# Triethylborane Induced Stereoselective Radical Addition of $R_3SiH$ to Acetylenes and Stereoselective Reduction of Alkenyl Iodides with Tris(trimethylsilyl)silane

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Triethylborane induced radical addition of various organosilanes ($R_3SiH$) to acetylenes has been studied. Among them, tris(trimethylsilyl)silane (TTMSS) proved to be the best reagent for the hydrosilylation of acetylenic compounds in terms of yield and stereoselectivity. For instance, reaction of 1-dodecyne with TTMSS at room temperature for 3 h under $Et_3B$ catalyst provided (*Z*)-1-tris(trimethylsilyl)silyl-1-dodecene selectively in 98% yield. The stereochemical course of reduction of alkenyl iodides with TTMSS–$Et_3B$ or *n*-$Bu_3SnH$–$Et_3B$ has been examined. Treatment of 1-dimethylphenylsilyl-2-iodo-1-dodecene with TTMSS–$Et_3B$ at room temperature afforded (*Z*)-1-dimethylphenylsilyl-1-dodecene selectively ($Z/E>30/1$). On the other hand, treatment with *n*-$Bu_3SnH$-$Et_3B$ gave (*E*)-1-dimethylphenylsilyl-1-dodecene exclusively.

**(1) Triethylborane Induced Stereoselective Radical Addition of $R_3SiH$ to Carbon–Carbon Triple Bonds.** Transition metal catalyzed hydrosilylation of acetylenes has been extensively studied and widely used for the preparation of alkenylsilanes.[1] In contrast, the synthetic use of hydrosilylation reaction catalyzed by various radical initiators such as peroxides and AIBN has serious limitations. Low stereoselectivity of the reaction is one of difficult problems. In addition, the choice of hydrosilanes is limited to silanes such as $Cl_3SiH$, $MeCl_2SiH$, and $Ph_3SiH$ because trialkylsilanes ($Me_3SiH$ and $Et_3SiH$) can not donate hydrogen to alkenyl radicals efficiently.[2]

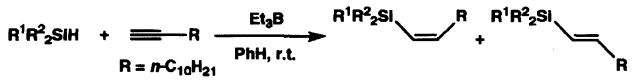
We have reported that $Et_3B$ facilitates the addition of $Ph_3SnH$[3] or $Ph_3GeH$[4] to acetylenes in the presence of oxygen. Hydrostannylation of 1-dodecyne with $Ph_3SnH$–$Et_3B$ provided a 7/3—8/2 mixture of (*E*)- and (*Z*)-1-triphenylstannyl-1-dodecene irrespective of the reaction conditions.[3] In contrast, $Et_3B$ induced hydrogermylation of 1-dodecyne with $Ph_3GeH$ gave (*E*)- or (*Z*)-1-triphenylgermyl-1-dodecene with excellent control of stereochemistry under equilibrating conditions or non-equilibrating conditions.[4] Whereas the reaction at −78 °C afforded (*Z*)-1-triphenylgermyl-1-dodecene exclusively, the addition at 60 °C provided (*E*)-1-triphenylgermyl-1-dodecene as a single product. Here we wish to report that $Et_3B$ mediated hydrosilylation of carbon–carbon triple bonds with a variety of organosilanes ($R_3SiH$) and that treatment of terminal acetylenes with tris(trimethylsilyl)silane (TTMSS)[5] in the presence of a catalytic amount of $Et_3B$ gave (*Z*)-1-tris(trimethylsilyl)silyl-1-alkenes with high stereoselectivity.

Triethylborane induced hydrosilylation of acetylenes with $Ph_3SiH$ proceeded very sluggishly as compared to hydrogermylation with $Ph_3GeH$ and hydrostannylation with $Ph_3SnH$. Stirring a hexane solution of 1-dodecyne (1.0 mmol) and $Ph_3SiH$ (2.0 mmol) in the presence of $Et_3B$ (2.0 mmol) at room temperature for 88 h gave a mixture of (*Z*)- and (*E*)-1-triphenylsilyl-1-dodecene only in 42% yield ($Z/E=12/1$). Then, hydrosilylation of 1-dodecyne was examined using various silanes such as $Ph_2SiH_2$, $Me_3SiSiPh_2H$, $(Me_3Si)_2SiPhH$, and $(Me_3Si)_3SiH$ (TTMSS). Reaction of each silane with 1-dodecyne at room temperature in the presence of $Et_3B$ provided the corresponding hydrosilylation products in poor to excellent yields. The results are shown in Table 1. The reaction with $Ph_2SiH_2$ was as slow as the hydrosilylation with $Ph_3SiH$ and gave alkenylsilane in low yield in spite of the use of excess amount of silane and $Et_3B$ even after prolonged reaction time (70—75 h). Substitution of phenyl group of $Ph_3SiH$ by trimethylsilyl group facilitated the free-radical hydrosilylation. Treatment of 1-dodecyne with $Me_3SiSiPh_2H$ or $(Me_3Si)_2SiPhH$ provided 1-[diphenyl(trimethylsilyl)silyl]-1-dodecene or 1-[bis(trimethylsilyl)phenylsilyl]-1-dodecene in good yield with high stereoselectivity ($Z/E=15/1$ or 16/1). TTMSS proved to be the best reagent and afforded (*Z*)-1-[tris(trimethylsilyl)silyl]-1-dodecene (**1**) in 98% yield ((*Z*)-isomer **1**/(*E*)-isomer **2**=17/1).[6] The reaction at room temperature completed within 3 h in the presence of a catalytic amount of $Et_3B$.

The stereoisomeric ratio of **1** to **2** depended on the reaction conditions. Whereas heating a benzene solution of 1-dodecyne (1.0 mmol) and TTMSS (1.1 mmol) at reflux for 30 min in the presence of AIBN (0.1 mmol) gave a mixture of (*Z*)-isomer **1** and (*E*)-isomer **2** (**1**/**2**=4/1) in 98% combined yield, $Et_3B$ initiated reaction in toluene at 0 °C provided **1** almost exclusively (96% yield, **1**/**2**>20/1).

Next, $Et_3B$ induced hydrosilylation of various alkynes with TTMSS at room temperature has been examined. Monosubstituted acetylenes provided the corresponding tris(trimethylsilyl)silyl substituted alkenes in good to excellent yields with high stereoselectivity (Table 2). In the case of phenylacetylene or ethyl propiolate, (*Z*)-isomeric product was obtained exclusively. But the reaction of *t*-butylacetylene gave only (*E*)-alkenylsilane as reported by B. Kopping et al.[6] Internal acetylene such as 6-dodecyne did not undergo hydrosilylation with TTMSS, and starting material was recovered unchanged under the same reaction conditions.

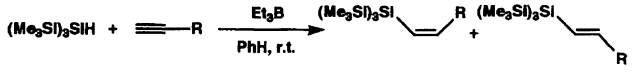
Table 1. Hydrosilylation of 1-Dodecyne with Various Silanes




| Entry | $R^1R^2{}_2SiH$ (mmol) | | $Et_3B$/mmol | Time/h | Yield/% | $Z/E$[a] |
|---|---|---|---|---|---|---|
| 1 | $Ph_3SiH$ | (2.0) | 2.0 | 88 | 42 | 12/1 |
| 2 | $Ph_2SiH_2$ | (2.0) | 2.0 | 75 | 20 | 2.4/1 |
| 3 | $Me_3SiSiPh_2H$ | (1.1) | 1.0 | 44 | 78 | 16/1 |
| 4 | $(Me_3Si)_2SiPhH$ | (1.1) | 0.1 | 12 | 74 | 15/1 |
| 5 | $(Me_3Si)_3SiH$ | (1.1) | 0.1 | 3 | 98 | 17/1 |

a) The stereoisomeric ratios were determined by the examination of $^1H$ NMR of isolated products.

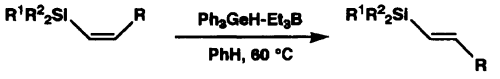
Table 2. Hydrosilylation of Alkynes with TTMSS[a]




| Entry | R | Time/h | Yield/% | $Z/E$[b] |
|---|---|---|---|---|
| 1 | $n$-$C_{10}H_{21}$ | 3 | 98 | 17/1 |
| 2 | Ph | 3 | 91 | >50/1 |
| 3 | COOEt | 3 | 90 | >50/1 |
| 4 | $CH_2OH$ | 5 | 50 | 17/1 |
| 5 | $CH_2OTHP$ | 5 | 72 | >20/1 |
| 6 | $CH_2CH_2OH$ | 5 | 81 | >20/1 |
| 7 | $t$-Bu | 2 | 88 | <1/100 |

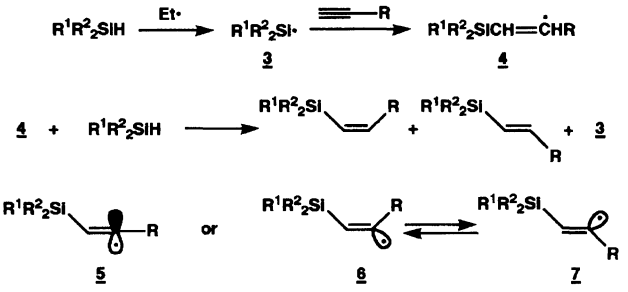
a) $(Me_3Si)_3SiH$ (1.1 mmol), acetylene (1.0 mmol), and $Et_3B$ (0.1 mmol) were employed. b) The stereoisomeric ratios were determined by the examination of $^1H$ NMR of isolated products.

