may be due to a competing reaction between Et_3SiH and sulfur, producing Et_3SiSH.[16]

2. Pyrolysis Reactions. Pyrolyses at 190 °C were carried out in refluxing decalin under an atmosphere of dry nitrogen. Dithiacyclohexasilanes **3a,b** (20 mg, 0.05 mmol) were stirred in 1 mL of refluxing decalin (190 °C), and the reaction was monitored by GLC. After 5 days a mixture containing 80% unreacted **3a,b**, 7% **4**, and 5% **5** was observed. Heating for an additional 7 days led to 63% unreacted **3a,b**, 14% **4**, and 12% **5**. A similar pyrolysis but in the presence of 10 equiv (0.5 mmol) of sulfur resulted in appreciably faster reaction and gave 19% **4**, 10% **5**, 2% **6**, and 59% **3a,b** after 3.5 days at 190 °C. The products were assigned by comparison of the GLC retention times, and **4** and **5** were additionally identified by mass spectroscopy. Reaction of **3a,b** (0.05 mmol), sulfur (0.5 mmol), and **8** (80 mg, 0.5 mmol) in 1 mL of decalin at 190 °C for 3.5 days produced 47% **9** (based on the elimination of $Et_2Si=S$ from starting material **3a,b**) in addition to **4** (17%) and **3a,b** (66%). Small amounts of minor products were present in each case.

Heating dithiacyclopentasilane **4** (10 mg, 0.03 mmol) in 0.5 mL of decalin at 190 °C for 4 days produced only traces of **5** in addition to unreacted **4**. Pyrolysis of **4** (0.03 mmol) and sulfur (9 mg, 0.3 mmol) in 0.5 mL of refluxing decalin (190 °C) led to 71% **4**, 16% **5**, and 4% **6** in addition to minor products in 3–7% yield after 3.5 days. No reaction of the thiacyclopentasilane **2** was detected in refluxing decalin, even after prolonged (8 days) reaction time.

3. Reaction of 10 with Sulfur. Silylene adduct **10** was synthesized from **8** and $(Et_2Si)_7$ in the following manner: 100 mg (0.17 mmol) of $(Et_2Si)_7$ and 240 mg (1.50 mmol) of **8** were dissolved in degassed, spectrograde isooctane and the solution was placed in a quartz tube. The tube was then irradiated at 254 nm in a Rayonet photochemical reactor for 3 h at 30 °C. Analysis by GLC showed $(Et_2Si)_4$ and **10** to be present as the major products. The solvent was evaporated, and pure **10** [85 mg, ca. 69% yield based on elimination of three units of Et_2Si from starting $(Et_2Si)_7$] was then isolated by preparative GLC: mass spectrum, selected m/e (relative intensity) 246 (53.6, M^+), 231 (28.1, M – CH_3), 217 (100,

M – C_2H_5), 203 (1.5, M – C_2H_5 – CH_2), 189 (6.3, M – C_2H_4), 145 (1.4, $(CH_2)_2Si_2Me_4H$), 87 (0.1, Et_2SiH), 57 (0.2, Me_2SiH); exact mass, calcd 246.1284, measd 246.1291, dev 2.8 ppm; ^{13}C NMR δ (number of carbons) 11.67 (1), 9.52 (1), 9.11 (2), 6.87 (2), 0.26 (2), –3.11 (2); ^{1}H NMR δ (CCl_4) 0.60–1.10 (m, 9 H), 0.12 (s, 6 H), 0.01 (s, 6 H); IR (cm^{-1}) 990–1020 (s, Si–O).

To test for a reaction between **10** and sulfur, a solution of 12 mg (0.05 mmol) of **10** and 16 mg (0.5 mmol) of sulfur in 0.5 mL of decalin was refluxed for 53 h; 87% unreacted **8** and 13% **7** were obtained as the only products.

4. Reaction of $(Et_2Si)_5$ with Sulfur. A solution of 216 mg (0.50 mmol) of $(Et_2Si)_5$ and 19 mg (0.60 mmol) of sulfur was refluxed in 10 mL of decalin for 4 days. GLC analysis showed the product mixture contained 39% unreacted $(Et_2Si)_5$ and 48% of the decaethylthiacyclohexasilane. Distillation (Kugelrohr method, 120 °C (0.1 torr)) of the product followed by preparative GLC gave 2,2,3,3,4,4,5,5,6,6-decaethyl-1-thiacyclohexasilane, a colorless oil: mass spectrum, selected m/e (relative intensity) 462 (23.4, M^+), 433 (100, M – C_2H_5), 375 (48.6), 289 (26.8), 172 (3.5), 87 (5.5); exact mass, calcd 462.2466, measd 462.2478, dev 2.6 ppm; ^{13}C NMR δ (number of carbons) 10.60 (4), 10.38 (6), 8.00 (4), 5.02 (2), 4.14 (4); ^{1}H NMR δ 0.80–1.30 (m).

