Stereoselective Syntheses of Allylic Silanes via Hydroalumination or Hydroboration of Propargylic Silanes

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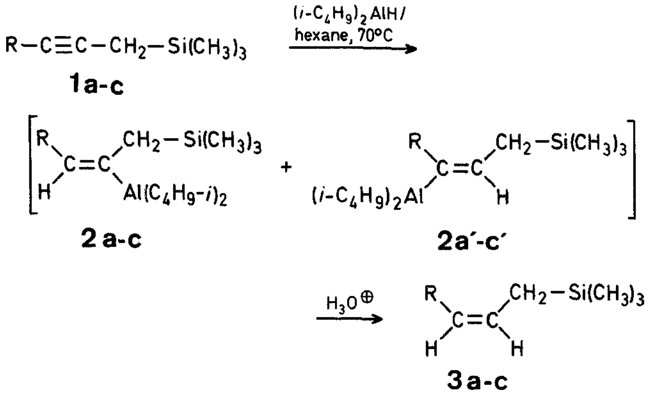
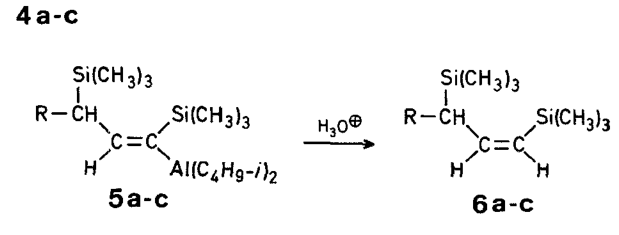
The usefulness of allylic silanes as synthons for a variety of chemical transformations has been amply demonstrated[1]. Although a number of procedures for their preparation have been reported, these often suffer from limitations in their general applicability and in their regio- and stereoselectivity. We now report that (*Z*)-1-trimethylsilyl-2-alkenes **3**, (*Z*)-1,3-bis[trimethylsilyl]-1-alkenes **6**, and 3-trimethylsilyl-1-alkenes **10** are conveniently synthesized by stereoselective reduction of the corresponding propargylic silanes, which are themselves readily accessible from simple precursors[2]. This new development should enhance the range of applications for allylic silanes in organic syntheses.

Monohydroalumination of 1-trimethylsilyl-2-heptyne[2] (**1a**) in *n*-hexane with two equivalents of diisobutylaluminum hydride[3] at 70 °C for 4 h proceeded in a stereoselective, but non-regioselective, manner to produce a 43 to 57 mixture of the alkenylalanes **2a** and **2a'**. Protonolysis of these with dilute hydrochloric acid afforded the (*Z*)-allylic silane **3a**[4].



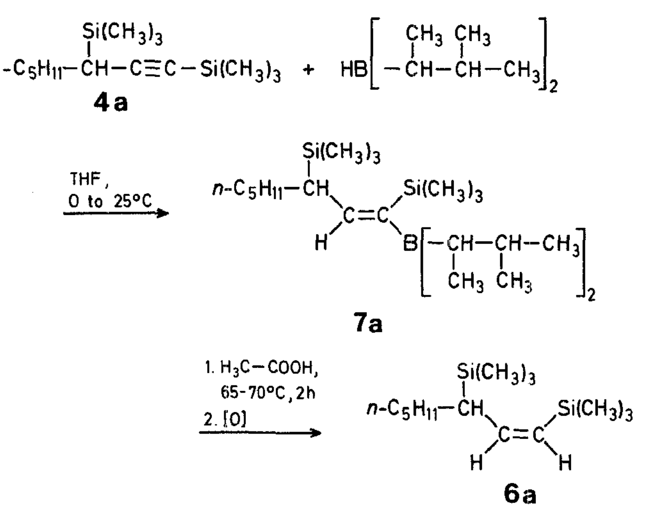
It should be noted that increasing the size of the R group from *n*-butyl to cyclohexyl or to *t*-butyl does not markedly affect the regiochemistry of the Al—H addition to the triple bond of **1**. Nevertheless, the hydroalumination-protonolysis reactions of 1-trimethylsilyl-2-alkynes **1a-c** provide the allylic silanes **3a-c** in high yields and isomeric purities.

