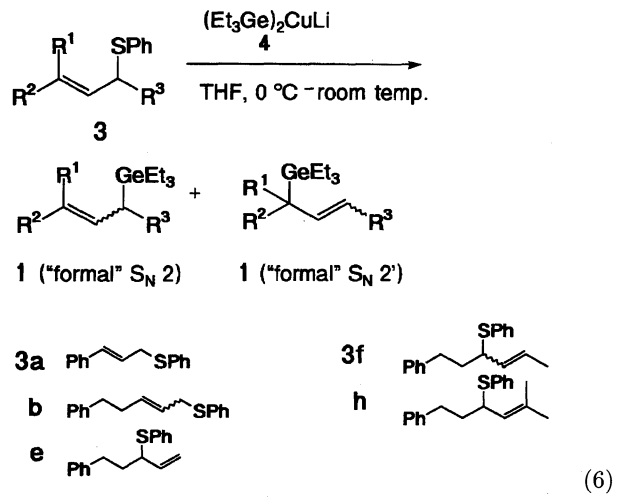
Run	2	Temp °C	Time h	1	Yield %
1	**2a**	−23	0.5	(*E*)-**1a**	95
2	**2b**	−23	0.5	(*E*)-**1b**	93
3	**2c**	−23	0.5	(*E*)-**1c**	80
4	**2d**	−23	0.8	(*E*,*Z*)-**1a**	97
5	**2e**	−23	0.5	(*E*,*Z*)-**1b**	94
6	**2f**	−23	0.5	(*E*,*Z*)-**1f**, (*E*,*Z*)-**1g**[b] (**1f** : **1g** = 92 : 8)	92
7	**2g**	−23	0.5	(*E*,*Z*)-**1f**, (*E*,*Z*)-**1g**[b] (**1f** : **1g** = 9 : 91)	85
8[c]	**2h**	−78	Overnight	**1h**	92
9	**2i**	−23	0.5	**1i**	96

a) All the reactions were performed with the similar procedure as described in the text, unless otherwise noted. b) The ratio of regioisomers was determined by ^{1}H NMR spectrum. c) Two equiv of **4** were used.

germanes (**1a**, **b**, and **c**), which resulted by the attack of **4** at the α-position to acetoxyl group, were obtained (Runs 1, 2, and 3). Furthermore, it was confirmed by NMR spectra of the products that the stereochemistry of the starting allyl acetates was retained through the reaction. On the other hand, the formal S_N2' products were exclusively produced when the allyl acetates (**2d**, **e**, and **i**) which possessed one substituent or two at the carbon atom α to acetoxyl group were employed (Runs 4, 5, and 9). However, these products were found to be the mixtures of *E*- and *Z*-isomers (see Run 4). What is interesting is a fact that the reactions of the allyl acetates (**1f** and **g**) possessing two secondary centers at the both ends of the allylic system gave the formal S_N2 products with high regioselectivity (Runs 6 and 7).

Desulfurizative Germylation of Allyl Sulfides (3). It is well-known that the alkylation of allyl sulfides proceeds with high regioselectivity. Therefore, the preparation of allylgermanes from substituted allyl sulfides is of special synthetic value. Ueno et al. reported the azobisisobutyronitrile- or di-*t*-butyl peroxide-initiated desulfurizative germylation of allyl sulfur compounds with triphenylgermane.[11a] However, they examined a limited number of compounds which all possessed a structure of terminal olefin, and their products were ones which formed with an allylic rearrangement. Then we next examined the desulfrizative germylation of allyl phenyl sulfide (**3**) with **4** (Eq. 6, Table 3).

As noted above, the desulfurizative stannylation using tributylstannyllithium proceeds in the presence of copper(I) bromide. On the contrary, the copper(I) bromide-catalyzed reaction of **3h** with triethylgermyllithium under the similar reaction conditions gave the corresponding allylgermane (**1h**) only in a poor or moderate yield (Runs 6 and 7). As was observed in the reaction of allyl acetates (**2**), the use of **4** also remarkably increased the yield of **1h** (Run 5).



(6)

The results listed in Table 3 show that the regioselectivity of the present reaction is identical with that of the reaction using allyl acetates (**2**). Although the desulfurizative stannylation of the α,γ-disubstituted allyl sulfide proceeds without regioselectivity,[18] the desulfurizative germylation of the similar substrate (**3f**) gave the allylgermane (**1f**) regioselectively. The reason for the difference of regioselectivity between these reactions is uncertain at present.