Table 3. Isomerization of Alkenylsilane by $Ph_3GeH$–$Et_3B$




| Entry | Alkenylsilane ($Z/E$) | $Ph_3GeH$ /equiv | $Et_3B$ /equiv | Time /h | Yield /% | $Z/E$[a] |
|---|---|---|---|---|---|---|
| 1 | $Ph_2(Me_3Si)Si$, $n$-$C_{10}H_{21}$ (16/1) | 0.2 | 0.2 | 16 | 97 | <1/20 |
| 2 | $Ph(Me_3Si)_2Si$, $n$-$C_{10}H_{21}$ (12/1) | 0.5 | 0.5 | 16 | 91 | 1/16 |
| 3 | $(Me_3Si)_3Si$, $n$-$C_{10}H_{21}$ (>20/1) | 0.5 | 0.5 | 15 | 90 | <1/30 |
| 4 | $(Me_3Si)_3Si$, $CH_2CH_2OH$ (17/1) | 0.5 | 0.5 | 15 | 76 | <1/20 |
| 5 | $(Me_3Si)_3Si$, Ph (>50/1) | 0.2 | 0.2 | 16 | 94 | <1/50 |

a) The stereoisomeric ratios were determined by the examination of $^1H$ NMR.

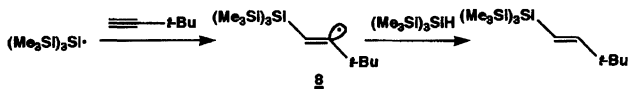



Scheme 1.

The isomerization of ($Z$)-1-tris(trimethylsilyl)silyl-1-alkenes into ($E$)-isomers by addition-elimination sequences of tris(trimethylsilyl)silyl radical did not proceed. Heating a mixture of **1**, TTMSS, and $Et_3B$ at 60 °C for 15 h gave only a small amount of ($E$)-isomer **2** (<5%) along with recovered **1**. This shows sharp contrast to a facile isomerization of ($Z$)-1-triphenylgermyl-1-dodecene or ($Z$)-1-triphenylstannyl-1-dodecene which was partially or completely isomerized to the corresponding ($E$)-isomers[7] at room temperature upon treatment with $Ph_3GeH$–$Et_3B$ or $Ph_3SnH$–$Et_3B$. ($Z$)-Alkenylsilane **1** was completely isomerized to ($E$)-isomer **2** at 60 °C by the use of $Ph_3GeH$–$Et_3B$[4] which is shown in Table 3 along with other examples. Thus, the procedure provides us with a synthetic method for the preparation of both ($Z$)- and ($E$)-alkenylsilanes.

We assume following reaction mechanism for the hydrosilylation of terminal acetylenes with $R^1R^2{}_2SiH$ (Scheme 1). Ethyl radical, generated by the attack of oxygen on triethylborane, abstracts hydrogen from silane to give silyl radical ($R^1R^2{}_2Si\cdot$, **3**). The silyl radical adds to terminal acetylenic carbon to provide alkenyl radical **4** which abstracts hydrogen from silane to produce alkenylsilane as a mixture of ($Z$)- and ($E$)-isomer under regeneration of silyl radical **3**. The selective formation of ($Z$)-alkenylsilane is due to steric hindrance of silyl group which prevents the *syn* attack of silane in the $\pi$-radical (**5**) or in the pair of $\sigma$-radicals (**6** or **7**).[8] In the hydrosilylation of $t$-butylacetylene with TTMSS, the steric repulsion between $t$-butyl and tris(trimethylsilyl)silyl group forces the intermediary $\sigma$-radical to possess ($E$)-stereochemistry (**8**), therefore, the reaction gave only ($E$)-isomer (Scheme 2).

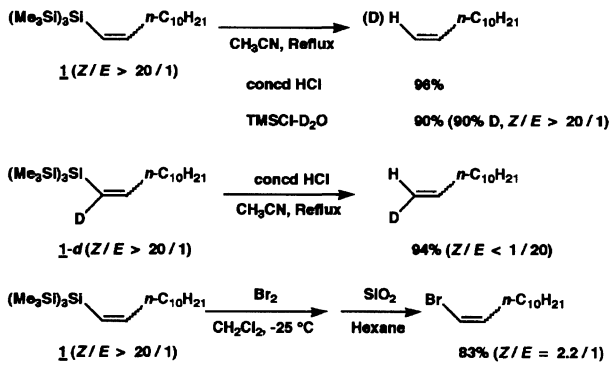
Hydrodesilylation of **1** with concd HCl proceeded in




Scheme 2.

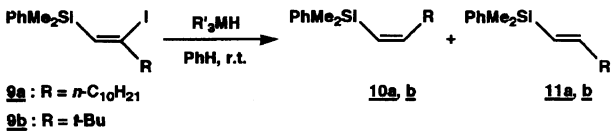
acetonitrile (Scheme 3). Treatment of **1** with TMSCl–$D_2O$ instead of concd HCl gave (*Z*)-1-deuterio-1-dodecene selectively. Moreover, the reaction of (*Z*)-1-deuterio-1-[tris(trimethylsilyl)silyl]-1-dodecene with concd HCl formed (*E*)-1-deuterio-1-dodecene exclusively. These results indicate that hydrodesilylation of **1** proceeds with retention of stereochemistry.[9] On the other hand, bromodesilylation of **1** gave 1-bromo-1-dodecene under low stereocontrol ($Z/E=2.2/1$).[10]

**(2) Reduction of Alkenyl Iodides with TTMSS.** It was anticipated that reduction of 1-silyl-2-iodo-1-alkenes with TTMSS would proceed via the same alkenyl radical as **4** in Scheme 1 and provide the same stereoisomeric mixtures of (*Z*)- and (*E*)-alkenylsilane as hydrosilylation of acetylenes. This was indeed the case as indicated by the following experiments. Treatment of 1-dimethylphenylsilyl-2-iodo-1-dodecene **9a** with TTMSS in the presence of $Et_3B$ at room temperature afforded (*Z*)-1-dimethylphenylsilyl-1-dodecene (**10a**) selectively ($Z/E>30/1$, Entry 1 in Table 4). In contrast, the use of *n*-$Bu_3SnH$ instead of TTMSS resulted in a reversal of stereoselectivity to give (*E*)-isomer **11a** as a predominant product (Entry 2). Although alkenyl iodide **9a** reacted with *n*-$Bu_3SnH$ smoothly even in the absence of radical initiator such as $Et_3B$, the product was a 2.7/1 mixture of **10a** and **11a** in favor of **10a** (Entry 3). These two experiments shown in entries 2 and 3 suggest that **10a** is a primary product in the reduction of **9a** with *n*-$Bu_3SnH$ as well as TTMSS, and $Et_3B$ induced the isomerization of **10a** to thermodynamically more stable **11a** by the addition–elimination sequences of *n*-$Bu_3Sn$ radical. Actually, **10a** was completely isomerized to **11a** by the treatment with *n*-$Bu_3SnH$–$Et_3B$ (0.1 equiv, respectively) for 2 h at room temperature.




Scheme 3.

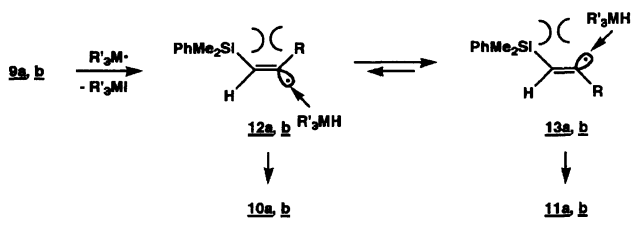
Table 4. Reduction of 1-Dimethylphenylsilyl-2-iodo-1-alkene




| Entry | Substrate | Method[a] | Yield/% | **10**/**11**[b] |
|---|---|---|---|---|
| 1 | **9a** | A | 84 | >30/1 |
| 2 | **9a** | B | 97 | <1/20 |
| 3 | **9a** | C | 96 | 2.7/1 |
| 4 | **9b** | A | 97 | 14/1 |
| 5 | **9b** | B | 100 | 1/19 |
| 6 | **9b** | C | 100 | 1/5.4 |

a) Method A: TTMSS (1.1 equiv)-$Et_3B$ (0.1 equiv), Method B: *n*-$Bu_3SnH$ (1.1 equiv)-$Et_3B$ (0.1 equiv), Method C: *n*-$Bu_3SnH$ (1.1 equiv). b) The stereoisomeric ratios of products were determined by the examination of $^1H$ NMR.

