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Stereoselective Syntheses of ((*E*)- and (*Z*)-1-Halo-1-alkenyl)silanes from Alkynes

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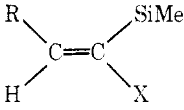
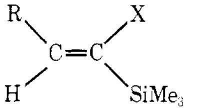
((*E*)-1-Haloalkenyl)trimethylsilanes are produced in high isomeric purities and yields by *N*-chlorosuccinimide, bromine, or iodine treatment of the monohydroalumination products derived from the reaction of (1-alkynyl)trimethylsilanes and diisobutylaluminum hydride in ether solvent. The corresponding ((*Z*)-1-chloro- and (*Z*)-1-bromoalkenyl)silanes may be obtained through bromine-catalyzed isomerization of the ((*E*)-1-chloro- and (*E*)-1-bromoalkenyl)silanes. Both (*E*)- and (*Z*)-1-haloalkenyl)silanes undergo metal–halogen exchange when treated with butyllithium to give ((*Z*)- and (*E*)-1-lithioalkenyl)silanes, respectively.

(α-Halovinyl)silanes ($H_2C{=}CXSiR_3$) are exceedingly versatile synthetic intermediates for use in a variety of chemical transformations,[1] and convenient procedures[2] for their synthesis are available. However, published procedures for preparation of the potentially valuable β-alkyl-substituted ((*E*)- and (*Z*)-1-halo-1-alkenyl)silanes are lacking. In connection with ongoing synthetic work, our need for ready access to these intermediates prompted us to explore their syntheses from 1-alkynes via conversion into (α-silylalkenyl)alanes.[3] Since we have previously shown that treatment of alkenylalanes with *N*-chlorosuccinimide,[4] bromine,[5] or iodine[5] results in preferential cleavage of the vinyl carbon–aluminum bond to afford the corresponding isomerically pure vinyl halides, it was hoped that halogenation of (α-silylalkenyl)alanes might provide the desired (α-haloalkenyl)silanes. Our investigations into these possibilities have uncovered operationally convenient stereoselective syntheses for ((*E*)- and (*Z*)-α-haloalkenyl)silanes **1** and **2**.

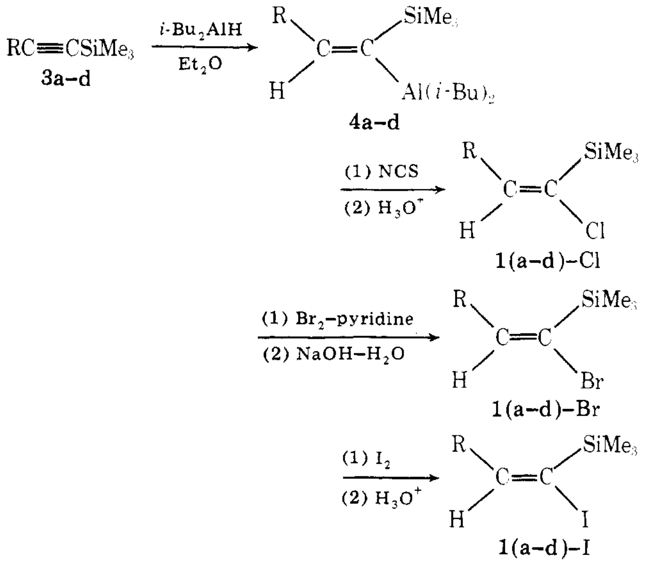

1(a–d)–X
X = Cl, Br, I


2(a–d)–X
X = Cl, Br

a, R = *n*-butyl; b, R = cyclohexyl; c, R = *tert*-butyl; d, R = cyclohexenyl

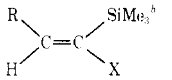
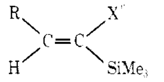
Results and Discussion

((*E*)-1-Halo-1-alkenyl)silanes. The hydroalumination of (1-alkynyl)silanes **3** with diisobutylaluminum hydride in ether solvent[6–8] proceeds in a stereo- and regiospecific manner to produce ((*Z*)-1-alumino-1-alkenyl)silanes **4** regardless of the steric requirements of the alkyl group at the β carbon of the (1-alkynyl)silanes. Attempts to chlorinate **4** with chlorine in methylene chloride at −78 °C resulted in low yields of the desired (α-chloroalkenyl)silane **1**–Cl. Fortunately, however, this difficulty could be obviated by the use of *N*-chlorosuccinimide (NCS) as the chlorinating agent. Thus, the silylacetylene **3** was treated with diisobutylaluminum hydride (1.0 equiv) in ether solvent and heated at 40 °C for 1 h. To the resultant ((*Z*)-1-alumino-1-alkenyl)silane **4**, NCS (1.1 equiv) was added in the dark with cooling to maintain the temperature between −25 and −20 °C. Stirring the reaction mixture for an additional 30 min at 0 °C followed by a hydrolytic workup afforded the ((*E*)-1-chloro-1-alkenyl)silanes **1**–Cl in greater than 80% yields (Table I).



a, R = *n*-butyl; b, R = cyclohexyl; c, R = *tert*-butyl; d, R = cyclohexenyl

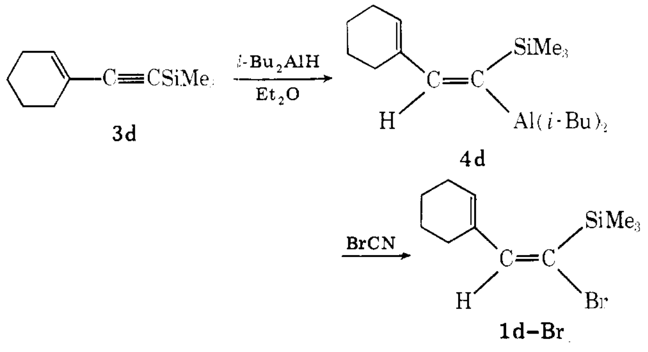
Table I. Isolated Yields of ((*E*)- and (*Z*)-1-Halo-1-alkenyl)trimethylsilanes Derived from (1-Alkynyl)trimethylsilanes[a]

