Bull. Chem. Soc. Jpn., ***70****, 245—251 (1997)*

Manganese-Catalyzed Silylmagnesiation of Acetylenes and 1,3-Dienes

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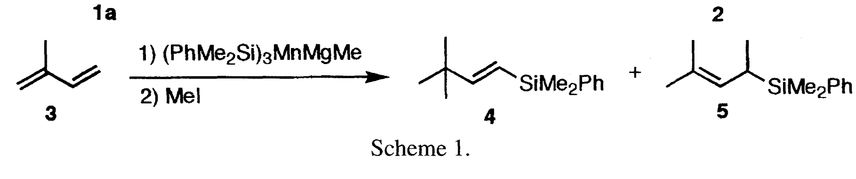
(Received August 7, 1996)

The treatment of 4-benzyloxy-1-butyne with PhMe$_2$SiMgMe in the presence of a catalytic amount of MnCl$_2$ gave a monosilylated product, (*E*)-PhCH$_2$OCH$_2$CH$_2$CH=CHSiMe$_2$Ph, selectively after an aqueous workup. Meanwhile, the reaction of isoprene with PhMe$_2$SiMgMe under manganese catalysis and the subsequent addition of iodomethane afforded 4-dimethylphenylsilyl-2,3-dimethyl-1-butene in good yield.

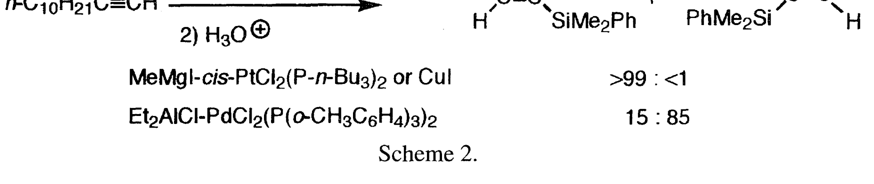
We have reported[1] on the preparation of tris(trialkylsilyl)manganate (R$_3$Si)$_3$MnMgMe and its reaction with acetylenes or 1,3-dienes. For instance, the treatment of 4-benzyloxy-1-butyne (**1a**) with (PhMe$_2$Si)$_3$MnMgMe, derived from PhMe$_2$SiLi, MeMgI, and MnCl$_2$, afforded a disilylated product, 4-benzyloxy-1,2-bis(dimethylphenylsilyl)-1-butene (**2**), in 51% yield as a stereoisomeric mixture ($Z/E = 42/58$). Meanwhile, a treatment of isoprene (**3**) with (PhMe$_2$Si)$_3$MnMgMe, followed by the addition of iodomethane, gave a mixture of (*E*)-3,3-dimethyl-1-dimethylphenylsilyl-1-butene (**4**) and 4-dimethylphenylsilyl-2-methyl-2-pentene (**5**) (**4** : **5** = 1 : 2) in 90% combined yield (Scheme 1). Here, we wish to report that the reaction of acetylenes or 1,3-dienes with PhMe$_2$SiMgMe in the presence of a catalytic amount of manganese(II) chloride has provided different types of products from those obtained by means of a stoichiometric reagent, (PhMe$_2$Si)$_3$MnMgMe.

(1) Manganese(II) Chloride Catalyzed Silylmagnesiation of Acetylenes. We have reported on the simultaneous cis addition of a silyl group and a metal to acetylenes with regioselectivity using PhMe$_2$SiLi and metal compounds, such as MeMgI, Et$_2$AlCl, ZnBr$_2$, and Et$_3$B, in the presence of a transition-metal catalyst.[2,3] Platinum- or copper-catalyzed silylmagnesiation (PhMe$_2$SiMgMe) of 1-dodecyne, followed by aqueous quenching, provided (*E*)-1-dimethylphenylsilyl-1-dodecene exclusively, which has the same regiochemistry as those products prepared from stoichiometric silylcupration[4] or silyltitanation.[5] On the other hand, palladium-catalyzed silylalumination (PhMe$_2$SiAlEt$_2$) afforded the regioisomer, 2-dimethylphenylsilyl-1-dodecene, with high regioselectivity (Scheme 2).

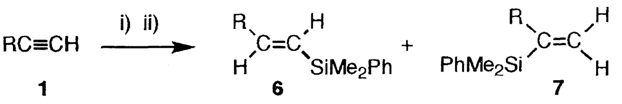
The treatment of 4-benzyloxy-1-butyne (**1a**, 1.0 mmol) with PhMe$_2$SiMgMe, prepared from PhMe$_2$SiLi (1.6 mmol)[6] and MeMgI (1.6 mmol) in situ, in the presence of a catalytic amount of MnCl$_2$ (0.08 mmol)[7,8] at 0 °C, gave a mixture of monosilylated products, **6a** and **7a**, in 90% combined yield after an aqueous workup.[9] The reaction proceeded with high regio- and stereoselectivities. (*E*)-4-Benzyloxy-1-dimethylphenylsilyl-1-butene (**6a**) was obtained as the major product, and only a small amount of the regioisomer, 4-benzyloxy-2-dimethylphenylsilyl-1-butene (**7a**), was detected in the reaction mixture (**6a**/**7a**=>95/5) (Scheme 3). The stereoisomer, (*Z*)-4-benzyloxy-1-dimethylphenylsilyl-1-butene, could not be observed in the reaction mixture. The use of tetrahydropyranyl ether of 3-butyn-1-ol (**1b**) in place of **1a** provided a regioisomeric mixture of **6b** and **7b** in 90%



Scheme 1.



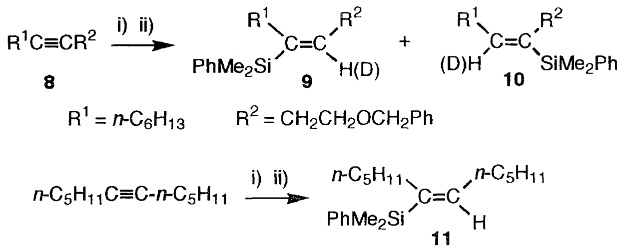
Scheme 2.



i) PhMe$_2$SiMgMe/cat. MnCl$_2$ ii) H$_3$O$^{\oplus}$

a: R = PhCH$_2$OCH$_2$CH$_2$	90%	>95 : <5
b: R = THPOCH$_2$CH$_2$	90%	85 : 15
c: R = n-C$_6$H$_{13}$	40%	80 : 20
d: R = n-C$_{10}$H$_{21}$	50%	76 : 24

Scheme 3.



i) PhMe$_2$SiMgMe/cat. MnCl$_2$ ii) H$_2$O (D$_2$O)

Scheme 4.