We also examined the reduction of 1-dimethylphenylsilyl-2-iodo-3,3-dimethyl-1-butene (**9b**) with TTMSS or *n*-$Bu_3SnH$ (Entries 4, 5, and 6 in Table 4). Since hydrosilylation of *t*-butylacetylene with TTMSS produced only (*E*)-isomer, it was expected that **9b** gave (*E*)-alkenylsilane selectively because of the steric repulsion between *t*-butyl and dimethylphenylsilyl group in alkenyl radical intermediate. The $Et_3B$-initiated reduction of **9b** with TTMSS, however, was found to be analogous to the reduction of **9a**, favoring (*Z*)-1-dimethylphenylsilyl-3,3-dimethyl-1-butene (**10b**) over the (*E*)-isomer (**11b**) in a ratio of 14/1 (Entry 4). This result indicates that unlike radical **8** the intermediary (*E*)-alkenyl radical (**13b**) can isomerize to (*Z*)-isomer (**12b**), because dimethylphenylsilyl group is less bulky than tris(trimethylsilyl)silyl group (Scheme 4). When *n*-$Bu_3SnH$ was used as the reducing agent with or without $Et_3B$, (*E*)-alkenylsilane was obtained predominantly (Entries 5 and 6). As shown in Entry 3 in Table 4, in the absence of $Et_3B$, the isomerization of product do not proceed effectively. For this reason, the selective formation of **11b** without $Et_3B$ is not attributed to the isomerization of **10b**, but the attack of *n*-$Bu_3SnH$ to (*E*)-alkenyl radical **13b**. Namely, the selectivity of hydrogen-abstraction from *n*-$Bu_3SnH$ is opposite to that from TTMSS. This difference can be explained by hydrogen-donating ability of the reducing agent. Chatgilialoglu et al.[5] have reported that the rate of hydrogen abstraction from TTMSS by primary alkyl radicals is ca. 4 times slower than the corresponding reaction with *n*-$Bu_3SnH$. It seems that, in the reduction of **9b** with TTMSS, hydrogen abstraction is slower than the isomerization of **13b**, therefore, TTMSS reacts with **12b** in preference to **13b** to avoid the steric hindrance of dimethylphenylsilyl group, and gives **10b** exclusively. On the other hand, hydrogen



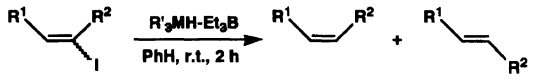

Scheme 4.

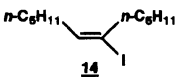
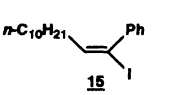
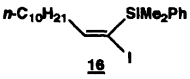
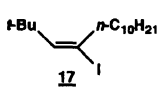
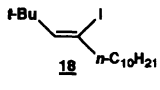
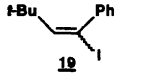
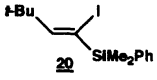
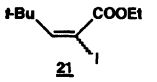
transfer from *n*-$Bu_3SnH$ to **13b** is faster than the isomerization of **13b**. Thus, thermodynamically favored (*E*)-alkenyl radical abstracted hydrogen from *n*-$Bu_3SnH$ to afford **11b** selectively. In Entry 3, the selective formation of **10a** is due to the facile isomerization of **13a** in comparison with **13b**. The steric repulsion between two substituents on double bond in **12a** is much smaller than that in **12b**.

Reduction of a variety of other alkenyl iodides with TTMSS under $Et_3B$ initiator has been studied. The results are summarized in Table 5. The stereochemical results by the reduction with *n*-$Bu_3SnH$ in the presence or absence of $Et_3B$ are also shown in Table 5. In general, the reduction with TTMSS–$Et_3B$ system produced (*Z*)-alkenes selectivity with an exceptional example shown in Entry 1. On the other hand, *n*-$Bu_3SnH$–$Et_3B$ gave (*E*)-alkenes as main products to the exclusion of Entry 12.

It is worth to note several points in the reduction

Table 5. Stereoselective Reduction of Various Alkenyl Iodides




| Entry | Substrate | Method[a] | Yield/% | $Z/E$[b] |
|---|---|---|---|---|
| 1 |  | A | 87 | 1/1.3 |
| 2 | **14** | B | 89 | 1/2.2 |
| 3 |  | A | 87 | 4.0/1 |
| 4 | **15** | B | 94 | 1/3.7 |
| 5 | | A | 96 | 5.8/1 |
| 6 |  | B | 95 | 1/15 |
| 7 | **16** | C | 97 | 1.3/1 |
| 8 |  | A | 97 | 2.1/1 |
| 9 | **17** | B | 98 | 1/2.8 |
| 10 |  **18** | A | 99 | 2.1/1 |
| 11 |  | A | 77 | >50/1 |
| 12 | **19** | B | 75 | 9/1 |
| 13 | | A | 94 | >50/1 |
| 14 |  | B | 90 | 1/16 |
| 15 | **20** | C | 96 | 6.0/1 |
| 16 |  | A | 70 | 5.7/1 |
| 17 | **21** | B | 77 | <1/100 |

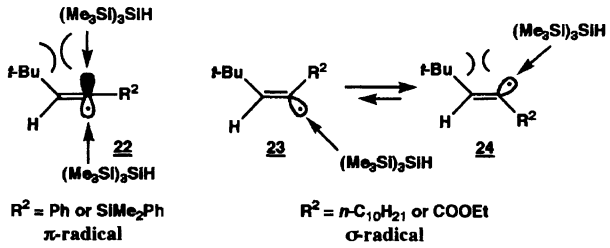
a), b) Refer to Table 4.

with TTMSS–$Et_3B$. First, the stereochemical outcome was independent on the stereochemistry of starting material. For instance, the treatment of (*E*)-2,2-dimethyl-4-iodo-3-tetradecene (**17**) or (*Z*)-isomer (**18**) with TTMSS–$Et_3B$ at room temperature for 2 h provided the same isomeric mixture of (*Z*)-2,2-dimethyl-3-tetradecene and (*E*)-isomer ($Z/E$=2.1/1, Entries 8 and 10). This result suggests that the firstly formed alkenyl radical isomerizes to the other isomer to reach the equilibrium before hydrogen abstraction from TTMSS. Secondary, comparisons of Entry 1 with 8, 3 with 11, and 5 with 13 show that (*Z*)-selectivity of the reduction improves with increase of the bulkiness of $R^1$ group. Thus, the severe steric repulsion between $R^1$ and TTMSS decrease in the formation of (*E*)-alkene. Moreover, when $R^2$ is phenyl (**19**) or dimethylphenylsilyl group (**20**), the reaction results in higher (*Z*)-selectivity than the case that $R^2$ is *n*-decyl (**17** or **18**) or ethoxycarbonyl group (**21**). The geometry of intermediary alkenyl radical is responsible for the change of selectivity.

As depicted in Scheme 5, it is known that α-phenylalkenyl radical is a π-radical (linear radical).[11] while α-alkyl- or α-alkoxycarbonylalkenyl is a σ-radical (bent radical).[12,13] The attack of TTMSS from the syn side of *t*-butyl group in **22** suffers the steric hindrance more severely than in **23**, because the direction of the attack of TTMSS is close to *t*-butyl group in **22**. Accordingly, the formation of (*E*)-alkene from **22** is strictly suppressed. The result shown in Entry 13 implies that α-silylalkenyl radical is a π-radical.[8] In addition, this assumption is supported by the following experiment. The reaction of **20** with *n*-$Bu_3SnH$ in the absence of $Et_3B$ gave (*Z*)-alkenylsilane selectively (Entry 15). If the intermediary radical is a σ-radical, it is considered that **20** affords (*E*)-alkenylsilane because of the steric repulsion between *t*-butyl and dimethylphenylsilyl and fast hydrogen abstraction from *n*-$Bu_3SnH$ as shown in the reaction of **9b** (Entry 6 in Table 4).

In *n*-$Bu_3SnH$–$Et_3B$ system, the reduction of alkenyl iodide bearing silyl or ethoxycarbonyl group (**16**, **20**, or **21**) gave (*E*)-alkene in high selectivity. Since addition of nucleophilic *n*-$Bu_3Sn$ radical to alkenylsilane or α,β-unsaturated ester is much faster than simple olefins, the isomerization of products in Entries 6, 14, and 17 proceeds easily.

In conclusion, the addition of TTMSS to acetylenes




Scheme 5.

provides us with a stereoselective synthetic method for (*Z*)-1-[tris(trimethylsilyl)silyl]-1-alkenes, since TTMSS radical cannot cause the isomerization of the resulting (*Z*)-alkenes into (*E*)-alkenes. Meantime, (*E*)-1-[tris(trimethylsilyl)silyl]-1-alkenes are produced on treatment of (*Z*)-1-[tris(trimethylsilyl)silyl]-1-alkenes with $Ph_3GeH$–$Et_3B$. Reduction of 1,2-disubstituted 1-iodo-1-alkenes with TTMSS–$Et_3B$ affords (*Z*)-1,2-disubstituted-1-alkenes selectively.

## Experimental

Distillation of the products was performed by use of Kugelrohr (Büchi), and boiling points are indicated by air-bath temperature without correction. Melting point was obtained on a Yanako MP-50929 melting point apparatus and are uncorrected, too. $^1$H NMR and $^{13}$C NMR spectra were taken on a Varian GEMINI 300 spectrometer, $CDCl_3$ was used as solvent, and chemical shifts being given in $\delta$ with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer and the mass spectra on a Hitachi M-80 machine. When $m/z$ is less than 100, mass spectra are described in only case where its relative intensity is more than 50. The analyses were carried out at the Elemental Analyses Center of Kyoto University.

