Table II. Oxidative Decarboxylation of **19t** in the Presence of Pyridine

pyridine			products, %^{b}	
μL	mol	mol %^{a}	pyruvate **19p**	carboxylate **19c**
0	0.00	0	<1	99
1	0.012	9	4	96
3	0.037	28	20	80
5	0.062	48	45	55
10	0.124	95	65	35
15	0.186	143	69	31
20	0.248	191	75	25
25	0.310	238	85	15
30	0.371	285	87	13

^{a}Relative to starting hydroxymalonic acid **19t**. ^{b}Relative yields determined by ^{1}H NMR analysis of the reaction product mixture.

s, 4 H), 1.45 (br s, 2 H), 2.30 (br s, 2 H), 2.77 (dt, $J = 11, 4$ Hz, 1 H), 3.18 (dd, $J = 11, 4$ Hz, 1 H), 3.33–3.53 (m, 1 H), 3.70 (s, 3 H), 5.73 (br s, 2 H). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.93; H, 8.35.

Methyl *cis*-bicyclo[3.3.0]oct-3-ene-2-*exo*-carboxylate (23c) was prepared from diethyl *cis*-bicyclo[3.3.0]oct-2-en-4-yl)hydroxypropanedioate (**23b**): ^{1}H NMR δ 1.2–2.2 (6 H), 2.7–3.5 (3 H), 3.70 (s, 3 H), 5.45–5.91 (m, 2 H). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.05; H, 8.45.

Methyl 1-(trimethylsilyl)cyclopent-1-ene-3-carboxylate (24c) was prepared from diethyl hydroxy[1-(trimethylsilyl)-1-cyclopenten-3-yl]-propanedioate (**24b**): ^{1}H NMR δ 0.0 (s, 9 H), 1.83–2.83 (m, 4 H), 3.35–4.00 (buried m, 1 H), 3.68 (s, 3 H), 5.78–5.95 (m, 1 H). Anal. Calcd for $C_{10}H_{18}O_2Si$: C, 60.56; H, 9.15. Found: C, 60.78; H, 9.08.

Methyl 1-(trimethylsilyl)cyclohex-1-ene-3-carboxylate (25c) was prepared from diethyl hydroxy(1-(trimethylsilyl)-1-cyclohexen-3-yl)-propanedioate (**25b**): ^{1}H NMR δ 0.0 (s, 9 H), 1.52–2.20 (m, 6 H), 2.88–3.33 (m, 1 H), 3.65 (s, 3 H), 5.88–6.08 (m, 1 H). Anal. Calcd for $C_{11}H_{20}O_2Si$: C, 62.21; H, 9.49. Found: C, 61.67; H, 9.24.

Methyl nona-3,8-dienoate (26c) was prepared from diethyl (octa-2,7-dienyl)hydroxypropanedioate (**26b**): ^{1}H NMR δ 1.17–1.75 (m, 2 H), 1.80–2.28 (m, 4 H), 3.00 (br d, $J = 5$ Hz, 2 H), 3.63 (s, 3 H), 4.77–5.18 (m, 2 H), 5.43–7.17 (m, 3 H). The corresponding ethyl ester was reported previously.[15]

Methyl 5-(cyclopenten-3-yl)pent-3-enoate (27c) was prepared from diethyl hydroxy[4-(cyclopenten-3-yl)but-3-enyl]propanedioate (**27b**): ^{1}H NMR δ 1.20–1.72 (m, 2 H), 1.78–2.87 (m, 5 H), 3.03 (br d, $J = 5$ Hz, 2 H), 3.73 (s, 3 H), 5.50–5.78 (m, 2 H), 5.75 (s, 2 H). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.79; H, 8.38.

Methyl 7-methylocta-3,6-dienoate (28c) was prepared from diethyl hydroxy(6-methylhepta-2,5-dienyl)propanedioate (**28b**): ^{1}H NMR δ 1.62 (br s, 3 H), 1.70 (br s, 3 H), 2.50–3.25 (m, 4 H), 3.70 (s, 3 H), 4.85–5.75 (m, 3 H). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.15; H, 9.62.

Methyl 2-(2-propenyl)hex-5-enoate (28c′) was prepared from diethyl hydroxy(2-methylhepta-1,6-dien-3-yl)propanedioate (**28b′**): ^{1}H NMR δ 1.5–2.3 (7 H), 3.09 (t, $J = 7$ Hz, 1 H) 3.70 (s, 3 H), 4.8–5.3 (4 H), 5.3–6.2 (H). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.40; H, 9.43.

