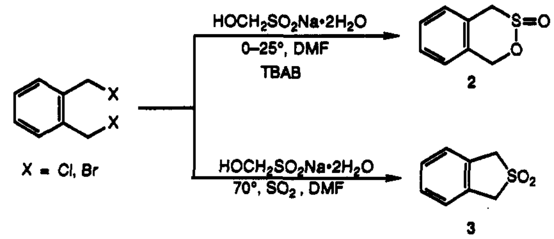
Table I. Yields of Sultine 2 from α,α′-Dihalo-o-xylenes and Rongalite

halide	temp, °C	catalyst	time, h	yield, %
Cl	60	–	48	0
Cl	25	NaI	26	70
Cl	25	TBAB	12	73
Br	0	–	48	64
Br	20	–	48	52
Br	40	–	48	46
Br	80	–	48	0
Br	0	TBAB	3	83

lyzed by Wilkinson's catalyst,[9] and by electrolysis of sulfur dioxide in the presence of α,α′-dibromo-o-xylene,[10] or by the photolysis of o-tolualdehyde in the presence of sulfur dioxide followed by borohydride reduction and cyclization by treatment with acid.[11] The sultine prepared by one of these methods has been used to generate 1 where gentle conditions and the avoidance of extraneous undesirable reagents (e.g. trimethylamine, reducing metals) are required.[12]

Earlier, we reported the trapping by norbornene of o-quinodimethane generated by treatment of α,α′-dibromo-o-xylene with sodium hydroxymethanesulfinate dihydrate (rongalite, sodium formaldehydesulfoxylate).[13] The sultine 2 was obtained in moderate yield (43–48%). Since the sultine is the likely precursor of the o-quinodimethane that was trapped, we reasoned that under milder conditions the sultine could be obtained in higher yield. Since the rongalite/α,α′-dibromo-o-xylene reaction involves only one step and less expensive reagents than the competitive photochemical o-tolualdehyde–SO_2–$NaBH_4$ route[11] to sultine 2, our new method might be preferred.[14] Related to our method is the reaction of α,α′-dibromo-o-xylene with reduced species of SO_2 obtained by electrolysis to give 2 in 67% yield.[10]

We wish to report an improved synthesis of 2 from rongalite and α,α′-dibromo- or α,α′-dichloro-o-xylene in which our previously reported yields[13] have been nearly doubled. The reaction of the dihalide with rongalite is done in N,N-dimethylformamide (DMF) in the absence of water but with addition of a catalytic amount of tetrabutylammonium bromide (TBAB) or sodium iodide. The dichloride is unreactive at 25 °C in the absence of the ammonium salt but in its presence gives 2 in 73% yield after 12 h. With a sodium iodide catalyst, a 70% yield of 2 is obtained after 26 h. The more reactive dibromide yields 83% of 2 after 3 h at 0 °C in the presence of the ammonium salt. The use of a relatively low temperature to prepare 2 is definitely advantageous since the higher temperatures needed in the absence of catalyst cause considerable polymerization of the o-quinodimethane. If benzothiophene sulfone (3) is required, the reaction of α,α′-dibromo-o-xylene with rongalite is conducted in the presence of SO_2 at 70 °C. To optimize the yield of 3, one should add the rongalite in four portions during 90 min. This periodic addition minimizes the exposure of rongalite to a temperature near its decomposition point, significant decomposition occurring at 80 °C. Sulfone 3 probably is formed by addition of sulfur dioxide to o-quinodimethane (generated in situ) as proposed by Durst et al.[7]



Experimental Section

General Procedure. A suspension of sodium hydroxymethanesulfinate (rongalite) (3.0 g, 20 mmol) was stirred with a solution of α,α′-dichloro- or α,α′-dibromo-o-xylene (10 mmol) and either sodium iodide or TBAB (2 mmol) in DMF (20 mL). The reaction mixture was worked up by addition of water (150 mL), removal of solids by filtration, extraction with ether, drying the ether solution with anhydrous magnesium sulfate, and removal of solvent. 1,4-Dihydro-2,3-benzoxathiin 3-oxide (2) was obtained as an oil whose spectroscopic properties were identical with those reported previously.[7,10,11,15] The yields and reaction conditions are given in Table I.