$RC{\equiv}CSiMe_3$, R=	Registry no.	 X =	Registry no.	 X =	Registry no.
n-Butyl	3844-94-8	Cl (84)	66270-61-9	Cl (81)[d]	66270-69-7
		Br (90)	66270-62-0	Br (81)[d]	66270-70-0
		I (90)	66270-63-1		
Cyclohexyl	66270-60-8	Cl (87)	66270-64-2	Cl (91)[d]	66270-71-1
		Br (96)	66270-65-3	Br (92)[d]	66270-72-2
				Br (89)[e]	
		I (90)	66270-66-4		
tert-Butyl	14630-42-3	Br (86)	65425-93-6	Br (89)[e]	65425-94-7
				Br (88)[f]	
		I (85)	66270-67-5		
Cyclohexenyl	17988-44-2	Br (84)	66270-68-6	Br (84)[f]	66270-73-3

[a] All compounds were at least 97% isomerically pure by GLC analysis on a 55-m OV-101 or SE-30 glass capillary column; % yields are in parentheses. [b] Via hydroalumination–halogenation. [c] Via hydroalumination–halogenation–isomerization. [d] Isomerization of crude *E* isomer in ether with bromine–pyridine while irradiating with a UV lamp. [e] Isomerization of quenched reaction mixture containing the *E* isomer with bromine in ambient light. [f] Via trans hydroalumination–bromination.

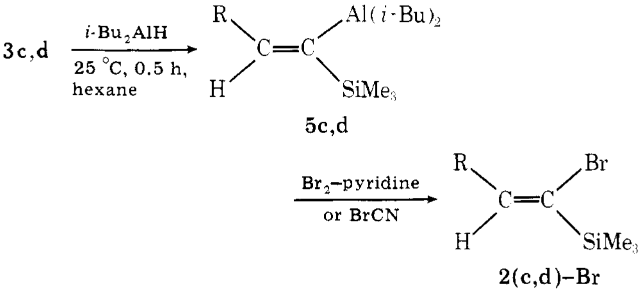
The synthesis of ((*E*)-1-bromo-1-alkenyl)silanes **1(a–c)**–Br required addition of bromine (1.3 equiv) in methylene chloride to a solution of 4 at low temperature in ether containing pyridine (2 equiv). This was followed by hydrolysis of the reaction mixture in cold dilute sodium hydroxide. A 30% excess of bromine was employed to compensate for some isobutyl group cleavage from the diisobutylalanyl moiety. The presence of pyridine in the bromination step represses addition of bromine to the double bond of 4 and/or 1–Br and results in higher yields of the desired (α-bromoalkenyl)silanes (Table I). Quenching of the bromination mixture was done in an aqueous solution of sodium hydroxide rather than in dilute hydrochloric acid because the latter procedure caused partial isomerization of the double bond.

Extension of the bromination reaction to (dienylsilyl)alane **4d**, accessible through the chemo- and regioselective hydroalumination of (2-cyclohexenylethynyl)trimethylsilane (**3d**), produced a mixture of products. This probably was the result of a competition for bromine between the carbon–carbon double bonds and the vinyl carbon–aluminum bond of **4d.** However, **4d** was successfully converted into the desired bromide **1d**–Br by treatment with a predried solution of cyanogen bromide.



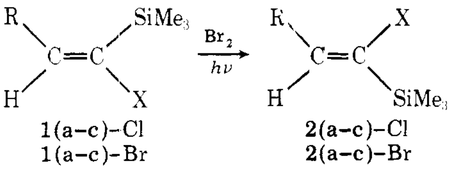
Finally, treatment of **4a–c** in ether solvent with iodine (1.3 equiv) furnished, after quenching the reaction mixture in dilute hydrochloric acid, the anticipated ((*E*)-1-iodo-1-alkenyl)silanes **1(a–c)**–I in better than 80% yields. A summary of the yields of ((*E*)-1-halo-1-alkenyl)silanes obtained using our procedures is presented in Table I.

((*Z*)-1-Halo-1-alkenyl)silanes. Having developed convenient syntheses for the ((*E*)-1-halo-1-alkenyl)silanes, we next turned our attention to finding routes to the corresponding *Z* halides. An obvious method for achieving this goal appeared to be through the halogenation of ((*E*)-1-alumino-1-alkenyl)silanes **5.** It has been shown that these are accessible through hydroalumination of (3,3-dimethyl-1-butynyl)trimethylsilane (**3c**) or (2-methylbut-1-en-3-yn-4-yl)trimethylsilane in hydrocarbon solvent.[3]



As expected, bromination of **5c** in the presence of pyridine indeed afforded the anticipated ((*Z*)-1-bromo-1-alkenyl)silane **2c**–Br containing only 1% of the *E* isomer. Also, treatment of enynylsilane **3d** with diisobutylaluminum hydride followed by addition of a solution of cyanogen bromide in methylene chloride yielded, after workup, the (*Z*)-dienylsilyl bromide **2d**–Br. Unfortunately, however, this approach to ((*Z*)-1-halo-1-alkenyl)silanes did not turn out to be general because hydroalumination of (1-alkynyl)trimethylsilanes containing primary or secondary β-alkyl substituents yielded mixtures of ((*Z*)- and (*E*)-1-alumino-1-alkenyl)silanes along with dihydroaluminated product. For example, when (1-hexynyl)trimethylsilane (**3a**) was treated with diisobutylaluminum hydride (1.1 equiv) in heptane solvent at 25 °C for 16 h followed by hydrolysis with dilute hydrochloric acid, GLC analysis of the products on a SE-30 glass capillary column (55 m) revealed (*cis*-1-hexenyl)trimethylsilane (11%), (*trans*-1-hexenyl)trimethylsilane (34%), and (*n*-hexyl)trimethylsilane (27%).[9,10]