Effect of Pyridine on the Bisdecarboxylation of [1-(1-Cyclohexenyl]-ethyl)hydroxypropanedioic Acid with Sodium Periodate. The diacid **19t** (30 mg, 0.13 mmol) was oxidized with $NaIO_4$ (15 mL of 0.25 M) in the presence of various amounts of pyridine (1–30 μL). After methylation of the resulting acids with diazomethane, the relative ratio of products was determined by ^{1}H NMR using the resonance of the methyl ester group at δ 3.85 for methyl 3-(1-cyclohexenyl)-2-oxobutanoate (**19p**) and δ 3.70 for methyl 2-(1-cyclohexenyl)propanoate (**19c**). The results are presented in Table II.

Acknowledgment. We thank the National Science Foundation for financial support.

Registry No. 2, 609-09-6; **6a**, 563-45-1; **6b**, 90046-55-2; **6c**, 2258-65-3; **7a**, 300-57-2; **7b**, 90107-07-6; **7c**, 24891-74-5; **8a**, 3290-53-7; **8b**, 73961-89-4; **8t**, 90107-23-6; **8c**, 52386-62-6; **9a**, 111-81-9; **9b**, 90107-08-7; **9t**, 90107-24-7; **9c**, 90107-89-8; **10a**, 112-19-6; **10b**, 90107-10-1; **10c**, 90107-11-2; **11a**, 872-05-9; **11b**, 90107·12-3; **11c**, 64749-23-1; **12a**, 98-83-9; **12b**, 78925-84-5; **12c**, 3461-38-9; **13a**, 625-27-4; **13b**, 90046-62-1; **13t**, 90107-27-0; **13c**, 58544-19-7; **13p**, 90107-28-1; **14a**, 513-35-9; **14b**, 73961-93-0; **14c**, 49714-67-2; **15a**, 1120-56-5; **15b**, 90046-63-2; **15c**, 71092-57-4; **16a**, 2505-03-5; **16b**, 90107-13-4; **16c**, 61704-65-2; **17a**, 127-91-3; **17b**, 90046-65-4; **17c**, 90107-14-5; **18a**, 2808-75-5; **18b**, 90046-68-7; **18b′**, 90046-67-6; **18c**, 90107-15-6; **19a**, 1003-64-1; **19b**, 90046-69-8; **19t**, 90107-25-8; **19c**, 62184-70-7; **19p**, 90107-26-9; **20a**, 771-98-2; **20b**, 73961-82-7; **20t**, 90107-29-2; **20p**, 90107-16-7; **21a**, 39599-89-8; **21b**, 90046-71-2; **21c**, 90046-83-6; **22a**, 2825-86-7; **22b**, 90046-73-4; **22c**, 90046-84-7; **23a**, 930-99-4; **23b**, 73961-80-5; **23c**, 65656-67-9; **24a**, 14579-08-9; **24b**, 78925-83-4; **24c**, 90107-17-8; **25a**, 40934-71-2; **25b**, 90046-74-5; **25c**, 90107-18-9; **26a**, 3710-30-3; **26b**, 90107-19-0; **26c**, 30463-55-9; **27a**, 73961-94-1; **27b**, 78925-82-3; **27c**, 90107-20-3; **28a**, 7270-50-0; **28b**, 77028-79-6; **28b′**, 73961-90-7; **28c**, 90107-21-4; **28c′**, 90107-22-5; carbon dioxide, 124-38-9; ceric ammonium nitrate, 16774-21-3.

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Regiochemistry of Alkenylsilyl and Alkenyldisilanyl Radical Cyclizations

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Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50011.

Received October 17, 1983

Abstract: The silyl radicals produced by hydrogen abstraction from a butenylsilane, an allyldisilane, a pentenylsilane, a butenyldisilane, and a (butenyloxy)silane all cyclize in an endo fashion, in contrast to the analogous carbon-centered radicals.