1,3-Dihydrobenzo[c]thiophene 2,2-Dioxide (3). The general procedure was applied to the reaction of rongalite (20 mmol) with α,α′-dibromo-o-xylene (10 mmol) except that SO_2 was passed through the reaction mixture for 20 min. The suspension was stirred at 70 °C for 4.5 h, and additional rongalite was added in four 10-mmol portions at intervals of 30 min. The reaction mixture was stirred for another 4.5 h. The workup, as described above, gave the sulfone 3 (1.26 g, 7.5 mmol, 75%): mp 146–148 °C (lit.[16] mp 150–151 °C). The ^1H NMR spectrum of 3 was identical with that previously reported.[17]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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Palladium(II) Acetate–*tert*-Alkyl Isocyanide as a Highly Efficient Catalyst for the Inter- and Intramolecular Bis-silylation of Carbon–Carbon Triple Bonds

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Much interest has been focused on the development of methodology for the introduction of silicon into organic molecules because such new methodology would be valuable for both the synthetic elaboration of organic molecules via organosilicon compounds and the synthesis of new silicon-containing materials.[1] Recently, new bis-silylation reactions of isocyanides[2] and alkenes[3] have been discov-

(1) *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: Chichester, 1989.

Scheme I

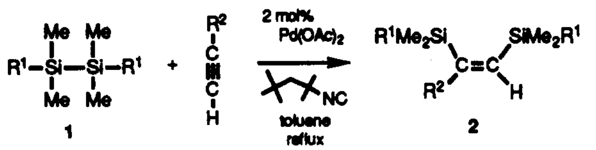


Table I. Bis-silylation of Alkynes with Disilanes

entry	R^1	R^2	product	% yield	Z:E
1	Me	Ph	**2a**	82	96:4
2	Me	*n*-Hex	**2b**	81	95:5
3	Ph	*n*-Hex	**2c**	96	100:0
4	Ph	H	**2d**	98	97:3

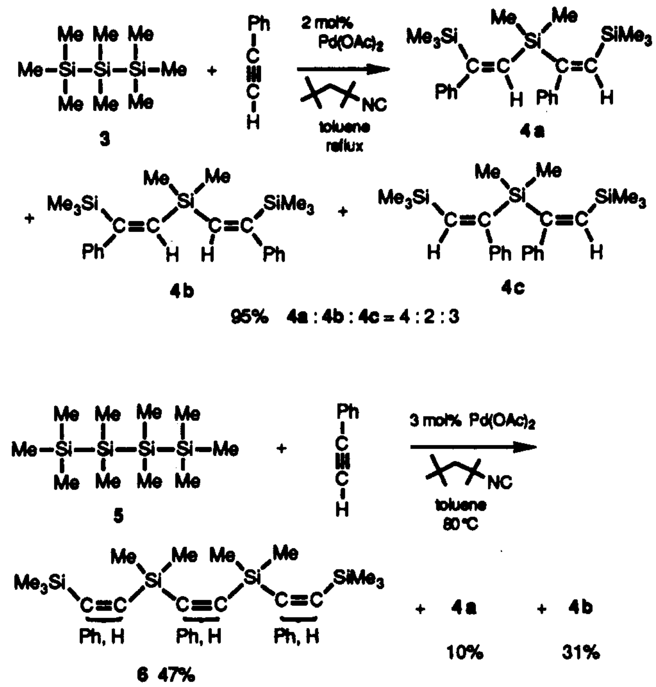
ered. The bis-silylation of alkynes by disilanes has also been reported.[4] However, satisfactory bis-silylations of alkynes were achieved only by disilanes with electron-withdrawing substituents (such as alkoxy and halogen) on silicon, and a few cyclic disilanes. Hexaalkyldisilanes, such as hexamethyldisilane, have afforded bis-silylation products in low yield (26% at most).[3c] The low reactivity of hexaalkyldisilanes discouraged attempts to employ other peralkylpolysilanes. Also, the *intra*molecular version of the reaction was unknown. We report here that a new catalyst, palladium(II) acetate–*tert*-alkyl isocyanide, permitted the *inter*molecular bis-silylation of alkynes by otherwise unreactive disilanes, such as hexamethyldisilane and 1,2-diphenyl-1,1,2,2-tetramethyldisilane, to give bis-silylated alkenes in yields up to 98%. Extension of the reaction of the *intra*molecular bis-silylation of carbon–carbon triple bonds led to the regioselective formation of cyclic organosilicon compounds in good yield.

