

(t, 6 H,  $J = 1.5$  Hz), 0.97 (s, 9 H), 0.15 (s, 6 H); IR (NaCl, film) 2900, 2850, 1355, 1255, 1160, 1094, 1016, 848, 830, 768  $\text{cm}^{-1}$ ; mass spectrum,  $m/e$  266, 251 ( $M - \text{CH}_3$ ), 209 ( $M - \text{C}_4\text{H}_9$ ).

Anal. Calcd for  $\text{C}_{16}\text{H}_{30}\text{OSi}$ : C, 72.1; H, 11.3. Found: C, 72.2; H, 11.0.

For 1-adamantyl *tert*-butyldiphenylsilyl ether:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.67 (m, 4 H), 7.30 (m, 6 H), 2.15 (br s, 3 H), 1.85-1.60 (m, 12 H), 1.07 (s, 9 H); IR (NaCl, film) 3070, 2925, 2900, 2850, 1585, 1423, 1350, 1120, 1013, 735, 700  $\text{cm}^{-1}$ ; mass spectrum,  $m/e$  390, 333 ( $M - \text{C}_4\text{H}_9$ ).

For  $\beta$ -methoxy-5 $\alpha$ -cholestyl *tert*-butyldimethylsilyl ether:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.78 (m, 1 H), 3.40 (s, 3 H), 2.20-0.80 (m), 1.07 (s, 3 H), 0.95 (s, 15 H), 0.90 (s, 3 H), 0.75 (s, 3 H), 0.09 (s, 6 H).

**Desilylation of  $\beta$ -Methoxy-5 $\alpha$ -cholestyl *tert*-Butyldimethylsilyl Ether.** A sample of the silyl ether (0.53 g, 1 mmol) was dissolved in 5 mL of 1 M tetra-*n*-butylammonium fluoride. After 4 h at reflux, the reaction mixture was diluted with ether and washed with water. The ether layer was concentrated. Recrystallization from methanol gave 0.4 g (95%) of a white solid (mp 131.5-132  $^\circ\text{C}$ ) identified as  $\beta$ -methoxy-5 $\alpha$ -cholestanol:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.68 (m, 1 H), 3.41 (s, 3 H), 2.20-0.80 (m), 1.07 (s, 3 H), 1.00 (s, 6 H), 0.93 (s, 3 H), 0.75 (s, 3 H).

Anal. Calcd for  $\text{C}_{28}\text{H}_{50}\text{O}_2$ : C, 80.5; H, 11.8. Found: C, 80.3; H, 11.9.

**Reaction of (Phenylseleno)trimethylsilane (1) with Hydrochloric Acid.** Hydrogen chloride gas was bubbled through a solution of 1 (4.58 g, 0.02 mol) in 40 mL of acetonitrile, giving an exothermic reaction. Distillation gave 2.1 g (97%) of trimethylsilyl chloride [bp 59-61  $^\circ\text{C}$  (atm)] and 2.93 g (93%) of benzeneselenol, bp 28-30  $^\circ\text{C}$  (0.03 torr).

**Reaction of (Phenylseleno)trimethylsilane (1) with Benzeneselenenyl Chloride.** Benzeneselenenyl chloride (1.91 g, 0.01 mol) was added to a solution of 1 (2.29 g, 0.01 mol) in 10 mL of acetonitrile cooled to 9  $^\circ\text{C}$ . Distillation gave 1.05 g (97%) of trimethylsilyl chloride, bp 59-61  $^\circ\text{C}$  (atm). Recrystallization of the pot residue from methanol gave 2.98 g (93%) of diphenyl diselenide, mp 61-62  $^\circ\text{C}$ .

**Acknowledgment.** We thank Dr. Thomas H. Whitesides for many helpful and stimulating discussions.

**Registry No.** 1, 33861-17-5; 2, 76358-43-5; 3, 72726-46-6; 4, 76358-44-6; 5, 75-77-4; 6, 2857-97-8; 7, 16029-98-4; 8, 994-30-9; 9, 1112-48-7; 10, 1112-49-8; 11, 18162-48-6; 12, 76358-45-7; 13, 72726-45-5; 14, 76358-46-8; diphenyl diselenide, 1666-13-3; triethylsilane, 617-86-7; benzeneselenol, 645-96-5; *tert*-butyldiphenylsilyl chloride, 58479-61-1; chlorine, 7782-50-5; bromine, 7726-95-6; iodine, 7553-56-2; methoxy-*tert*-butyldiphenylsilyl ether, 76358-47-9; cyclopentene oxide, 285-67-6; *trans*-2-iodocyclopentyl *tert*-butyldimethylsilyl ether, 76358-48-0; cyclopent-2-enyl *tert*-butyldimethylsilyl ether, 68845-73-8; cyclohexene oxide, 286-20-4; *trans*-2-iodocyclohexyl *tert*-butyldimethylsilyl ether, 76358-49-1; cyclohex-2-enyl *tert*-butyldimethylsilyl ether, 72726-49-9; cycloheptene oxide, 286-45-3; *trans*-2-iodocycloheptyl *tert*-butyldimethylsilyl ether, 76358-50-4; cyclohept-2-enyl *tert*-butyldimethylsilyl ether, 72726-50-2; 2-cyclo-