Possibly the most frequency encountered radical rearrangement is the exo cyclization of 5-hexenyl radicals.[2] The somewhat surprising kinetic control of this reaction to afford the five-membered-ring exo radicals rather than the thermodynamically favored six-membered-ring endo radicals has been rationalized[3,4] as stereoelectronic control and generalized as the familiar Baldwin–Beckwith rules.[5,6]

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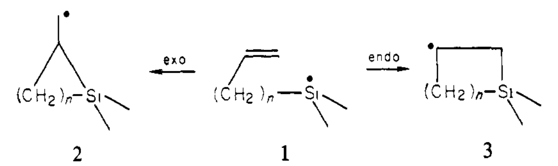
[1] Dow Corning Predoctoral Minority Fellow, 1981–1983.

[2] For an excellent and critical review of this subject, see: Suzur, J-M. In "Reactive Intermediates"; Abramovitch, R. A., Ed.; Wiley: New York, 1981; Vol. 2, Chapter 3.

[3] Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Essay 4.

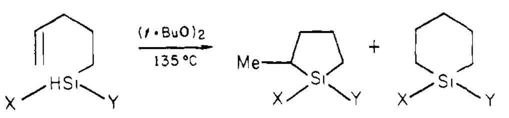
[4] Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073.

The purpose of the work reported herein was to determine whether the Baldwin–Beckwith rules could be extended to the cyclizations of alkenyl silicon-centered radicals. The question was whether radicals of type **1** would undergo kinetically controlled exo cyclization to afford **2** or thermodynamically controlled endo cyclization to afford **3**.



There is a wealth of literature on the subject of intermolecular addition of silyl radicals to carbon–carbon double bonds—the so-called free-radical hydrosilylation reaction. This reaction has been extensively reviewed.[7] The generation of silyl radicals for addition of R_3SiH across multiple bonds has been accomplished thermally, photochemically, with organic peroxides, and with γ-irradiation. However, in recent years little work has been done on this reaction due to the tremendous success of metal-catalyzed hydrosilylation.

At the inception of this project, there existed only a single mention (in a review article) of silyl radical cyclization.[7] Sakurai reported that di-*tert*-butyl peroxide initiated intramolecular hydrosilylation of (4-pentenyl)silanes (**4**) produced a confusing picture of substituent control of both regiochemistry and yield. This work has never been published in complete form.



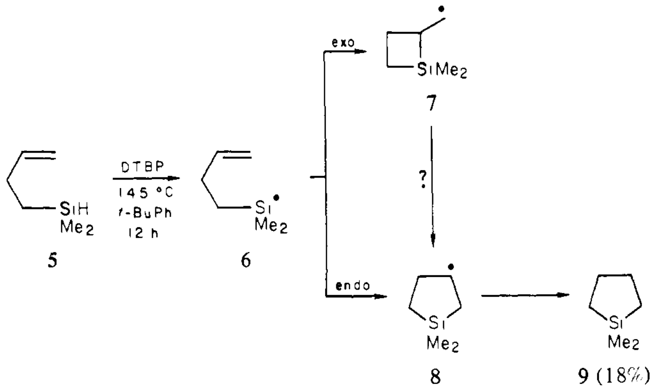
4	X	Y	% A	% B
	Me	Ph	0.65	5.46
	Me	Cl	71.60	12.60
	Ph	Ph	0.74	6.1
	i-Pr	Cl	3.94	5.47

This report of our findings to date in the area of alkenylsilyl radical cyclizations was prompted by a recent publication of Ingold and Davies[8] that describes an ESR study of the radicals formed during photolysis of di-*tert*-butyl peroxide (DTBP) and several alkenyldimethylsilanes. No evidence for the cyclization of (3-butenyl)silyl radicals was found, and in all cases intermolecular radical addition was found to predominate. However, it was demonstrated that (4-pentenyl)silyl radicals strongly favored endo cyclization over exo cyclization. Since in only one case were products actually isolated and identified, our report will be complementary and supportive of the conclusions of Ingold and Davies with regard to pentenylsilyl radical cyclizations and will present a new picture of butenylsilyl radical intramolecular reactions.

Results

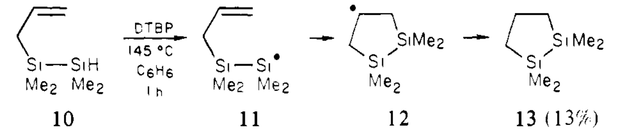
Five alkenylsilyl hydrides were synthesized in order to probe the effects of varied chain length and heteroatom substitution in the chain on intramolecular reactions of the corresponding radicals. These five systems will first be discussed individually. All reactions were conducted both in *tert*-butylbenzene and in benzene solutions, although only one set of conditions will be reported here. No effect of solvent change was noted. In all cases, only a single major volatile product was obtained. Searching the gas chromatographic (GC) trace of the product mixtures by GCMS revealed no significant products isomeric with the major product. Product yields are corrected for unreacted starting material.

