An Efficient Synthesis of Unsymmetrical 1,1-Bis(silyl)ethenes

Grzegorz Hreczycho, Piotr Pawluć, Bogdan Marciniec*

Department of Organometallic Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland
Fax +48(61)8291508; E-mail: marcinb@amu.edu.pl

Received 17 October 2005; revised 8 December 2005

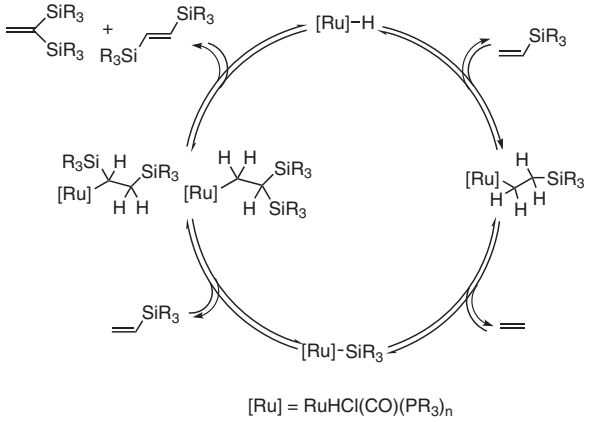
Abstract: A new convenient and effective method for the synthesis of unsymmetrical 1,1-bis(silyl)ethenes is described. The synthetic methodology involves selective silylative coupling cyclization of *N*-methyl-*N*-(dimethylvinylsilyl)-2-(dimethylvinylsilyloxy)ethanamine catalyzed by a ruthenium hydride complex and subsequent one-pot reaction of the cyclic bis(silyl)derivative with Grignard reagents followed by alcoholysis. As a result, a variety of 1,1-bis(silyl)ethenes containing different substituents at the silicon atoms were produced in regiocontrolled manner with considerably high efficiency.

Key words: vinylsilanes, silylative coupling, amino alcohol, Grignard reactions, organometallic reagents

Vinylsilanes are important synthetic intermediates in stereocontrolled organic synthesis.[1] Due to similar properties of 1,1-bis(silyl)alkenes to those of vinylsilanes, they have gained significant attention as potential intermediates in the organic and organosilicon syntheses.[2] The potential use of the 1,1-bis(silyl)alkenes as precursors for the preparation of ketones and isoxazoline derivatives as well as a variety of important organosilicon intermediates such as acylsilanes, epoxysilanes, silanols, etc., has greatly stimulated their synthetic advancements.[3]

To date however, the complexity of 1,1-bis(silyl)alkene synthesis has been limiting their use as synthetic precursors. Unsymmetrical 1,1-bis(silyl)ethenes have been previously prepared by multistep reactions involving commercially unavailable substrates, e.g. dihalodisilylmethanes or 1-halo-1-silylethenes.[4] Application of these methods are limited not only by complicated synthetic procedures involving the use of harmful starting materials and very reactive organolithium compounds, but also by only moderate yields of the obtained products.[3c,4] Therefore, in view of the growing interest in 1,1-bis(silyl)ethenes, the development of more efficient and straightforward synthetic methods is of great significance.

In the last two decades in the series of our studies we have developed the silylative coupling reaction of vinylsilane derivatives in the presence of transition-metal complexes (e.g. ruthenium and rhodium) initially containing or generating M–H and M–Si bonds.[5] The silylative coupling reaction of monovinyl organosilicon compounds occurs by cleavage of the =C–Si bond of the vinyl-substituted silicon compound and the activation of the =C–H bond of the second vinylsilane (or other olefin) molecule. The mechanism of this reaction (Scheme 1) involving β-silyl elimination and insertion of a C=C double bond into the resulting M–Si bond has been proved by insertion of ethylene and vinylsilane into M–Si (where M = Ru, Rh, Co) bonds as well as by a series of elaborate mass spectrometric studies with deuterated styrene and vinylsilanes.[6]