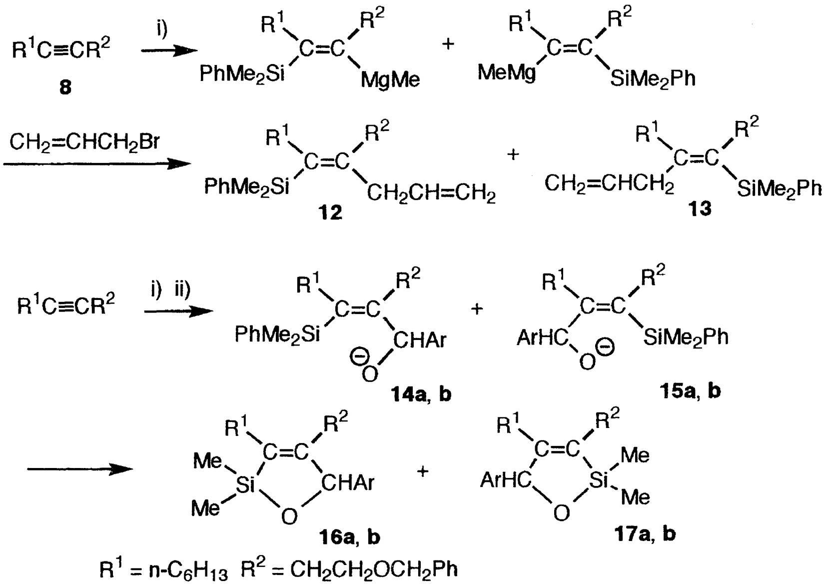
combined yield (**6b**/**7b** = 85/15). The oxygen atom of 3-butynyl ether played a critical role in the case of terminal acetylenes, since the yield dropped to 40 and 50% in the manganese-catalyzed reaction of 1-octyne (**1c**) and 1-dodecyne (**1d**).

(Dimethylphenylsilyl)magnesium reagent was added effectively to internal acetylenes as well as to terminal acetylenes to provide alkenylsilanes. The reaction proceeded with high regio- and stereoselectivities. For instance, a treatment of 1-benzyloxy-3-decyne (**8**) with PhMe$_2$SiMgMe in the presence of a catalytic amount of MnCl$_2$ at 25 °C for 2 h afforded a mixture of (*E*)-1-benzyloxy-4-dimethylphenylsilyl-3-decene (**9**) and its regioisomer **10** in 95% combined yield (**9**/**10** = 73/72). Quenching the reaction mixture with D$_2$O gave the corresponding mixture of (*E*)-alkenylsilane and regioisomer (**9**-*d*/**10**-*d* = 70/30, 95% combined yield). 6-Dodecyne provided (*E*)-6-dimethylphenylsilyl-6-dodecene (**11**) as a single product in 95% yield. The yield was much higher than that of the reaction between 1-dodecyne and PhMe$_2$SiMgMe (Scheme 4).

The intermediary alkenylmagnesium compound could be trapped by various electrophiles. The addition of allyl bromide provided allylated products **12** and **13** (**12**/**13** = 8/2) in 68% yield. The addition of benzaldehyde afforded 4-[(2-benzyloxy)ethyl]-3-hexyl-2,2-dimethyl-5-phenyl-1-oxa-2-silacyclopent-3-ene **16a** and regioisomer **17a** (**16a**/**17a** = 8/2) in 65% yield. *p*-Methoxybenzaldehyde also gave the corresponding silyl ether, **16b** and **17b** (**16b**/**17b** = 7/3), in 70% yield (Scheme 5). The use of butyraldehyde in place of aromatic aldehydes provided a complex mixture containing the corresponding oxasilacyclopentene derivative in only < 20% yield. The formation of silyl ether, **16** and **17**, might be explained by an internal attack of oxides **14** and **15** on silicon under cleavage of silicon–phenyl bond.[10,11] In these reactions, (*E*)-1-benzyloxy-4-dimethylphenylsilyl-3-decene (**9**), (*E*)-1-benzyloxy-3-dimethylphenylsilyl-3-decene (**10**), and 1-benzyloxy-3,4-bis(dimethylphenylsilyl)-3-decene were obtained as by-products (10—15% combined yield).

(2) Manganese(II) Chloride Catalyzed Silylmagnesiation of 1,3-Dienes. We have reported that a reaction of 1,3-diene, such as isoprene with (PhMe$_2$Si)$_3$MnMgMe, gave a mixture of (*E*)-3,3-dimethyl-1-dimethylphenylsilyl-1-butene (**4**) and 4-dimethylphenylsilyl-2-methyl-2-pentene (**5**) after quenching with iodomethane (vide supra).[1b] Here, we describe that manganese-catalyzed silylmagnesiation of 1,3-diene has provided different products from those generated in the stoichiometric reaction with (PhMe$_2$Si)$_3$MnMgMe.

The treatment of isoprene (**3**) with PhMe$_2$SiMgMe in the



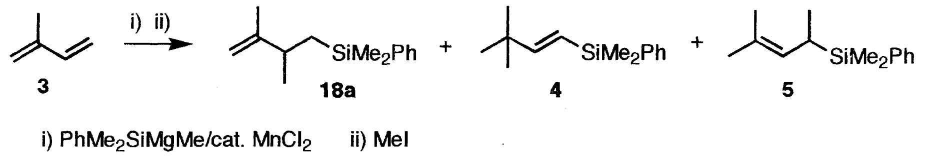
R^1 = n-C$_6$H$_{13}$ R^2 = CH$_2$CH$_2$OCH$_2$Ph

i) PhMe$_2$SiMgMe/cat. MnCl$_2$ ii) a: PhCHO, b: p-MeOC$_6$H$_4$CHO

Scheme 5.

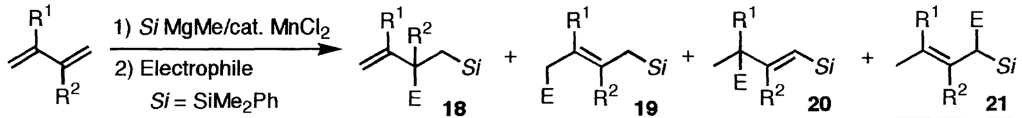
presence of $MnCl_2$ catalyst under an argon atmosphere, followed by the addition of iodomethane, afforded 4-dimethylphenylsilyl-2,3-dimethyl-1-butene (**18a**) as a main product, along with **4** and **5** (Scheme 6).