(3-Butenyl)dimethylsilane (5).[9] Heating a 1% solution of **5** and DTBP (2:1) in *tert*-butylbenzene at 145 °C for 12 h produced a complex mixture as evidenced by gas chromatographic (GC) analysis. Preparative GC isolation of the only major volatile product allowed identification of 1,1-dimethylsilacyclopentane (**9**)[9,10] by comparison of its spectral properties with those of an authentic sample of **9**. The GC yield of **9**, based on 91% reacted **5**, was 18%. Thus, in contrast to Ingold and Davies,[8] who saw no evidence for intramolecular reaction of radical **6**, it appears that under our conditions **6** does indeed cyclize and that it does so in an endo fashion.



Although the endo cyclization of **6** is an apparent violation of the Baldwin–Beckwith rules, caution must be exercised in interpretation of this result as it is possible that initially formed exo radical **7** rearranges to endo radical **8**. It will be necessary to independently generate **7**, not a simple task, to answer this question. Unfortunately, there seem to be no definitive results on the cyclization of 4-pentenyl radicals in the literature for comparison of **6** with the carbon analogue.[3]

Allyl-1,1,2,2-tetramethyldisilane (10). The radical produced from hydrogen abstraction from disilanyl hydride **10** was also reported[8] to provide no ESR evidence for intramolecular reaction. However, heating a 1% solution of **10** and DTBP in benzene at 145 °C for 1 h afforded a product mixture that contained, in addition to 14% unreacted **10**, a 13% yield (GC) of a sole major volatile product, 1,1,2,2-tetramethyl-1,2-disilacyclopentane (**13**).[11] Thus, the disilanyl radical analogue of **6**, **11**, also undergoes apparent predominant or exclusive intramolecular π-addition in an endo sense. The formation of endo radical **12** may be simply another manifestation of the well-known stability of β-silyl radicals as **12** possesses two β-silyl substituents. Even so, the net result is thermodynamic rather than kinetic control over cyclization.



(4-Pentenyl)dimethylsilane (14).[9] In order to provide a close comparison with the classic 5-hexenyl radical, hydrogen abstraction from the analogous silyl hydride **14** was effected. After **14** was heated with DTBP at 145 °C for 4 h, GC analysis revealed 48% of unreacted **14** and 19% of 1,1-dimethyl-1-silacyclohexane (**18**),[9,10] which was isolated pure by preparative GC.

Since radical **16** (and not **17**) has been identified as arising from **15** in the ESR studies of Ingold and Davies,[8] it is reasonable to assume that endo cyclization of **15** has occurred, in a dramatic reversal from the behavior of the analogous carbon-centered radical.

4-(Tetramethyldisilanyl)-1-butene (19). Analogue extension of the 5-hexenyl system to a disilanyl radical was accomplished

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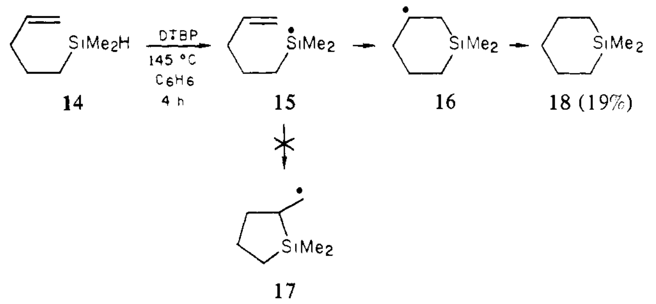
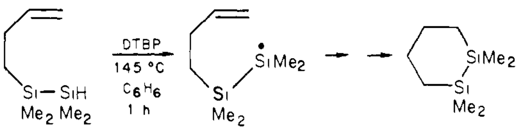
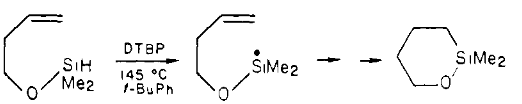


by synthesis of **19** via magnesium-induced coupling of 1,2-dichloro-1,1,2,2-tetramethyldisilane and 4-bromo-1-butene followed by $LiAlH_4$ reduction. After a 1% benzene solution of **19** with DTBP was heated for 1 h at 145 °C, only 11% of **19** remained. The sole major volatile product (23%) was isolated by preparative GC and spectrally identified as 1,1,2,2-tetramethyl-1,2-disilacyclohexane (**21**).[11] Thus, the substitution of a second silicon in the radical chain does not deter the cyclization of **20** from an endo pathway.