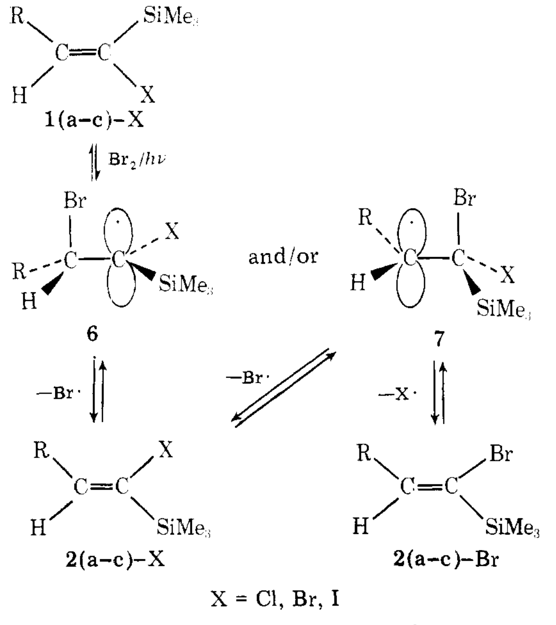
Fortunately, a general method for preparing ((*Z*)-1-bromo-1-alkenyl)silanes **2**–Br emerged when it was discovered that bromine in the presence of light catalyzes isomerization of the *E* bromides **1**–Br into the desired *Z* isomers **2**–Br. Thus, after hydrolysis of the bromination mixture containing **1b**–Br or **1c**–Br with dilute hydrochloric acid, 10 mol % of bromine was added in two equal portions at the beginning and middle of a 60-min period while exposing the two-phase mixtures to ambient light and stirring vigorously at 25 °C. Then they were treated with aqueous sodium sulfite to decompose the excess bromine. Extraction with pentane and distillation afforded the ((*Z*)-1-bromo-1-alkenyl)silanes **2b**–Br and **2c**–Br in at least 97% isomeric purities.



This operationally simple procedure, which does not require prior isolation of the *E* bromide precursors **1**–Br, is very effective and proceeds rapidly when applied to alkynylsilanes containing secondary or tertiary alkyl groups. However, it was noted that under the above conditions isomerization of **1a**–Br, containing a primary alkyl group, proceeded much more slowly. This may result from a relatively fast, irreversible reaction of bromine with the substrate. However, this difficulty was obviated by slight modification of the experimental procedure. Thus, after hydrolysis with dilute hydrochloric acid, the *E* bromide **1a**–Br was extracted into ether, and the combined extract was washed successively with dilute hydrochloric acid, saturated sodium bicarbonate, and saturated sodium chloride. After drying over magnesium sulfate and filtration, the ethereal solution containing **1a**–Br was treated at room temperature with pyridine (6 equiv based on Br_2) and with 15 mol % of bromine in methylene chloride in three equal portions after 0, 30, and 60 min during a 90-min period while irradiating with a UV sunlamp (275 W). After workup and distillation, there was obtained an 81% yield of **2a**–Br containing only 3% of the *E* isomer **1a**–Br.

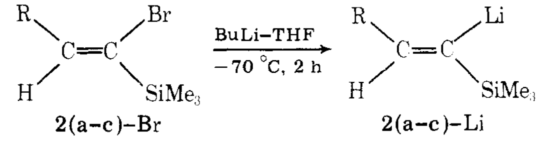
The above isomerization procedures were also very effective for the conversion of ((*E*)-1-chloro-1-alkenyl)silanes to the corresponding *Z* isomers (Table I). However, attempts to isomerize ((*E*)-1-iodo-1-alkenyl)silanes in the presence of bromine–pyridine while irradiating the mixture with a sunlamp resulted in appreciable exchange of iodine by bromine. A summary of the yields of ((*Z*)-1-chloro- and (*Z*)-1-bromo-1-alkenyl)silanes obtained via the bromine-catalyzed isomerizations is shown in Table I.

The isomerization of ((*E*)-1-halo-1-alkenyl)silanes (**1** → **2**) is reminiscent of the bromine-catalyzed cis–trans isomerization of 1,2-dibromoethylene, which has been subjected to a detailed mechanistic study.[11] Thus, addition of bromine atoms resulting from photolytic dissociation of Br_2 to **1**–X produces the radicals **6** and/or **7**, depicted in their most stable conformations. Since both a trialkylsilyl moiety[12] and a halogen[13] are known to stabilize an adjacent radical center, formation of radical **6** should be favored over that of **7**. When X = Br, loss of a bromine from either **6** or **7** leads to the observed sterically less hindered *Z* bromides **2**–Br. However, when X represents either Cl or I in radical **7**, these halogen atoms may be lost competitively with the bromine atom, thus producing mixtures of products containing both **2**–Br and **2**–Cl or **2**–I, respectively. The fact that the bond dissociation energy of the C–Cl bond is larger than that of the C–Br bond suggests the preferential ejection of the bromine atom. In agreement with this is the observation that bromine-catalyzed isomerizations of ((*E*)-1-chloro-1-alkenyl)silanes **1**–Cl afford the corresponding *Z* isomers **2**–Cl in high isomeric purities and essentially free of the corresponding bromides **2**–Br. A different situation exists when X in **7** is iodine. In this case, loss of the iodine atom from radical **7** (X = I) should be favored over dissociation of the bromine atom. This was born out by the fact that attempted isomerization of **1a**–I afforded, besides the *Z* iodide **2a**–I, a mixture of the corresponding *Z* bromide **2a**–Br and the thermodynamically less favored *E* bromide **1a**–Br.