In conclusion, it should be noted that present reactions provide the most convenient and regioselective methods for the preparation of highly substituted allyltrialkyl germanes.

Experimental

General. ^{1}H NMR spectra (200 MHz) and ^{13}C NMR

Table 3. The Desulfurizative Germylation of Allyl Sulfides (**3**)[a]

Run	3	Product (1)	Yield % (Recovered **3**)
1	**3a**	(*E*)-**1a**	71 (5)
2	**3b**	(*E*,*Z*)-**1b**	86 (8)
3	**3e**	(*E*,*Z*)-**1b**	77 (16)
4	**3f**	(*E*,*Z*)-**1f**, (*E*,*Z*)-**1g**[b] (**1f** : **1g** = 89 : 11)	73 (19)
5[c]	**3h**	**1h**	60 (12)
6[d]	**3h**	**1h**	9
7[e]	**3h**	**1h**	40 (44)

a) All the reactions were performed with the similar procedure as described in the text, unless otherwise noted. b) The ratio of regioisomers was determined by ^{1}H NMR spectrum. c) Two equiv of **4** were used. d) The reaction was carried out using 0.1 equiv of CuBr and 4.0 equiv of Et_3GeLi in the presence of HMPA (1.6 ml/1 mmol of **3h**) in THF (5 ml/1 mmol of **3h**) at 0°C overnight. e) The reaction was carried out using 2.0 equiv of CuBr and 4.0 equiv of Et_3GeLi under the same conditions employed in Run 6.

spectra (50.1 MHz) were recorded on a JEOL JNM-FX200 spectrometer using deuteriochloroform as a solvent with tetramethylsilane as an internal standard. IR spectra were measured with JASCO A-100 spectrometer. Short-path distillations of products were carried out in a Kugelrohr apparatus. All reactions were carried out under argon. Allyl acetates (**2**) were prepared by the acetylation of corresponding alcohols by the method reported by Steglich et al.[20] Cinnamyl phenyl sulfide (**3a**) and 5-phenyl-2-pentenyl phenyl sulfide (**3b**) were prepared by the reaction of potassium benzenethiolate with cinnamyl chloride and 5-phenyl-2-pentenyl bromide, respectively.[21] Allyl sulfides (**3e**, **3f**, and **3h**) were prepared by the reaction of phenethyl bromide with the lithium salts of allyl, crotyl, and 3-methyl-2-butenyl phenyl sulfides, respectively.[22] Triethylgermane was prepared by the method reported by Sakurai et al.[23]

Preparation of Cinnamyltriethylgermane (1a) by the Reaction of Cinnamylmagnesium Chloride with Triethylgermyl Chloride. To magnesium turnings (1.57 g, 0.0647 g. atom) in ether (21 ml), a small piece of iodine and a few drops of cinnamyl chloride was added successively. After the color of iodine disappeared, an ethereal (10 ml) solution of cinnamyl chloride (0.797 g, 5.2 mmol) and triethylgermyl chloride (0.816 g, 4.2 mmol) was added dropwise to the reaction mixture. After being stirred overnight, the reaction was quenched by addition of a saturated NH_4Cl aqueous solution. The organic material was extracted with ether, dried (Na_2SO_4), and condensed under reduced pressure. The purification of the residue by flash chromatography (silica gel, hexane) gave a mixture of (*E* and *Z*)-cinnamyltriethylgermane (**1a**) and 3-phenyl-3-triethylgermyl-1-propene (**5**) (***E*-1a** : ***Z*-1a** : **5**=71 : 3 : 26) (1.103 g, 95%); an oil; IR (neat) 3036, 2958, 2924, 2890, 1642, 1603, 1459, 957, 733, and 696 cm^{-1}; ^1H NMR δ=0.65—0.88 (6H, m), 0.91—1.12 (9H, m), 1.83 (1.42H, d, J=7.2 Hz), 2.00 (0.06H, d, J=9.1 Hz), 3.28 (0.26H, d, J=11.0 Hz), 4.88 (0.26H, d, J=8.3 Hz), 4.94 (0.26H, d, J=15.9 Hz), 6.12—6.41 (1.74H, m), and 6.99—7.38 (5H, m); ^{13}C NMR δ=3.44, 4.20, 4.36, 8.89, 8.93, 18.49, 42.13, 111.06, 124.43, 125.46, 126.08, 126.86, 127.37, 128.34, 128.44, 129.20, 138.65, 139.02, and 143.21.