Scheme 1 Silylative coupling reaction mechanism

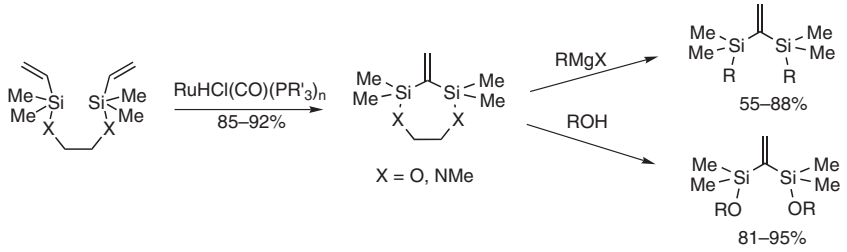
The notable peculiarity of silylative coupling reaction, distinguishing it from cross-metathesis, which starts with the same substrates, is the formation of 1,1-bis(silyl)ethene fragment under the given conditions.[6b] Previous reports have shown that silylative coupling reactions of divinyl-substituted organosilicon monomers catalyzed by ruthenium and rhodium complexes under optimum conditions yielded silacyclic compounds containing *exo*-methylene bond between silicon atoms.[7]

We have recently reported a new facile and efficient protocol for the synthesis of alkyl-, aryl-, alkenyl- or alkoxy-substituted symmetrical 1,1-bis(silyl)ethenes using cyclic silyl ether or cyclic silyl amine selectively obtained via ruthenium-catalyzed silylative coupling cyclization of divinyl-substituted monomers, followed by their reaction with Grignard reagents or alcohols (Scheme 2).[8]

While this reaction sequence leads to a wide range of 1,1-bis(silyl)ethenes with moderate and high yields, this particular method cannot be applied to the synthesis of unsymmetrical bis(silyl) derivatives, which also seem to be desirable reagents in the organic and organosilicon syntheses.

Herein we present the results of our synthetic studies of unsymmetrical 1,1-bis(silyl)ethenes. The products de-

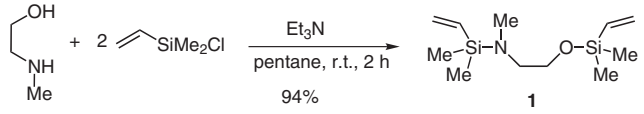
SYNTHESIS 2006, No. 8, pp 1370–1374
Advanced online publication: 27.03.2006
DOI: 10.1055/s-2006-926406; Art ID: T14505SS



Scheme 2 Synthesis of symmetrical 1,1-bis(silyl)ethenes

sired were obtained via ruthenium complex catalyzed silylative coupling cyclization of *N*-methyl-*N*-(dimethylvinylsilyl)-2-(dimethylvinylsilyloxy)ethanamine (**1**) to give 1-aza-1,2,2,4,4-pentamethyl-3-methylene-5-oxa-2,4-disilacycloheptane (**2**), followed by the treatment of the resulting cyclic product **2** with Grignard reagent, introduction of the alkoxy group via alcoholysis and reaction with another Grignard reagent.

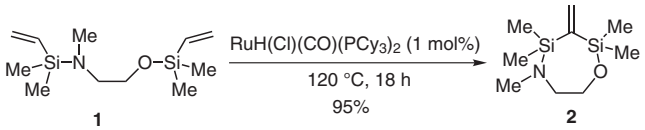
The starting *N*-methyl-*N*-(dimethylvinylsilyl)-2-(dimethylvinylsilyloxy)ethanamine (**1**) has been conveniently prepared by the reaction of commercially available and relatively inexpensive chlorodimethylvinylsilane and 2-(methylamino)ethanol in the presence of triethylamine in high yield (94%) as outlined in Equation 1.



Equation 1 Synthesis of *N*-methyl-*N*-(dimethylvinylsilyl)-2-(dimethylvinylsilyloxy)ethanamine

Two ruthenium-hydride complexes, [RuHCl(CO)(PCy_3)$_2$] and [RuHCl(CO)(PPh_3)$_3$], have been recently reported as effective catalysts for selective silylative coupling cyclization of 1,2-bis(dimethylvinylsilyloxy)ethane and *N*,*N*′-dimethyl-*N*,*N*′-bis(dimethylvinylsilyl)ethane-1,2-diamine.[8] Considering the structural similarity of **1** to earlier reported substrates, one can expect compound **1** to undergo also the silylative coupling cyclization catalyzed by ruthenium hydride complexes to give cyclic bis(silyl) product. The conditions for an effective transformation of *N*-methyl-*N*-(dimethylvinylsilyl)-2-(dimethylvinylsilyloxy)ethanamine (**1**) into the 1-aza-1,2,2,4,4-pentamethyl-3-methylene-5-oxa-2,4-disilacycloheptane (**2**) in the presence of ruthenium catalysts have been optimized via catalytic screenings of the substrate conversion and yield of cyclic product using GC and GC-MS methods. At 1 mol% catalyst loading the catalysis of the pentacoordinated ruthenium hydride complex containing tricyclohexylphosphine, [RuHCl(CO)(PCy_3)$_2$], was found to be more efficient than the catalysis of [RuHCl(CO)(PPh_3)$_3$].