heptenol, 4096-38-2; cyclooctene oxide, 286-62-4; *trans*-2-iodocyclooctyl *tert*-butyldimethylsilyl ether, 76358-51-5; cyclooct-2-enyl *tert*-butyldimethylsilyl ether, 72726-51-3; *trans*-2,3-dibutyloxirane, 2165-61-9; *erythro*-6-iodo-5-decyl *tert*-butyldimethylsilyl ether, 76358-52-6; *trans*-6-decen-5-yl *tert*-butyldimethylsilyl ether, 72726-52-4; 5-decanone, 820-29-1; 2,2-dimethyl-3-ethyloxirane, 1192-22-9; 2-methylpent-1-en-3-yl *tert*-butyldimethylsilyl ether, 72726-53-5; 6-oxaspiro[5.2]octane, 185-70-6; (cyclohexen-1-yl)methyl *tert*-butyldimethylsilyl ether, 76358-53-7; 1-(iodomethyl)cyclohex-1-yl *tert*-butyldimethylsilyl ether, 72726-54-6; 1-methylcyclohexene oxide, 1713-33-3; 2-methylcyclohex-2-enyl *tert*-butyldimethylsilyl ether, 72726-55-7; 2-methylenecyclohexyl *tert*-butyldimethylsilyl ether, 72726-56-8; *cis*-2-iodo-2-methylcyclohexanol, 76358-54-8; *trans*-2-iodo-1-methylcyclohexyl *tert*-butyldimethylsilyl ether, 72726-47-7; tetramethyloxirane, 5076-20-0; 2,3-dimethyl-3-buten-2-yl *tert*-butyldimethylsilyl ether, 72726-57-9; butyloxirane, 1436-34-6; 1-iodo-2-hexyl *tert*-butyldimethylsilyl ether, 76358-55-9; 2-iodo-1-hexyl *tert*-butyldimethylsilyl ether, 76358-56-0; *trans*-2-iodocyclopentyl *tert*-butyldiphenylsilyl ether, 76376-85-7; cyclopent-2-enyl *tert*-butyldiphenylsilyl ether, 76358-57-1; *trans*-2-iodocyclohexyl *tert*-butyldiphenylsilyl ether, 76358-58-2; cyclohex-2-enyl *tert*-butyldiphenylsilyl ether, 76358-59-3; *trans*-2-iodocycloheptyl *tert*-butyldiphenylsilyl ether, 76358-60-6; cyclohept-2-enyl *tert*-butyldiphenylsilyl ether, 76358-61-7; *trans*-2-iodocyclooctyl *tert*-butyldiphenylsilyl ether, 76358-62-8; cyclooct-2-enyl *tert*-butyldiphenylsilyl ether, 76358-63-9; *erythro*-6-iododec-5-yl *tert*-butyldiphenylsilyl ether, 76358-64-0; *trans*-dec-6-en-5-yl *tert*-butyldiphenylsilyl ether, 76358-65-1; 2-methylpent-1-en-3-yl *tert*-butyldiphenylsilyl ether, 76358-66-2; (cyclohexen-1-yl)methyl *tert*-butyldiphenylsilyl ether, 76358-67-3; 1-(iodomethyl)cyclohexyl *tert*-butyldiphenylsilyl ether, 76358-68-4; 2-methylenecyclohexyl *tert*-butyldiphenylsilyl ether, 76358-69-5; *trans*-2-iodo-1-methylcyclohexyl *tert*-butyldiphenylsilyl ether, 76358-70-8; 3-iodo-2,3-dimethyl-2-butyl *tert*-butyldiphenylsilyl ether, 76358-71-9; 2,3-dimethylbut-3-en-2-yl *tert*-butyldiphenylsilyl ether, 76358-72-0; 3-bromo-2-methylpentan-2-ol, 76358-73-1; 1-(bromomethyl)cyclohexyl *tert*-butyldimethylsilyl ether, 76376-86-8; cyclooctene, 931-88-4; *trans*-2-iodocyclooctyl trimethylsilyl ether, 76358-74-2; *trans*-2-iodocyclooctanol, 76358-75-3; *trans*-dec-5-ene, 7433-56-9; *erythro*-6-iododec-5-yl trimethylsilyl ether, 76358-76-4; *erythro*-6-iododecan-5-ol, 76358-77-5; *trans*-dec-6-en-5-yl trimethylsilyl ether, 76358-78-6; *trans*-2-bromocyclooctyl trimethylsilyl ether, 76358-79-7; cyclooct-2-enyl trimethylsilyl ether, 31059-41-3; 1-hexadecyl *tert*-butyldimethylsilyl ether, 76358-80-0; (-)-menthyl *tert*-butyldimethylsilyl ether, 76358-81-1; cholesteryl *tert*-butyltrimethylsilyl ether, 57711-50-9; 3-ethyl-3-pentyl *tert*-butyldimethylsilyl ether, 76376-87-9; 3-ethyl-3-pentyl *tert*-butyldiphenylsilyl ether, 76358-82-2; 1-methylcyclohexyl *tert*-butyldimethylsilyl ether, 76358-83-3; 1-methylcyclohexyl *tert*-butyldiphenylsilyl ether, 76358-84-4; 1-adamantyl *tert*-butyldimethylsilyl ether, 76358-85-5; 1-adamantyl *tert*-butyldiphenylsilyl ether, 76358-86-6;  $\beta$ -methoxy-5 $\alpha$ -cholestyl *tert*-butyldimethylsilyl ether, 76376-88-0; 1-hexadecanol, 36653-82-4; (-)-menthol, 2216-51-5; cholesterol, 57-88-5; 3-ethyl-3-pentanol, 597-49-9; 1-methylcyclohexanol, 590-67-0; 1-adamantol, 768-95-6;  $\beta$ -methoxy-5 $\alpha$ -cholesterol, 76376-89-1; hydrochloric acid, 7647-01-0; benzeneselenenyl chloride, 5707-04-0; 3-bromo-2-methylpent-2-yl *tert*-butyldimethylsilyl ether, 76376-90-4; 2-methylcyclohex-2-enyl *tert*-butyldiphenylsilyl ether, 76358-87-7.