The representative results of the reaction of 1,3-butadiene and 2,3-dimethyl-1,3-butadiene as well as isoprene are summarized in Table 1. Several comments are worth making: (1) The distribution of the products heavily depended on the reaction temperature. For instance, when iodomethane was added at −78 °C to silyl-substituted allylic magnesium compound, prepared from isoprene and $PhMe_2SiMgMe$ at 0 °C in the presence of $MnCl_2$ catalyst, 4-dimethylphenylsilyl-2,3-dimethyl-1-butene (**18a**) was obtained exclusively (Entry 1). In contrast, the addition of iodomethane at 0 °C provided 3,3-dimethyl-1-dimethylphenylsilyl-1-butene (**4**) and 4-dimethylphenylsilyl-2-methyl-2-pentene (**5**) in addition to **18a** (**18a** : **4** : **5** = 88 : 6 : 6) (Entry 2). Moreover, the addition at 25 °C afforded 4-dimethylphenylsilyl-2-methyl-2-pentene (**5**) as the main product in 37% yield in addition to **18a** (14% yield) (Entry 3). To prevent the formation of a complex isomeric mixture, other electrophiles, such as allyl bromide and carbonyl compounds, where added at −78 °C (Entry 4—15 except 13). (2) The addition of aldehyde or ketone at −78 °C to the intermediary magnesium compound, derived from manganese-catalyzed silylmagnesiation of isoprene, afforded homoallylic silane derivatives **18e**, **18f**, and **18g** exclusively. In contrast, quenching with CH_3COOH, even at −78 °C, gave a mixture of 4-dimethylphenylsilyl-2-methyl-1-butene (**18c**, 70%) and 1-dimethylphenylsilyl-3-methyl-2-butene (**19c**, 8%) (Entry 5). The addition of D_2O at −78 °C also provided an isomeric mixture of **18d** and **19d** (**18d**/**19d** = 77/23). (3) Manganese salts, such as $Mn_2(CO)_{10}$ and $CH_3C_5H_4Mn(CO)_3$, were also effective as $MnCl_2$. For example, the treatment of isoprene (1.0 mmol) with silylmagnesium reagent (1.6 mmol) in the presence of $Mn_2(CO)_{10}$ and $CH_3C_5H_4Mn(CO)_3$ (0.08 mmol each) provided a mixture of 4-dimethylphenylsilyl-2-methyl-1-butene (**18c**) and 1-dimethylphenylsilyl-3-methyl-2-butene (**19c**) in 90% (**18c**/**19c** = 62/38) and 70% (**18c**/**19c** = 72/28) combined yields, respectively, after quenching with H_2O at −78 °C. (4) The reagent $PhMe_2SiLi$ or $PhMe_2SiMgMe$ did not react with isoprene without manganese(II) chloride, which suggests that the manganese salts played a critical role for the silylmagnesiation reaction. The addition of MeMgI was also essential for a successful reaction. The treatment of isoprene with $PhMe_2SiLi$ instead of $PhMe_2SiMgMe$ in the presence



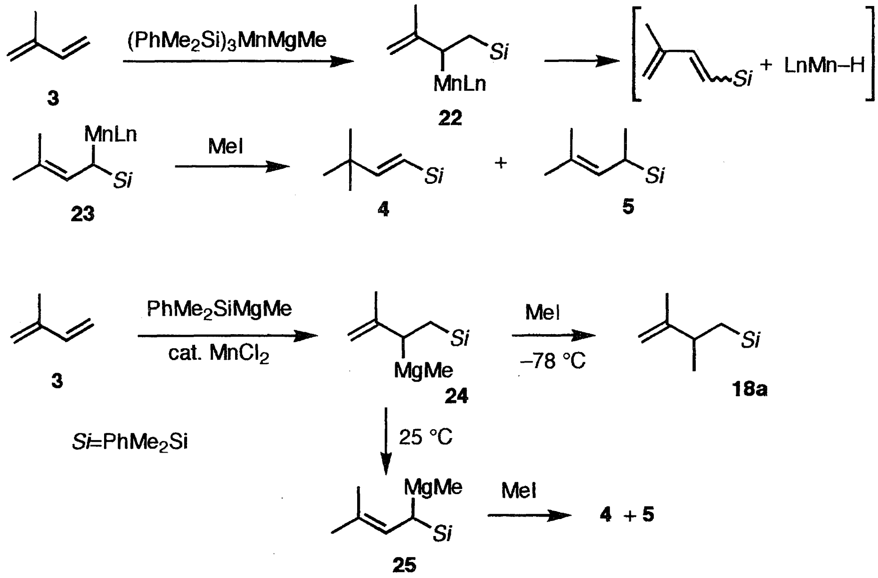
Scheme 6.

Table 1. Manganese-Catalyzed Silylmagnesiation of 1,3-Dienes[a)]

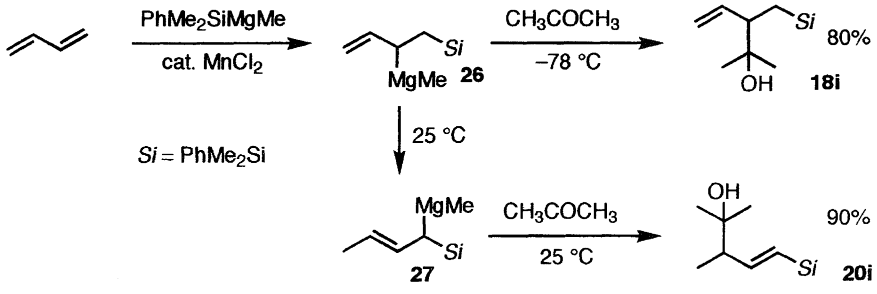


Entry	Diene			Product / %			
	R^1	R^2	Electrophile	**18**	**19**	**20**	**21**
1	Me	H	MeI	83 (**18a**)	0	0	0
2			$\text{MeI}^{b)}$	86	0	6 (**4**)	6 (**5**)
3			$\text{MeI}^{c)}$	14	0	2	37
4			$CH_2{=}CHCH_2Br$	83 (**18b**)	0	0	0
5			CH_3COOH	70 (**18c**)	8 (**19c**)	0	0
6			D_2O	74 (**18d**)	22 (**19d**)	0	0
7			*n*-BuCHO	88 (**18e**)	0	0	<2
8			PhCHO	95 (**18f**)	0	0	<2
9			CH_3COCH_3	90 (**18g**)	0	0	<2
10	H	H	MeI	63 (**18h**)	0	0	10 (**21h**)
11			CH_3COCH_3	80 (**18i**)	0	0	0
12			$D_2O^{d)}$	48 (**18j**)	47 (**19j**)	0	0
13			$H_2O^{e)}$	7 (**18k**)	**19k**$^{f)}$	39 (**20k**)	**21k**$^{f,g)}$
14	Me	Me	MeI	53 (**18l**)	0	0	0
15			CH_3COCH_3	47 (**18m**)	0	0	0

a) $PhMe_2SiMgMe$ and 1,3-diene were stirred at 0 °C in the presence of $MnCl_2$ catalyst for 10 min and then electrophiles were added at −78 °C unless otherwise noted. b) MeI was added at 0 °C. c) The reaction between $PhMe_2SiMgMe$ and isoprene was performed at 25 °C for 0.5 h and then MeI was added at 25 °C. d) D_2O was added at −78 °C. e) H_2O was added at 0 °C. f) **19k**+**21k** = 54%. g) E/Z = 70/30.