**General Procedure for $Et_3B$ Induced Hydrosilylation of 1-Dodecyne with $Ph_3SiH$, $Ph_2SiH_2$, or $Me_3SiSiPh_2H$.** Hydrosilylation of 1-dodecyne with $Ph_3SiH$ is representative. A hexane solution of $Et_3B$ (0.96 M, 1 M=1 mol dm$^{-3}$, 2.1 mL, 2.0 mmol) was added to a mixture of 1-dodecyne (0.166 g, 1.00 mmol) and $Ph_3SiH$ (0.520 g, 2.00 mmol) at room temperature under argon atmosphere. After stirring for 88 h, the reaction mixture was concentrated and distilled to remove 1-dodecyne and $Ph_3SiH$ in vacuo (0.50 Torr, 1 Torr=133.322 Pa, bath temp, 120 °C, 1 h). The residual oil was purified by silica-gel column chromatography using hexane as an eluent to give 1-triphenylsilyl-1-dodecene (0.179 g) in 42% yield.

**(*Z*)-1-(Triphenylsilyl)-1-dodecene:** Bp 160—164 °C (0.27 Torr, bath temp); IR (neat) 3062, 2920, 2850, 1602, 1428, 1110, 712, 698 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=0.85—1.32 (m, 19H, included 0.88 (t, $J$=6.9 Hz)), 1.86—1.95 (m, 2H), 6.02 (dt, $J$=14.0, 1.3 Hz, 1H), 6.71 (dt, $J$=14.0, 7.5 Hz, 1H), 7.31—7.42 (m, 9H), 7.54—7.59 (m, 6H); $^{13}$C NMR ($CDCl_3$) $\delta$=14.14, 22.70, 29.04, 29.19, 29.33 (two carbons), 29.51 (two carbons), 31.91, 34.57, 122.52, 127.80, 129.28, 135.64, 135.71, 154.06; MS (70 eV) $m/z$ (rel intensity) 427 ($M^+$+1, 3.5), 426 ($M^+$, 7.9), 286 (42), 285 (100), 259 (47), 207 (19), 184 (17), 183 (70), 182 (21), 181 (27), 105 (16). Found: C, 84.34; H, 9.04%. Calcd for $C_{30}H_{38}Si$: C, 84.44; H, 8.98%.

**(*Z*)-1-(Diphenylsilyl)-1-dodecene:** Bp 139—143 °C (0.55 Torr, bath temp); IR (neat) 2952, 2920, 2850, 2120, 1603, 1429, 1115, 800, 730, 697 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=0.88 (t, $J$=6.8 Hz, 3H), 1.15—1.36 (m, 16H), 2.15—2.23 (m, 2H), 5.27 (d, $J$=5.3 Hz, 1H), 5.83 (ddt, $J$=13.8, 5.4, 1.2 Hz, 1H), 6.66 (dt $J$=13.8, 7.4 Hz, 1H), 7.31—7.42 (m, 6H), 7.54—7.60 (m, 4H); $^{13}$C NMR ($CDCl_3$) $\delta$=14.14, 22.69, 29.14, 29.23, 29.34, 29.42, 29.57 (two carbons), 31.91, 33.76, 121.31, 127.97, 129.44, 134.57, 135.23, 153.74; MS (70 eV) $m/z$ (rel intensity) 351 ($M^+$+1, 0.3), 350 ($M^+$, 1.4), 184 (20), 183 (100), 182 (30), 181 (24), 107 (15), 105 (34). Found: C, 82.44; H, 9.83%. Calcd for $C_{24}H_{34}Si$: C, 82.21; H, 9.77%.

**(*E*)-1-(Diphenylsilyl)-1-dodecene:** Bp 139—143 °C (0.55 Torr, bath temp); IR (neat) 2950, 2922, 2850, 2116, 1615, 1429, 1114, 807, 727, 696 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=0.88 (t, $J$=6.7 Hz, 3H), 1.18—1.48 (m, 16H), 2.16—2.23 (m, 2H), 5.08 (d, $J$=3.1 Hz, 1H), 5.92 (ddt, $J$=18.5, 3.1, 1.5 Hz, 1H), 6.29 (dt, $J$=18.5, 6.2 Hz, 1H), 7.32—7.43 (m, 6H), 7.54—7.60 (m, 4H); $^{13}$C NMR ($CDCl_3$) $\delta$=14.14, 22.69, 28.41, 29.19, 29.35, 29.47, 29.61 (two carbons), 31.91, 36.97, 121.78, 127.92, 129.53, 134.24, 135.40, 154.03; MS (70 eV) $m/z$ (rel intensity) 351 ($M^+$+1, 0.5), 350 ($M^+$, 1.9), 184 (20), 183 (100), 182 (33), 181 (24), 107 (15), 105 (29). Found: C, 82.38; H, 9.93%. Calcd for $C_{24}H_{34}Si$: C, 82.21; H, 9.77%.

**(*Z*)-1-[Diphenyl(trimethylsilyl)silyl]-1-dodecene:** Bp 145—149 °C (0.33 Torr, bath temp); IR (neat) 2950, 2922, 2850, 1598, 1428, 1244, 1102, 851, 834, 736, 698 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=0.15 (s, 9H), 0.88 (t, $J$=6.9 Hz, 3H), 0.98—1.32 (m, 16H), 1.85—1.92 (m, 2H), 5.84 (dt, $J$=13.6, 1.2 Hz, 1H), 6.60 (dt, $J$=13.6, 7.3 Hz, 1H), 7.28—7.36 (m, 6H), 7.45—7.53 (m, 4H); $^{13}$C NMR ($CDCl_3$) $\delta$=−1.21, 14.15, 22.70, 29.20 (two carbons), 29.29, 29.41, 29.52 (two carbons), 31.91, 34.92, 122.97, 127.81, 128.57, 135.28, 136.71, 152.49; MS (70 eV) $m/z$ (rel intensity) 423 ($M^+$+1, 1.4), 422 ($M^+$, 2.2), 349 (36), 287 (68), 197 (53), 183 (100), 135 (50), 121 (38), 107 (18), 105 (43). Found: C, 76.41; H, 10.01%. Calcd for $C_{27}H_{42}Si_2$: C, 76.70; H, 10.01%.

**(*E*)-1-[Diphenyl(trimethylsilyl)silyl]-1-dodecene:** Bp 141—145 °C (0.21 Torr, bath temp); IR (neat) 2920, 2850, 1428, 1244, 1103, 852, 834, 735, 698 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=0.17 (s, 9H), 0.88 (t, $J$=6.7 Hz, 3H), 1.20—1.44 (m, 16H), 2.16—2.23 (m, 2H), 5.94 (dt, $J$=18.5, 1.2 Hz, 1H), 6.11 (dt, $J$=18.5, 6.1 Hz, 1H), 7.29—7.38 (m, 6H), 7.44—7.51 (m, 4H); $^{13}$C NMR ($CDCl_3$) $\delta$=−1.31, 14.14, 22.70, 28.71, 29.14, 29.36, 29.48, 29.62, 29.65, 31.92, 37.19, 123.74, 127.79, 128.68, 135.52, 136.35, 151.94; (MS (70 eV) $m/z$ (rel intensity) 424 ($M^+$+2, 0.6), 423 ($M^+$+1, 1.5), 422 ($M^+$, 2) 349 (31), 287 (61), 197 (52), 183 (100), 135 (36), 121 (25), 105 (25). Found: C, 76.65; H, 9.80%. Calcd for $C_{27}H_{42}Si_2$: C, 76.70; H, 10.01%.

**General Procedure for $Et_3B$ Induced Hydrosilylation of Acetylenes with $(Me_3Si)_2SiPhH$ or $(Me_3Si)_3SiH$.** Typical procedure is as follows. Under argon atmosphere, $Et_3B$ (0.96 M hexane solution, 0.10 mL, 0.10 mmol) was added to a solution of 1-dodecyne (0.166 g, 1.00 mmol) and $(Me_3Si)_3SiH$ (0.274 g, 1.10 mmol) in benzene (2.0 mL) at room temperature. After stirring for 3 h, the reaction mixture was concentrated in vacuo. Purification by silica-gel column (hexane) yielded 1-[tris(trimethylsilyl)-silyl]-1-dodecene (0.407 g, 98%, $Z/E$=17/1).

**(*Z*)-1-[Phenylbis(trimethylsilyl)silyl]-1-dodecene:** Bp 128—132 °C (0.35 Torr, bath temp); IR (neat) 2952, 2922, 2850, 1244, 835, 697, 622 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=0.14 (s, 18H), 0.88 (t, $J$=6.8 Hz, 3H), 1.14—1.35 (m, 16H), 1.91—1.99 (m, 2H), 5.67 (dt, $J$=13.3, 1.3 Hz, 1H), 6.53 (dt, $J$=13.3, 7.2 Hz, 1H), 7.25—7.31 (m, 3H), 7.40—7.45 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$=−0.49, 14.15, 22.70, 29.32, 29.48 (two carbons), 29.54 (three carbons), 31.91, 35.39, 121.37, 127.60, 135.12, 136.96, 151.11; MS (70 eV) $m/z$ (rel intensity) 419 ($M^+$+1, 1.0), 418 ($M^+$, 2.5), 179 (26), 178 (53), 163 (19), 135 (99), 121 (41), 116 (36), 73 (100). Found: C, 69.05; H, 11.36%. Calcd for $C_{24}H_{46}Si_3$: C, 68.82; H, 11.07%.