These catalytic results provide a basis for the synthesis of desired cyclic product from divinyl-substituted monomer **1**. Silylative coupling cyclization of **1** was effectively catalyzed by [RuHCl(CO)(PCy_3)$_2$] (1 mol%), without solvent under argon (glass ampoule), and divinyl-substituted compound was exclusively transformed into cyclic product **2** (Equation 2) in 18 hours at 120 °C. The reaction occurred efficiently also in toluene, in the open system, without affecting either the activity of the catalyst or the selectivity of this process, however, it required a longer time (48 h). It is worth noting that the process described gives regioselectively cyclic product **2** with no linear oligomeric products observed.

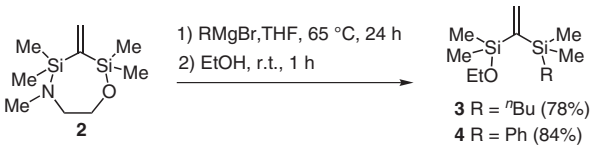


Equation 2 Synthesis of 1-aza-1,2,2,4,4-pentamethyl-3-methylene-5-oxa-2,4-disilacycloheptane

The cyclic product, 1-aza-1,2,2,4,4-pentamethyl-3-methylene-5-oxa-2,4-disilacycloheptane (**2**), was easily isolated by 'bulb-to-bulb' distillation from the reaction flask in 95% yield. Results of the spectroscopic analyses (^{13}C NMR, DEPT) of **2** unambiguously confirmed the existence of quaternary carbon atom (the signal observed at 157.7 ppm), i.e. 1,1-bis(silyl)ethene fragment in the molecule.

Inspired by recently reported[8] successful transformations of cyclic products containing *exo*-methylene bond and either SiOR or SiN(Me)R functionalities into symmetrical 1,1-bis(silyl)ethenes, as well as by the difference in the reactivity of Si–O and Si–N bonds, we envisioned compound **2** as a good substrate candidate for the synthesis of unsymmetrical 1,1-bis(silyl)ethenes containing both alkoxy and alkyl (aryl) functionalities.

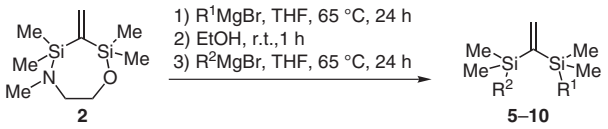
To test this hypothesis, we synthesized a series of 1-(ethoxydimethylsilyl)-1-(organyldimethylsilyl)ethenes. We found that the treatment of the cyclic compound **2** with 1.2 equivalents of the corresponding Grignard reagent in THF at 65 °C for 24 hours and subsequent alcoholysis with ethanol, yielded unsymmetrical 1,1-bis(silyl)ethenes containing both alkoxy and alkyl (aryl) substituents at the silicon atoms (Equation 3) as expected. Using this procedure we synthesized two new organosilicon compounds: 1-(ethoxydimethylsilyl)-1-(butyldimethylsilyl)ethene (**3**) (isolated yield 78%) and 1-(ethoxydimethylsilyl)-1-(dimethylphenylsilyl)ethene (**4**) (isolated yield 84%).



Equation 3 Synthesis of 1-(ethoxydimethylsilyl)-1-(organyldimethylsilyl)ethenes.

The structures of these products were confirmed by DEPT spectrum analysis. Surprisingly, a detailed GC-MS analysis of the reaction by-products revealed the presence of small amounts (about 5%) of 1,1-bis(ethoxydimethylsilyl)ethene, which can be easily removed by distillation under reduced pressure.

Consequently we turned our attention towards the one-pot synthesis of unsymmetrical 1,1-bis(silyl)ethenes containing alkyl-, alkenyl- or aryl substituents at the silicon atoms. These unsymmetrical compounds were formed in the reaction of **2** with the first Grignard reagent, followed by alcoholysis and reaction with the second Grignard reagent without isolation of the alkoxy-substituted organosilicon intermediate (Equation 4). Treatment of **2** with 1.2 equivalents of Grignard reagent R^1MgBr in THF at 65 °C for 24 hours under argon, followed by addition of 1.5 equivalents of ethanol and subsequent reaction with 2 equivalents of the second Grignard compound (R^2MgBr,) at 65 °C for 24 hours resulted in the desired 1,1-bis(silyl)ethenes **5**–**10** in moderate to good yields (Table 1). To obtain the methyl substituted product methylmagnesium iodide was used. In all cases excellent regioselectivities were attained.