Scheme 7.



Scheme 8.

of a catalytic amount of $MnCl_2$ gave 4-dimethylphenylsilyl-2-methyl-1-butene in only < 20% yield after quenching with water. (5) 1,3-Butadiene was equally reactive toward a $MnCl_2$-catalyzed silylmagnesiation reaction, and 2,3-dimethyl-1,3-butadiene was less reactive than 1,3-butadiene and isoprene. 1,3-Pentadiene and 1,3-cyclooctadiene were too sluggish to react with $PhMe_2SiMgMe$ in the presence of a $MnCl_2$ catalyst.

We are tempted to assume the following reaction mechanism for stoichiometric silylmanganation and manganese-catalyzed silylmagnesiation reactions of isoprene (Scheme 7). In the stoichiometric reaction with $(PhMe_2Si)_3MnMgMe$, regioselective silylmanganation of isoprene occurs to give silylated allylmanganese compound **22** in the first step of the reaction sequence. Then, a β-elimination of Mn–H from **22**, followed by hydromanganation (1, 4-fashion), generates a more stable allylmanganese species **23**. The addition of iodomethane to **23** affords two isomeric products, **4** and **5**. Meanwhile, the catalytic reaction proceeds as follows. Manganese-catalyzed silylmagnesiation takes place regioselectively to introduce a silyl group at the least-hindered position, giving an allylmagnesium compound **24**. The allylic metal species **24** reacts at a secondary carbon with electrophiles, such as iodomethane and carbonyl compounds, regioselectively at −78 °C to give **18**. However, at a higher temperature, such as 25 °C, a partial manganese-catalyzed isomerization of **24** into **25** competes with the reaction between **24** and iodomethane, and a complex isomeric mixture containing **18**, **20**, and **21** is obtained upon a treatment with electrophiles. Heating a solution of **24** accelerated the isomerization, which was exemplified by the following experiment. The mixture of isoprene and $PhMe_2SiMgMe$ containing a $MnCl_2$ catalyst was stirred for 10 min at 0 °C, and then heated at 80 °C for 30 min. The addition of iodomethane to the resulting mixture at 25 °C provided a mixture of three isomers, **18a**, **4**, and **5** (**18a** : **4** : **5** = 11 : 12 : 77), in 40% combined yield.

The manganese-catalyzed isomerization by β-elimination and a subsequent readdition of Mn–H took place more easily in the adduct of 1,3-butadiene with $PhMe_2SiMgMe$ compared to the adduct derived from isoprene and $PhMe_2SiMgMe$. For instance, when D_2O was added at −78 °C to allylic magnesium compound **26**, prepared from butadiene and $PhMe_2SiMgMe$ at 0 °C in the presence of $MnCl_2$ catalyst, a mixture of **18j** and **19j** (**18j** : **19j** = 1 : 1) was obtained (Entry 12). In contrast, an addition of H_2O at 0 °C afforded **20k** and **21k** in addition to **18k** and **19k** (**18k** : **19k**+**21k** : **20k** = 7 : 54 : 39). Moreover, two stereoisomers could be prepared separately by changing the reaction temperature without any contamination by the other isomer in the reaction of 1,3-butadiene and acetone. The addition of acetone to the reaction mixture, derived from 1,3-butadiene and silylmagnesium in the presence of $MnCl_2$ at −78 °C, afforded 2-methyl-3-[(dimethylphenylsilyl)methyl]-4-penten-2-ol (**18i**) as a single product (Entry 11 in Table 1). In contrast, 2,3-dimethyl-5-dimethylphenylsilyl-4-penten-2-ol (**20i**) was obtained exclusively upon the addition of acetone at 25 °C (Scheme 8).

Experimental

Distillation of the products was performed using Kugelrohr (Büchi); the boiling points are indicated by the air-bath temperature values without any correction. The NMR spectra (^1H and ^{13}C) were recorded on a Varian GEMINI 300 spectrometer in $CDCl_3$; tetramethylsilane (TMS) was used as an internal standard. The IR spectra were determined on a JASCO IR-810 spectrometer. The analyses were carried out at the Elemental Analysis Center of Kyoto University.

General Procedure for the Reaction of Acetylene with $PhMe_2SiMgMe$ in the Presence of a Catalytic Amount of $MnCl_2$. The reaction of 3-decyn-1-ol benzyl ether (**8**) with $PhMe_2SiMgMe$ is representative. A tetrahydrofuran (THF) solution of $PhMe_2SiLi$ (0.7 M, 2.2 mL, 1.6 mmol, $M = mol\,dm^{-3}$) and MeMgI (1.0 M, ether solution, 1.6 mL, 1.6 mmol) was added to a suspension of $MnCl_2$ (10 mg, 0.08 mmol) in THF (2 mL) at 0 °C under an argon atmosphere, After being stirred for 30 min at 0 °C, a THF solution of **8** (0.24 g, 1.0 mmol) was added, and the resulting mixture was stirred for 2 h at 0 °C and warmed up to 25 °C. The mixture was poured into ice-cooled water and extracted with ethyl acetate (20 mL×3). The combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residual oil was submitted to silica-gel column chromatography (hexane/ethyl acetate = 20/1) to give a mixture of (*E*)-1-benzyloxy-4-dimethylphenylsilyl-3-decene (**9**) and its regioisomer (**10**) in 95% yield (0.36 g, **9**/**10** = 73/27).

(*E*)-1-Benzyloxy-4-dimethylphenylsilyl-3-decene (9) and (*E*)-1-Benzyloxy-3-dimethylphenylsilyl-3-decene (10)=(73 : 27): IR (neat) 2952, 2924, 2854, 1110, 812, 730, 697 cm^{-1}; ^1HNMR ($CDCl_3$) $\delta = 0.30$ (s, 1.62H), 0.32 (s, 4.38H), 0.82 (t, $J = 6.9$ Hz, 2.19H), 0.85 (t, $J = 6.9$ Hz, 0.81H), 1.06—1.35 (m, 8H), 2.09 (m, 2H), 2.46 (dt, $J = 6.9$, 6.9 Hz, 2H), 3.22 (t, $J = 8.1$ Hz, 0.54H), 3.49 (t, $J = 6.9$ Hz, 1.46H), 4.36 (s, 0.54H), 4.51 (s, 1.46H), 5.80 (t, $J = 6.9$ Hz, 0.73H), 5.87 (t, $J = 6.6$ Hz, 0.27H), 7.32 (m, 8H), 7.48 (m, 2H); ^{13}CNMR ($CDCl_3$, major isomer) $\delta = -2.79$, 13.95, 22.49, 29.22, 29.54, 29.89, 30.02, 31.53, 69.83, 72.85, 127.59, 127.67, 128.44, 128.80, 134.07, 133.77, 138.64, 139.16, 141.61. Found: C, 78.60; H, 9.56%. Calcd for $C_{25}H_{36}OSi$: C, 78.88; H, 9.53%.