Results and Discussion

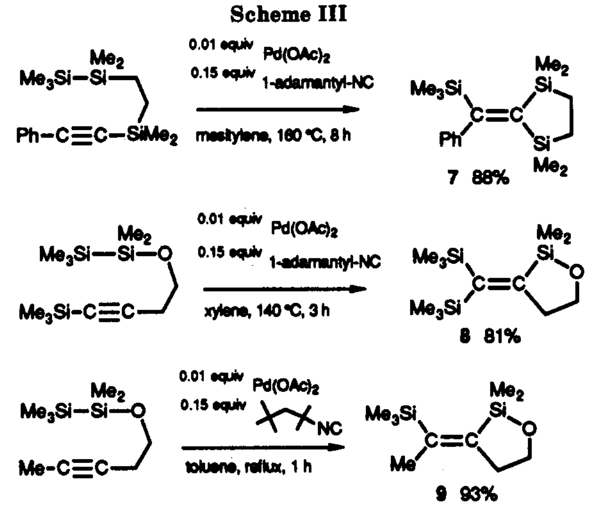
Heating a toluene solution of hexamethyldisilane and phenylethyne (1.5 equiv) in the presence of palladium(II) acetate (0.02 equiv)[5] and 1,1,3,3-tetramethylbutyl isocyanide (*tert*-octyl isocyanide) (0.30 equiv) at reflux for 6 h, followed by preparative TLC of the cooled reaction mixture on silica gel, furnished 1,2-bis(trimethylsilyl)-1-phenylethene (**2a**) (Z:E = 96:4) in 82% yield (Scheme I). The results of similar bis-silylations of selected alkynes are summarized in Table I. Z isomers, which arose from cis addition of the Si–Si linkage to the carbon–carbon triple bond, were predominantly produced. Not only phenylethyne but also other alkyl-substituted terminal alkynes and acetylene itself afforded (Z)-1,2-bis(organosilyl)alkenes in good yield. However, disubstituted alkynes were unreactive.

A significant feature of the palladium catalyst is the use of excess *tert*-alkyl isocyanide as a ligand. However, the role of the isocyanide in the remarkable promotion of bis-silylation is yet to be clarified. 1-Adamantyl and *tert*-butyl isocyanides also efficiently promoted the catalytic activity of palladium(II) acetate. In the absence of

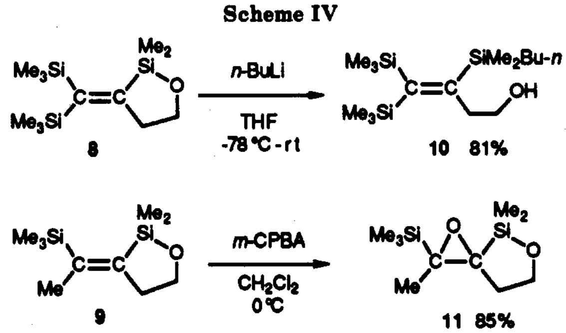
Scheme II



Scheme III



Scheme IV



tert-alkyl isocyanide, reaction failed to occur.

The reaction was extended to include bis-silylation by octamethyltrisilane (**3**) and decamethyltetrasilane (**5**). The reaction of **3** with phenylethyne (3 equiv) gave a mixture of regioisomeric double bis-silylation products **4** in high total yield (Scheme II). Bis-silylation with **5** gave the desired triple bis-silylation product **6**[6] in 47% yield, to-

(2) Ito, Y.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1988**, *110*, 3692.