Equation 4 Synthesis of 1,1-bis(organyldimethylsilyl)ethenes

Table 1 Synthesis of Unsymmetrical 1,1-Bis(organyldimethylsilyl)ethenes

Product	R^1	R^2	Yield (%)[a]
5	Ph	Me	68
6	Ph	Et	71
7	Ph	*n*-Bu	63
8	*n*-Bu	Me	58
9	*n*-Bu	Et	69
10	Ph	$CH=CH_2$	63

[a] Isolated yields of chromatographically pure products.

All products were isolated and spectroscopically characterized. The presence of a quaternary carbon and $(R^1Me_2Si)(R^2Me_2Si)C=CH_2$ structure was elucidated by DEPT spectrum analysis. A detailed GC-MS analysis of the by-products of the reaction discussed revealed the presence of a small amount (less than 5%) of symmetrical organosilicon derivatives: $(R^1Me_2Si)_2C=CH_2$ and $(R^2Me_2Si)_2C=CH_2$, which can be easily separated by column chromatography.

In conclusion, we have described a novel regioselective and efficient method for the synthesis of unsymmetrical 1,1-bis(silyl)ethenes from easily available starting materials. Otherwise difficult to synthesize compounds of the general formula $(R^1Me_2Si)(R^2Me_2Si)C=CH_2$ were obtained as predominant products via selective silylative coupling cyclization of *N*-methyl-*N*-(dimethyl-vinylsilyl)-2-(dimethylvinylsilyloxy)ethanamine catalyzed by ruthenium-hydride complex and subsequent treatment of the resulted cyclic bis(silyl) derivative with various Grignard reagents.

^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Varian XL 300 spectrometer using $CDCl_3$ as a solvent and TMS as reference. GC analyses were performed on a Varian 3400 with a Megabore column (30 m) and TCD. Mass spectra of the products were determined by GC-MS analysis on a Varian Saturn 2100T, equipped with a BD-5 capillary column (30 m) and a Finnigan Mat 800 ion trap detector. All reactions were performed under an atmosphere of deoxygenated and dried argon. Et_3N and pentane were dried over CaH_2, distilled under argon and stored over molecular sieves type 4A. THF and toluene were dried over sodium and benzophenone and freshly distilled prior to use. Grignard reagents were synthesized via well-known procedures described in the literature. $[RuHCl(CO)(PCy_3)_2]$ was prepared by adaptation of a procedure described in literature.[9]

***N*-Methyl-*N*-(dimethylvinylsilyl)-2-(dimethylvinylsilyloxy)ethanamine (1)**

A solution of anhyd Et_3N (28.6 mL, 0.205 mol) in anhyd pentane (200 mL) was introduced into a flame-dried three-necked, 500-mL round-bottomed flask equipped with a magnetic stirring bar, rubber septum cap and argon bubbling tube. To the resulting solution was added 2-(methylamino)ethanol (7.44 mL, 0.093 mol). Chlorodimethylvinylsilane (25.3 mL, 0.186 mol) was subsequently added over 1 h and the mixture was stirred under the flow of argon for 2 h at r.t. After the substrate disappearance was confirmed by GC, the resulting salt was filtered off and the volatiles were removed in a rotary evaporator. Distillation under reduced pressure afforded compound **1**; yield: 21.3 g (94%); colorless liquid; bp 55–57 °C/0.5 mm Hg.

^1H NMR ($CDCl_3$): δ = 0.16 (s, 6 H), 0.18 (s, 6 H) 2.43 (s, 3 H), 2.87–2.92 (t, *J* = 6.0 Hz, 2 H), 3.51–3.55 (t, *J* = 6.0 Hz, 2 H), 5.68–5.80 (m, 2 H), 5.91–5.97 (dd, *J* = 4.4, 14.8 Hz, 2 H), 6.09–6.19 (m 2 H).

^{13}C NMR ($CDCl_3$): δ = –2.0, –1.9, 35.3, 53.3, 61.4, 131.9, 133.9, 138.0, 139.7.