## (*E*)- and (*Z*)-(1-Iodo-1-alkenyl)silanes. Their Preparation and Their Conversion into (*E*)- and (*Z*)-(1-Lithio-1-alkenyl)silanes<sup>1</sup>

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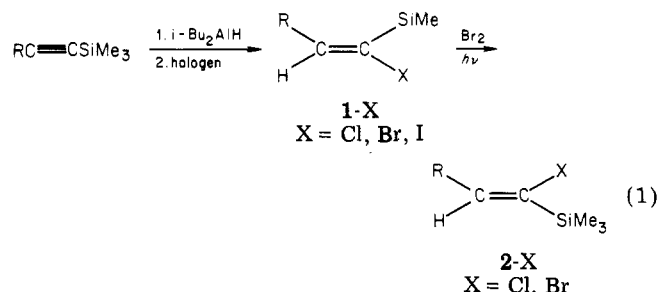
Received August 13, 1980

(*Z*)-(1-Iodo-1-alkenyl)trimethylsilanes can be conveniently obtained by isomerization of the readily available *E* isomers through the intermediacy of (1-lithioalkenyl)silanes formed by addition of catalytic amounts of *tert*-butyllithium. Reaction of (*E*)- and (*Z*)-(1-iodoalkenyl)silanes with 2.1 equiv of *tert*-butyllithium produces the (*E*)- and (*Z*)-(1-lithio-1-alkenyl)silanes. These synthetically important alkenyllithiums have been found to be configurationally stable at -70  $^\circ\text{C}$ . However, they isomerize at higher temperatures, reaching an *E/Z* equilibrium distribution at 0  $^\circ\text{C}$  of 86:14 ( $\pm 5\%$ ) irrespective of the size of the  $\beta$ -alkyl substituent.

Recently we reported that (*E*)-(1-haloalkenyl)silanes 1-X (X = Cl, Br, I) are produced in high isomeric purities and

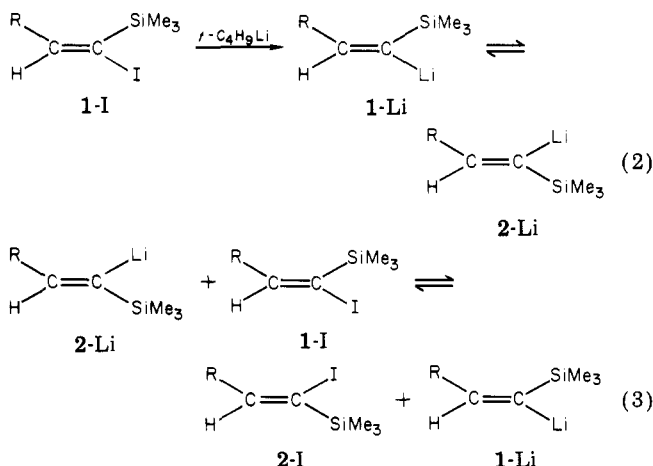
yields by halogenation of the monohydroalumination products derived from the reaction of (1-alkynyl)tri-

methylsilanes with diisobutylaluminum hydride in ether solvent (eq 1).<sup>2</sup> Upon UV irradiation in the presence of



catalytic amounts of bromine the (E)-(1-chloroalkenyl)- and (E)-(1-bromoalkenyl)silanes can be isomerized almost exclusively into the corresponding (Z)-(1-halo-1-alkenyl)silanes 2-X (X = Cl, Br). Unfortunately, however, attempts to isomerize the (E)-(1-iodo-1-alkenyl)silanes 1-I in a similar manner resulted in appreciable exchange of iodine by bromine.<sup>2</sup> Since the trifunctional  $\alpha$ -halovinylsilyl moiety represents a uniquely constituted synthon for stereoselective syntheses of substituted olefins,<sup>3</sup> it was desirable to also have access to the (Z)-iodides 2-I. Thus, we continued to search for suitable approaches for their preparation.