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(4) (a) Tamao, K.; Hayashi, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *114*, C19. (b) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1975**, *97*, 931. (c) Watanabe, H.; Kobayashi, M.; Higuchi, K.; Nagai, Y. *J. Organomet. Chem.* **1980**, *186*, 51 and references cited therein.

(5) The use of tetrakis(triphenylphosphine)palladium(0) and *tert*-octyl isocyanide gave unsatisfactory results. The catalytic species in the bis-silylation reaction thus may be a palladium(0) isocyanide complex, to which otherwise unreactive hexaalkyldisilanes can undergo oxidative addition. In the case of tetrakis(triphenylphosphine)palladium(0), triphenylphosphine may possibly coordinate to palladium(0) species so strongly as to seriously retard the exchange of ligands.

(6) ^1H and ^{13}C NMR indicate that the product (**6**) is a single isomer of unknown regiochemistry.

gether with the double bis-silylation products **4a** and **4b** (41%). The latter may possibly have been formed by fragmentation of **5** to **3** and subsequent bis-silylation by **3**.

Furthermore, palladium(II) acetate–*tert*-alkyl isocyanide catalyzed the first known *intra*molecular bis-silylations, that is, cyclizations of pentaalkyldisilyl-substituted alkynes, which permitted bis-silylation of disubstituted alkynes for the first time. Thus, intramolecular regioselective cis addition of the Si–Si linkage to the carbon–carbon triple bond furnished the exocyclic olefins **7–9** in good yield. Of particular note was that olefins **7** and **8**, which are sterically very congested, were easily formed (Scheme III).

The synthetic transformations possible for the bis-silylation products are exemplified by the ring-opening of **8** to yield silyl-substituted homoallylic alcohol **10** and by the oxidation of **9** to afford epoxide **11** (Scheme IV).

A new catalyst, palladium(II) acetate–*tert*-alkyl isocyanide, thus has made the bis-silylation of alkynes a synthetically useful reaction. Studies of a variety of synthetically useful transformations of the bis-silylation products are now in progress.

Experimental Section

Electron impact mass spectra (EIMS) were recorded with a JEOL JMS-D300 spectrometer and a JMA-2000 data system. Fast atom bombardment mass spectra (FABMS) were recorded with a JEOL JMS-SX102 spectrometer and a JMA-DA6000 data system. A Xe beam source (10-kV acceleration potential) was used, and the spectra were obtained from 2-hydroxyethyl disulfide solutions. Melting points are uncorrected.

1,1,3,3-Tetramethylbutyl isocyanide was purchased from Aldrich. 1-Adamantyl isocyanide was prepared by dehydration of *N*-formyl-1-adamantanamine with thionyl chloride–triethylamine. Toluene, xylene, and mesitylene were freshly distilled under nitrogen from lithium aluminum hydride before use.

1,2-Bis(trimethylsilyl)-1-phenylethene (2a). A toluene solution (1 mL) of hexamethyldisilane (100 mg, 0.68 mmol), phenylethyne (105 mg, 1.03 mmol), palladium(II) acetate (3.1 mg, 0.014 mmol), and 1,1,3,3-tetramethylbutyl isocyanide (29 mg, 0.21 mmol) was heated at reflux for 6 h under nitrogen. Preparative TLC of the cooled reaction mixture on silica gel (*n*-hexane) afforded 1,2-bis(trimethylsilyl)-1-phenylethene (**2a**, 140 mg, 82%, *Z*:*E* = 96:4).