MS (EI): *m*/*z* (%) = 243 (M^+, 3), 228 (5), 159 (5), 143 (5), 128 (100), 117 (7), 85 (45), 73 (5), 59 (20).

HRMS: *m*/*z* calcd for $C_{11}H_{25}NOSi_2$ [M^+]: 243.14748; found: 243.14759.

1-Aza-1,2,2,4,4-pentamethyl-3-methylene-5-oxa-2,4-disilacycloheptane (2)

Compound **1** (10.0 g, 0.041 mol) and $[RuHCl(CO)(PCy_3)_2]$ (0.283 g, 4×10^{-4} mol) were placed in a glass ampoule, which was sealed under argon and heated for 18 h at 120 °C. After the substrate disappearance was confirmed by GC, the cyclic product was isolated

by 'bulb-to-bulb' distillation to give compound **2**; yield: 8.4 g (95%); colorless liquid; bp 45 °C/0.5 mm Hg.

^{1}H NMR ($CDCl_3$): δ = 0.11 (s, 6 H), 0.13 (s, 6 H), 2.42 (s, 3 H), 2.89–2.92 (t, *J* = 4.1 Hz, 2 H), 3.68–3.71 (t, *J* = 4.1 Hz, 2 H), 6.13 (s, 2 H).

^{13}C NMR ($CDCl_3$): δ = –2.7, –1.7, 34.9, 54.4, 61.7, 138.8, 132.9, 157.7.

MS (EI): *m*/*z* (%) = 215 (M^+, 10), 200 (100), 172 (25), 143 (45), 132 (40), 116 (15), 85 (10), 73 (20), 58 (20).

HRMS: *m*/*z* calcd for $C_9H_{21}NOSi_2$ [M^+]: 215.11617; found: 215.11678.

1-(Ethoxydimethylsilyl)-1-(organyldimethylsilyl)ethenes 3 and 4; General Procedure

The glass reactor (50-mL, two-necked, round-bottomed flask equipped with a magnetic stirring bar, reflux condenser and argon bubbling tube) was evacuated and flushed with argon. 1-Aza-1,2,2,4,4-pentamethyl-3-methylene-5-oxa-2,4-disilacycloheptane (**2**; 1 equiv) and THF (10 mL) were added to the reactor. Then *n*-butylmagnesium (1.2 equiv, 1.3 M in THF) or phenylmagnesium bromide (1.2 equiv, 2.5 M in THF) was added dropwise. The mixture was refluxed under argon for 24 h. Then at r.t., EtOH (1.5 equiv) was added dropwise. The mixture was stirred under argon for 1 h. After the reaction was complete, the excess of alcohol and the solvent were evaporated in vacuo. The crude product was distilled under reduced pressure to afford the analytically pure product.

1-(Butyldimethylsilyl)-1-(ethoxydimethylsilyl)ethene (3)

Colorless liquid; yield: 78%; bp 70–72 °C/0.5 mm Hg.

^{1}H NMR ($CDCl_3$): δ = 0.02 (s, 6 H), 0.18 (s, 6 H), 0.42–0.48 (t, *J* = 3.3 Hz, 2 H), 0.84–0.89 (t, *J* = 7.1 Hz, 3 H), 1.06–1.12 (t, *J* = 6.9 Hz, 3 H), 1.14–1.26 (m, 4 H), 3.52–3.62 (q, *J* = 6.9 Hz, 2 H), 6.44 (d, *J* = 5.4 Hz, 1 H), 6.48 (d, *J* = 5.4 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = –2.2, –1.4, 13.7, 15.7, 18.4, 26.1, 26.5, 58.2, 142.0, 151.6.

MS (EI): *m*/*z* (%) = 229 (30), 187 (75), 159 (100), 145 (40), 74 (50), 60 (70), 54 (20).

Anal. Calcd for $C_{12}H_{28}OSi_2$: C, 58.94; H, 11.54. Found: C, 58.72; H, 11.29.

1-(Ethoxydimethylsilyl)-1-(dimethylphenylsilyl)ethene (4)

Colorless liquid; yield: 84%; bp 118 °C/0.5 mm Hg.

^{1}H NMR ($CDCl_3$): δ = 0.20 (s, 6 H), 0.46 (s, 6 H) 1.08–1.14 (t, *J* = 6.8 Hz, 3 H), 3.56–3.64 (q, *J* = 7.1 Hz, 2 H), 6.40 (d, *J* = 5.2 Hz, 1 H), 6.48 (d, *J* = 5.2 Hz, 1 H), 7.41–7.62 (m, 5 H).