**(*E*)-1-[Phenylbis(trimethylsilyl)silyl]-1-dodecene:**

Bp 125—129 °C (0.30 Torr, bath temp); IR (neat) 2948, 2922, 2850, 1244, 835, 697 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=0.14 (s, 18H), 0.88 (t, $J$=6.7 Hz, 3H), 1.18—1.47 (m, 16H), 2.15—2.22 (m, 2H), 5.77 (dt, $J$=18.4 1.4 Hz, 1H), 6.13 (dt, $J$=18.4, 6.5 Hz, 1H), 7.26—7.32 (m, 3H), 7.40—7.46 (m, 2H); $^{13}C$ NMR ($CDCl_3$) $\delta$=−0.66, 14.14, 22.69, 29.00, 29.07, 29.36, 29.48, 29.62, 29.67, 31.92, 37.47, 122.63, 127.65, 127.75, 135.21, 136.80, 150.50; MS (70 eV) $m/z$ (rel intensity) 419 ($M^+$+1, 1.0), 418 ($M^+$, 1.9), 193 (19), 179 (30), 178 (54), 163 (21), 135 (100), 121 (40), 116 (35), 73 (99). Found: C, 68.59; H, 11.25%. Calcd for $C_{24}H_{46}Si_3$: C, 68.82; H, 11.07%.

**(*Z*)- 1- [Tris(trimethylsilyl)silyl]- 1- dodecene (1):** Bp 127—131 °C (0.38 Torr, bath temp); IR (neat) 2948, 2922, 2850, 1244, 832, 686, 621 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=0.18 (s, 27H), 0.88 (t, $J$=6.7 Hz, 3H), 1.22—1.41 (m, 16H), 2.03—2.10 (m, 2H), 5.47 (dt, $J$=13.0, 1.5 Hz, 1H), 6.38 (dt, $J$=13.0, 7.0 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$=1.09, 14.15, 22.70, 29.33, 29.59 (three carbons), 29.69, 29.80, 31.91, 35.65, 119.55, 149.48; MS (70 eV) $m/z$ (rel intensity) 415 ($M^+$+1, 0.6), 414 ($M^+$, 1.7), 175 (16), 174 (68), 131 (12), 129 (12), 117 (11), 73 (100). Found: C, 60.51; H, 11.87%. Calcd for $C_{21}H_{50}Si_4$: C, 60.78; H, 12.14%.

**(*E*)- 1- [Tris(trimethylsilyl)silyl]- 1- dodecene (2):** Bp 116—120 °C (0.33 Torr, bath temp); IR (neat) 2946, 2922, 2850, 1244, 832, 685, 622 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=0.16 (s, 27H), 0.88 (t, $J$=6.7 Hz, 3H), 1.21—1.39 (m, 16H), 2.05—2.13 (m, 2H), 5.47 (dt, $J$=18.2, 1.3 Hz, 1H), 5.97 (dt, $J$=18.2, 6.5 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$=0.78, 14.14, 22.69, 28.99, 29.18, 29.35, 29.47, 29.61, 29.67, 31.92, 37.64, 120.36, 149.50; MS (70 eV) $m/z$ (rel intensity) 416 ($M^+$+2, 0.5), 415 ($M^+$+1, 0.7), 414 ($M^+$, 2.0), 189 (11), 175 (21), 174 (76), 131 (14), 129 (13), 117 (14), 73 (100). Found: C, 60.60; H, 12.35%. Calcd for $C_{21}H_{50}Si_4$: C, 60.78; H, 12.14%.

**(*Z*)- 1- Deuterio- 1- [tris(trimethylsilyl)silyl]- 1- dodecene (1-d):** Bp 130—134 °C (0.40 Torr, bath temp); IR (neat) 2946, 2922, 2850, 1244, 834, 685, 615 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=0.18 (s, 27H), 0.88 (t, $J$=6.7 Hz, 3H), 1.22—1.40 (m, 16H), 2.03—2.10 (m, 2H), 6.38 (t, $J$=7.0 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$=1.09, 14.14, 22.70 29.33, 29.59 (three carbons), 29.69, 29.80, 31.91, 35.61, 119.19 (t, $J_{CD}$=21.4 Hz), 149.38; MS (70 eV) $m/z$ (rel intensity) 416 ($M^+$+1, 0.6), 415 ($M^+$, 1.6), 175 (20), 174 (70), 131 (10), 117 (11), 73 (100). Found: C, 60.38; H, 11.84; D, 0.47%. Calcd for $C_{21}H_{49}DSi_4$: C, 60.64; H, 11.87; D, 0.48%.

**(*E*)- 1- Deuterio- 1- [tris(trimethylsilyl)silyl]- 1- dodecene (2-d):** Bp 116—120 °C (0.30 Torr, bath temp); IR (neat) 2946, 2922, 2852, 1244, 835, 686, 621 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=0.16 (s, 27H), 0.88 (t, $J$=6.7 Hz, 3H), 1.21—1.38 (m, 16H), 2.06—2.12 (m, 2H), 5.93—5.99 (m, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$=0.79, 14.14, 22.70, 28.99, 29.18, 29.36, 29.48, 29.62, 29.68, 31.92, 37.57, 119.99 (t, $J_{CD}$=21.2 Hz), 149.43; MS (70 eV) $m/z$ (rel intensity) 416 ($M^+$+1, 0.6), 415 ($M^+$, 1.8), 176 (11), 175 (19), 174 (74), 131 (10), 73 (100). Found: C, 60.54; H, 11.74; D, 0.47%. Calcd for $C_{21}H_{49}DSi_4$: C, 60.64; H, 11.87; D, 0.48%.

**(*Z*)-3-[Tris(trimethylsilyl)silyl]-2-propen-1-ol:** Mp 105—107 °C (Hexane); IR ($CDCl_3$) 3610, 2948, 2890, 1246, 1005, 922, 836, 714, 707, 687, 621 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=0.19 (s, 27H), 1.42 (bs, 1H), 4.14 (dd, $J$=6.6, 1.1 Hz, 2H), 5.78 (dt, $J$=13.2, 1.1 Hz, 1H), 6.56 (dt, $J$=13.2, 6.6 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$=0.89, 65.00, 124.90, 146.27; MS (20 eV) $m/z$ (rel intensity) 233 ($M^+$+2−$SiMe_3$, 2.1), 232 ($M^+$+1−$SiMe_3$, 4.5), 231 ($M^+$−$SiMe_3$, 18), 215 (46), 157 (16), 141 (17), 131 (26), 117 (20), 73 (100). Found: C, 47.20; H, 10.33%. Calcd for $C_{12}H_{32}OSi_4$; C, 47.30; H, 10.58%.

**(*E*)-3-[Tris(trimethylsilyl)silyl]-2-propen-1-ol:** Mp 76—78 °C (Hexane); IR ($CDCl_3$) 3608, 2946, 2890, 1245, 1074, 984, 837, 758, 731, 728, 687, 622 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=0.17 (s, 27H), 1.47 (bs, 1H), 4.15 (dd, $J$=4.9, 1.6 Hz, 2H), 5.84 (dt, $J$=18.5, 1.6 Hz, 1H), 6.18 (dt, $J$=18.5, 4.9 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$=0.76, 66.41, 122.73, 146.38; MS (20 eV) $m/z$ (rel intensity) 231 ($M^+$−$SiMe_3$, 2.7), 215 (28), 199 (29), 175 (32), 141 (32), 131 (55), 117 (33), 73 (100). Found: C, 47.16; H, 10.70%. Calcd for $C_{12}H_{32}OSi_4$: C, 47.30; H, 10.58%.

**(*Z*)-1-(2-Tetrahydropyranyloxy)-3-[tris(trimethylsilyl)silyl]-2-propene:** Bp 96—100 °C (0.23 Torr, bath temp); IR (neat) 2944, 2892, 1258, 1245, 1119, 1061, 1028, 834, 686, 620 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=0.19 (s, 27H), 1.48—1.92 (m, 6H), 3.47—3.54 (m, 1H), 3.84—3.92 (m, 1H), 3.97 (ddd, $J$=12.1, 7.0, 1.3 Hz, 1H), 4.28 (ddd, $J$=12.1, 5.6, 1.5 Hz, 1H), 4.64 (dd, $J$=3.9, 3.1 Hz, 1H), 5.77 (ddd, $J$=13.5, 1.5, 1.3 Hz, 1H), 6.54 (ddd, $J$=13.5, 7.0, 5.6 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$=0.93, 19.47, 25.47, 30.67, 62.17, 69.46, 98.47, 124.20, 144.72; MS (20 eV) $m/z$ (rel intensity) 231 ($M^+$−$C_5H_8O$−$SiMe_3$, 18), 215 (14), 199 (6.3), 157 (5.1), 147 (6.3), 141 (5.8), 133 (7.7), 131 (10), 117 (8.5), 85 (100). Found: C, 52.40; H, 10.62%. Calcd for $C_{17}H_{40}O_2Si_4$: C, 52.51; H, 10.37%.