1,2-Bis(trimethylsilyl)-1-octene (2b). Bis-silylation product **2b** was obtained from 1-octyne and hexamethyldisilane, by the procedure described for **2a**, in 81% yield (*Z*:*E* = 95:5): IR (neat) 2932, 1466, 1250, 844 cm^{-1}; ^1H NMR of the *Z* isomer (200 MHz, $CDCl_3$) δ 0.12 (s, 9 H), 0.15 (s, 9 H), 0.88 (t, *J* = 6.2 Hz, 3 H), 1.23–1.42 (m, 8 H), 2.12–2.22 (m, 2 H), 6.26 (s, 1 H); ^{13}C NMR of the *Z* isomer ($CDCl_3$) δ 0.81, 1.08, 14.10, 22.67, 29.15, 30.26, 31.77, 44.30, 143.33, 162.72; MS (EI, 20 eV) *m*/*z* 256 (M^+). Anal. Calcd for $C_{14}H_{32}Si_2$: C, 65.54; H, 12.37. Found: C, 65.80; H, 12.54.

1,2-Bis(dimethylphenylsilyl)-1-octene (2c). Bis-silylation product **2c** was obtained from 1-octyne and 1,1,2,2-tetramethyl-1,2-diphenyldisilane, by the procedure described for **2a**, in 96% yield (*Z*:*E* = 100:0): IR (neat) 2932, 1430, 1252, 1112, 844 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.17 (s, 6 H), 0.27 (s, 6 H), 0.87 (t, *J* = 6.2 Hz, 3 H), 1.19–1.47 (m, 8 H), 2.21–2.31 (m, 2 H), 6.60 (s, 1 H), 7.25–7.36 (m, 3 H), 7.41–7.50 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −0.35, −0.22, 14.09, 22.66, 29.12, 30.30, 31.70, 44.13, 127.60, 128.64, 128.79, 133.88, 134.18, 139.55, 140.41, 143.20, 162.05; EIMS (20 eV) *m*/*z* 380 (M^+). Anal. Calcd for $C_{24}H_{36}Si_2$: C, 75.72; H, 9.53. Found: C, 75.85; H, 9.64.

1,2-Bis(dimethylphenylsilyl)ethene (2d). To a toluene solution (5 mL) of 1,1,2,2-tetramethyl-1,2-diphenyldisilane (100 mg, 0.37 mmol), palladium(II) acetate (1.7 mg, 0.0076 mmol), and 1,1,3,3-tetramethylbutyl isocyanide (15 mg, 0.11 mmol) in an autoclave cooled in a liquid N_2 bath was introduced gaseous ethyne to a pressure of 10 kg/cm^2. The autoclave was heated at 120 °C for 60 h. Preparative TLC of the cooled reaction mixture on silica gel (*n*-hexane) afforded 1,2-bis(dimethylphenylsilyl)ethene (**2d**, 108 mg, 98%, *Z*:*E* = 97:3): IR (neat) 2964, 1430, 1252, 1114 cm^{-1}; ^1H NMR of the *Z* isomer (200 MHz, $CDCl_3$) δ 0.35 (s, 12 H), 7.16 (s, 2 H), 7.39–7.46 (m, 3 H), 7.54–7.60 (m, 2 H); ^{13}C NMR of the *Z* isomer ($CDCl_3$) δ −0.93, 127.71, 128.89, 133.96, 139.22, 151.41; EIMS (20 eV) *m*/*z* 296 (M^+). Anal. Calcd for $C_{18}H_{24}Si_2$: C, 72.90; H, 8.16. Found: C, 72.64; H, 8.22.

Reaction of Phenylethyne with Octamethyltrisilane. A toluene solution (1 mL) of octamethyltrisilane (100 mg, 0.49 mmol), phenylethyne (150 mg, 1.47 mmol), palladium(II) acetate (2.2 mg, 0.0098 mmol), and 1,1,3,3-tetramethylbutyl isocyanide (21 mg, 0.15 mmol) was heated at reflux for 6 h under nitrogen. Preparative TLC of the cooled reaction mixture on silica gel (*n*-hexane) afforded a mixture of regioisomeric double bis-silylation products **4a** + **4b** + **4c** (190 mg, 95%). Anal. Calcd for $C_{24}H_{36}Si_3$: C, 70.51; H, 8.88. Found: C, 70.72; H, 9.12. The regiochemistry of each isomer was determined from the ^1H NMR spectra of authentic samples.[7] **4a**: ^1H NMR (200 MHz, $CDCl_3$) δ 0.08 (s, 9 H), 0.18 (s, 9 H), 0.34 (s, 6 H), 6.47 (s, 1 H), 6.56 (s, 1 H), 6.9–7.3 (m, 10 H). **4b**: ^1H NMR (200 MHz, $CDCl_3$) δ 0.14 (s, 18 H), 0.37 (s, 6 H), 6.56 (s, 2 H), 7.0–7.3 (m, 10 H). **4c**: ^1H NMR (200 MHz, $CDCl_3$) δ 0.13 (s, 18 H), 0.41 (s, 6 H), 6.38 (s, 2 H), 6.8–7.3 (m, 10 H).