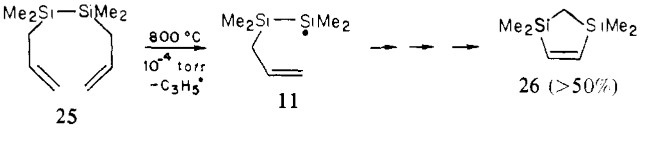
4-(Dimethylsiloxy)-1-butene (22). A final heterosubstitution, that of oxygen, in the 5-hexenyl radical chain was provided by the decomposition of **22** to afford silyl radical **23**. All of **22** was reacted after 1 h at 145 °C in the presence of DTBP, and the only major volatile product was found to be 2,2-dimethyl-2-silaoxacyclohexane (**24**)[13] formed in 24% yield.



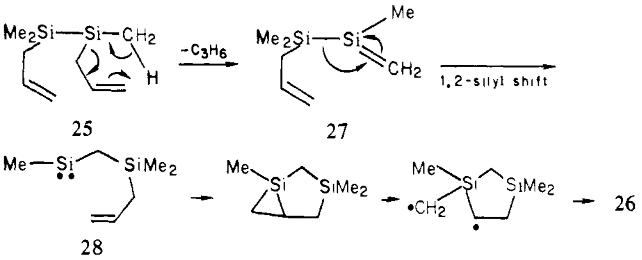
Discussion

Our results coupled with those of Ingold and Davies,[8] as well as those of Mochida and Asami[14] for the analogous cyclizations of alkenyldimethylgermyl radicals, make it abundantly clear that the Baldwin–Beckwith rules for homolytic ring closures cannot be extended beneath carbon in group 4. Since the reasons for the contrathermodynamic behavior of the carbon-centered radicals are not totally clear,[2] it is not possible to pinpoint the origins of the changeover in behavior with certainty. Certainly, the most obvious and most likely responsible differences are the increased chain length due to the longer bonds to silicon (both in the chain and for the incipient Si–C bonds in the activated complex) and the pyramidal configuration of silyl radicals as opposed to the planar configuration of carbon radicals. The possible roles of these factors are well discussed in ref 8.

With regard to the cyclization of alkenyldisilanyl radicals, it is interesting to note that radical **11** has been invoked[15] in a complex effort to explain the remarkably clean, but puzzling, formation of **26** in the flash vacuum pyrolysis of 1,2-diallyldisilane (**25**). Although the experimental conditions are vastly different,



the demonstration that **11** undergoes endo cyclization would seem to make it unlikely that **11** is a precursor to **26**. Thus, we suggest that **25** decomposes by a retroene elimination of propene,[16] followed by rearrangement[17] of silene **27** to silylene **28**, intramolecular π-addition,[18] C–C homolysis, and prototropic shift. Indeed, we now believe[19] that retroene elimination of propene from allylsilanes is far more important that previously thought.[20]



Experimental Section

^{1}H NMR spectra were obtained on a Nicolet Model 1280 300-MHz spectrometer. ^{13}C NMR spectra were obtained on a JEOL Model FX90Q 90-MHz spectrometer. GCMS data were collected at 70 eV on a Finnegan Model 4023 quadrupole mass spectrometer, and exact mass measurements were obtained on an AEI MS-902 mass spectrometer. IR spectra were recorded on an IBM IR/90 Series FTIR spectrometer. Gas chromatographic separations were performed on a Varian-Aerograph Series 1700 instrument. All reported yields were obtained by GC using an internal standard and predetermined response factors. Product yields are based on the amount of reacted silyl hydride. The radical cyclization experiments were carried out in degassed, evacuated, sealed Pyrex Ampules in a heated oil bath. Radical generation was accomplished by heating a 1 wt % solution of the silyl hydride in either *tert*-butylbenzene or benzene with di-*tert*-butyl peroxide (DTBP). All radical reactions were conducted both in *tert*-butylbenzene and in benzene, but yields were determined in only one solvent. Each product mixture was carefully screened by GCMS in a search for minor products. Combustion analyses were performed for all previously unreported compounds by MicAnal, Tucson, AZ.