In the course of investigating the iodine-lithium exchange of (E)-(1-iodo-1-hexenyl)trimethylsilane (1-I, R = *n*-C<sub>4</sub>H<sub>9</sub>) with *tert*-butyllithium, we noted that the resultant (Z)-(1-lithiohexenyl)silane (1-Li) rearranged to a mixture predominating in the (E)-vinyl lithium (2-Li) when its solution was allowed to warm up to 0 °C. It occurred to us that this tendency of the (Z)-alkenyl lithium (1-Li) to isomerize at higher temperature might be exploited in a catalytic procedure converting the readily accessible (E)-iodides 1-I into the corresponding (Z)-isomers 2-I via a sequence of isomerization and iodine-lithium-exchange reactions (eq 2 and 3).



For the initial isomerization studies, two different procedures were investigated. In the first of these, a solution of *tert*-butyllithium (1.0 mmol, 2.0 M)<sup>4</sup> in pentane was diluted with anhydrous ether and added at -70 °C to the pure (E)-(1-iodo-1-alkenyl)trimethylsilane (0.5 mmol). The

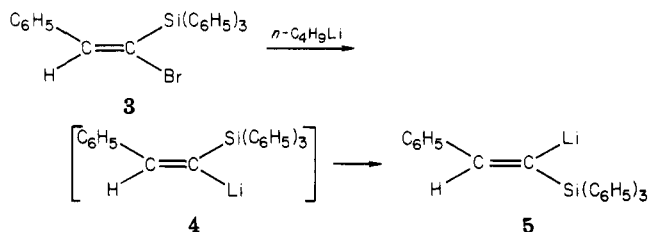
Table I. Yields of (Z)-(1-Iodo-1-alkenyl)trimethylsilanes (2-I) Derived from (E)-(1-Iodo-1-alkenyl)trimethylsilanes (1-I)

R =	isolated yields, % <sup>b</sup>		vinyl protons, <sup>c</sup> $\delta$
	1-I	2-I	
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	7.1 (t, <i>J</i> = 8 Hz)	85 <sup>d</sup> 72 <sup>e</sup>	6.1 (t, <i>J</i> = 6 Hz)
<i>c</i> -C <sub>6</sub> H <sub>11</sub>	7.0 (d, <i>J</i> = 10 Hz)	89 <sup>d</sup> 82 <sup>e</sup>	5.8 (d, <i>J</i> = 8 Hz)
<i>t</i> -C <sub>4</sub> H <sub>9</sub>	7.5 (s)	83 <sup>d</sup>	6.5 (s)

<sup>a</sup> Reference 2. <sup>b</sup> The isolated iodides were at least 97% isomerically pure. <sup>c</sup> The spectra were run in CCl<sub>4</sub> solvent, using an internal Me<sub>3</sub>Si standard. <sup>d</sup> Utilization of pure (E)-iodides. <sup>e</sup> Utilization of (E)-iodides prepared in situ.

resultant solution was treated with an additional 9.5 mmol of the iodide and then allowed to slowly warm up to room temperature before workup. In the second procedure, we investigated to determine the feasibility of using crude instead of distilled (E)-iodides. For this purpose, the (E)-iodides 1-I (20 mmol) derived via the sequence of reactions shown in eq 1 were freed from their solvents. Then, without isolation, they were added to a mixture of ether and *tert*-butyllithium (3.0 mmol) in pentane maintained at -70 °C. The resultant solutions, after being brought slowly to room temperature, were worked up. We were pleased to observe that using both procedures the (Z)-iodides were isolated in at least 97% isomeric purities.<sup>6</sup> A summary of yields of (Z)-iodides realized by using the pure and crude (E)-iodide precursors is shown in Table I.

Having ready access to both the (E)- and (Z)-(1-iodo-1-alkenyl)trimethylsilanes, we next turned our attention toward their conversion into the synthetically important (Z)- and (E)-(1-lithio-1-alkenyl)trimethylsilanes, respectively. It is apparent that for their efficient application as intermediates for stereoselective transformations, an understanding of the factors of temperature, time, and reaction medium influencing their configurational stabilities is necessary. Although isolated observations regarding the isomerization of (1-lithioalkenyl)silanes have been reported, no detailed study concerning the configurational stability of isomeric pairs of these reagents has appeared thus far in the literature. Brook and co-workers<sup>7</sup> reported that bromine-lithium exchange of  $\beta$ -bromo- $\beta$ -(triphenylsilyl)styrene (3) with *n*-butyllithium at low temperature followed by hydrolysis afforded *trans*-(triphenylsilyl)styrene, indicating that the (Z)-(1-lithio-1-silyl)styrene (4) initially formed isomerized to the (E)-vinyl lithium 5. Also,



Cunico<sup>8</sup> observed that the vinyl lithium derived from

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

(2) Zweifel, G.; Lewis, W. *J. Org. Chem.* 1978, 43, 2739.