Although it has not yet been actually demonstrated, the incorporation of both the allylic- and vinylic silyl moieties into a molecule should allow their selective elaboration into a variety of derivatives. An operationally convenient route to the bifunctional 1,3-bis[trimethylsilyl]-1-alkenes **6** is via reduction of the corresponding propargylic silanes **4**. Thus, hydroalumination of 1,3-bis[trimethylsilyl]-1-octyne (**4a**) with 1.1 equivalents of diisobutylaluminum hydride in ether at 40 °C furnished the alkenylalane **5a**. Protonolysis of **5a** yielded nearly isomerically pure (*Z*)-1,3-bis[trimethylsilyl]-1-octene (**6a**).



Deuterolysis of the alkenylalane **5a** and examination of the resultant deuterated 1,3-bis[trimethylsilyl]-1-alkene by ^{1}H-N.M.R. revealed that the deuterium was attached nearly exclusively at the 1-position of the double bond. Hence, the hydroalumination must have proceeded in a regioselective manner, placing the aluminum at the terminal carbon of the triple bond. The hydroalumination-protonolysis reactions worked equally well for the conversion of the cyclohexyl- and phenyl substituted propargylic silanes **4b, c** into the corresponding unsaturated silanes **6b, c**[5,6].

Although the hydroalumination-protonolysis is the method of choice for the reduction of simple propargylic silanes **4**, the presence of other functional groups in the molecule might interfere with the use of diisobutylaluminum hydride. Thus, we briefly examined the more chemoselective hydroboration reaction for the conversion of **4** to **6**. Treatment of **4a** with bis[1,2-dimethylpropyl]borane[7] afforded regioselectively the alkenylborane **7a**. Protonolysis of **7a** with glacial acetic acid followed by oxidation of the remaining 1,2-dimethylpropyl groups on boron with alkaline hydrogen peroxide afforded the bis-silane **6a** in 87% yield (G.L.C. analysis).



In this case, however, the bis-silane **6a** has to be separated from the oxidation byproduct, 3-methyl-2-butanol.

In connection with the above syntheses of 1,3-bis[trimethylsilyl]-1-alkenes, it should be noted that the intermediate regio- and stereodefined alkenylalanes **5** and alkenylboranes **7** might prove to be synthetically useful themselves in that the presence of a vinylic carbon-aluminum or a vinylic carbon-boron bond provides an additional site for further elaboration.

In contrast with the observed facile hydroalumination of the propargylic silanes **1** and **4**, treatment of 3-trimethylsilyl-1-octyne (**8a**) with various stoichiometries of diisobutylaluminum hydride in a hydrocarbon or ether produced the alkenylalane in only modest yield. Fortunately, hydroboration of **8a** with bis[1,2-dimethylpropyl]borane proceeded without difficulty to furnish the alkenyl borane **9a**. Treatment of **9a** with glacial acetic acid followed by an oxidative work up yielded the desired allylic silane **10a**[8].

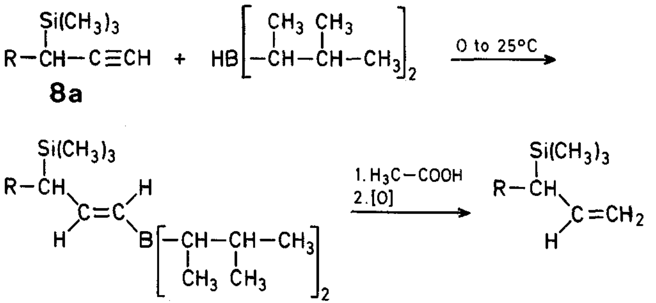
Table. Yields of (*Z*)-1-Trimethylsilyl-2-alkenes (**3**), (*Z*)-1,3-Bis[trimethylsilyl]-1-alkenes (**6**), and 3-Trimethylsilyl-1-alkenes (**10**)