**(*E*)-1-(2-Tetrahydropyranyloxy)-3-[tris(trimethylsilyl)silyl]-2-propene:** Bp 97—101 °C (0.39 Torr, bath temp); IR (neat) 2944, 2890, 1245, 1120, 1078, 1025, 867, 831, 686, 622 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=0.17 (s, 27H), 1.48—1.92 (m, 6H), 3.45—3.53 (m, 1H), 3.85—3.93 (m, 1H), 4.05 (ddd, $J$=13.2, 6.1, 1.3 Hz, 1H), 4.22 (ddd, $J$=13.2, 4.6, 1.5 Hz, 1H), 4.62 (dd, $J$=4.2, 2.8 Hz, 1H), 5.84 (ddd, $J$=18.4, 1.5, 1.3 Hz, 1H), 6.08 (ddd, $J$=18.4, 6.1, 4.6 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$=0.77, 19.63, 25.49, 30.69, 62.39, 70.27, 97.23, 124.85, 143.86; MS (20 eV) $m/z$ (rel intensity) 215 ($M^+$−$C_5H_8O$−$SiMe_3$, 10), 199 (11), 191 (15), 175 (11), 147 (18), 141 (13), 133 (22), 131 (24), 117 (21), 85 (94), 73 (100). Found: C, 52.71; H, 10.64%. Calcd for $C_{17}H_{40}O_2Si_4$: C, 52.51; H, 10.37%.

**(*Z*)-4-[Tris(trimethylsilyl)silyl]-3-buten-1-ol:** Bp 86—90 °C (0.24 Torr, bath temp); IR (neat) 3310 (bs), 2946, 2890, 1244, 1047, 833, 686, 621 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=0.19 (s, 27H), 1.45 (bs, 1H), 2.39 (dtd, $J$=7.1, 6.6, 1.4 Hz, 2H), 3.71 (t, $J$=6.6 Hz, 2H), 5.71 (dt, $J$=13.1, 1.4 Hz, 1H), 6.40 (dt, $J$=13.1, 7.1 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$=1.09, 38.49, 62.31, 124.32, 144.16; MS (20 eV) $m/z$ (rel intensity) 247 ($M^+$+2−$SiMe_3$, 2.5), 246 ($M^+$+1−$SiMe_3$, 4.8), 245 ($M^+$−$SiMe_3$, 18), 229 (32), 201 (20), 191 (21), 175 (27), 133 (26), 131 (37), 117 (27), 73 (100). Found: C, 48.79; H, 10.96%. Calcd for $C_{13}H_{34}OSi_4$: C, 48.99; H, 10.75%.

**(*E*)-4-[Tris(trimethylsilyl)silyl]-3-buten-1-ol:** Bp 92—96 °C (0.30 Torr, bath temp); IR ($CDCl_3$) 3618, 2946, 2890, 1245, 1044, 982, 837, 687, 623 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=0.17 (s, 27H), 1.48 (bs, 1H), 2.40 (dtd, $J$=6.7, 6.4, 1.2 Hz, 2H), 3.64 (t, $J$=6.4 Hz, 2H), 5.70 (dt, $J$=18.2, 1.2 Hz, 1H), 5.96 (dt, $J$=18.2, 6.7 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$=0.76, 40.93, 61.68, 125.91, 144.19; MS (20 eV)

*m/z* (rel intensity) 318 ($M^+$, 0.4), 201 (16), 191 (55), 175 (44), 155 (17), 133 (26), 131 (49), 117 (27), 73 (100). Found: C, 49.22; H, 10.82%. Calcd for $C_{13}H_{34}OSi_4$: C, 48.99; H, 10.75%.

**AIBN Induced Hydrosilylation of 1-Dodecyne with $(Me_3Si)_3SiH$.** A solution of 1-dodecyne (0.166 g, 1.00 mmol), $(Me_3Si)_3SiH$ (0.273 g, 1.10 mmol), and AIBN (0.016 g, 0.10 mmol) in benzene (2 mL) was refluxed for 30 min. The reaction mixture was concentrated in vacuo, followed by purification by silica-gel column to give 1-[tris(trimethylsilyl)silyl]-1-dodecene (0.407 g, 98%, $Z/E=4/1$).

**General Procedure for Isomerization of (*Z*)-Alkenylsilane to (*E*)-Isomer.** $Et_3B$ (0.96 M hexane solution, 0.52 mL, 0.50 mmol) was added to a benzene (5.0 mL) solution of (*Z*)-rich alkenylsilane (1.00 mmol) and $Ph_3GeH$ (0.152 g, 0.500 mmol), and the resulting mixture was heated at 60 °C under argon atmosphere. After stirring for 12—16 h, the reaction mixture was concentrated in vacuo. Purification by silica-gel column afforded (*E*)-rich alkenylsilane.

**Hydrodesilylation of 1-[Tris(trimethylsilyl)silyl]-1-dodecene.** Concd HCl (ca. 36%, 0.35 mL) was added to a solution of 1-[tris(trimethylsilyl)silyl]-1-dodecene (0.415 g, 1.00 mmol) in acetonitrile (5.0 mL) and the mixture was heated at reflux. After stirring for 2 h, the reaction mixture was cooled to room temperature, and aqueous NaOH (1.0 M, 10 mL) was poured. The mixture was stirred for 1 h, then extracted with hexane (20 mL×3). Concentration of the dried ($Na_2SO_4$) organic layer and purification by silica-gel column gave 1-dodecene (0.161 g) in 96% yield. The use of $Me_3SiCl$ (0.50 mL, 4.0 mmol) and $D_2O$ (0.072 mL, 4.0 mmol) instead of concd HCl afforded 1-deuterio-1-dodecene (0.152 g, 90% D, $Z/E>20/1$) in 90% yield. Hydrodesilylation of (*Z*)-1-deuterio-1-[tris(trimethylsilyl)silyl]-1-dodecene was performed according to the same procedure as described above.

**Bromodesilylation of 1-[Tris(trimethylsilyl)silyl]-1-dodecene.** Bromine (1.0 M $CH_2Cl_2$ solution, 2.0 mL, 2.0 mmol) was added dropwise to a solution of 1-[tris(trimethylsilyl)silyl]-1-dodecene (0.207 g, 0.500 mmol) in $CH_2Cl_2$ at −25 °C. After stirring for 30 min, the reaction mixture was treated with aqueous $Na_2S_2O_3$ (10%, 2.0 mL), and immediately warmed to room temperature. The resulting mixture was poured into water (20 mL), and extracted with $Et_2O$ (20 ml×2). The combined organic layer was dried over $Na_2SO_4$, then concentrated in vacuo. The crude product was treated with silica-gel (1.0 g) in hexane (5 ml) for 2 h at room temperature. After filtration of the mixture through $Na_2SO_4$ column, the filtrate was concentrated in vacuo. The residual oil was purified by silica-gel column (hexane) to give 1-bromo-1-dodecene in 83% yield (0.103 g, $Z/E=2.3/1$).

**Synthesis of Alkenyl Iodide.** Silylmagnesation of 1-dodecyne and *t*-butylacetylene followed by quenching with iodine afforded (*Z*)-1-dimethylphenylsilyl-2-iodo-1-alkene **9a** and **9b**.[14] Alkenyl iodide **14** or **15** were prepared by hydroiodination of the corresponding acetylene according to the reported procedure.[15] Alkenyl iodide **16** was derived from 1-dimethylphenylsilyl-1-dodecyne by hydroalumination followed by the treatment with iodine.[16] On the other hand, $Et_3B$-induced radical additions of *t*-butyl iodide to 1-dodecyne, phenylacetylene, (dimethylphenylsilyl)acetylene, and ethyl propiolate gave alkenyl iodide **17** with **18**, **19**, **20**, and **21**, respectively.[17]

**(*Z*)-1-Dimethylphenylsilyl-2-iodo-1-dodecene (9a):** Bp 118—122 °C (0.44, Torr, bath temp); IR (neat) 2952, 2922, 2850, 1593, 1247, 1112, 833, 814, 728, 696 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta=0.47$ (s, 6H), 0.88 (t, $J=6.7$ Hz, 3H), 1.26 (bs, 14H), 1.48—1.60 (m, 2H) 2.53—2.58 (m, 2H), 6.50 (s, 1H), 7.33—7.38 (m, 3H), 7.55—7.59 (m, 2H); $^{13}C$ NMR ($CDCl_3$) $\delta=-2.19$, 14.14, 22.69, 28.11, 29.25, 29.32, (two carbons), 29.55, (two carbons), 31.90, 50.99, 125.53, 127.55, 128.98, 133.99, 134.89, 138.04; MS (70 eV) *m/z* (rel intensity) 302 ($M^+ +1-I$, 8.5), 301 ($M^+ -I$, 22), 286 (4.3), 285 (14), 247 (6.3), 137 (5.4), 136 (17), 135 (100), 121 (9.5), 105 (5.2). Found: C, 56.32; H, 7.91%. Calcd for $C_{20}H_{33}SiI$: C, 56.06; H, 7.76%.