Registry No. 1, 75375-74-5; 2, 87451-22-7; **3a**, 87451-23-8; **3b**, 87451-29-4; 4, 87451-24-9; 5, 18236-36-7; 6, 15287-09-9; 7, 87451-25-0; 8, 7418-20-4; 9, 87451-26-1; 10, 87451-27-2; 11, 87451-28-3; S, 7704-34-9; $(Et_2Si)_7$, 75399-05-2; $(Et_2Si)_5$, 75217-22-0; 2,2,3,3,4,4,5,5,6,6-decaethyl-1-thiacyclohexasilane, 87451-30-7.

Ring-Insertion and Ring-Opening Reactions of Octaethylcyclotetrasilane

Corey W. Carlson and Robert West*

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

The strained cyclotetrasilane $(Et_2Si)_4$ (1) reacts with alkynes in the presence of palladium catalysts to yield 3,4,5,6-tetrasilacyclohexenes and, ultimately, 1,4-disilacyclohexa-2,5-dienes. With isoprene, 1 forms two addition products in which one and two isoprene units, respectively, are inserted into the silicon ring. The reaction of 1 with m-chloroperbenzoic acid leads to rapid oxidation, forming the siloxanes $(Et_2Si)_4O_n$, $n = 1–4$. Ring-opening reactions of 1 take place rapidly with Cl_2, Br_2, I_2, $LiAlH_4$, HCl, HBr, H_2O, EtOH, and HOAc and slowly with PhLi to give 1,4-disubstituted linear tetrasilanes.

Introduction

Cyclotetrasilanes are generally more reactive than larger polysilane rings. Reactions of $(Ph_2Si)_4$, mainly of the ring-opening type, have been extensively examined,[1] but those of other cyclotetrasilanes have been little studied. Known reactions of the peralkylcyclotetrasilanes include chlorination, chlorodemethylation, and oxidation reactions, each of which has been described for $(t\text{-BuMeSi})_4$.[2]

Preliminary reports describing several ring-opening reactions of $(i\text{-Pr}_2Si)_4$[3] and a sulfur-insertion reaction of $(Me_2Si)_4$[4] have also appeared.

Octaethylcyclotetrasilane, $(Et_2Si)_4$ (1), is readily prepared in good yields from the reaction of Et_2SiCl_2 with sodium in toluene.[5] Tetrasilane 1 is much less reactive than the very labile $(Me_2Si)_4$ but appears to be more reactive than cyclotetrasilanes which bear more sterically

(1) (a) Gilman, H.; Schwebke, G. L. *Adv. Organomet. Chem.* **1964**, *1*, 89. (b) Gilman, H.; Atwell, W. H.; Cartledge, F. K. *Ibid.* **1966**, *4*, 1.
(2) (a) Biernbaum, M.; West, R. *J. Organomet. Chem.* **1977**, *131*, 189. (b) Helmer, B. J.; West, R. *Organometallics* **1982**, *1*, 1463.

(3) Watanabe, H.; Muraoko, T.; Kageyama, M.; Nagai, Y. *J. Organomet. Chem.* **1981**, *216*, C45.
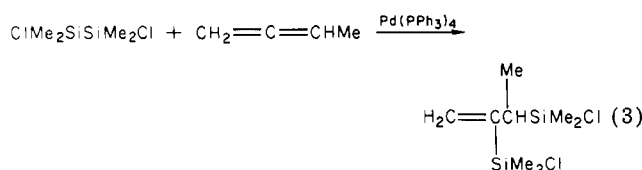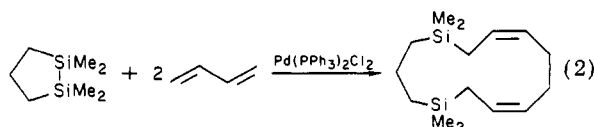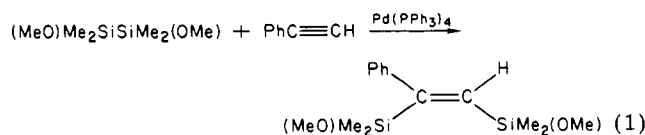(4) Hengge, E.; Schuster, H. C. *J. Organomet. Chem.* **1982**, *231*, C17.
(5) Carlson, C. W.; West, R. *Organometallics*, preceding paper in this issue.