((*E*)- and (*Z*)-1-Lithio-1-alkenyl)silanes. Having both ((*E*)- and (*Z*)-1-halo-1-alkenyl)silanes readily available, we finally directed our efforts to their conversion into the corresponding (α-lithioalkenyl)silanes. This reaction is of considerable interest not only in connection with synthetic methodology, but it also provides a convenient tool for establishing the stereochemistries of the (α-haloalkenyl)silanes obtained in the present study.

Previous attempts to prepare (α-lithioalkenyl)silanes by metalation of (*cis*- and *trans*-alkenyl)silanes have resulted in isomeric mixtures of products and/or competing metalation of the trimethylsilyl moiety.[14] On the other hand, we have now found that metal–halogen exchange of the ((*E*)- and (*Z*)-1-bromo- or (*E*)-1-iodoalkenyl)silanes with butyllithium provides efficient, stereoselective syntheses for ((*E*)- and (*Z*)-1-lithioalkenyl)silanes.[15] Thus, addition of butyllithium (1.1 equiv) in hexane to a solution of ((*E*)-1-iodoalkenyl)silanes **1(a–c)**–I in ether at −70 °C produces the corresponding ((*Z*)-1-lithioalkenyl)silanes **1(a–c)**–Li in better than 90% yields and containing less than 7% of the trans isomers. This was evidenced by the stereochemistries of the vinyl silanes formed on protonolysis of the intermediate (α-lithioalkenyl)-silanes with methanol (Table II). For metal–halogen exchange involving *E* bromides **1(a–c)**–Br, the presence of tetrahydrofuran was required. To repress coupling of the product **1**–Li with the accompanying butyl bromide,[16,17] the reaction had to be carried out at −95 °C for 30 min using a mixture of tetrahydrofuran–ether–*n*-hexane.[18]



Exchange of the sterically more hindered bromide in ((*Z*)-1-bromo-1-alkenyl)silanes **2(a–c)**–Br by butyllithium occurred more slowly and had to be carried out at −70 °C for 2 h. With either isomer, however, nearly quantitative conversions into the lithio compounds **1**–Li and **2**–Li with retention of stereochemistry were achieved (Table II).

Table II. Lithiation–Protonation of ((*E*)- and (*Z*)-1-Halo-1-alkenyl)trimethylsilanes

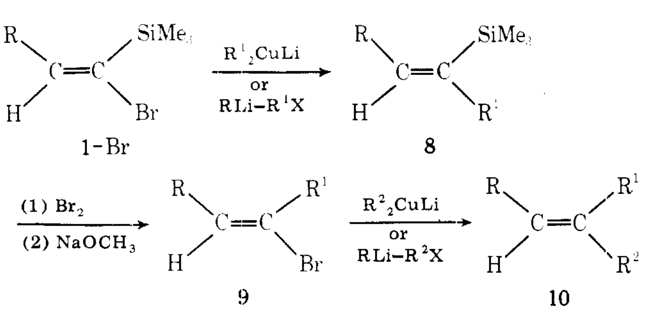
(1-Halo-1-alkenyl)silane	Lithiation[a]			Alkenylsilane[b]	GLC yield of alkenylsilanes,[c] %
	Solvent	Temp, °C	Time, min	Cis:trans	
1a–Br	Trapp[d]	−95	30	99:1[e]	88
1b–Br	Trapp	−95	30	99:1[f]	92
1c–Br	Trapp	−95	30	90:10[g]	89
2a–Br	THF	−70	120	1:99	96
2b–Br	THF	−70	120	1:99	96
2c–Br	THF	−70	120	1:99	99
1a–I	Et_2O	−70	20	93:7	93
1b–I	Et_2O	−70	20	98:2	98
1c–I	Et_2O	−70	20	96:4	99

[a] By treatment with *n*-butyllithium (1.1 equiv) under the specified conditions. [b] After quenching of the (1-lithio-1-alkenyl)silanes with excess methanol. Isomeric purities were determined by GLC comparison with authentic samples. [c] The GLC chromatogram also revealed peaks with retention times corresponding to the starting material and to the coupling product derived from the (1-lithio-1-alkenyl)silane with butyl bromide. [d] Mixture of THF–Et_2O–*n*-hexane (4:1:1). [e] Registry no.: cis, 54731-58-7; trans, 66270-75-5. [f] Registry no.: cis, 52835-06-0; trans, 20107-37-3. [g] Registry no.: cis, 66270-74-4; trans, 26567-95-3.

Finally, attempted metal–halogen exchange on the (α-chloroalkenyl)silane **1a**–Cl using *n*-butyl- or *sec*-butyllithium did not furnish the anticipated (*cis*-1-hexenyl)trimethylsilane after hydrolysis, but afforded a mixture of products containing starting material, (1-hexynyl)trimethylsilane, and several unidentified compounds. Conclusive proof of the stereochemistries of both the ((*E*)- and (*Z*)-1-chloro-1-hexenyl)trimethylsilanes **1a**–Cl and **2a**–Cl was obtained by their conversion into (*Z*)- and (*E*)-2-trimethylsilyl-2-heptenes via alkylation with methyllithium in the presence of a catalytic amount of cuprous iodide.[19,20]

Summary

Operationally simple syntheses of ((*E*)- and (*Z*)-1-halo-1-alkenyl)silanes are described. The precursors are readily available via the regio- and stereoselective monohydroalumination of (1-alkynyl)trimethylsilanes. Treatment of the resultant ((*Z*)-1-alumino-1-alkenyl)silanes with NCS, bromine, or iodine produces the corresponding ((*E*)-1-halo-1-alkenyl)silanes in high yields and isomeric purities. Bromine-catalyzed isomerization of ((*E*)-1-chloro- and (*E*)-1-bromo-1-alkenyl)silanes affords the corresponding *Z* isomers. As exemplified below, these (α-haloalkenyl)silanes provide a valuable entry to stereoselective synthesis of dialkyl-substituted (vinyl)silanes (**8**),[19] alkenyl halides (**9**),[19,21] and trisubstituted olefins (**10**).[19] The corresponding compounds with opposite stereochemistries are available using the ((*Z*)-1-bromo-1-alkenyl)silanes.[19]