(3) Miller, R. B.; McGarvey, G. *J. Org. Chem.* 1979, 44, 4623.

(4) It should be noted that half of the *tert*-butyllithium employed is consumed in the dehydrohalogenation of the resultant *tert*-butyl iodide to isobutene.<sup>5</sup>

(5) Corey, E. J.; Beams, D. J. *J. Am. Chem. Soc.* 1972, 94, 7210. Kluge, H. F.; Untch, K. G.; Fried, J. H. *Ibid.* 1972, 94, 7827. Cahiez, G.; Bernard, D.; Normant, J. F. *Synthesis* 1976, 245.

(6) Recently, we have found that the conversion of 1-I to 2-I may also be accomplished in the presence of a catalytic amount of LiAlH<sub>4</sub> instead of *tert*-butyllithium. In this case, however, the isomerizations have to be carried at 65 °C in THF solvent. Lewis, W. Ph.D. Thesis, University of California, Davis, CA, 1979.

(7) Brook, A. G.; Duff, J. M.; Reynolds, W. F. *J. Organomet. Chem.* 1976, 121, 293.

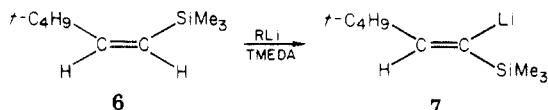
Table II. Configurational Stability of (1-Lithio-1-alkenyl)trimethylsilanes Derived via Lithiation of (1-Iodo-1-alkenyl)trimethylsilanes<sup>a</sup>

starting alkenyllithiums	R =	temp, °C	time, h	solvent	E/Z ratios of protonation products 8 <sup>b</sup>
	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	-70	1	Et <sub>2</sub> O	0/100
		-35	1	Et <sub>2</sub> O	15/85
		0	1	Et <sub>2</sub> O	86/14
		0	2	Et <sub>2</sub> O	86/14
		25	1	Et <sub>2</sub> O	83/17
		0	1	THF	84/16
	<i>c</i> -C <sub>6</sub> H <sub>11</sub>	-70	1	Et <sub>2</sub> O-HMPA	83/17
		0	1	Et <sub>2</sub> O	1/99
		0	1	Et <sub>2</sub> O	83/17
		0	1	Et <sub>2</sub> O	3/97
	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	-70	1	Et <sub>2</sub> O	88/12
		0	1	Et <sub>2</sub> O	99/1
	<i>c</i> -C <sub>6</sub> H <sub>11</sub>	0	1	Et <sub>2</sub> O	88/12
		0	1	Et <sub>2</sub> O	85/15
	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	0	1	Et <sub>2</sub> O	91/9
		0	1	Et <sub>2</sub> O	

<sup>a</sup> Results at 0 and 25 °C represent equilibrium distributions. (GLC analysis).

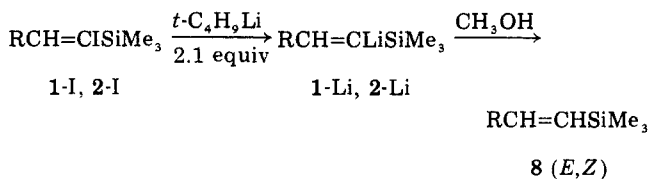
<sup>b</sup> The alkenylsilanes were obtained in better than 90% yields

metalation of **6** at the  $\alpha$ -silylvinyl position is not the anticipated *Z* but rather the *E* isomer **7**. It was suggested



that the severe *syn-tert*-butyltrimethylsilyl group interaction might provide the driving force for the observed isomerization.<sup>8</sup>

For the present study, the appropriate (*E*)- and (*Z*)-iodides (**1-I**, **2-I**) were added at -70 °C to 2.1 equiv<sup>4</sup> of *tert*-butyllithium in *n*-pentane. After the mixture was stirred for an additional 2 h at this temperature, the resultant alkenyllithiums (**1-Li**, **2-Li**) were protonated with methanol. In related experiments, the alkenyllithiums prepared at -70 °C were allowed to warm up to various higher temperatures, maintained there for various periods of time, and then treated with methanol. The (*E*)- and (*Z*)-alkenylsilanes **8** formed under the various conditions were analyzed for their isomeric compositions by GLC on a 90-m SE-30 glass capillary column (J & W column), and the results are summarized in Table II.

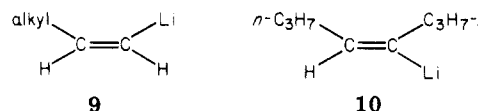


The salient conclusions emerging from this study are that both the (*E*)- and (*Z*)- $\alpha$ -lithioalkenylsilanes (**1-Li**, **2-Li**) are configurationally stable at low temperature but do isomerize at higher temperatures. These observations have important implications when applying the  $\alpha$ -lithioalkenylsilanes as intermediates for organic syntheses. Thus, their reactions with electrophiles have to be carried out at sufficiently low temperature to ensure retention of stereochemistry of the double bond in the products.