Reaction of Phenylethyne wtih Decamethyltetrasilane. A toluene solution (0.7 mL) of decamethyltetrasilane (67 mg, 0.25 mmol), phenylethyne (116 mg, 1.14 mmol), palladium(II) acetate (1.7 mg, 0.0076 mmol), and 1,1,3,3-tetramethylbutyl isocyanide (15 mg, 0.11 mmol) was heated at 80 °C for 4 h under nitrogen. Preparative TLC of the cooled reaction mixture on silica gel (*n*-hexane) afforded **6** (68 mg, 47%) and **4a** + **4b** (42 mg, 41%). **6**: IR (neat) 2968, 1596, 1490, 1250 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.08 (s, 9 H), 0.12 (s, 9 H), 0.388 (s, 6 H), 0.394 (s, 6 H), 6.53 (s, 1 H), 6.57 (s, 1 H), 6.64 (s, 1 H), 6.87–7.32 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 0.96, 1.07, 1.78, 2.21, 125.59, 125.83, 126.10, 126.15, 126.64, 127.75, 127.80, 147.93, 148.36, 149.25, 150.49, 150.57, 150.73, 163.54, 164.69, 164.75; HRFABMS calcd for $C_{34}H_{48}Si_4$ + Li 575.2993, found 575.2997.

Synthesis of 7 by Intramolecular Bis-silylation. A mesitylene solution (0.5 mL) of 3,3,6,6,7,7-hexamethyl-1-phenyl-3,6,7-trisila-1-octyne (103 mg, 0.32 mmol), palladium(II) acetate (1.4 mg, 0.0062 mmol), and 1-adamantyl isocyanide (15 mg, 0.093 mmol) was heated at 160 °C for 8 h under nitrogen. Preparative TLC of the cooled reaction mixture on silica gel (*n*-hexane) afforded **7** (91 mg, 88%): mp 53.4–54.4 °C; IR (KBr) 2960, 1248, 840 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ −0.37 (s, 6 H), 0.04 (s, 9 H), 0.28 (s, 6 H), 0.55–0.80 (m, 4 H), 6.81–6.87 (m, 2 H), 7.10–7.25 (m, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ −0.13, 0.27, 0.90, 9.84, 11.35, 125.28, 127.06, 127.33, 149.44, 161.92, 177.58; HREIMS (20 eV) calcd for $C_{17}H_{30}Si_3$ 318.1655, found 318.1627.

Synthesis of 8 by Intramolecular Bis-silylation. A xylene solution (0.5 mL) of 4-((pentamethyldisilyl)oxy)-1-(trimethylsilyl)-1-butyne (138 mg, 0.51 mmol), palladium(II) acetate (1.2 mg, 0.0053 mmol), and 1-adamantyl isocyanide (13 mg, 0.081 mmol) was heated at 140 °C for 3 h under nitrogen. Kugelrohr distillation [120–125 °C (1 mmHg)] of the reaction mixture afforded **8** (112 mg, 81%): IR (neat) 2964, 1252, 1084 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.16 (s, 9 H), 0.21 (s, 9 H), 0.35 (s, 6 H), 2.75 (t, *J* = 6.3 Hz, 2 H), 3.91 (t, *J* = 6.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 1.37, 2.46, 2.90, 42.49, 63.97, 157.26, 172.62; EIMS (20 eV) *m*/*z* 272 (M^+). Anal. Calcd for $C_{12}H_{28}OSi_3$: C, 52.87; H, 10.35. Found: C, 52.60; H, 10.56.