Synthesis of (3-Butenyl)dimethylsilane (5). To a stirred mixture of excess Mg turnings in 125 mL of dry THF under nitrogen was added dropwise a solution containing 20.0 g (0.15 mol) of chlorodimethylsilane and 14.1 g (0.15 mol) of 4-bromo-1-butene in 100 mL of THF. After 8 h the reaction mixture was hydrolyzed with excess H_2O and transferred to a separatory funnel containing 100 mL of pentane. The pentane layer was extracted with H_2O, separated, dried over Na_2SO_4, and filtered. Distillation (65–75 °C) afforded 13.6 g (80%) of **5**, whose spectral properties matched those in the literature:[9] ^{1}H NMR ($DCCl_3$) δ 0.13 (d, J = 3.69 Hz, 6 H), 0.71–0.78 (m, 2 H), 2.11–2.19 (m, 2 H), 3.89–3.94 (m, 1 H), 4.95 (d of d, 1 H, J_{gem} = 1.61 Hz, J_{cis} = 10.06 Hz), 5.04 (d of d, J_{gem} = 1.61 Hz, J_{trans} = 17.06 Hz, 1 H), 5.86–6.06 (m, 1 H); ^{13}C NMR ($DCCl_3$) δ -4.36, 13.46, 28.52, 113.09, 141.2; *m/e* (% rel intens) 113 (M − 1, 1%) 99 (16), 86 (14), 72 (22), 71 (26), 59 (100), 58 (23); calcd for SiC_6H_{13} (m − 1) *m/e* 113.07866, measured *m/e* 113.07872; IR (neat) 2116 cm^{-1} (SiH). Anal. Calcd for $C_6H_{14}Si$: C, 63.06; H, 12.38. Found: C, 63.41; H, 12.54.

Synthesis of Allyl-1,1,2,2-tetramethyldisilane (10). To a stirred mixture of excess Mg turnings and 18.6 g (0.1 mol) of 1,2-dichlorotetramethyldisilane in 50 mL dry THF under N_2 was added a small portion of allyl chloride for initiation. The remainder of the allyl chloride (7.7 g, 0.1 mol total) was dissolved in 100 mL of THF and added dropwise to the stirred solution. After 5 h the liquid phase was removed by vacuum distillation (ca. 0.05 torr) at room temerature and collected at −78 °C.

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This solution was then added to a stirred suspension of excess $LiAlH_4$ in 200 mL of Et_2O. The organic hase was removed by distillation (0.05 torr, 25 °C), diluted with 200 mL of pentane, extracted with H_2O, separated, and dried over Na_2SO_4. Distillation afforded 5.0 g of **10** (32%): bp 140–145 °C; ^1H NMR ($DCCl_3$) δ 0.09 (s, 6 H), 0.13 (d, 6 H, J = 4.68 Hz), 1.62 (d, 2 H, J = 8.09 Hz), 3.63–3.69 (m, 1 H), 4.81–4.88 (m, 2 H), 5.71–5.86 (m, 1 H); ^{13}C NMR ($DCCl_3$) δ −6.53, −4.20, 22.94, 112.87, 135.08; *m/e* (% rel intens) 158 (3), 143 (13), 127 (8), 119 (8), 118 (20), 117 (92), 116 (81), 101 (8), 99 (31), 85 (8), 83 (8), 74 (9), 72 (100), 71 (17), 59 (77); calcd for $Si_2C_7H_{18}$ *m/e* 158.09471, measured *m/e* 158.09433; IR (neat) 2093 cm^{-1} (SiH). Anal. Calcd for $C_7H_{18}Si_2$: C, 53.07; H, 11.48. Found: C, 52.78; H, 11.48.