Experimental Section

All boiling points are uncorrected. Infrared spectra were obtained on a Beckman IR-8 spectrometer. ^1H NMR spectra were recorded on a Varian A-60 spectrometer, and chemical shifts are reported in ppm downfield from a Me_4Si internal standard. High-resolution mass measurements were obtained on a DuPont 21-492B mass spectrometer. GLC analyses were performed on a Varian 600-D gas chromatograph equipped with 5-ft columns packed with 20% dodecamethylenedinitrile, didecyl phthalate, or SF-96 on Gas-Chrome R, Q, or Q, respectively, or on a Varian 1400 gas chromatograph equipped with either a 55-m OV-101 or SE-30 glass capillary column.

The hydrocarbons (Phillips) and anhydrous diethyl ether (Mallinckrodt) were used as received. NCS (Aldrich) was recrystallized from methylene chloride and dried over phosphorus pentoxide. All alkynes employed in the study were purchased from Farchan and were used after checking their ^1H NMR spectra, indices of refraction, and GLC retention times. The concentration of butyllithium (Ventron or Aldrich) in *n*-hexane was determined by titration using 2,2′-biquinoline as an indicator.[22] Diisobutylaluminum hydride (Texas Alkyls) was transferred from the lecture bottle into a storage flask which was maintained under an N_2 atmosphere. The neat reagent (5.4 M) was transferred by means of a syringe.

All glassware for reactions involving organoaluminum or organolithium reagents was oven-dried at 150 °C for 6 h, assembled hot, and cooled under a stream of purified nitrogen before use. All reactions involving these materials were stirred magnetically and carried out under an atmosphere of nitrogen.

General Procedure for the Preparation of (1-Alkynyl)trimethylsilanes. (1-Hexynyl)trimethylsilane (3a). A solution of 1-hexyne (24.7 g, 0.300 mol) in 100 mL of anhydrous ether was treated consecutively at −70 °C with a solution of butyllithium (0.306 mol) in *n*-hexane and with trimethylchlorosilane (33.2 g, 0.306 mol). The reaction mixture was allowed to exotherm to room temperature, where it was stirred for 2 h and then quenched in ice water. The layers were separated, and the aqueous layer was extracted with *n*-pentane. The combined pentane extracts were washed with water and brine, dried ($MgSO_4$), and concentrated. Distillation of the residue gave 41.2 g (89%) of **3a**: bp 71–73 °C (36 Torr); n^{23}_{D} 1.4305 (lit.[23] bp 155 °C, n^{20}_{D} 1.4318); IR (neat) 2185, 1251, and 843 cm^{-1}; NMR (CCl_4) δ 2.3–0.9 (m, 9 H) and 0.11 (s, 9 H).

(2-Cyclohexylethynyl)trimethylsilane (3b). Following the general procedure described above, cyclohexylacetylene was converted to **3b** in 86% yield: bp 82–83 °C (7 Torr); n^{22}_{D} 1.4615; IR (neat) 2185, 1250, and 845 cm^{-1}; NMR (CCl_4) δ 2.5–1.0 (m, 11 H) and 0.12 (s, 9 H); exact mass, *m/e* 180.1340 (calcd for $C_{11}H_{20}Si$, 180.1335).

(3,3-Dimethyl-1-butynyl)trimethylsilane (3c). Following the general procedure, *tert*-butylacetylene was converted to **3c** in 82% yield: bp 80–81 °C (150 Torr); n^{23}_{D} 1.4161 (lit.[24] bp 57 °C (60 Torr), n^{20}_{D} 1.4161); IR (neat) 2165, 1252, and 842 cm^{-1}; NMR (CCl_4) δ 1.22 (s, 9 H) and 0.11 (s, 9 H).

(2-Cyclohexenylethynyl)trimethylsilane (3d). Following the general procedure described previously, 1-ethynylcyclohexene was converted to **3d** in 89% yield: bp 55–57 °C (1 Torr); n^{23}_{D} 1.4915 (lit.[25] bp 107–108 °C (20 Torr), n^{20}_{D} 1.4940); IR (neat) 2160, 1250, 870, and 845 cm^{-1}; NMR (CCl_4) δ 6.07 (m, 1 H), 2.05 (m, 4 H), 1.60 (m, 4 H), and 0.14 (s, 9 H).

General Procedure for the Preparation of ((*E*)-1-Chloro-1-alkenyl)trimethylsilanes. ((*E*)-1-Chloro-1-hexenyl)trimethylsilane (1a–Cl). Into a dry 25-mL three-neck round-bottom flask equipped with a nitrogen inlet and thermometer and kept under a static pressure of nitrogen was added **3a** (1.54 g, 10 mmol) and anhydrous ether (5 mL). Diisobutylaluminum hydride (1.85 mL, 10 mmol) was added dropwise using a syringe while maintaining the temperature during the addition at 25–30 °C by means of a water bath. The solution was stirred at room temperature for 15 min and then heated at 40 °C for 1 h. After cooling to −25 °C (aqueous $CaCl_2$–dry ice bath[26]) and diluting with anhydrous ether (5 mL), the reaction mixture was treated in the dark with dry solid *N*-chlorosuccinimide (1.47 g, 11 mmol) at such a rate as to maintain the temperature below −20 °C. After completion of the NCS addition, the reaction mixture was stirred in the dark for an additional 15 min at −25 °C and then for 30 min at 0 °C. The resultant yellowish solution was slowly poured into chilled, stirred 10% hydrochloric acid (50 mL). Stirring was continued until the resulting phases became clear. The layers were separated, the water layer was extracted with *n*-pentane, and the combined organic extracts were washed with 10% hydrochloric acid followed by saturated aqueous sodium bicarbonate. After drying (MgSO$_4$) and concentration, distillation from a small amount of calcium carbonate afforded 1.60 g (84%) of **1a**–Cl: bp 63–64 °C (5 Torr); $n^{19}{}_{\mathrm{D}}$ 1.4580; IR (neat) 1600, 1251, 867, and 842 cm^{-1}; NMR (CCl$_4$) δ 6.37 (t, 1 H, J = 8 Hz), 2.2–0.8 (m, 9 H), and 0.23 (s, 9 H); exact mass, *m/e* 190.0971 (calcd for $C_9H_{19}ClSi$, 190.0946).