**(*Z*)-1-Dimethylphenylsilyl-2-iodo-3,3-dimethyl-1-butene (9b):** Bp 75—79 °C (0.60 Torr, bath temp); IR (neat) 2964, 1247, 1222, 1115, 903, 836, 813, 728, 697, 645 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta=0.48$ (s, 6H), 1.18 (s, 9H), 6.65 (s, 1H), 7.33—7.39 (m, 3H), 7.54—7.59 (m, 2H); $^{13}C$ NMR ($CDCl_3$) $\delta=-1.88$, 30.36, 43.49, 127.73, 128.87, 131.78, 133.99, 138.40, 142.24; MS (70 eV) *m/z* (rel intensity) 218 ($M^+ +1-I$, 9.7), 217 ($M^+ -I$, 36), 201 (17), 136 (16), 135 (100), 105 (13). Found: C, 48.63; H, 6.09%. Calcd for $C_{14}H_{21}SiI$: C, 48.84; H, 6.15%.

**(*E*)-1-Iodo-1-phenyl-1-dodecene (15):** Bp 108—112 °C (0.28 Torr, bath temp); IR (neat) 2950, 2920, 2850, 752, 691 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta=0.88$ (t, $J=6.6$ Hz, 3H), 1.23—1.42 (m, 14H), 1.46—1.56 (m, 2H), 2.27—2.34 (m, 2H), 5.89 (t, $J=6.8$ Hz, 1H), 7.21—7.32 (m, 3H), 7.42—7.46 (m, 2H); $^{13}C$ NMR ($CDCl_3$) $\delta=14.14$, 22.69, 28.31, 29.27, 29.34, 29.50, 29.59 (two carbons), 31.90, 37.76, 104.75, 128.11, 128.54, 139.11, 139.19, 143.23; MS (70 eV) *m/z* (rel intensity) 371 ($M^+ +1$, 1.7), 370 ($M^+$, 4.7), 131 (12), 117 (100), 126 (34), 115 (29), 91 (95). Found: C, 58.36; H, 7.17%. Calcd for $C_{18}H_{27}I$: C, 58.38; H, 7.35%.

**(*E*)-1-Dimethylphenylsilyl-1-iodo-1-dodecene (16):** Bp 104—108 °C (0.22 Torr, bath temp); IR (neat) 2950, 2920, 2850, 1250, 1112, 836, 822, 776, 732, 699 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta=0.54$ (s, 6H), 0.88 (t, $J=6.7$ Hz, 3H), 1.02—1.34 (m, 16H), 1.78—1.87 (m, 2H), 7.26 (t, $J=8.0$ Hz, 1H), 7.33—7.40 (m, 3H), 7.53—7.59 (m, 2H); $^{13}C$ NMR ($CDCl_3$) $\delta=0.35$, 14.14, 22.69, 28.84, 28.99, 29.30 (two carbons), 29.49, 29.54, 31.89, 35.47, 103.25, 127.91, 129.41, 133.76, 137.56, 158.52; MS (70 eV) *m/z* (rel intensity) 428 ($M^+$, 0.4), 302 (5.1), 301 (17), 247 (15), 185 (8.4), 145 (7.7), 136 (14), 135 (100), 121 (9). Found: C, 56.07; H, 7.58%. Calcd for $C_{20}H_{33}SiI$: C, 56.06; H, 7.76%.

**(*E*)-4-Iodo-2,2-dimethyl-3-tetradecene (17):** Bp 75—80 °C (0.44 Torr, bath temp); IR (neat) 2954, 2922, 2850, 1465, 1364 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta=0.88$ (t, $J=6.7$ Hz, 3H), 1.12 (s, 9H), 1.27 (bs, 14H), 1.50—1.59 (m, 2H), 2.41—2.46 (m, 2H), 6.23 (s, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta=14.13$, 22.68, 28.77, 29.32, 29.50, 29.57 (two carbons), 30.28, 30.91, 31.89, 36.84, 40.51, 106.31, 150.65; MS (70 eV) *m/z* (rel intensity) 351 ($M^+ +1$, 0.9), 350 ($M^+$, 5.2), 224 (1.4), 223 (1.6), 111 (16), 97 (59), 83 (100), 69 (62), 57 (64). Found: C, 54.61; H, 9.08%. Calcd for $C_{16}H_{31}I$: C, 54.86; H, 8.92%.

**(*Z*)-4-Iodo-2,2-dimethyl-3-tetradecene (18):** Bp 78—82 °C (0.45 Torr, bath temp); IR (neat) 2952, 2922, 2852, 1460, 1362, 1201 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta=0.88$ (t,

$J$=6.7 Hz, 3H), 1.18 (s, 9H), 1.26 (bs, 14H), 1.45—1.55 (m, 2H), 2.41—2.46 (m, 2H), 5.88 (s, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$=14.13, 22.69, 27.99, 29.34 (two carbons), 29.43, 29.58 (two carbons), 29.83, 31.90, 33.11, 47.97, 102.70, 143.07; MS (70 eV) $m/z$ (rel intensity) 351 ($M^+$+1, 1.0), 350 ($M^+$, 6.7), 224 (1.1), 223 (5.4), 111 (14), 97 (81), 83 (100), 69 (71), 57 (66), 55 (55). Found: C, 54.76; H, 9.09%. Calcd for $C_{16}H_{31}I$: C, 54.86; H, 8.92%.

**1- Iodo- 3, 3- dimethyl- 1- phenyl- 1- butene (19, *E*: *Z*=91 : 9):** Bp 57—61 °C (0.22 Torr, bath temp); IR (neat) 2956, 830, 765, 697, 681 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=0.89 (s, 8.19H), 1.29 (s, 0.81H), 6.24 (s, 0.09H), 6.47 (s, 0.91H), 7.20—7.42 (m, 5H); $^{13}$C NMR ($CDCl_3$) for (*E*)-isomer $\delta$=30.58, 38.10, 93.70, 127.89 (bs), 144.16, 152.46; MS (70 eV) $m/z$ (rel intensity) 286 ($M^+$, 1.6), 160 (16), 159 (100), 144 (12), 143 (13), 129 (25), 128 (23), 117 (28), 115 (14), 103 (13), 102 (17), 57 (63). Found: C, 50.61; H, 5.37%. Calcd for $C_{12}H_{15}I$: C, 50.37; H, 5.28%.

**(*Z*)-1-Dimethylphenylsilyl-1-iodo-3,3-dimethyl-1-butene (20):** Mp 53—54 °C (Hexane); IR ($CDCl_3$) 2958, 1251, 1114, 866, 828, 796, 777, 732, 701 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=0.45 (s, 6H), 1.21 (s, 9H), 6.58 (s, 1H), 7.33—7.43 (m, 3H), 7.52—7.56 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$=−2.39, 29.35, 36.17, 103.34, 127.77, 129.33, 134.19, 136.53, 157.27; MS (70 eV) $m/z$ (rel intensity) 345 ($M^+$+1, 0.3), 344 ($M^+$, 1.2), 247 (7.5), 218 (5.4), 217 (21), 136 (14), 135 (100). Found: C, 48.59; H, 5.98%. Calcd for $C_{14}H_{21}SiI$: C, 48.84; H, 6.15%.

**Ethyl 2- Iodo- 4, 4- dimethyl- 2- pentenoate (21, *E*: *Z*=9 : 1):** Bp 66—70 °C (5 Torr, bath temp); IR (neat) 2956, 1727, 1367, 1219, 1194, 1026 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=1.10 (s, 8.1H), 1.27 (s, 0.9H), 1.32 (t, $J$=7.1 Hz, 3H), 4.24 (q, $J$=7.1 Hz, 1.8H), 4.25 (q, $J$=7.1 Hz, 0.2H), 6.34 (s, 0.9H), 7.63 (s, 0.1H); $^{13}$C NMR ($CDCl_3$) for (*E*)-isomer $\delta$=13.76, 29.12, 38.43, 61.95, 79.14, 154.74, 166.79; MS (70 eV) $m/z$ (rel intensity) 283 ($M^+$+1, 2.1), 282 ($M^+$, 15), 239 (12), 237 (11), 112 (18), 110 (19), 109 (100), 81 (65), 41 (76). Found: C, 38.49; H, 5.31%. Calcd for $C_9H_{15}O_2I$: C, 38.31; H, 5.36%.

**General Procedure for Reduction of Alkenyl Iodide with $(Me_3Si)_3SiH$–$Et_3B$ or *n*-$Bu_3SnH$–$Et_3B$.** $Et_3B$ (0.96 M, 0.10 mL, 0.10 mmol) was added to a benzene (2.0 mL) solution of alkenyl iodide (1.00 mmol) and $(Me_3Si)_3SiH$ (0.274 g, 1.10 mmol) at room temperature under argon atmosphere. The mixture was stirred for 2 h, followed by an addition of aqueous NaOH (1.0 M, 10 mL). After stirring for another 2 h, the resultant mixture was extracted with hexane (10 mL×3). Combined organic layers were dried over $Na_2SO_4$, and concentrated in vacuo. The residual oil was purified by silica-gel column.

The reaction conditions for reduction with *n*-$Bu_3SnH$ was similar to those with $(Me_3Si)_3SiH$. The work-up procedure is as follows. After stirring for 2 h, the reaction mixture was concentrated in vacuo, and the residue was dissolved in $CH_2Cl_2$ (10 mL). Anhydrous KF (1.0 g) and saturated aqueous KF (2.0 mL) was added to the $CH_2Cl_2$ solution. After stirring for several hours, resulting precipitate was filtered through $Na_2SO_4$, and the filtrate was concentrated in vacuo. After the residue was dissolved in hexane (1.0 mL), the solution was submitted to silica-gel column.