(*E*)-1-Benzyloxy-3-deuterio-4-dimethylphenylsilyl-3-decene (9-d) and (*E*)-1-Benzyloxy-4-deuterio-3-dimethylphenylsilyl-3-decene (10-d) (73 : 27): IR (neat) 2952, 2924, 2852, 1598, 1248, 1109, 830, 814, 771, 731, 697 cm^{-1}; ^1HNMR ($CDCl_3$) $\delta = 0.30$ (s, 1.62H), 0.32 (s, 4.38H), 0.82 (t, $J = 6.9$ Hz, 2.19H), 0.85 (t, $J = 6.9$ Hz, 0.81H), 1.06—1.35 (m, 8H), 2.09 (m, 2H), 2.46 (t, $J = 7.2$ Hz, 2H), 3.22 (t, $J = 8.1$ Hz, 0.54H), 3.49 (t, $J = 6.9$ Hz, 1.46H), 4.36 (s, 0.54H), 4.51 (s, 1.46H), 7.32 (m, 8H), 7.48 (m, 2H); ^{13}CNMR ($CDCl_3$, major isomer) $\delta = -2.78$, 13.94, 22.49, 29.13, 29.55, 29.90, 30.00, 31.54, 69.84, 72.86, 127.59, 127.68, 128.45, 128.80, 134.08, 138.67, 139.19, 141.48. Found: C, 78.68; H+D, 9.91%. Calcd for $C_{25}H_{35}DOSi$: C, 78.68; H+D, 9.69%.

4-[(2-Benzyloxy)ethyl]-5-dimethylphenylsilyl-1,4-undecadiene (12) and 7-Benzyloxy-5-dimethylphenylsilyl-4-hexyl-1,4-heptadiene (13) (80 : 20): IR (neat) 2952, 2924, 2852, 1455, 1428, 1249, 1109, 832, 814, 771, 729, 698 cm^{-1}; ^1HNMR ($CDCl_3$) $\delta = 0.340$ (s, 1.2H), 0.344 (s, 4.8H), 0.86 (t, $J = 6.9$ Hz, 3H), 1.23 (m, 8H), 2.13 (m, 2H), 2.49 (t, $J = 7.5$ Hz, 1.6H), 2.54 (t, $J = 7.5$ Hz, 0.4H), 2.73 (d, $J = 6.3$ Hz, 2H), 3.50 (t, $J = 7.5$ Hz, 1.6H), 3.52 (t, $J = 7.5$ Hz, 0.4H), 4.44 (s, 0.4H), 4.50 (s, 1.6H), 4.85 (m, 1H), 4.89 (m, 1H), 5.45 (m, 1H), 7.30 (m, 8H), 7.47 (m, 2H); ^{13}CNMR ($CDCl_3$, major isomer) $\delta = -0.29$, 13.97, 22.59, 29.64, 31.05, 31.63, 32.35, 41.75, 69.15, 72.75, 116.25, 127.56, 127.66, 127.75, 128.43, 128.64, 133.83, 134.11, 135.69, 136.80, 138.68, 140.65. Found: C, 79.73; H, 9.71%. Calcd for $C_{26}H_{36}SiO_2$: C, 79.95; H, 9.51%.

4-[(2-Benzyloxy)ethyl]-3-hexyl-2,2-dimethyl-5-phenyl-1-oxa-2-silacyclopent-3-ene (16a) and 3-[(2-Benzyloxy)ethyl]-4-hexyl-2,2-dimethyl-5-phenyl-1-oxa-2-silacyclopent-3-ene (17a) (80 : 20): IR (neat) 3026, 2952, 2922, 2852, 1455, 1249, 1098, 1079, 1054, 1027, 863, 833, 779, 733, 697 cm^{-1}; ^1HNMR ($CDCl_3$) $\delta = 0.21$ (s, 0.6H), 0.29 (s, 2.4H), 0.29 (s, 0.6H), 0.37 (s, 2.4H), 0.88 (t, $J = 6.9$ Hz, 2.4H), 0.95 (m, 0.6H), 1.15—1.50 (m, 8H), 1.50—1.65 (m, 0.2H), 2.08 (ddd, $J = 6.6$, 8.5, 14.1 Hz, 0.8H), 2.13 (m, 0.2H), 2.25 (t, $J = 7.5$ Hz, 1.6H), 2.47 (ddd, $J = 6.0$, 8.5, 14.1 Hz, 0.8H), 2.55—2.65 (m, 0.4H), 3.13 (dt, $J = 6.0$, 8.5 Hz, 0.8H), 3.32 (dt, $J = 6.6$, 8.5 Hz, 0.8H), 3.55 (t, $J = 6.6$ Hz, 0.4H), 4.38 (s, 1.6H), 4.55 (s, 0.4H), 5.45 (s, 0.2H), 5.49 (m, 0.8H), 7.19—7.60 (m, 10H); ^{13}CNMR ($CDCl_3$, major isomer) $\delta = 0.72$, 1.54, 13.97, 22.54, 28.03, 28.16, 29.49, 30.34, 31.63, 68.37, 72.6, 86.79, 127.32, 127.52, 127.56, 127.86, 128.39, 128.52, 137.41, 138.42, 142.29, 151.33. Found: C, 76.41; H, 8.87%. Calcd for $C_{26}H_{36}SiO_2$: C, 76.42; H, 8.87%.