Preparation of Triethylgermyllithium. To a THF (1 ml) solution of triethylgermane (161 mg, 1.0 mmol) and TMEDA (0.17 ml, 1.1 mmol) was added a pentane solution of *t*-butyllithium (0.70 ml, 1.1 mmol) at 0°C. After being stirred for 30 min at the same temperature, the resultant solution of triethylgermyllithium was used for the subsequent reactions.

Preparation of Cinnamyltriethylgermane (1a) by the Reaction of Cinnamyl Chloride with Triethylgermyllithium. To a THF solution of triethylgermyllithium (0.5 mmol) was added a THF (1 ml) solution of cinnamyl chloride (83 mg, 0.5 mmol) at −23°C. After being stirred for 1 h, the reaction was quenched by addition of a phosphate buffer solution (pH 7). The organic material was extracted with ether. The ethereal layer was washed with 3.5% aqueous NH_3 solution and water successively and dried (Na_2SO_4). After evaporation of solvent, the residue was purified by preparative TLC (silica gel, hexane) and a mixture of (*E* and *Z*)-**1a** and **5** (***E*-1a** : ***Z*-1a** : **5**=53 : 1 : 46) (116 mg, 84%) was obtained.

The reaction of cinnamyl chloride with bis(triethylgermyl)cuprate reagent (**4**) was carried out according to the procedure B described below.

Preparation of 5-Phenyl-1-triethylgermyl-2-pentene (1b) Using 3-Acetoxy-5-phenyl-1-pentene (2e). Procedure A: To a THF (3 ml) suspension of CuI (95 mg, 0.5 mmol) and 3-acetoxy-5-phenyl-1-pentene (**2e**) (102 mg, 0.5 mmol) was added a THF solution of triethylgermyllithium (1.0 mmol) at −23°C. The resulting solution was stirred for 1 h at the same temperature. Then the reaction was quenched by addition of a phosphate buffer solution (pH 7). The usual work-up described above gave a mixture of (*E* and *Z*)-5-phenyl-1-triethylgermyl-2-pentene (**1b**) (141 mg, 92%); bp 150°C/0.7 mmHg (1 mmHg=133.322 Pa); IR (neat) 3028, 2940, 2886, 1643, 1608, 1458, 969, 728, and 698 cm^{-1}; ^1H NMR δ=0.73 (6H, q, J=7.7 Hz), 1.01 (9H, t, J=7.7 Hz), 1.57 and 1.62 (2H, 2d, J=8.1 Hz, and J=9.5 Hz), 2.29 and 2.33 (2H, 2q, J=7.2 Hz and J=7.5 Hz), 2.64 and 2.65 (2H, 2t, J=7.8 Hz and J=7.8 Hz), 5.16—5.36 (1H, m), 5.38—5.57 (1H, m), and 7.09—7.34 (5H, m); ^{13}C NMR δ=3.93, 4.16, 8.95, 12.98, 16.97, 29.03, 34.56, 36.18, 36.57, 125.64, 125.71, 127.00, 127.33, 128.20, 128.26, 128.44, 142.25, and 142.39. Found: C, 66.93; H, 9.27%. Calcd for $C_{17}H_{28}Ge$: C, 66.94; H, 9.25%.

Procedure B: To a suspension of CuI (95 mg, 0.5 mmol) in THF (2 ml) was added a THF solution of triethylgermyllithium (1.0 mmol) at 0°C, and the reaction mixture was stirred for 10 min. After the resulting dark red solution was cooled to −23°C, **2e** (102 mg, 0.5 mmol) in THF (1 ml) was added to the solution. The mixture was stirred for 30 min and then quenched by addition of a phosphate buffer solution (pH 7). The usual work-up described above gave **1b** (143 mg) in 94% yield.

According to procedure B, various allylgermanes (**1**) were synthesized from the corresponding allyl acetates (**2**).