^{13}C NMR ($CDCl_3$): δ = –2.6, –1.3, 18.3, 56.2, 127.9, 128.4, 134.7, 137.8, 143.1, 151.6.

MS (EI): *m*/*z* (%) = 250 (45), 235 (15), 219 (20), 188 (30), 144 (100), 136 (90), 103 (40), 76 (30), 46 (35).

Anal. Calcd for $C_{14}H_{24}OSi_2$: C, 63.57; H, 9.15. Found: C, 63.42; H, 9.44.

1,1-Bis(organyldimethylsilyl)ethenes 5–10; General Procedure

The glass reactor (50-mL, two-necked, round-bottomed flask equipped with a magnetic stirring bar, reflux condenser and argon bubbling tube) was evacuated and flushed with argon. 1-Aza-1,2,2,4,4-pentamethyl-3-methylene-5-oxa-2,4-disilacycloheptane (**2**; 2g, 1 equiv) and THF (10 mL) were added to the reactor. Then the corresponding organylmagnesium bromide (R^1MgBr, 1.2 equiv) in anhyd THF (7.5 mL) was added dropwise. The mixture was refluxed under argon for 24 h. After cooling to r.t., EtOH (1.5 equiv) was added dropwise. The mixture was stirred under argon at r.t. for 1 h. After that time, a solution of R^2MgBr (2 equiv) in THF (12 mL) was added dropwise and the mixture was heated at 65 °C for 24 h. The excess amount of Grignard reagent was quenched by adding MeOH–Et_2O and after adding H_2O, the mixture was extracted with Et_2O. The ethereal phase was dried ($MgSO_4$) and filtered, the volatiles removed in a rotary evaporator and the mixture was passed through a silica gel column (eluent: hexane). After evaporation, the crude product was distilled under reduced pressure to afford the analytically pure product.

1-(Dimethylphenylsilyl)-1-(trimethylsilyl)ethene (5)

Colorless liquid; yield: 68%; bp 92–94 °C/0.5 mm Hg.

^{1}H NMR ($CDCl_3$): δ = 0.15 (s, 9 H), 0.54 (s, 6 H), 6.45–6.48 (d, *J* = 4.9 Hz, 1 H), 6.54–6.60 (d, *J* = 4.9 Hz, 1 H), 7.44–7.47 (m, 3 H), 7.62–7.64 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = –1.5, –0.1, 127.5, 128.7, 134.0, 138.9, 141.8, 152.6.

MS (EI): *m*/*z* (%) = 220 (100), 206 (25), 146 (20), 136 (80), 122 (10), 74 (30), 60 (30).

Anal. Calcd for $C_{13}H_{22}Si_2$: C, 66.59; H, 9.46. Found: C, 66.53; H, 9.76.

1-(Ethyldimethylsilyl)-1-(dimethylphenylsilyl)ethene (6)

Colorless liquid; yield: 71%; bp 110 °C/0.5 mm Hg.

^{1}H NMR ($CDCl_3$): δ = 0.03 (s, 6 H), 0.44 (s, 6 H), 0.52–0.57 (q, *J* = 7.7 Hz, 2 H), 0.89–0.92 (t, *J* = 7.1 Hz, 3 H), 6.42 (d, *J* = 5.2 Hz, 1 H), 6.46 (d, *J* = 5.2 Hz, 1 H), 7.37–7.39 (m, 3 H), 7.53–7.56 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = –2.5, –1.6, 7.5, 7.8, 127.5, 128.7, 133.9, 138.9, 142.3, 151.4.

MS (EI): *m*/*z* (%) = 248 (M^+, 3), 234 (30), 220 (100), 172 (10), 146 (15), 136 (74), 122 (10), 106 (15), 74 (15), 60 (30).

Anal. Calcd for $C_{14}H_{24}Si_2$: C, 67.66; H, 9.73. Found: C, 67.73; H, 9.95.

1-(Butyldimethylsilyl)-1-(dimethylphenylsilyl)ethene (7)

Colorless liquid; yield: 63%; bp 125–127 °C/0.5 mm Hg.