Synthesis of 9 by Intramolecular Bis-silylation. A toluene solution (1.2 mL) of 5-((pentamethyldisilyl)oxy)-2-pentyne (137 mg, 0.64 mmol), palladium(II) acetate (1.4 mg, 0.0062 mmol), and 1,1,3,3-tetramethylbutyl isocyanide (13 mg, 0.093 mmol) was heated at reflux for 1 h under nitrogen. Kugelrohr distillation [140–150 °C (10 mmHg)] of the reaction mixture afforded **9** (128 mg, 93%): IR (neat) 2968, 1252, 1066 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.11 (s, 9 H), 0.30 (s, 6 H), 1.81 (t, *J* = 1.3 Hz, 3 H), 2.55 (t q, *J* = 6.6 and 1.3 Hz, 2 H), 3.96 (t, *J* = 6.6 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −0.21, 0.86, 20.71, 35.77, 64.28, 148.45, 150.67; MS (EI,

(7) Bis-silylation of phenylethyne (1 equiv) by **3** afforded (*Z*)-2-(pentamethyldisilyl)-1-phenyl-1-(trimethylsilyl)ethene (34%) and (*Z*)-1-(pentamethyldisilyl)-1-phenyl-2-(trimethylsilyl)ethene (29%). The two were separated by HPLC and were identified by an ^1H NMR NOE experiment. The regioisomers were transformed to **4a** + **4b** and **4a** + **4c** by further reaction with phenylethyne.

20 eV) m/z 214 (M^+). Anal. Calcd for $C_{10}H_{22}OSi_2$: C, 56.01; H, 10.34. Found: C, 56.21; H, 10.57.

Synthesis of Homoallylic Alcohol 10. To a THF solution (1 mL) of 8 (67 mg, 0.25 mmol) was added a hexane solution of n-butyllithium (0.49 mmol) at −78 °C under nitrogen. The temperature of the mixture was allowed to rise to room temperature over 12 h, and then 1 N aqueous HCl (1 mL) was added. Extraction with ether and preparative TLC of the extract (n-hexane/ether = 9:1) afforded 10 (66 mg, 81%): IR (neat) 3324, 2964, 1252, 1040 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.20 (s, 6 H), 0.21 (s, 9 H), 0.24 (s, 9 H), 0.65–0.74 (m, 2 H), 0.89 (t, J = 6.6 Hz, 3 H), 1.26–1.43 (m, 4 H), 2.87 (t, J = 6.8 Hz, 2 H), 3.62 (t, J = 6.8 Hz, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.33, 3.50, 3.72, 13.64, 17.67, 26.21, 26.48, 46.78, 62.24, 167.99, 174.64; HREIMS (20 eV) calcd for $C_{16}H_{38}OSi_3$ 330.2231, found 330.2221.

Epoxidation of 9. To a dichloromethane solution (1 mL) of m-chloroperbenzoic acid (45 mg, 0.26 mmol) was added 9 (47 mg, 0.22 mmol) at 0 °C. The mixture was stirred for 45 min and was then extracted with ether. Evaporation of solvent from the extract afforded 11 (43 mg, 85%): IR (neat) 2968, 1254, 1064 cm^{-1}; ^1H NMR (200 MHz, C_6D_6) δ 0.05 (s, 9 H), 0.31 (s, 3 H), 0.42 (s, 3 H), 1.25 (s, 3 H), 1.57 (ddd, J = 14.1, 4.5, and 2.1 Hz, 1 H), 1.86–2.03 (m, 1 H), 3.88–4.05 (m, 2 H); ^{13}C NMR (50 MHz, C_6D_6) δ −2.02, −1.61, 0.36, 18.55, 36.83, 56.94, 63.42; EIMS (20 eV) m/z 230 (M^+). Anal. Calcd for $C_{10}H_{22}O_2Si_2$: C, 52.12; H, 9.62. Found: C, 51.84; H, 9.60.