4-[(2-Benzyloxyethyl)]-3-hexyl-5-(4-methoxyphenyl)-2,2-dimethyl-1-oxa-2-silacyclopent-3-ene (16b) and 3-[(2-Benzyloxy)ethyl]-3-hexyl-5-(4-methoxyphenyl)-2,2-dimethyl-1-oxa-2-silacyclopent-3-ene (17b) (70 : 30): IR (neat) 2954, 2926, 2854, 1613, 1513, 1456, 1362, 1304, 1249, 1173, 1132, 1100, 1077, 1038, 1010, 864, 827, 780, 734, 697 cm^{-1}; ^1HNMR ($CDCl_3$) $\delta = 0.20$ (s, 0.9H), 0.28 (s, 3H), 0.35 (s, 2.1H), 0.78—0.90 (m, 0.9H), 0.90 (t, $J = 6.6$ Hz, 2.1H), 1.10—1.48 (m, 8H), 1.58—1.70 (m, 0.3H), 2.03—2.18 (m, 0.3H), 2.08 (ddd, $J = 6.6$, 8.4, 14.7 Hz, 0.7H), 2.25 (t, $J = 8.4$ Hz, 1.4H), 2.46 (ddd, $J = 6.3$, 8.7, 14.7 Hz, 0.7H), 2.50—2.61 (m, 0.6H), 3.16 (dt, $J = 6.3$, 9 Hz, 0.7H), 3.53 (t, $J = 6.6$ Hz, 0.6H), 3.32 (dt, $J = 6.3$, 9 Hz, 0.7H), 3.77 (s, 0.9H), 3.79 (s, 2.1H), 4.39 (s, 1.4H), 4.52 (s, 0.6H), 5.41 (s, 0.3H), 5.45 (s, 0.7H), 6.82 (m, 0.6H), 6.84 (m, 1.4H), 7.13 (m, 1.4H), 7.25 (m, 0.6H), 7.22—7.38 (m, 5H); ^{13}CNMR ($CDCl_3$, major isomer) $\delta = 0.70$, 1.61, 13.99, 22.56, 28.07, 28.23, 29.52, 30.37, 31.65, 55.21, 68.40, 72.61, 86.30, 113.90, 127.55, 127.58, 128.40, 128.54, 134.59, 137.33, 138.46, 151.46, 159.34. Found: C, 73.74; H, 8.62%. Calcd for $C_{27}H_{38}SiO_3$: C, 73.94; H, 8.73%.

The physical data for **6a**, **6b**, **6c**, **7a**, **7b**, **7c**, and **11** were identical with those which have been described in the literature.[3b)]

General Procedure for the Reaction of Silylmagnesium Reagent with 1,3-Dienes. A THF solution of $PhMe_2SiLi$ (0.7 M, 2.2 ml, 1.6 mmol) and MeMgI (1.0 M ether solution, 1.6 ml, 1.6 mmol) were added to a suspension of $MnCl_2$ (0.08 mmol) in THF (2 ml) at 0 °C under an argon atmosphere. After being stirred for 30 min at 0 °C, isoprene (THF solution, 1.0 mmol) was added and the whole was stirred for 10 min. The reaction flask was cooled to −78 °C in a dry ice bath, and iodomethane (3.2 mmol) was added. The resulting mixture was stirred for 30 min at −78 °C, and then warmed up to 25 °C. An extractive workup followed by silica-gel column chromatography gave 4-dimethylphenylsilyl-2,3-dimethyl-1-butene (**18a**) in 83% yield: Bp 111—115 °C (3 Torr, 1 Torr = 133.322 Pa); IR (neat) 2870, 1644, 1427, 1373, 1248, 1112, 887, 812, 697 cm^{-1}; ^1HNMR ($CDCl_3$) $\delta = 0.29$ (s, 3H), 0.30 (s, 3H), 0.84 (dd, $J = 7.5$, 15.9 Hz, 1H), 0.97 (dd, $J = 7.5$, 15.9 Hz, 1H), 1.00 (d, $J = 6.9$ Hz, 3H), 1.64 (s, 3H), 2.36 (tq, $J = 7.5$, 6.9

Hz, 1H), 4.60 (s, 1H), 4.68 (s, 1H), 7.35 (m, 3H), 7.52 (m, 2H); ^{13}C NMR ($CDCl_3$) $\delta = -2.59$, -2.36, 18.44, 22.51, 22.95, 37.38, 108.46, 127.74, 128.80, 133.65, 139.99, 152.36. Found: C, 76.77; H, 10.18%. Calcd for $C_{14}H_{22}Si$: C, 77.05; H, 10.08%.

3-[(Dimethylphenylsilyl)methyl]-2-methyl-1,5-hexadiene (18b): Bp 125—127 °C (3 Torr); IR (neat) 2904, 1642, 1427, 1373, 1248, 1112, 991, 889, 698 $\mathrm{cm^{-1}}$; ^{1}H NMR ($CDCl_3$) $\delta = 0.27$ (s, 3H), 0.29 (s, 3H), 0.92 (d, $J = 7.8$ Hz, 2H), 1.57 (m, 3H), 2.06 (m, 2H), 2.29 (tt, $J = 7.2$, 7.2 Hz, 1H), 4.66 (s, 2H), 4.93 (m, 2H), 5.64 (m, 1H), 7.35 (m, 3H), 7.52 (m, 2H); ^{13}C NMR ($CDCl_3$) $\delta = -2.87$, -2.29, 17.83, 20.19, 41.24, 43.23, 111.09, 115.31, 127.72, 128.81, 133.66, 137.49, 139.86, 148.87. Found: C, 78.54; H, 10.11%. Calcd for $C_{16}H_{24}Si$: C, 78.67; H, 9.83%.

4-Dimethylphenylsilyl-2-methyl-1-butene (18c): Bp 104—106 °C (3 Torr); IR (neat) 2888, 1649, 1427, 1374, 1248, 1171, 1113, 883, 811, 771, 697 $\mathrm{cm^{-1}}$; ^{1}H NMR ($CDCl_3$) $\delta = 0.28$ (s, 6H), 0.90 (m, 2H), 1.71 (s, 3H), 2.00 (m, 2H), 4.66 (s, 1H), 4.69 (s, 1H), 7.35 (m, 3H), 7.52 (m, 2H); ^{13}C NMR ($CDCl_3$) $\delta = -3.28$, 13.63, 22.13, 31.71, 108.48, 127.83, 128.93, 133.66, 139.35, 148.51. Found: C, 76.46; H, 10.09%. Calcd for $C_{13}H_{20}Si$: C, 76.45; H, 9.79%.

3-Deuterio-4-dimethylphenylsilyl-2-methyl-1-butene (18d) and 1-Deuterio-4-dimethylphenylsilyl-2-methyl-2-butene (19d) (78 : 22): Bp 104—106 °C (3 Torr); IR (neat) 2956, 2910, 1649, 1427, 1248, 1113, 873, 837, 698 $\mathrm{cm^{-1}}$; ^{1}H NMR ($CDCl_3$) $\delta = 0.24$ (s, 1.32H), 0.26 (s, 4.68H), 0.87 (d, $J = 9.3$ Hz, 1.56H), 1.46 (m, 0.44H), 1.61 (d, $J = 8.4$ Hz, 0.44H), 1.67 (s, 0.66H), 1.69 (s, 2.34H), 1.97 (t, $J = 9.3$ Hz, 0.78H), 4.65 (s, 0.78H), 4.68 (s, 0.78H), 5.14 (t, $J = 8.4$ Hz, 0.22H), 7.35 (m, 3H), 7.50 (m, 2H); ^{13}C NMR ($CDCl_3$, major isomer) $\delta = -3.28$, 13.53, 22.10, 31.35 (t, $J = 19.5$ Hz), 108.49, 127.83, 128.93, 133.66, 139.36, 148.51. Found: C, 75.96; H+D, 10.45%. Calcd for $C_{13}H_{19}DSi$: C, 76.08; H+D, 10.23%.