^{1}H NMR ($CDCl_3$): δ = 0.01 (s, 6 H), 0.41 (s, 6 H), 0.50–0.52 (t, *J* = 3.4 Hz, 2 H), 0.84–0.88 (t, *J* = 7.1 Hz, 3 H), 1.15–1.30 (m, 4 H), 6.36–6.38 (d, *J* = 4.9 Hz, 1 H), 6.42–6.43 (d, *J* = 4.9 Hz, 1 H), 7.35–7.37 (m, 3 H), 7.50–7.53 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = –2.2, –1.7, 13.8, 15.7, 26.1, 26.5, 127.6, 128.8, 134.0, 139.1, 142.3, 151.8.

MS (EI): *m*/*z* (%): 276 (M^+, 1), 219 (100), 205 (30), 135 (80), 74 (30), 60 (30).

Anal. Calcd for $C_{16}H_{28}Si_2$: C, 69.49; H, 10.20. Found: C, 69.42; H, 10.43.

1-(Butyldimethylsilyl)-1-(trimethylsilyl)ethene (8)

Colorless liquid; yield: 58%; bp 190–192 °C/760 mm Hg.

^{1}H NMR ($CDCl_3$): δ = 0.02 (s, 9 H), 0.06 (s, 6 H), 0.42–0.46 (t, *J* = 3.6 Hz, 2 H), 0.72–0.77 (t, *J* = 7.3 Hz, 3 H), 1.05–1.10 (m, 4 H), 6.32–6.35 (d, *J* = 5.4 Hz, 1 H), 6.44–6.47 (d, *J* = 5.4 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = –1.7, –1.5, 13.8, 14.4, 25.9, 26.0, 139.1, 152.0.

MS (EI): *m*/*z* (%): 215 (M^+, 15), 142 (35), 128 (20), 86 (10), 74 (100), 60 (30), 46 (30).

Anal. Calcd for $C_{11}H_{26}Si_2$: C, 61.59; H, 12.22. Found: C, 61.89; H, 11.96.

1-(Butyldimethylsilyl)-1-(ethyldimethylsilyl)ethene (9)

Colorless liquid; yield: 69%; bp 66–68 °C/0.5 mm Hg.

^{1}H NMR ($CDCl_3$): δ = 0.06 (s, 6 H), 0.08 (s, 6 H), 0.42–0.46 (q, *J* = 7.2 Hz, 2 H), 0.56–0.59 (t, *J* = 3.4 Hz, 2 H), 0.78–0.83 (t, *J* = 7.1 Hz, 3 H), 0.90–0.94 (t, *J* = 6.9 Hz, 3 H), 1.10–1.15 (m, 4 H), 6.38–6.42 (d, *J* = 5.4 Hz, 1 H), 6.47–6.49 (d, *J* = 5.4 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = –1.9, –1.4, 7.4, 8.1, 14.1, 15.2, 26.1, 27.0, 138.0, 151.4.

MS (EI): *m*/*z* (%) = 199 (2), 172 (25), 157 (40), 143 (100), 129 (10), 87 (35), 73 (65), 60 (75), 46 (20).

Anal. Calcd for $C_{12}H_{28}Si_2$: C, 63.07; H, 12.35. Found: C, 63.37; H, 12.19.

1-(Dimethylphenylsilyl)-1-(dimethylvinylsilyl)ethene (10)
Colorless liquid; yield: 63%; bp 114–116 °C/0.5 mm Hg.

^{1}H NMR ($CDCl_3$): δ = 0.19 (s, 6 H), 0.38 (s, 6 H), 5.62–5.70 (d, *J* = 4.0, 20.2 Hz, 1 H), 5.90–5.98 (d, *J* = 4.0, 14.4 Hz, 1 H), 6.10–6.22 (d, *J* = 14.4, 20.0 Hz, 1 H), 6.32–6.34 (d,, *J* = 4.8 Hz, 1 H), 6.46–6.48 (d, *J* = 4.8 Hz, 1 H), 7.28–7.32 (m, 3 H), 7.48–7.52 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = –2.2, –1.9, 127.6, 128.8, 131.0, 134.0, 139.2, 142.3, 152.1.

MS (EI): *m*/*z* (%) = 246 (M^+, 10), 232 (15), 219 (15), 192 (15), 145 (25), 135 (100), 105 (25), 85 (20), 74 (25), 60 (70), 46 (15).

Anal. Calcd for $C_{14}H_{22}Si_2$: C, 68.22; H, 9.00. Found: C, 63.41; H, 9.22.