Synthesis of (4-Pent-1-enyl)dimethylsilane (14).[9] Synthesis of **14** was accomplished by the same procedure as for **5** using 29.6 g (0.2 mol) of 5-bromo-1-butene and 18.9 g (0.2 mol) of chlorodimethylsilane to provide 17.8 g (70%) of **14** after distillation at 108–118 °C: ^1H NMR ($DCCl_3$) δ 0.06 (d, 6 H, J = 3.62 Hz), 0.57–0.63 (d of t, 2 H, J = 3.24 Hz, J = 8.28 Hz), 1.39–1.50 (m, 2 H), 2.04–2.12 (q, 2 H, J = 7.1 Hz), 3.83–3.87 (m, 1 H), 4.94 (d, 1 H, J = 10.39 Hz), 5.00 (d, 1 H, J = 19.07 Hz), 5.73–5.86 (m, 1 H); ^{13}C NMR ($DCCl_3$) δ −4.41, 13.79, 23.97, 37.24, 114.55, 138.87; *m/e* (% rel intens) 127 (M − 1, 1), 113 (6), 100 (7), 87 (44), 85 (18), 60 (9), 59 (100); calcd for SiC_7H_{15} *m/e* 127.09431, measured *m/e* 127.09489; IR (neat) 2112 cm^{-1} (SiH). Anal. Calcd for $C_7H_{16}Si$: C, 65.52; H, 12.59. Found: C, 65.72; H, 12.72.

Synthesis of (3-Butenyl)-1,1,2,2-tetramethyldisilane (19). Synthesis of **19** was performed by the same procedure as for **10** using 5.32 g (39.4 mmol) of 4-bromo-1-butene and 7.33 g (39.4 mmol) of 1,2-dichlorotetramethyldisilane. Isolation of 2.0 g of pure **19** was accomplished by preparative GC on a 9-ft, 20% SE-30/Chromosorb W column at 140 °C. The GC-determined yield was 30% of **19**: ^1H NMR ($DCCl_3$) δ 0.09 (s, 6 H), 0.13 (d, 6 H, J = 4.63 Hz), 0.70–0.76 (m, 2 H), 2.02–2.12 (m, 2 H), 3.60–3.67 (m, 1 H), 4.88 (d of d, J_{gem} = 1.32, J_{cis} = 10.12Hz, 1 H), 4.98 (d of d, J_{gem} = 1.32, J_{trans} = 17.06, 1 H), 5.82–5.95 (m, 1 H); ^{13}C NMR ($DCCl_3$) δ −6.53, −3.82, 14.55, 28.68, 112.92, 141.58; *m/e* (% rel intens) 172 (1), 157 (4), 144 (15), 129 (7), 117 (18), 116 (19), 114 (7), 113 (53), 112 (8), 99 (8), 98 (10), 86 (11), 85 (74), 73 (47), 72 (7), 71 (7), 60 (10), 59 (100); calcd for $Si_2C_8H_{20}$ *m/e* 172.11036, measured *m/e* 172.11129; IR (neat) 2091 cm^{-1} (SiH). Anal. Calcd for $C_8H_{20}Si_2$: C, 55.72; H, 11.71. Found: C, 55.94; H, 11.72.

Synthesis of 4-(Dimethylsiloxy)-1-butene (22).[21] To a stirred solution of 5.0 g (69.4 mmol) of 3-buten-1-ol and 5.5 g (69.4 mmol) of pyridine in dry Et_2O was added 1 equiv of chlorodimethylsilane in a dropwise fashion. The reaction mixture was diluted with 75 mL of pentane and then washed twice with saturated $NaHCO_3$ solution. The organic layer was separated, dried over Na_2SO_4, and distilled (98–104 °C) to afford 7.2 g (80%) of **22**: ^1H NMR ($DCCl_3$) δ 0.19 (d, 6 H, J = 2.85 Hz), 2.29 (q, 2 H, J = 6.78 Hz), 3.66 (t, 2 H, J = 6.8 Hz), 4.59–4.62 (m, 1 H), 5.02 (d of d, 1 H, J_{gem} = 1.11 Hz, J_{cis} = 9.77 Hz), 5.07 (d of d, 1 H, J_{gem} = 1.11 Hz, J_{trans} = 6.69 Hz), 5.72–5.86 (m, 1 H); ^{13}C NMR ($DCCl_3$) δ −1.49, 37.03, 63.73, 116.55, 135.19; *m/e* (% rel intens) 129 (M − 1, 1), 115 (20), 90 (9), 89 (99), 87 (15), 85 (7), 61 (13), 60 (9), 59 (100); IR (neat) 2112 cm^{-1} (SiH), 1094 (Si–O).