((*E*)-1-Chloro-2-cyclohexylethenyl)trimethylsilane (1b–Cl). Using the procedure described for the preparation of **1a**–Cl, 1.80 g (10 mmol) of **3b** was converted into 1.88 g (87%) of **1b**–Cl: bp 57–58 °C (0.5 Torr); $n^{26}{}_{\mathrm{D}}$ 1.4820; IR (neat) 1600, 1252, 865, 840, and 760 cm^{-1}; NMR (CCl$_4$) δ 6.22 (d, 1 H, J = 10 Hz), 2.3–1.0 (m, 11 H), and 0.22 (s, 9 H); exact mass, *m/e* 216.1112 (calcd for $C_{11}H_{21}ClSi$, 216.1102).

((*E*)-1-Bromo-1-hexenyl)trimethylsilane (1a–Br). According to the general hydroalumination procedure described above for the preparation of **1a**–Cl, 2.32 g (15 mmol) of **3a** contained in ether (7.5 mL) was treated with 16.5 mmol (10% excess) of diisobutylaluminum hydride (3.06 mL) and heated at 40 °C for 1 h. The hydroalumination product formed was diluted at 0 °C with ether (15 mL) and pyridine (2.4 mL). To the resultant yellow reaction mixture was added at −70 °C a solution of bromine (19.5 mmol, 1.5 M) in methylene chloride at such a rate as to maintain the temperature during the addition below −60 °C. The yellow slurry that formed was kept for an additional 15 min at −70 °C and then was poured slowly into a vigorously stirred mixture of 1 N sodium hydroxide (60 mL), ice (20 g), and *n*-pentane (15 mL). After shaking the mixture until it became clear, it was extracted with *n*-pentane. The combined organic extracts were washed successively with 1 N hydrochloric acid, a 20% aqueous solution of cadmium chloride (to remove small amounts of remaining pyridine), 1 N hydrochloric acid, and saturated aqueous sodium bicarbonate and then dried (MgSO$_4$). Distillation from a small amount of calcium carbonate afforded 3.17 g (90%) of **1a**–Br: bp 48 °C (1 Torr); $n^{23}{}_{\mathrm{D}}$ 1.4755; IR (neat) 1595, 1251, and 841 cm^{-1}; NMR (CCl$_4$) δ 6.71 (t, 1 H, J = 8 Hz), 2.1–0.9 (m, 9 H), and 0.25 (s, 9 H); exact mass, *m/e* 234.0413 (calcd for $C_9H_{19}BrSi$, 234.0440).

((*E*)-1-Bromo-2-cyclohexylethenyl)trimethylsilane (1b–Br). Following the procedure described above for the preparation of **1a**–Br, 1.80 g (10 mmol) of **3b** was subjected to hydroalumination–bromination. Distillation from calcium carbonate gave 2.51 g (96%) of **1b**–Br: bp 47–51 °C (10^{-3} Torr); $n^{23}{}_{\mathrm{D}}$ 1.5008; IR (neat) 1592, 1250, 860, and 840 cm^{-1}; NMR (CCl$_4$) δ 6.55 (d, 1 H, J = 10 Hz), 2.4–1.0 (m, 11 H), and 0.25 (s, 9 H); exact mass, *m/e* 260.0627 (calcd for $C_{11}H_{21}BrSi$, 260.0596).

((*E*)-1-Bromo-3,3-dimethyl-1-butenyl)trimethylsilane(1c–Br). Following the procedure described above for the preparation of **1a**–Br, 1.54 g (10 mmol) of **3c** yielded 2.01 g (86%) of **1c**–Br on hydroalumination–bromination: bp 54–55 °C (2 Torr); $n^{23}{}_{\mathrm{D}}$ 1.4821; IR (neat) 1570, 1251, and 845 cm^{-1}; NMR (CCl$_4$) δ 7.06 (s, 1 H), 1.12 (s, 9 H), and 0.32 (s, 9 H); exact mass, *m/e* 234.0422 (calcd for $C_9H_{19}BrSi$, 234.0440).

((*E*)-1-Bromo-2-cyclohexenylethenyl)trimethylsilane (1d–Br). Using the hydroalumination procedure described for the preparation of **1a**–Cl, 3.56 g (20 mmol) of **3d** was treated with 20 mmol of diisobutylaluminum hydride (no excess) and heated. To the resulting organoalane was added at 0 °C a 2 M solution of cyanogen bromide (22 mmol) in ether (dried over Drierite) at such a rate as to maintain the temperature below 10 °C. After stirring the mixture for 30 min at ambient temperature, it was transferred by means of the double-ended needle technique[27] to vigorously stirred, chilled, aqueous 6 N sodium hydroxide (100 mL). The reaction mixture was shaken vigorously to bring any remaining solid material into solution. The layers were separated, and the aqueous phase was extracted with *n*-pentane. The combined organic extracts were washed with aqueous 6 N sodium hydroxide and brine and dried (MgSO$_4$). Distillation from a small amount of calcium carbonate afforded 4.38 g (84%) of **1d**–Br: bp 46–47 °C (10^{-3} Torr); $n^{20}{}_{\mathrm{D}}$ 1.5235; IR (neat) 1628, 1592, 1260, 950, 904, and 855 cm^{-1}; NMR (CCl$_4$) δ 7.10 (s, 1 H), 5.53 (m, 1 H), 2.02 (m, 4 H), 1.63 (m, 4 H), and 0.21 (s, 9 H); exact mass, *m/e* 258.0418 (calcd for $C_{11}H_{19}BrSi$, 258.0439).