hindering groups. These properties of moderate reactivity and ease of preparation make 1 a good choice for the study of polysilane reactions. In this paper, some ring-insertion and ring-opening reactions of 1 will be reported.
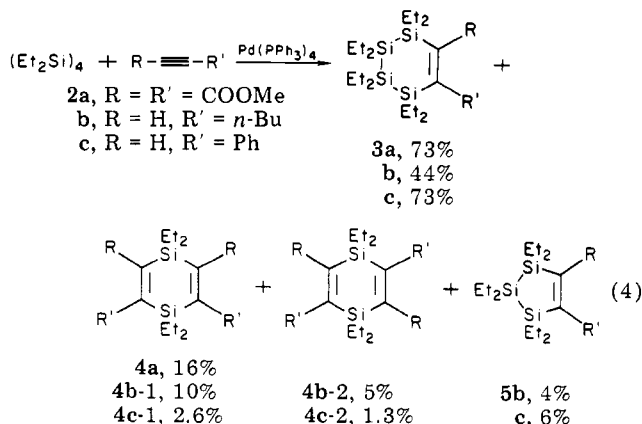
Results and Discussion

Reactions of 1 with Acetylenes and Dienes. Recent literature has described novel transition-metal-catalyzed reactions of the Si–Si bond of disilanes with alkynes (eq 1),[6] dienes (eq 2),[7] and allenes (eq 3).[8] These reactions

$$(MeO)Me_2SiSiMe_2(OMe) + PhC\equiv CH \xrightarrow{Pd(PPh_3)_4}$$

$$(1)$$

$$(2)$$

$$ClMe_2SiSiMe_2Cl + CH_2=C=CHMe \xrightarrow{Pd(PPh_3)_4}$$

$$(3)$$

are similar to $[\sigma 2s + \pi 2s]$ reactions in carbon chemistry, which are thermally forbidden but may be allowed in the presence of a catalyst. The corresponding reactions of polysilanes containing more than two silicon atoms, however, have not been examined. We find that 1 reacts with alkynes in the presence of palladium catalysts to give double silylation reactions. The products include not only the expected tetrasilacyclohexenes but also products arising from additional Si–Si bond cleavage.

When 1, dimethyl acetylenedicarboxylate (2a), and a catalytic amount of tetrakis(triphenylphosphine)palladium(0) [Pd(PPh₃)₄] were mixed in benzene and refluxed under nitrogen for 4 h, the addition product, dimethyl 3,3,4,4,5,5,6,6-octaethyl-3,4,5,6-tetrasilacyclohexene-1,2-dicarboxylate, 3a, was obtained in high yield. The products also included a small amount of unreacted 1 and, unexpectedly, tetramethyl 1,1,4,4-tetraethyl-1,4-disilacyclohexa-2,5-diene-2,3,5,6-tetracarboxylate, 4a (eq 4). In
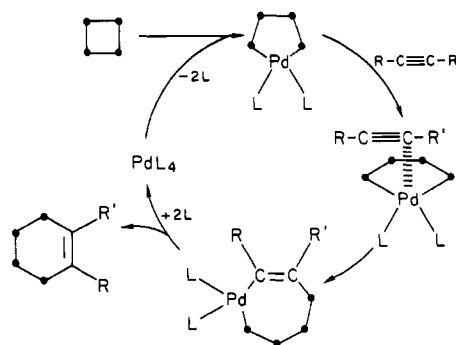
$$(Et_2Si)_4 + R-\equiv-R' \xrightarrow{Pd(PPh_3)_4}$$

2a, R = R' = COOMe
b, R = H, R' = *n*-Bu
c, R = H, R' = Ph

3a, 73%
b, 44%
c, 73%

$$(4)$$

4a, 16%
4b-1, 10%
4c-1, 2.6%

4b-2, 5%
4c-2, 1.3%

5b, 4%
c, 6%

Scheme I. Possible Mechanism for Double Silylation of $(Et_2Si)_4$[a]

[a] Each dot represents Et₂Si.

a similar fashion, 1-hexyne (2b) reacts with 1 in the presence of Pd(PPh₃)₄ at 80 °C to give a complex mixture consisting mainly of insertion product 3b but also containing disilacyclohexadiene 4b and 1-*n*-butyl-3,3,4,4,5,5-hexaethyl-3,4,5-trisilacyclopentene, 5b. A fourth product, present in 2% yield, was suggested to be a trisilacycloheptadiene by its mass spectrum. Phenylacetylene, 2c, and 1 reacted under similar conditions to form 3c, 4c, and 5c as the new cyclic products.