3-[(Dimethylphenylsilyl)methyl]-2-methyl-1-octen-4-ol (*erythro*/*threo*=1 : 1 mixture) (18e): Bp 160 °C (0.5 Torr, decomp); IR (neat) 3410, 2954, 2858, 1643, 1427, 1248, 1112, 837, 730, 698 $\mathrm{cm^{-1}}$; ^{1}H NMR ($CDCl_3$) $\delta = 0.24$ (s, 1.5H), 0.25 (s, 1.5H), 0.26 (s, 1.5H), 0.28 (s, 1.5H), 0.83—1.59 (m, 15H), 2.13 (m, 1H), 3.34 (m, 1H), 4.72 (s, 0.5H), 4.77 (s, 0.5H), 4.78 (s, 0.5H), 4.87 (m, 0.5H), 7.33 (m, 3H), 7.47 (m, 2H); ^{13}C NMR ($CDCl_3$) $\delta = -3.18$, -2.96, -2.31, -2.05, 13.95, 13.99, 14.03, 15.78, 18.73, 20.57, 22.59, 22.74, 27.74, 28.18, 33.72, 34.13, 48.80, 49.61, 73.63, 74.18, 112.93, 115.20, 127.72, 127.76, 128.83, 128.94, 133.64, 133.68, 139.44, 139.78, 146.55, 147.17. Found: C, 74.40; H, 10.41%. Calcd for $C_{18}H_{30}OSi$: C, 74.50; H, 10.34%.

2-[(Dimethylphenylsilyl)methyl]-3-methyl-1-phenyl-3-buten-1-ol (18f): Bp 160 °C (0.5 Torr, decomp); IR (neat) 3404, 2896, 1492, 1427, 1248, 1181, 1112, 999, 814, 698 $\mathrm{cm^{-1}}$; ^{1}H NMR ($CDCl_3$) $\delta = 0.15$ (s, 1.5H), 0.17 (s, 1.5H), 0.20 (s, 1.5H), 0.21 (s, 1.5H), 0.52 (dd, $J = 3$, 15 Hz, 0.5H), 0.81 (dd, $J = 12.3$, 15 Hz, 0.5H), 1.00 (dd, $J = 1.5$, 15 Hz, 0.5H), 1.14 (dd, $J = 3.0$, 15 Hz, 0.5H), 1.55 (s, 1.5H), 1.66 (s, 1.5H), 1.96 (s, 0.5H), 2.21 (s, 0.5H), 2.45 (m, 1H), 4.31 (d, $J = 9$ Hz, 0.5H), 4.54 (d, $J = 6$ Hz, 0.5H), 4.69 (m, 0.5H), 4.77 (m, 0.5H), 4.92 (m, 0.5H), 4.98 (m, 0.5H), 7.29 (m, 3H), 7.37 (m, 2H); ^{13}C NMR ($CDCl_3$) $\delta = -3.34$, -2.90, -2.33, -2.03, 13.37, 15.14, 17.83, 21.46, 50.26, 51.67, 76.67, 77.08, 113.34, 116.25, 126.35, 127.22, 127.58, 127.66, 127.67, 127.83, 128.12, 128.36, 128.77, 128.87, 133.60, 133.65, 139.03, 139.56, 142.42, 143.04, 146.15, 146.51. Found: C, 77.59; H, 8.67%. Calcd for $C_{20}H_{26}OSi$: C, 77.42; H, 8.38%.

3-[(Dimethylphenylsilyl)methyl]-2,4-dimethyl-4-penten-2-ol (18g): Bp 135—137 °C (1 Torr); IR (neat) 3444, 2894, 1638, 1427, 1375, 1248, 1111, 945, 818, 728, 698 $\mathrm{cm^{-1}}$; ^{1}H NMR ($CDCl_3$) $\delta = 0.26$ (s, 3H), 0.29 (s, 3H), 1.02 (m, 2H), 1.15 (s, 6H), 1.51 (s, 1H), 1.66 (m, 3H), 2.16 (m, 1H), 4.76 (m, 1H), 4.85 (m, 1H), 7.35 (m, 3H), 7.52 (m, 2H); ^{13}C NMR ($CDCl_3$) $\delta = -3.26$, -2.23, 14.54, 21.83, 27.61, 27.75, 53.28, 72.89, 114.95, 127.72, 128.87, 133.66, 139.56, 146.87. Found: C, 73.27; H, 10.19%. Calcd for $C_{16}H_{26}OSi$: C, 73.27; H, 9.91%.

4-Dimethylphenylsilyl-3-methyl-1-butene (18h): Bp 99—100 °C (3 Torr); IR (neat) 2874, 1638, 1248, 1113, 908, 786, 697 $\mathrm{cm^{-1}}$; ^{1}H NMR ($CDCl_3$) $\delta = 0.29$ (s, 3H), 0.30 (s, 3H), 0.83 (dd, $J = 7.2$, 14.7 Hz, 1H), 0.93 (dd, $J = 7.2$, 14.7 Hz, 1H), 1.00 (d, $J = 6.6$ Hz, 3H), 2.32 (m, 1H), 4.82 (m, 1H), 4.90 (m, 1H), 5.74 (ddd, $J = 7.2$, 9.9, 17.4 Hz, 1H), 7.35 (m, 3H), 7.52 (m, 2H); ^{13}C NMR ($CDCl_3$) $\delta = -2.30$, -2.02, 23.77, 23.82, 34.15, 111.09, 127.76, 128.80, 133.65, 139.99, 146.98. Found: C, 76.22; H, 9.93%. Calcd for $C_{13}H_{20}Si$: C, 76.48; H, 9.80%.