((*E*)-1-Iodo-1-hexenyl)trimethylsilane (1a–I). Following the general hydroalumination procedure described for the preparation of **1a**–Br, 7.72 g (50 mmol) of **3a** was reacted with 10.2 mL of diisobutylaluminum hydride (55 mmol). The resultant organoalane was diluted with ether (25 mL) and then treated at −70 °C with a solution of iodine (16.5 g, 65 mmol) in ether (100 mL) at such a rate as to maintain the temperature during the addition below −65 °C. The resulting brown reaction mixture was stirred for 1 h at −70 °C and then allowed to exotherm to 0 °C. After stirring for an additional 15 min at 0 °C, the yellow reaction mixture was slowly poured into a stirred mixture of 10% hydrochloric acid (200 mL) and ice (50 g). The two-phase mixture was shaken until the precipitate that had formed dissolved, and the mixture then was extracted with *n*-pentane. The combined organic extracts were washed successively with aqueous 1 N sodium hydroxide (50 mL), 1 M sodium thiosulfate, and brine and then dried (MgSO$_4$). Distillation from a small amount of calcium carbonate yielded 12.7 g (90%) of **1a**–I: bp 56–57 °C (1 Torr); $n^{22}{}_{\mathrm{D}}$ 1.5084; IR (neat) 1580, 1251, and 841 cm^{-1}; NMR (CCl$_4$) δ 7.12 (t, 1 H, J = 8 Hz), 2.1–0.9 (m, 9 H), and 0.26 (s, 9 H); exact mass, *m/e* 282.0321 (calcd for $C_9H_{19}ISi$, 282.0302).

((*E*)-1-Iodo-2-cyclohexylethenyl)trimethylsilane (1b–I). By a procedure similar to that described for the preparation of **1a**–I, 1.80 g (10 mmol) of **3b** was converted into 2.75 g (90%) of **1b**–I: bp 53–54 °C (10^{-4} Torr); $n^{23}{}_{\mathrm{D}}$ 1.5320; IR (neat) 1581, 1249, and 850 cm^{-1}; NMR (CCl$_4$) δ 6.96 (d, 1 H, J = 10 Hz), 2.4–1.0 (m, 11 H), and 0.25 (s, 9 H); exact mass, *m/e* 308.0458 (calcd for $C_{11}H_{21}ISi$, 308.0458).

((*E*)-1-Iodo-3,3-dimethyl-1-butenyl)trimethylsilane (1c–I). By a procedure similar to that described for the preparation of **1a**–I, 3.86 g (25 mmol) of **3c** yielded 6.07 g (85%) of **1c**–I: bp 64–65 °C (2 Torr); $n^{23}{}_{\mathrm{D}}$ 1.5183; IR (neat) 1555, 1251, and 845 cm^{-1}; NMR (CCl$_4$) δ 7.52 (s, 1 H), 1.02 (s, 9 H), and 0.25 (s, 9 H); exact mass, *m/e* 282.0278 (calcd for $C_9H_{19}ISi$, 282.0302).

((*Z*)-1-Chloro-1-hexenyl)trimethylsilane (2a–Cl). Using the procedure described above for the preparation of **1a**–Cl, 3.09 g (20 mmol) of **3a** was treated sequentially with diisobutylaluminum hydride and NCS. The reaction mixture containing the *E* chloride **1a**–Cl was poured slowly into vigorously stirred, chilled 10% hydrochloric acid (100 mL). The resulting mixture containing some solid material was shaken until the organic phase became clear. It then was extracted with three 10-mL portions of ether. The combined extracts were washed with 10% hydrochloric acid (10 mL), saturated aqueous sodium bicarbonate, and brine. After drying over MgSO$_4$ and filtration, the ethereal solution containing **1a**–Cl was stirred and treated three times at room temperature (water bath, cooled as needed) under a UV sunlamp (275 W) with 0.50 mL of pyridine followed by 1.0 mL of a 1.0 M solution of bromine in methylene chloride after 0, 30, and 60 min during a 90-min period. The reaction mixture was decanted from a gummy residue and washed with 10% hydrochloric acid (70 mL), 20% aqueous cadmium chloride (to remove traces of pyridine), water, 1 M sodium hydroxide, and brine. GLC analysis of the extract revealed, in addition to the *Z* chloride **2a**–Cl, a small amount of an unknown product of longer retention time. After drying (MgSO$_4$) and distillation there was obtained 3.08 g (81%) of **2a**–Cl: bp 74–77 °C (10 Torr); $n^{20}{}_{\mathrm{D}}$ 1.4517; IR (neat) 1610, 1252, and 838 cm^{-1}; NMR (CCl$_4$) δ 5.91 (t, 1 H, J = 7 Hz), 2.30 (d of t, 2 H, J = 7 Hz), 1.6–0.8 (m, 7 H), and 0.16 (s, 9 H); exact mass, *m/e* 190.0948 (calcd for $C_9H_{19}ClSi$, 190.0946).