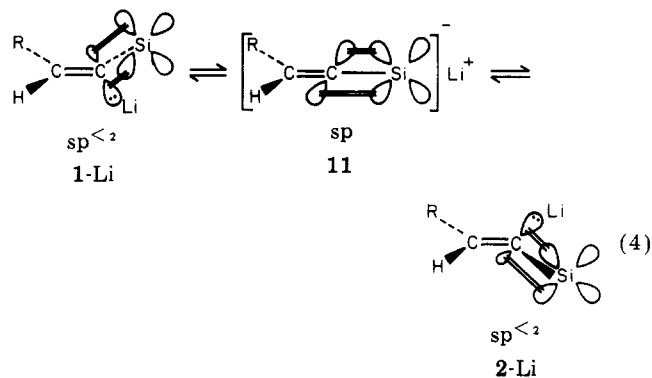
Another interesting facet of the results in Table II is the observation that the *E/Z* equilibrium ratios at 0 °C of the alkenyllithiums (**1-Li**, **2-Li**) are close to 86:14 ( $\pm 5\%$ ), irrespective of the size of the alkyl group at the double bond. Also, the reaction medium used for the halogen-metal exchange reactions, whether ether, ether-HMPA, or tet-

rahydrofuran, affects the equilibrium *E/Z* ratios of the alkenyllithiums at 0 °C only slightly. That equilibrium was indeed attained was evidenced by the fact that either of the isomeric  $\alpha$ -lithioalkenylsilanes furnished similar mixtures of (*Z*)- and (*E*)-alkenylsilanes **8** when maintained at 0 °C for 1 h prior to protonation.

In view of the observed configurational stability in ethereal solvents of the simple alkyl-substituted alkenyllithiums **9**<sup>6</sup> and **10**,<sup>9</sup> which do not possess  $\alpha$ -substituents



capable of stabilizing an adjacent negative charge, the isomerization mechanism for the (1-lithio-1-alkenyl)silanes (**1-Li**, **2-Li**) must involve the silicon center. The tendency of these organolithiums to isomerize can be accounted for in terms of a silicon-assisted ionization of the carbon-lithium bond to provide the linear intermediate (or activated complex) **11** (eq 4). Thus, through its known  $\alpha$ -



anion stabilizing effect, the silicon facilitates isomerization in a manner similar to that provided by a phenyl group in  $\alpha$ -arylvinylolithiums, which are also configurationally labile in ethereal solvents.<sup>10,11</sup>

Finally, it is interesting to contrast the 86/14 ( $\pm 5\%$ ) *E/Z* equilibrium distribution of the  $\alpha$ -lithioalkenylsilanes with those observed in other isomerization studies in-

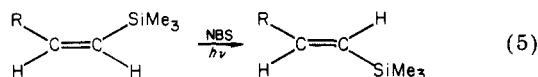
(9) The (*Z*)-4-octenyllithium (**10**) was prepared by treatment of the corresponding iodide in ether and maintained at -70 °C with 2.1 equiv of *tert*-butyllithium.

(10) Curtin, D. Y.; Crump, J. W. *J. Am. Chem. Soc.* **1958**, *80*, 1922. Curtin, D. Y.; Koehl, W. J. *Ibid.* **1962**, *84*, 1967.

(11) Knorr, R.; Lattke, E.; *Tetrahedron Lett.* **1977**, 3969.

(8) Cunico, R. F. *J. Organomet. Chem.* **1973**, *60*, 219.

volving alkenylsilanes. We have shown that  $\alpha$ -halo- and simple alkenylsilanes possessing the trimethylsilyl and the  $\beta$ -alkyl substituents in a *cis* relation undergo bromine-catalyzed inversion (eq 1 and 5), producing the corre-



sponding *trans* isomers in 97% isomeric purities.<sup>2,12</sup> Also, the  $\alpha$ -lithioalkenylsilane-catalyzed isomerization of (*E*)-(1-iodo-1-alkenyl)silanes (eq 3) affords at least 97% isomerically pure (*Z*)-iodides 2-I (*vide infra*). These results clearly point to the strong preference of the trimethylsilyl group in alkenylsilanes to occupy the sterically more favorable *trans* position. Consequently, the silicon moiety in (*Z*)- $\alpha$ -lithioalkenylsilanes 2-Li must experience less steric compression as compared to that in (*E*)-halo- (1-X, eq 1) and (*Z*)-alkenylsilanes (eq 5) mentioned above.

A possible explanation for this behavior is that electron delocalization from the C-Li bond into the silicon d orbitals in (1-lithio-1-alkenyl)silanes changes the hybridization of the  $\alpha$ -carbon from  $sp^2$  to  $sp^{<2}$  (eq 4). Concomitant with this is a decrease in nonbonded interaction between the *cis*-trimethylsilyl and the  $\beta$ -alkyl groups in 1-Li. Nevertheless, at equilibrium the *trans*-vinyl lithium 2-Li is still favored over the *cis* isomer 1-Li.