(*E*)-1-Phenyl-3-triethylgermyl-1-propene (1a); bp 130°C/2 mmHg; IR (neat) 3034, 2948, 2922, 2886, 1640, 1599, 1457, 957, 732, and 690 cm^{-1}; ^1H NMR δ=0.78 (6H, q, J=7.7 Hz), 1.05 (9H, t, J=7.7 Hz), 1.84 (2H, d, J=7.1 Hz), 6.17—6.40 (2H, m), and 7.07—7.32 (5H, m); ^{13}C NMR δ= 4.13, 8.93, 18.43, 125.42, 126.04, 127.25, 128.44, 129.24, and 138.60. Found: C, 65.21; H, 8.76%. Calcd for $C_{15}H_{24}Ge$: C, 65.05; H, 8.73%.

(*E*)-5-Phenyl-1-triethylgermyl-2-pentene (1b); an oil; IR (neat) 3044, 2956, 2892, 1661, 1609, 1458, 964, 733, and 697 cm^{-1}; ^1H NMR δ=0.69 (6H, q, J=7.7 Hz), 0.99 (9H, t, J=7.7 Hz), 1.56 (2H, d, J=7.8 Hz), 2.41 (2H, q, J=7.2 Hz), 2.64 (2H, t, J=7.8 Hz), 5.28 (1H, dt, J=15.2 and 7.8 Hz), 5.47 (1H, dt, J=15.2 and 7.2 Hz), and 7.06—7.32 (5H, m); ^{13}C NMR δ=3.95, 8.91, 16.99, 34.54, 36.59, 125.64, 127.02, 128.18, 128.22, 128.46, and 142.27.

(*E*)-3,7-Dimethyl-1-triethylgermyl-2,6-octadiene (1c); bp 100°C/3 mmHg; IR (neat) 2950, 2884, 1661, 1457, 1380, 969, and 703 cm^{-1}; ^1H NMR δ=0.72 (6H, q, J=7.7 Hz), 1.01 (9H, t, J=7.7 Hz), 1.57 (3H, S), 1.60 (3H, S), 1.52—1.63 (2H, m), 1.67 (3H, d, J=1.0 Hz), 1.89—2.16 (4H, m), 5.01—5.14 (1H, m), and 5.22 (1H, t, J=8.6 Hz); ^{13}C NMR δ=4.24, 8.97, 13.17, 15.68, 17.67, 25.69, 26.97, 40.05, 121.53, 124.76, 131.03, and 131.36. Found: C, 64.24; H, 10.78%. Calcd for $C_{16}H_{32}Ge$: C, 64.70; H, 10.86%.

(*E* and *Z*)-1-Phenyl-3-triethylgermyl-1-propene (1a); an oil; IR (neat) 3032, 2960, 2894, 1637, 1607, 1455, 961, 736, and 698 cm^{-1}; ^1H NMR δ=0.63—0.84 (6H, m), 0.89—1.12 (9H, m), 1.84 (0.98H, d, J=7.3 Hz), 2.00 (1.02H,

dd, J=9.5 and 1.0 Hz), 5.76 (0.51H, dt, J=11.5 and 9.5 Hz), 6.14—6.42 (1.49H, m), and 7.05—7.36 (5H, m); ^{13}C NMR δ=4.20, 4.38, 8.87, 8.93, 14.58, 18.49, 125.46, 125.87, 125.93, 126.08, 127.37, 128.11, 128.46, 128.63, 129.24, 130.36, 138.38, and 138.67.

(*E* and *Z*)-6-Phenyl-4-triethylgermyl-2-hexene (1f) contaminated by (*E* and *Z*)-1-Phenyl-5-triethylgermyl-3-hexene (1g) (1f : 1g=92 : 8); bp 128°C/2 mmHg; IR (neat) 3048, 2970, 2896, 1661, 1610, 1460, 968, 746, and 698 cm^{-1}; ^{1}H NMR δ=0.72 (6H, q, J=7.7 Hz), 0.98 (9H, t, J=7.7 Hz), 1.11 (0.24H, d, J=7.3 Hz), 1.69 (2.76H, d, J=4.9 Hz), 1.61—1.95 (2.84H, m), 2.22—2.85 (2.16H, m), 5.17—5.62 (2H, m), and 7.07—7.33 (5H, m); ^{13}C NMR δ= 2.82, 3.06, 9.05, 9.09, 15.18, 17.98, 18.06, 31.27, 32.65, 32.69, 34.74, 35.83, 36.66, 121.68, 124.12, 125.52, 125.62, 128.20, 128.50, 133.44, 135.03, and 142.94. Found: C, 67.71; H, 9.54%. Calcd for $C_{18}H_{30}Ge$: C, 67.76; H, 9.48%.