Acknowledgment

This work was supported by The State Committee for Scientific Research, Projects No. 3 TO9A 009 29 and 3 T09A 145 26.

References

(1) (a) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, **1988**. (b) *The Chemistry of Organosilicon Compounds*; Patai, S.; Rappoport, Z., Eds.; Wiley: Chichester, **1988**, Chap. 3. (c) Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev.* **1997**, *97*, 2063.

(2) (a) Padwa, A.; MacDonald, J. G. *J. Org. Chem.* **1983**, *48*, 3189. (b) Hodgson, D. M.; Comina, P. J.; Drew, M. G. B. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2279. (c) Inoue, A.; Kondo, J.; Shinokubo, H.; Oshima, K. *J. Am. Chem. Soc.* **2001**, *123*, 11109. (d) Inoue, A.; Kondo, J.; Shinokubo, H.; Oshima, K. *Chem. Commun.* **2002**, 114.

(3) (a) Narasaka, K.; Saito, N.; Hayashi, Y.; Ichida, H. *Chem. Lett.* **1990**, 1411. (b) Fleming, I.; Ghosh, U. *J. Chem. Soc., Perkin Trans. 1* **1994**, 257. (c) Inoue, A.; Kondo, J.; Shinokubo, H.; Oshima, K. *Chem. Lett.* **2001**, 956. (d) Kondo, J.; Inoue, A.; Shinokubo, H.; Oshima, K. *Tetrahedron Lett.* **2002**, *43*, 2399.

(4) (a) Kondo, J.; Inoue, A.; Shinokubo, H.; Oshima, K. *Chem. Eur. J.* **2002**, *8*, 1730. (b) Jones, P. R.; Bates, T. F. *J. Am. Chem. Soc.* **1987**, *109*, 913. (c) Miura, K.; Hondo, T.; Okajima, S.; Nakagawa, T.; Takahashi, T.; Hosomi, A. *J. Org. Chem.* **2002**, *67*, 6082. (d) Ohmiya, H.; Yorimitsu, H.; Oshima, K. *Angew. Chem. Int. Ed.* **2005**, *44*, 3488.

(5) For reviews, see: (a) Marciniec, B.; Pietraszuk, C.; Kownacki, I.; Zaidlewicz, M. *Vinyl and Aryl Silicon, Germanium, and Boron Compounds,* In *Comprehensive Organic Functional Group Transformations II*, Vol. 2; Katritzky, A. R.; Taylor, R. J. K., Eds.; Elsevier: Oxford, **2005**, 941–1023. (b) Marciniec, B.; Pietraszuk, C. *Curr. Org. Chem.* **2003**, *7*, 691. (c) Marciniec, B.; Pietraszuk, C. In *Topics in Organometallic Chemistry. Synthesis of Silicon Derivatives with Ruthenium Catalysts*; Dixneuf, P., Ed.; Springer: Berlin, **2004**, 197–248.

(6) (a) Wakatsuki, Y.; Yamazaki, H.; Nakano, N.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 703. (b) Marciniec, B.; Pietraszuk, C. *J. Chem. Soc., Chem. Commun.* **1995**, 2003. (c) Marciniec, B.; Pietraszuk, C. *Organometallics* **1997**, *16*, 4320.

(7) (a) Marciniec, B.; Lewandowski, M. *Tetrahedron Lett.* **1997**, *38*, 3777. (b) Mise, T.; Takaguchi, Y.; Umemiya, T.; Shimizu, S.; Wakatsuki, Y. *Chem. Commun.* **1998**, 699. (c) Marciniec, B.; Lewandowski, M.; Bijpost, E.; Małecka, E.; Kubicki, M.; Walczuk-Guściora, E. *Organometallics* **1999**, *20*, 3968. (d) Marciniec, B.; Małecka, E. *Macromol. Symp.* **2001**, *174*, 137. (e) Majchrzak, M.; Marciniec, B.; Kubicki, M.; Pawelczyk, A. *Organometallics* **2005**, *24*, 3731.

(8) (a) Pawluć, P.; Marciniec, B.; Hreczycho, G.; Gaczewska, B.; Itami, Y. *J. Org. Chem.* **2005**, *70*, 370. (b) Pawluć, P.; Hreczycho, G.; Marciniec, B. *Synlett* **2005**, 1105.

(9) Yi, C. S.; Lee, D. W.; Chen, Y. *Organometallics* **1999**, *18*, 2043.