### Experimental Section

The glassware for reactions involving 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 reagents were stirred magnetically and carried out under an atmosphere of nitrogen.

Boiling points are uncorrected. Infrared spectra were obtained on a Beckman IR-8 spectrophotometer. <sup>1</sup>H NMR spectra were recorded on a Varian A-60A spectrometer, and chemical shifts are reported in parts per million downfield from a Me<sub>4</sub>Si internal standard. High-resolution mass measurements were obtained on a Du Pont 21-492B mass spectrometer. The isomeric purities of the compounds obtained in this study were determined on a 90-m SE-30 glass capillary column (J & W column).

(*E*)-(1-Iodo-1-hexenyl)trimethylsilane, (*E*)-(1-iodo-2-cyclohexenylethenyl)trimethylsilane, and (*E*)-(1-iodo-3,3-dimethyl-1-butenyl)trimethylsilane were prepared as described in the literature.<sup>2</sup>

**Preparation of (*Z*)-(1-Iodo-1-hexenyl)trimethylsilane (2-I) from (*E*)-(1-Iodo-1-hexenyl)trimethylsilane (1-I). Procedure A.** To a solution of *tert*-butyllithium (1.0 mmol, 2.0 M) in pentane diluted with anhydrous ether (2 mL) and maintained at -70 °C was added 0.5 mmol of freshly distilled (*E*)-(1-iodo-1-hexenyl)trimethylsilane. After the solution was stirred at -70 °C for 2 h, a further 9.5 mmol of the (*E*)-iodide was added and the mixture was allowed to slowly warm to 25 °C. The resulting solution was stirred for 2 h at 25 °C, and then was poured into 5 mL of water. The layers were separated, the water layer was extracted with *n*-pentane, and the combined organic extracts were washed to neutrality with a saturated sodium chloride solution. After the solution was dried (MgSO<sub>4</sub>) and concentrated, distillation afforded 2.4 g (85%) of (*Z*)-(1-iodo-1-hexenyl)trimethylsilane: bp 45 °C (0.03 torr);  $n_D^{25}$  1.5005; IR (neat) 1595, 1250, 875, 835 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>)  $\delta$  6.1 (t, 1 H,  $J$  = 6 Hz), 2.3–0.9 (m, 9 H), 0.2 (s, 9 H); exact mass,  $m/e$  282.0312 (calcd for C<sub>9</sub>H<sub>19</sub>ISi 282.0302).

**(*Z*)-(1-Iodo-2-cyclohexylethenyl)trimethylsilane.** By the preceding procedure, (*E*)-(1-iodo-2-cyclohexylethenyl)trimethylsilane was converted to the corresponding *Z* isomer in 89% yield: bp 52 °C ( $3 \times 10^{-4}$  torr);  $n_D^{25}$  1.5220; IR (neat) 1600, 1250, 875, 845 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>)  $\delta$  5.8 (d, 1 H,  $J$  = 8 Hz), 2.8–2.3 (m, 1 H), 2.1–0.8 (m, 10 H), 0.2 (s, 9 H); exact mass,  $m/e$  308.0448 (calcd for C<sub>11</sub>H<sub>21</sub>ISi 308.0458).

**(*Z*)-(1-Iodo-3,3-dimethyl-1-butenyl)trimethylsilane.** By the procedure described above, (*E*)-(1-iodo-3,3-dimethyl-1-butenyl)trimethylsilane was isomerized to the *Z* isomer in 83% yield: bp 52 °C (2 torr);  $n_D^{25}$  1.4994; IR (neat) 1580, 1250, 880, 840 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>)  $\delta$  6.5 (s, 1 H), 1.2 (s, 9 H), 0.2 (s, 9 H); exact mass,  $m/e$  282.0287 (calcd for C<sub>9</sub>H<sub>19</sub>ISi 282.0302).