(*E* and *Z*)-1-Phenyl-5-triethylgermyl-3-hexene (1g) Contaminated by (*E* and *Z*)-6-Phenyl-4-triethylgermyl-2-hexene (1f) (1g : 1f=91 : 9); an oil; IR (neat) 3044, 2954, 2894, 1610, 1460, 969, 744, and 700 cm^{-1}; ^{1}H NMR δ=0.70 (6H, q, J=7.7 Hz), 1.01 (9H, t, J=7.7 Hz), 1.11 (2.73H, d, J=7.3 Hz), 1.69 (0.27H, d, J=4.9 Hz), 1.65—2.00 (1.18H, m), 2.31 (1.82H, q, J=5.8 Hz), 2.65 (1.82H, t, J=7.8 Hz), 2.22—2.82 (0.18H, m), 5.12—5.43 (1.09H, m), 5.55 (0.91H, dd, J=15.5 and 7.8 Hz), and 7.07—7.32 (5H, m); ^{13}C NMR δ=2.88, 3.13, 9.13, 15.22, 18.02, 24.62, 31.33, 32.69, 34.72, 35.85, 36.70, 121.70, 124.18, 125.54, 125.64, 128.22, 128.48, 133.48, 135.05, 142.31, and 142.96.

2-Methyl-6-phenyl-4-triethylgermyl-2-hexene (1h); bp 150°C/2 mmHg; IR (neat) 3046, 2934, 2892, 1607, 1459, 966, 741, and 697 cm^{-1}; ^{1}H NMR δ=0.70 (6H, q, J=7.7 Hz), 0.97 (9H, t, J=7.7 Hz), 1.51—1.91 (2H, m), 1.54 (3H, d, J=1.5 Hz), 1.73 (3H, s), 2.05 (1H, td, J=11.5 and 3.3 Hz), 2.39 (1H, ddd, J=13.5, 9.3, and 7.3 Hz), 2.71 (1H, ddd, J=13.5, 8.9, and 4.8 Hz), 5.03 (2H, d, J=11.5 Hz), and 7.07—7.38 (5H, m); ^{13}C NMR δ=3.09, 9.13, 18.25, 25.88, 27.22, 33.72, 36.04, 125.46, 127.46, 127.87, 128.14, 128.55, and 142.88. Found: C, 68.73; H, 9.72%. Calcd for $C_{19}H_{32}Ge$: C, 68.52; H, 9.68%.

[2-(Triethylgermyl)ethylidene]cyclohexane (1i); bp 105°C/3 mmHg; IR (neat) 2948, 2894, 1667, 1451, 970, 782, and 721 cm^{-1}; ^{1}H NMR δ=0.72 (6H, q, J=7.7 Hz), 1.00 (9H, t, J=7.7 Hz), 1.41—1.53 (6H, m), 1.57 (2H, d, J=8.8 Hz), 1.99—2.16 (4H, m), and 5.13 (1H, tt, J=8.8 and 1.0 Hz); ^{13}C NMR δ=4.07, 9.01, 12.20, 27.17, 27.67, 28.30, 28.82, 37.38, 118.07, and 135.93. Found: C, 62.04; H, 10.44%. Calcd for $C_{14}H_{28}Ge$: C, 62.51; H, 10.49%.

Desulfurizative Germylation of 5-Phenyl-3-phenylthio-1-pentene (3e) with Bis(triethylgermyl)-cuprate Reagent (4). To a stirred solution of bis(triethylgermyl)cuprate reagent (**4**) (0.5 mmol, see Procedure B) was added a THF solution of 5-phenyl-3-phenylthio-1-pentene (**3e**) (127 mg, 0.5 mmol) at 0°C. The mixture was stirred overnight at room temperature and quenched by addition of a phosphate buffer solution (pH 7). The usual work-up described above gave 5-phenyl-1-triethylgermyl-2-pentene (**1b**) (131 mg) in 86% yield; IR, ^{1}H NMR, and ^{13}C NMR spectra were the identical with ones given above.

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