Decomposition of 5. A 1% (by weight) solution of **5** (0.140 g, 1.23 mmol) in *tert*-butylbenzene containing 0.085 g (0.58 mmol) of DTBP was heated at 145 °C for 12 h. The products were analyzed and separated by GC on a 9-ft, 20% SE-30/Chromosorb W column at 80 °C isothermal. Other than **5** (9%), the only volatile silicon-containing product was **9**[9,10] (18%): ^1H NMR (D_6C_6) δ 0.04 (s, 6 H), 0.50–0.55 (m, 4 H), 1.54–1.62 (m, 4 H); ^{13}C NMR (D_6C_6) δ −1.78, 13.17, 27.42; *m/e* (% rel intens) 114 (18), 100 (5), 99 (44), 97 (16), 87 (11), 86 (100), 71 (26), 59 (24), 58 (54); the GC retention time and spectral properties exactly matched with an authentic sample of **9** prepared by coupling butane-1,4-diylbis(magnesium bromide) with dichlorodimethylsilane.

Decomposition of 10. A 1% (by weight) solution of **10** (25.2 mg, 0.159 mmol) in benzene containing 7.1 mg (0.049 mmol) of DTBP was heated at 145 °C for 1 h. GC separation and isolation of the products were carried out on a 15-ft, 20% OV-101/Chromosorb W colmn at 130 °C. In addition to **10** (14%), the only volatile silicon-containing product was **13**[11] (13%): ^1H NMR (D_6C_6) δ 0.12 (s, 12 H), 0.70 (t, 4 H, J = 6.77 Hz), 1.73 (pentet, 2 H, J = 6.77 Hz); ^{13}C NMR (D_6D_6) δ −4.11, 18.96, 22.92; *m/e* (% rel intens) 159 (10), 158 (57), 143 (40), 131 (10), 130 (56), 117 (43), 116 (43), 115 (100), 99 (19), 85 (26), 83 (15), 73 (87), 72 (29), 59 (75). The spectral properties matched those reported in the literature.[11,22]

Decomposition of 14. A 1% (by weight) solution of **14** (48.1 mg, 0.376 mmol) in benzene contaiing 19.7 mg (0.135 mmol) of DTBP was heated for 4 h. The products were separated and isolated by GC on a 9-ft, 20% OV-101/Chromosorb W column at 130 °C. In addition to unreacted **14** (48%), the only major product containing silicon was **18**[9,10] (19%): ^1H NMR (D_6C_6) δ 0.01 (s, 6 H), 0.57 (t, 4 H, J = 6.62), 1.33–1.41 (m, 4 H), 1.62–1.70 (m, 2 H); ^{13}C NMR (D_6C_6) δ −3.08, 14.36, 24.65, 30.29; *m/e* (% rel intens) 128 (26), 113 (100), 85 (99), 72 (19), 59 (53). The GC retention time and spectral properties exactly matched those of an authentic sample prepared by coupling pentane-1,5-diylbis(magnesium bromide) with dichlorodimethylsilane.

decomposition of 19. The reaction of **19** (51.1 mg, 0.297 mmol) and DTBP (17.0 mg, 0.116 mmol) in benzene was carried out as described for **5**, **10**, and **14** for 1 h. Separation and isolation of the products by GC were performed on a 9-ft, 20% OV-101/Chromosorb W column at 130 °C. In addition to unreacted **19** (11%), the only silicon-containing volatile product was **21**[11] (23%): ^1H NMR ($DCCl_3$) δ 0.05 (s, 12 H), 0.68–0.72 (m, 4 H), 1.54–1.59 (m, 4 H); ^{13}C NMR ($DCCl_3$) δ −3.98, 17.09, 26.24; *m/e* (% rel intens) 173 (12), 172 (M^+, 62), 157 (59), 144 (22), 129 (37), 116 (46), 99 (34), 98 (21), 97 (100), 85 (39), 73 (74), 59 (48).

Decomposition of 22. Reaction of **22** (0.63 g, 4.85 mmol) and DTBP (0.20 g, 1.37 mmol) in *tert*-butylbenzene was carried out for 1 h as described for **5**, **10**, 14, and **19**. GC isolation (10 ft, 15% OV-101/Chromosorb W, 120 °C) afforded **22** (14%) and **24**[12,13] (21%): ^1H NMR (60 MHz, $DCCl_3$) δ 0.05 (s, 6 H), 0.55 (broadened t, 2 H, J = 8 Hz), 1.22–1.88 (m, 4 H), 3.72 (broad t, 2 H, J = 5.8 Hz); *m/e* (% rel intens) 130 (M^+, 14), 115 (100), 87 (74), 61 (22), 59 (20), 47 (10). The NMR spectrum matched that previously reported.[12]

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