Compound	R	Yield [%]	Isomeric purity[a] [%]	b.p. [°C]/torr	n_D [°C]	Molecular Formula[b]	
3a	*n*-C_4H_9	85	98	72°/13	1.4352 (25°)	$C_{10}H_{22}Si$	(170.1)
3b	*c*-C_6H_{11}	85	99	78°/3	1.4642 (25°)	$C_{12}H_{24}Si$	(196.1)
3c	*t*-C_4H_9	83	97	90°/60	1.4340 (23°)	$C_{10}H_{22}Si$	(170.1)
6a	*n*-C_5H_{11}	89	99	87°/2	1.4550 (23°)	$C_{14}H_{32}Si_2$	(256.2)
6b	*c*-C_6H_{11}	82	99	88°/1	1.4805 (22°)	$C_{15}H_{32}Si_2$	(268.2)
6c	C_6H_5	75	94[c]	94–96°/1	1.5095 (23°)	$C_{15}H_{26}Si_2$	(262.2)
10a	*n*-C_5H_{11}	79	97	64°/4	1.4345 (23°)	$C_{11}H_{24}Si$	(184.2)

[a] The isomeric purities of the compounds were determined on a SE-54 glass capillary column (30 m).

[b] The microanalyses were in satisfactory agreement with the calculated values: C, ±0.28; H, ±0.22.

[c] The compound contained about 6% of the corresponding allenic isomer, which was also present in the starting material.



(*Z*)-1-Trimethylsilyl-2-heptene (3a); Typical Procedure:

Into a dry 50-ml three-necked flask equipped with a nitrogen inlet tube, reflux condenser, thermometer, and magnetic stirrer kept under a static pressure of nitrogen is placed 1-trimethylsilyl-2-heptyne[2] (2.5 g, 15 mmol) and *n*-hexane (15 ml). To this solution is added diisobutylaluminum hydride (neat, 5.5 ml, 30 mmol) while maintaining the temperature during the addition at 25–30°C by means of a water bath. The solution is stirred at room temperature for 30 min, then heated at 70°C for 4 h. After cooling to room temperature, the reaction mixture is transferred by means of a double ended needle to a vigorously stirred mixture of 10% hydrochloric acid (30 ml), ice (30 g), and *n*-pentane (15 ml). The mixture is stirred for 15 min, the organic phase formed is separated, and the aqueous phase is extracted with *n*-pentane (3 × 20 ml). The combined organic extracts are washed with water (25 ml) and a saturated solution of sodium chloride (25 ml), then dried with magnesium sulfate. The solvents are removed and the residue is distilled through a short Vigreux column; yield: 2.18 g (85%); b.p. 71–72°C/13 torr; n_D^{25}: 1.4352.

$C_{10}H_{22}Si$	calc.	C 70.44	H 13.02
(170.1)	found	70.62	12.87

M.S.: *m/e* = 170.1459 (M^+); $C_{10}H_{22}Si$ requires 170.1492.

I.R. (neat): ν = 3030 (C=C—H); 1645 (C=C); 1250; 850 [$Si(CH_3)_3$] cm^{-1}.

^{1}H-N.M.R. (CCl_4): δ = 5.4–5 (m, 2H, CH=CH); 2–1.8 (m, 2H, C=C—CH_2); 1.4–1.2 (m, 6H); 0.9 (t, 3H, *J* = 6 Hz, CH_3); 0.0 ppm [s, 9H, $Si(CH_3)_3$].