((*Z*)-1-Chloro-2-cyclohexylethenyl)trimethylsilane (2b–Cl). Using the procedure described above for the preparation of **2a**–Cl, the crude *E* chloride **1b**–Cl derived from **3b** (20 mmol) was isomerized to afford 91% of **2b**–Cl: bp 70–71 °C; $n^{19}{}_{\mathrm{D}}$ 1.4798; IR (neat) 1610, 1251, and 838 cm^{-1}; NMR (CCl$_4$) δ 5.73 (d, 1 H, J = 8.5 Hz), 2.72 (m, 1 H), 2.0–1.0 (m, 10 H), and 0.17 (s, 9 H); exact mass, *m/e* 216.1078 (calcd for $C_{11}H_{21}ClSi$, 216.1102).

((*Z*)-1-Bromo-1-hexenyl)trimethylsilane (2a–Br). Using the procedure described above for the preparation of **2a**–Cl, the crude *E* bromide **1a**–Br derived from **3a** (30 mmol) was isomerized to yield 81% of **2a**–Br: bp 67–69 °C (4 Torr); $n^{22}{}_{\mathrm{D}}$ 1.4697; IR (neat) 1610, 1250, 880, and 840 cm^{-1}; NMR (CCl$_4$) δ 6.19 (t, 1 H, J = 6.5 Hz), 2.3–0.9 (m, 9 H), and 0.17 (s, 9 H); exact mass, *m/e* 234.0430 (calcd for $C_9H_{19}BrSi$, 234.0440).

((*Z*)-1-Bromo-2-cyclohexylethenyl)trimethylsilane (2b–Br). The reaction mixture containing the *E* bromide **1b**–Br derived from **3b** (25 mmol) was quenched in chilled 10% hydrochloric acid (125 mL) and then allowed to warm to room temperature. To the well-stirred two-phase mixture was added at room temperature (water bath) under ambient light conditions at the beginning and middle of a 60-min period 1.0 mL each time of a solution of bromine (1.25 M) in methylene chloride. The mixture was extracted with *n*-pentane, and the extract was washed with 10% hydrochloric acid (20 mL), 20% aqueous cadmium chloride (to remove traces of pyridine), water, aqueous sodium thiosulfate, 1 N sodium hydroxide, and brine. After drying (MgSO4) and distillation there was obtained an 89% yield of **2b**–Br: bp 80–82 °C (2 Torr); $n^{22}{}_{\mathrm{D}}$ 1.4958; IR (neat) 1606, 1248, 884, and 843 cm^{-1}; NMR (CCl$_4$) δ 5.99 (d, 1 H, J = 8 Hz), 2.9–1.1 (m, 11 H), and 0.15 (s, 9 H); exact mass, *m/e* 260.0603 (calcd for $C_{11}H_{21}BrSi$, 260.0596.

((*Z*)-1-Bromo-3,3-dimethyl-1-butenyl)trimethylsilane (2c-Br). Using the procedure described above for the preparation of **2b**-Br, the crude *E* bromide **1c**-Br derived from **3c** (5.0 mmol) was isomerized to afford 89% of **2c**-Br: bp 51–53 °C (5 Torr); $n^{23}{}_D$ 1.4670; IR (neat) 1596, 1251, 897, and 844 cm^{-1}; NMR (CCl$_4$) δ 6.30 (s, 1 H), 1.23 (s, 9 H), and 0.16 (s, 9 H); exact mass, *m/e* 234.0458 (calcd for $C_9H_{19}BrSi$, 234.0440).

((*Z*)-1-Bromo-2-cyclohexenylethenyl)trimethylsilane (2d-Br). To a solution of **3d** (3.56 g, 20 mmol) in hexane (10 mL) was added dropwise at 25–30 °C diisobutylaluminum hydride (3.70 mL, 20 mmol). The reaction mixture was stirred for an additional 30 min at room temperature and then cooled in an ice bath and treated with a dried solution (Drierite) of cyanogen bromide (22 mmol, 2M) in ether. After stirring at ambient temperature for 1 h, the mixture was worked up as described above for the isolation of the corresponding *E* bromide **1d**-Br. Distillation from a small amount of calcium carbonate gave 4.37 g (84%) of **2d**-Br: bp 47–49 °C (10^{-3} Torr); $n^{23}{}_D$ 1.5309; IR (neat) 1656, 1586, 1260, and 855 cm^{-1}; NMR δ 6.60 (s, 1 H), 6.00 (m, 1 H), 2.28 (m, 2 H), 2.10 (m, 2 H), 1.62 (m, 4 H), and 0.18 (s, 9 H); exact mass, *m/e* 258.0433 (calcd for $C_{11}H_{19}BrSi$, 258.0439).

General Procedure for Lithium–Halogen Exchange Reactions of (1-Bromo- and 1-Iodo-1-alkenyl)silanes. To a solution of the (α-haloalkenyl)silane (10 mmol) in 20 mL of the appropriate solvent or solvent mixture at the indicated temperature was added a solution of *n*-butyllithium (11 mmol, 1.5–2.5 M) in hexane at such a rate as to limit the temperature rise to 5 °C. After stirring the reaction mixture for an appropriate length of time, it was treated dropwise with 1 mL of methanol, warmed to room temperature, and diluted with 10% hydrochloric acid. The resultant (1-alkenyl)silane was extracted with *n*-pentane, dried (MgSO$_4$), and analyzed by GLC using a hydrocarbon as an internal standard to measure the yield. The isomeric purity of the compound was determined on a glass capillary column (SE-30; 50 m) by comparing the retention times of the peaks observed with those from authentic samples of the corresponding ((*E*)- and (*Z*)-1-alkenyl)silanes. The results of these experiments are summarized in Table II.

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Registry No.—1-Hexyne, 693-02-7; cyclohexylacetylene, 931-48-6; *tert*-butylacetylene, 917-92-0; 1-ethynylcyclohexene, 931-49-7.

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