**Preparation of (*Z*)-(1-Iodo-1-alkenyl)trimethylsilanes (2-I) from (*E*)-(1-Iodo-1-alkenyl)trimethylsilanes (1-I). Procedure B.** A solution of diisobutylaluminum hydride (22 mmol, 1.0 M) in hexane was placed in a flask. The solvent was removed under reduced pressure (25 °C, 1 torr). After introduction of nitrogen, the alane was diluted with anhydrous ether (10 mL). Hydroalumination was achieved by dropwise addition of the appropriate (1-alkenyl)trimethylsilane (20 mmol) while the temperature was maintained between 25–30 °C (water bath). The resultant solution was stirred at room temperature for 15 min and then heated at 40 °C for 1 h. The organoalane formed was diluted with ether (10 mL) and then treated with a solution of iodine (6.6 g, 26 mmol) in ether (60 mL) at such a rate as to maintain the temperature during the addition below -65 °C. After the reaction was stirred for 1 h at -70 °C, it was allowed to warm to 0 °C; then it was slowly poured into a stirred mixture of 10% hydrochloric acid (100 mL) and crushed ice (25 g). The two-phase mixture was shaken until the precipitate that had formed dissolved, and the mixture was then extracted with *n*-pentane. The combined organic extracts were washed successively with aqueous 1 N sodium hydroxide (40 mL), 10% aqueous sodium thiosulfate, and saturated sodium chloride solution and then dried (MgSO<sub>4</sub>). Removal of the solvent (25 °C, 1 torr) gave the crude (*E*)-iodide 1-I. This was slowly added to a mixture of ether (10 mL) and *tert*-butyllithium (3.0 mmol, 2.0 M) in pentane while the temperature during the addition was maintained below -65 °C (dry ice-acetone bath). The flask containing the (*E*)-iodide was rinsed with ether (4 mL) which then was added to the *tert*-butyllithium solution. The resultant solution was allowed to exotherm to room temperature, stirred for 30 min, and then was poured into water. The layers were separated and the aqueous layer was extracted with *n*-pentane. The combined extracts were washed with a saturated sodium chloride solution and then dried (MgSO<sub>4</sub>). As shown in Table II, distillation afforded the (*Z*)-iodides 2-I in yields and isomeric purities similar to those obtained by using procedure A (Table I).

**General Procedure for the Isomerization of (1-Lithio-1-alkenyl)silanes.** Into a three-necked flask equipped with a nitrogen inlet and thermometer and kept under a static pressure of nitrogen was added anhydrous ether (6 mL). The flask was cooled to -70 °C (dry ice-acetone bath) and a solution of *tert*-butyllithium (4.2 mmol, 2.0 M) in *n*-pentane was slowly added to the ether. To the lithium reagent maintained at -70 °C was added the appropriate (*E*- or (*Z*)-(1-iodo-1-alkenyl)silane (2.0 mmol) at such a rate as to limit the temperature rise to 5 °C. The mixture was stirred at -70 °C for 2 h, then allowed to warm to the appropriate temperature, and maintained there for a period of time. After slow addition of methanol (1 mL) and a hydrocarbon standard, the mixture was poured into 10% hydrochloric acid (10 mL). The layers were separated, the water layer was extracted with *n*-pentane, and the combined organic extracts were washed to neutrality with saturated aqueous sodium chloride. The solution containing the alkenylsilanes 8 was dried (MgSO<sub>4</sub>) and analyzed by GLC, using the hydrocarbon as an internal standard to measure the yield. The isomeric purity of the compound was determined on a glass capillary column (SE-30, 90 m) by comparing the retention times of the peaks observed with those from authentic samples of the corresponding (*E*- and (*Z*)-alkenylsilanes. The results from these experiments are summarized in Table II.

**Registry No.** 1-I (R = *n*-C<sub>4</sub>H<sub>9</sub>), 66270-63-1; 1-I (R = *c*-C<sub>6</sub>H<sub>11</sub>), 66270-66-4; 1-I (R = *t*-C<sub>4</sub>H<sub>9</sub>), 66270-67-5; 1-Li (R = *n*-C<sub>4</sub>H<sub>9</sub>), 76346-95-7; 1-Li (R = *c*-C<sub>6</sub>H<sub>11</sub>), 76346-96-8; 1-Li (R = *t*-C<sub>4</sub>H<sub>9</sub>), 76346-97-9; 2-I (R = *n*-C<sub>4</sub>H<sub>9</sub>), 76346-98-0; 2-I (R = *c*-C<sub>6</sub>H<sub>11</sub>), 76346-99-1; 2-I (R = *t*-C<sub>4</sub>H<sub>9</sub>), 76359-30-3; 2-Li (R = *n*-C<sub>4</sub>H<sub>9</sub>), 76347-00-7; 2-Li (R = *c*-C<sub>6</sub>H<sub>11</sub>), 76347-01-8; 2-Li (R = *t*-C<sub>4</sub>H<sub>9</sub>), 76347-02-9; 8(*E*) (R = *n*-C<sub>4</sub>H<sub>9</sub>), 54731-58-7; 8(*Z*) (R = *n*-C<sub>4</sub>H<sub>9</sub>), 52835-06-0; 8(*E*) (R = *c*-C<sub>6</sub>H<sub>11</sub>), 66270-74-4; 8(*Z*) (R = *c*-C<sub>6</sub>H<sub>11</sub>), 66270-75-5; 8(*E*) (R = *t*-C<sub>4</sub>H<sub>9</sub>), 20107-37-3; 8(*Z*) (R = *t*-C<sub>4</sub>H<sub>9</sub>), 26567-95-3; RC≡CSiMe<sub>3</sub> (R = *n*-C<sub>4</sub>H<sub>9</sub>), 3844-94-8; RC≡CSiMe<sub>3</sub> (R = *c*-C<sub>6</sub>H<sub>11</sub>), 66270-60-8; RC≡CSiMe<sub>3</sub> (R = *t*-C<sub>4</sub>H<sub>9</sub>), 14630-42-3.