(*Z*)-1,3-Bis[trimethylsilyl]-1-octene (6a); Typical Procedure:

Into a dry, nitrogen-flushed 50-ml three-necked flask is placed 1,3-bis[trimethylsilyl]-1-octyne[2] (1.75 g, 7.0 mmol) and anhydrous diethyl ether (3.5 ml). To the solution is added diisobutylaluminum hydride (neat, 1.4 ml, 7.6 mmol) while maintaining the temperature during the addition at 25–30°C by means of a water bath. The solution is stirred at 40°C for 2 h. The alkenylalane-containing mixture is cooled to room temperature, then is added by means of a double ended needle to a vigorously stirred mixture of 10% hydrochloric acid (15 ml), ice (15 g), and *n*-pentane (15 ml). The mixture is stirred for 15 min, the organic phase formed is separated, and the aqueous phase is extracted with *n*-pentane (2 × 15 ml). The combined organic extracts are washed successively with ice cold 10% hydrochloric acid (20 ml), water (20 ml), and saturated aqueous sodium chloride solution (20 ml), then dried with magnesium sulfate. The solvents are removed and the residue is distilled through a short Vigreux column; yield: 1.59 g (89%); b.p. 86–87°C/2 torr; n_D^{23}: 1.4550.

$C_{14}H_{32}Si_2$	calc.	C 65.48	H 12.57
(256.2)	found	65.63	12.47

M.S.: *m/e* = 256.2063 (M^+); $C_{14}H_{32}Si_2$ requires 256.2044.

I.R. (neat): ν = 1590 (C=C); 1250, 850 [$Si(CH_3)_3$] cm^{-1}.

^{1}H-N.M.R. (CCl_4): δ = 6.0 (dd, 1H, *J* = 14 Hz, 11 Hz, C=CH—C—Si); 5.2 (d, 1H, *J* = 14 Hz, C=CH—Si); 1.5–1.1 (m, 9H); 1.0–0.7 (m, 3H); 0.0 [s, 9H, C=C—$Si(CH_3)_3$]; −0.1 ppm [s, 9H, C=C—C—$Si(CH_3)_3$].

3-Trimethylsilyl-1-octene (10a):

To a stirred 1.5 molar solution (3.4 ml, 5.1 mmol) of bis[1,2-dimethylpropyl]borane[7] in tetrahydrofuran is added at 0°C 3-trimethylsilyl-1-octyne[2] (0.9 g, 5.0 mmol). The resultant mixture is stirred at 0–5°C for 30 min and then at room temperature for an additional 30 min. The resultant alkenylborane is treated with glacial acetic acid (0.6 ml) and then is heated at 65–70°C for 2 h. The remaining 1,2-dimethylpropyl groups on boron are oxidized with 3 molar sodium acetate (6 ml) and 30% hydrogen peroxide (1.4 ml) at 35–40°C. The mixture is maintained for 30 min at ambient temperature, saturated with potassium carbonate (1.5 H_2O), then extracted with ether (2 × 10 ml). The combined extracts are washed with a saturated solution of sodium chloride (20 ml), then dried with magnesium sulfate. The solvents are removed and the residue is distilled through a short Vigreux column; yield: 0.72 g (79%); b.p. 63–64°C/4 torr; n_D^{23}: 1.4345.

$C_{11}H_{24}Si$	calc.	C 71.59	H 13.12
(184.2)	found	71.67	12.98

M.S.: *m/e* = 184.1672 (M^+); $C_{11}H_{24}Si$ requires 184.1648.

I.R. (neat): ν = 3100 (C=C—H); 1625 (C=C); 1250, 850 [$Si(CH_3)_3$] cm^{-1}.

^{1}H-N.M.R. (CCl_4/C_6H_6): δ = 5.6–5.2 (m, 1H, C=CH—C—Si); 4.9–4.5 (m, 2H, C=CH_2); 1.5–0.7 (m, 12H); −0.1 [s, 9H, $Si(CH_3)_3$].

We thank the National Science Foundation for support of this investigation.

Received: July 22, 1983

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