**(*Z*)-1-Dimethylphenylsilyl-1-dodecene (10a):** Bp 96—100 °C (0.58 Torr, bath temp); IR (neat) 2952, 2920, 2850, 1605, 1248, 1112, 834, 820, 777, 727, 698 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=0.37 (s, 6H), 0.88 (t, $J$=6.8 Hz, 3H), 1.14—1.33 (m, 16H), 1.99—2.07 (m, 2H), 5.61 (dt, $J$=13.9, 1.2 Hz, 1H), 6.43 (dt, $J$=13.9, 7.5 Hz, 1H), 7.32—7.37 (m, 3H), 7.52—7.57 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$=−0.80, 14.13, 22.69, 29.28, 29.33, 29.50 (two carbons), 29.58 (two carbons), 31.91, 33.78, 126.36, 127.70, 128.71, 133.69, 139.80, 151.14; MS (70 eV) $m/z$ (rel intensity) 303 ($M^+$+1, 1.2), 302 ($M^+$, 4.1), 288 (16), 287 (50), 162 (39), 161 (50), 148 (21), 135 (91), 121 (100), 105 (23). Found: C, 79.42; H, 11.48%. Calcd for $C_{20}H_{34}Si$: C, 79.39; H, 11.33%.

**(*Z*)-1-Dimethylphenylsilyl-3,3-dimethyl-1-butene (10b):** Bp 67—71 °C (5 Torr, bath temp); IR (neat) 2952, 1596, 1248, 1112, 834, 821, 785, 729, 699, 670 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=0.41 (s, 6H), 0.96 (s, 9H), 5.51 (d, $J$=15.6 Hz, 1H), 6.48 (d, $J$=15.6 Hz, 1H), 7.31—7.37 (m, 3H), 7.52—7.57 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$=0.84, 30.06, 35.65, 122.51, 127.62, 128.60, 133.70, 140.86, 161.66; MS (70 eV) $m/z$ (rel intensity) 219 ($M^+$+1, 0.2), 218 ($M^+$, 1.7), 203 (34), 161 (56), 136 (15), 135 (100), 125 (10), 121 (38), 105 (17). Found: C, 77.01; H, 10.39%. Calcd for $C_{14}H_{22}Si$: C, 76.99; H, 10.15%.

**(*E*)-1-Dimethylphenylsilyl-3,3-dimethyl-1-butene (11b):** Bp 74—78 °C (5 Torr, bath temp); IR (neat) 2954, 1612, 1248, 1113, 994, 844, 824, 731, 697 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=0.32 (s, 6H), 1.02 (s, 9H), 5.65 (d, $J$=19.0 Hz, 1H), 6.13 (d, $J$=19.0 Hz, 1H), 7.33—7.38 (m, 3H), 7.49—7.56 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$=−2.37, 29.04, 35.22, 120.19, 127.66, 128.72, 133.82, 139.59, 159.53; MS (70 eV) $m/z$ (rel intensity) 219 ($M^+$+1, 0.8), 218 ($M^+$, 4.1), 203 (34), 162 (10), 161 (61), 148 (11), 136 (14), 135 (100), 121 (51), 105 (21), 73 (56). Found: C, 77.25; H, 10.12%. Calcd for $C_{14}H_{22}Si$: C, 76.99; H, 10.15%.

**(*Z*)-1-Phenyl-1-dodecene:** Bp 78—82 °C (0.45 Torr, bath temp); IR (neat) 2952, 2920, 2850, 1466, 767, 697 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=0.88 (t, $J$=6.6 Hz, 3H), 1.25 (bs, 14H), 1.40—1.48 (m, 2H), 2.28—2.36 (m, 2H), 5.66 (dt, $J$=11.6, 7.3 Hz, 1H), 6.40 (d, $J$=11.6 Hz, 1H), 7.19—7.35 (m, 5H); $^{13}$C NMR ($CDCl_3$) $\delta$=14.14, 22.69, 28.65, 29.36 (two carbons), 29.52, 29.61 (two carbons), 29.99, 31.91, 126.37, 128.07, 128.59, 128.70, 133.30, 137.79; MS (70 eV) $m/z$ (rel intensity) 245 ($M^+$+1, 7.6), 244 ($M^+$, 20), 118 (21), 117 (74), 116 (10), 115 (18), 105 (16), 104 (100). Found: C, 88.71; H, 11.76%. Calcd for $C_{18}H_{28}$; C, 88.45; H, 11.55%.

**(*E*)-1-Phenyl-1-dodecene:** Bp 79—84 °C (0.43 Torr, bath temp); IR (neat) 2922, 2850, 962, 690 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=0.88 (t, $J$=6.7 Hz, 3H), 1.27 (bs, 14H), 1.41—1.50 (m, 2H), 2.17—2.24 (m, 2H), 6.23 (dt, $J$=15.8 Hz, 1H), 6.37 (d, $J$=15.8 Hz, 1H), 7.15—7.21 (m, 1H), 7.25—7.36 (m, 4H); $^{13}$C NMR ($CDCl_3$) $\delta$=14.14, 22.70, 29.24, 29.36 (two carbons), 29.54, 29.63 (two carbons), 31.91, 33.06, 125.86, 126.71, 128.43, 129.60, 131.25, 137.91; MS (70 eV) $m/z$ (rel intensity) 245 ($M^+$+1, 7.5), 244 ($M^+$, 19), 118 (20), 117 (86), 115 (18), 105 (12), 104 (100). Found: C, 88.50; H, 11.74%. Calcd for $C_{18}H_{28}$: C, 88.45; H, 11.55%.

**(*Z*)-2,2-Dimethyl-3-tetradecene:** Bp 63—67 °C (0.55 Torr, bath temp); IR (neat) 2996, 2952, 2920, 2852, 1466, 1362 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=0.88 (t, $J$=6.6 Hz, 3H), 1.10 (s, 9H), 1.26 (bs, 16H), 2.12—2.19 (m, 2H), 5.15 (dt, $J$=12.0, 7.3 Hz, 1H), 5.30 (dt, $J$=12.0, 1.6 Hz, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$=14.13, 22.69, 28.38, 29.35, 29.42, 29.64 (two carbons), 30.31, 31.16 (two carbons), 31.91, 33.05,

129.15, 139.54; MS (70 eV) $m/z$ (rel intensity) 225 ($M^+ + 1$, 0.7), 224 ($M^+$, 3.2), 111 (7.3), 83 (100), 69 (57). Found: C, 85.68; H, 14.63%. Calcd for $C_{16}H_{32}$: C, 85.63; H, 14.37%.

**(*E*)-2,2-Dimethyl-3-tetradecene:** Bp 63—67 °C (0.55 Torr, bath temp); IR (neat) 2954, 2922, 2852, 1460, 970 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=0.88 (t, $J$=6.6 Hz, 3H), 0.98 (s, 9H), 1.20—1.35 (m, 16H), 1.92—1.99 (m, 2H), 5.30 (dt $J$=15.6, 6.4 Hz, 1H), 5.42 (dt, $J$=15.6, 1.0 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$=14.14, 22.70, 29.14, 29.36, 29.52, 29.64 (two carbons), 29.75, 29.81 (two carbons), 31.92, 32.67, 124.76, 141.36; MS (70 eV) $m/z$ (rel intensity) 225 ($M^+ + 1$, 0.8), 224 ($M^+$, 4.5), 111 (11), 83 (100), 69 (71). Found: C, 85.83; H, 14.45%. Calcd for $C_{16}H_{32}$: C, 85.63; H, 14.37%.

**Ethyl (*Z*)-4,4-Dimethyl-2-pentenoate:** Bp 64—68 °C (80 Torr, bath temp); IR (neat) 2956, 2906, 1728, 1638, 1385, 1363, 1202, 1179, 1032 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=1.20 (s, 9H), 1.30 (t, $J$=7.1 Hz, 3H), 4.17 (q, $J$=7.1 Hz, 2H), 5.65 (d, $J$=13.0 Hz, 1H), 6.00 (d, $J$=13.0 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$=14.15, 29.59, 33.83, 60.17, 118.61, 154.77, 166.82; MS (70 eV) $m/z$ (rel intensity) 157 ($M^+ + 1$, 0.8), 156 ($M^+$, 7.5), 141 (34), 113 (52), 111 (61), 83 (100), 55 (55), 41 (69). Found: C, 69.43; H, 10.50%. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32%.

**Ethyl (*E*)-4,4-Dimethyl-2-pentenoate:** Bp 72—76 °C (53 Torr, bath temp); IR (neat) 2960, 1721, 1651, 1367, 1311, 1300, 1260, 1204, 1165 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=1.08 (s, 9H), 1.30 (t, $J$=7.1 Hz, 3H), 4.19 (q, $J$=7.1 Hz, 2H), 5.73 (d, $J$=15.9 Hz, 1H), 6.97 (d, $J$=15.9 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$=14.28, 28.62, 33.74, 60.20, 116.62, 159.09, 167.35; MS (70 eV) $m/z$ (rel intensity) 157 ($M^+ + 1$, 1.5), 156 ($M^+$, 15), 141 (37), 113 (38), 111 (68), 83 (100), 41 (56). Found: C, 68.89; H, 10.51%. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32%.

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