3-[(Dimethylphenylsilyl)methyl]-2-methyl-4-penten-2-ol (18i): Bp 133—135 °C (1 Torr); IR (neat) 3552, 3424, 3066, 2968, 2886, 1638, 1427, 1372, 1249, 1156, 1113, 1000, 914, 832, 728, 699 $\mathrm{cm^{-1}}$; ^{1}H NMR ($CDCl_3$) $\delta = 0.25$ (s, 3H), 0.27 (s, 3H), 0.75 (dd, $J = 12$, 14.7 Hz, 1H), 1.03 (dd, $J = 2.4$, 14.7 Hz, 1H), 1.10 (s, 3H), 1.12 (s, 3H), 1.55 (s, 1H), 2.12 (ddd, $J = 2.4$, 9.9, 12 Hz, 1H), 5.04 (ddd, $J = 1.8$, 10.2, 18 Hz, 2H), 5.54 (ddd, $J = 9.9$, 10.2, 18 Hz, 1H), 7.35 (m, 3H), 7.52 (m, 2H); ^{13}C NMR ($CDCl_3$) $\delta = -2.87$, -1.90, 16.02, 26.11, 26.22, 51.75, 72.69, 117.85, 127.75, 128.88, 133.68, 136.60, 140.67. Found: C, 72.52; H, 9.93%. Calcd for $C_{15}H_{24}OSi$: C, 72.60; H, 9.67%.

A Mixture of 3-Deuterio-4-dimethylphenylsilyl-1-butene (18j), (*E*)-1-Deuterio-4-dimethylphenylsilyl-2-butene (19j-*E*), and (*Z*)-1-Deuterio-4-dimethylphenylsilyl-2-butene (19j-*Z*) (50 : 39 : 11): Bp 83—85 °C (3 Torr); IR (neat) 2954, 2902, 1638, 1427, 1249, 1113, 836, 728, 697, 459, 442, 418 $\mathrm{cm^{-1}}$; ^{1}H NMR ($CDCl_3$) $\delta = 0.24$ (s, 0.66H), 0.26 (s, 5.34H), 0.83 (d, $J = 8.1$ Hz, 1H), 1.48 (m, 0.78H), 1.58 (m, 0.22H), 1.63 (d, $J = 8.1$ Hz, 0.22H), 1.70 (d, $J = 7.2$ Hz, 0.78H), 2.04 (m, 0.5H), 4.87 (ddd, $J = 10.2$, 1.2, 1.2 Hz, 0.5H), 4.97 (ddd, $J = 17.1$, 1.2, 1.2 Hz, 0.5H), 5.37 (m, 1H), 5.86 (ddd, $J = 6.0$, 10.2, 17.1 Hz, 0.5H), 7.34 (m, 3H), 7.49 (m, 2H); ^{13}C NMR ($CDCl_3$, **18j** and **19j**-*E*) $\delta = -3.45$, -3.18, 12.19 (t, $J = 19.5$ Hz), 14.59, 17.02, 27.48 (t, $J = 19.5$ Hz), 112.88, 122.04, 125.87, 127.78, 127.82, 128.93, 129.01, 133.65, 133.71, 139.14, 139.35, 141.58. Found: C, 75.27; H+D, 10.02%. Calcd for $C_{12}H_{17}DSi$: C, 75.45; H+D, 9.95%.

A Mixture of (*E*)-1-Dimethylphenylsilyl-2-butene (21k-*E*), (*Z*)-1-Dimethylphenylsilyl-2-butene (21k-*Z*), and (*E*)-1-Dimethylphenylsilyl-1-butene (20k) (43 : 17 : 40): Bp 83—85 °C (3 Torr); IR (neat) 2952, 1248, 1113, 824, 696 $\mathrm{cm^{-1}}$; ^{1}H NMR ($CDCl_3$) $\delta = 0.26$ (s, 1.02H), 0.29 (s, 2.58H), 0.33 (s, 2.40H), 1.02 (t, $J = 7.5$ Hz, 1.2H), 1.51 (d, $J = 5.7$ Hz, 1.29H), 1.64 (d, $J = 5.7$ Hz, 0.51H), 1.66 (d, $J = 6.9$ Hz, 0.34H), 1.73 (d, $J = 7.5$ Hz, 0.86H), 2.17 (qd, $J = 7.5$, 5.7 Hz, 0.8H), 5.41 (m, 1.2H), 5.76 (d, $J = 18.6$ Hz, 0.4H), 6.19 (dt, $J = 18.6$, 5.7 Hz, 0.4H), 7.35 (m, 3H), 7.53 (m, 2H); ^{13}C NMR ($CDCl_3$) $\delta = -3.54$, -3.45, -2.60, 12.47, 12.60, 17.01, 17.93, 21.46, 29.35, 112.85, 122.07, 124.02, 125.85, 125.95, 126.44, 127.76, 127.78, 127.83, 128.87, 128.95, 129.01, 133.65, 133.71, 133.91, 139.13, 139.47, 150.84. Found: C, 75.84; H, 9.57%. Calcd for $C_{12}H_{18}Si$: C, 75.80; H, 9.47%.

4-Dimethylphenylsilyl-2,3,3-trimethyl-1-butene (18l): Bp 113—115 °C (3 Torr); IR (neat) 2958, 1636, 1427, 1376, 1248, 1190, 1112, 890, 816, 698 $\mathrm{cm^{-1}}$; ^{1}H NMR ($CDCl_3$) $\delta = 0.29$ (s, 6H), 1.06 (s, 6H), 1.07 (s, 2H), 1.69 (s, 3H), 4.63 (m, 1H), 4.70 (m, 1H), 7.35 (m, 3H), 7.52 (m, 2H); ^{13}C NMR ($CDCl_3$) $\delta = -1.27$, 19.63, 29.16, 29.90, 30.44, 38.41, 108.28, 127.68, 128.61, 133.59, 140.94, 154.20. Found: C, 77.31; H, 10.42%. Calcd for $C_{15}H_{24}Si$:

C, 77.57; H, 10.33%.

3-[(Dimethylphenylsilyl)methyl]-2,3,4-trimethyl-4-penten-2-ol (18m): Bp 139—141 °C (1 Torr); IR (neat) 3462, 2974, 1628, 1427, 1369, 1248, 1111, 1044, 947, 892, 815, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 0.27$ (s, 3H), 0.32 (s, 3H), 0.99 (d, $J = 14.4$ Hz, 1H), 1.07 (s, 3H), 1.12 (s, 3H), 1.17 (s, 3H), 1.54 (d, $J = 14.4$ Hz, 1H), 1.69 (s, 1H), 1.80 (s, 3H), 4.84 (s, 1H), 5.00 (s, 1H), 7.35 (m, 3H), 7.52 (m, 2H); ^{13}C NMR ($CDCl_3$) $\delta = -1.02$, -0.82, 22.41, 23.24, 23.85, 25.45, 25.58, 48.20, 75.28, 114.54, 127.71, 128.65, 133.60, 141.10, 150.39. Found: C, 73.98; H, 10.42%. Calcd for $C_{17}H_{28}OSi$: C, 73.93; H, 10.14%.

The physical data for **19c**, **20i**, and **21h** were identical with those which have been described in the literature.[1c)]

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