Supplementary Material Available: ^1H and ^{13}C NMR spectra of compounds 6, 7, and 10 (6 pages). Ordering information is given on any current masthead page.

C-Centered Optically Active Organosilanes. A Rational Approach to an Efficient Silylated Chiral Auxiliary

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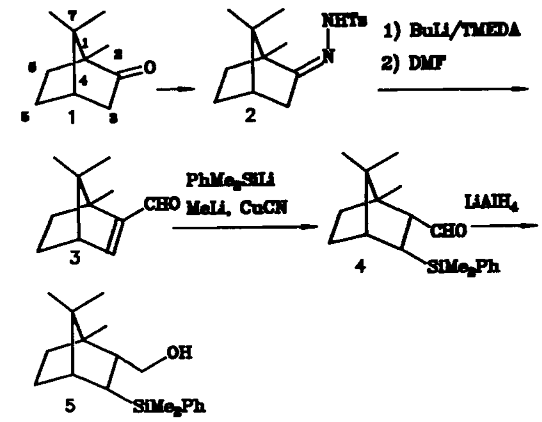
We recently reported the preparation[1] of some C-centered optically active organosilanes and their use[2] as chiral auxiliaries in the rections of allylsilanes with electrophiles. The modest enantiomeric excess (ee) values obtained in these reactions, comparable with results reported by other authors,[3] prompted us to consider a different approach to the preparation of such auxiliaries.

We looked at the possibility of performing an enantiocontrolled electrophilic attack at the double bond of an allylsilane by using a C-centered optically active auxiliary bonded to silicon, one which efficiently hinders one side of the double bond.

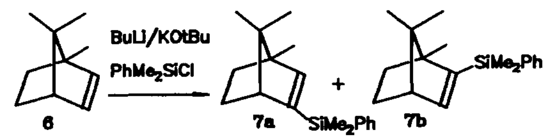
We report here the preparation of a chlorosilyl derivative with one of the ligands to silicon having a bornane-like structure, some applications which show the efficacy of this auxiliary in stereocontrolled reactions of allylsilanes, and some observations on the possible limitations of wider applications of this approach.

We first attempted to prepare a $PhMe_2Si$ derivative, as the precursor of a $ClMe_2Si$ group, by silyl cupration of the

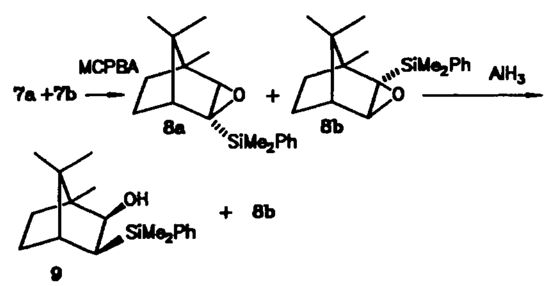
Scheme I



Scheme II



Scheme III



α,β-unsaturated bornyl aldehyde 3, prepared by a modification of the Shapiro reaction[4] (Scheme I).

Aldehyde 3, isolated in 56% yield,[5] underwent silyl cupration with $PhMe_2SiLi$ and CuCN at 0 °C, giving, after column chromatography, product 4 as the syn-endo isomer. The silyl cuprate attacks the double bond from the endo face, and the addition of the proton from the opposite direction[6] gives the product with the stereochemistry shown in Scheme I for 4.

Aldehyde 4 was easily enolized by treatment with organometallic reagents such as BuLi, BuMgBr, $PhCH_2MgBr$, and MeLi. Reduction of 4 with $LiAlH_4$ gave alcohol 5 only in poor yield. These results suggested that 4 was not a suitable intermediate for preparation of the required auxiliary.

The introduction of the $PhMe_2Si$ group into the bornyl skeleton was then attempted by coupling $PhMe_2SiCl$ with

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(5) This product has been prepared by an analogous reaction starting from the camphor trisylhydrazone. Chamberlin, A. R.; Stemke, J. E.; Bond, F. T. *J. Org. Chem.* 1978, *43*, 147.
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