The silylation products, all air-stable oils or solids, were identified on the basis of their ^{13}C NMR and mass spectra. The ^{13}C NMR resonances of the ethyl groups in these cyclic compounds fall into two sets, between 8–11 and 3–7 ppm, assignable to the methyl and methylene carbons, respectively. In each case, the correct pattern of ethyl resonances were observed, and the remaining ^{13}C signals were consistent with the structural assignment.

Tetrasilacyclohexenes 3 contained only a single isomer, assigned to the *cis* configuration. Examination of molecular models showed that the alternative trans form should be highly strained. The reactions of disilanes with alkynes, which form predominantly *cis*-alkenes, also suggest that the formation of the trans isomer is unlikely. Compound 4b, when purified, showed only a single peak on the GLC and gave the correct IR and mass spectra but produced five lines in the ethyl region of its ^{13}C NMR (in ratio of 2:1:1:1:1) and two alkene proton resonances (in a 2:1 ratio) in its ^1H NMR spectrum. These observations suggested the presence of two unresolved isomers of 4b, the 2,6-di-*n*-butyl derivative, 4b-1, and the 2,5-di-*n*-butyl derivative 4b-2, in a 2:1 ratio. The expected ^{13}C intensity patterns of the ethyl groups would be 1:1:1:1 for 4b-1 and 1:1 for 4b-2. Disilacyclohexadiene 4c, by similar reasoning, was also found to contain two unresolved isomers, 4c-1 and 4c-2, again in 2:1 ratio.[9]

All of the reactions proceeded in a nearly identical fashion when bis(triphenylphosphine)palladium(II) chloride [Pd(PPh₃)₂Cl₂] was used as the silylation catalyst. Diphenylacetylene, bis(trimethylsilyl)acetylene, 2-hexyne, and 3-hexyne gave no reaction with 1 when using either Pd(PPh₃)₄ or Pd(PPh₃)₂Cl₂ as the catalysts; in this, 1 resembles the disilanes, which are also less reactive toward bissubstituted acetylenes.[6]

A simple catalytic scheme can be proposed for the formation of tetrasilacyclohexenes (Scheme I) by analogy to that suggested by Kumada[6b] or Watanabe and Nagai[6c] for the disilanes. However, the mechanism for rearrangement to the disilacyclohexadienes is not known. In the reaction

(6) (a) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* 1975, *97*, 931. (b) Tamao, K.; Hayashi, T.; Kumada, M. *J. Organomet. Chem.* 1976, *114*, C19. (c) Watanabe, H.; Kobayashi, M.; Higuchi, K.; Nagai, Y. *Ibid.* 1980, *186*, 51. (d) Watanabe, H.; Kobayashi, M.; Saito, M.; Nagai, Y. *Ibid.* 1981, *216*, 149.
(7) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *Chem. Lett.* 1975, 887.
(8) Watanabe, H.; Saito, M.; Sutou, N.; Kishimoto, K.; Inose, J.; Nagai, N. *J. Organomet. Chem.* 1982, *225*, 343.

(9) A small peak at δ 5.89 is also observed in the ^{13}C NMR of several samples of 4c and may arise from small amounts of a 1,2-disilacyclohexadiene isomer.

of 1 with both 2a and 2b, higher yields of the disilacyclohexadienes are obtained when an excess of the alkyne and extended reaction times are used.[10] High yields of 4a are also formed when 3a is stirred in refluxing benzene in the presence of Pd(PPh$_3$)$_2$Cl$_2$ and an excess of 2a.[11] These results suggest that recoordination of the initially formed tetrasilacyclohexene to the catalyst occurs, followed by successive silylation steps in which the remaining Si-Si bonds are cleaved. The 1,4-disilacyclohexadienes, which contain no Si-Si bonds, appear to be the stable end products of these catalyzed reactions.

Double silylation of a diene by 1 was also observed but is much less facile than the corresponding reactions with alkynes. A solution of isoprene (7), 1, and Pd(PPh$_3$)$_2$Cl$_2$ in benzene was heated in an evacuated sealed tube for 72 h, giving new cyclic compounds 1-methyl-4,4,5,5,6,6,7,7-octaethyl-4,5,6,7-tetrasilacyclooctene (8, 9%) and 1,10-dimethyl-4,4,5,5,6,6,7,7-octaethyl-4,5,6,7-tetrasilacyclododeca-1,9-diene (9, 6%) in addition to unreacted 1 (71%) (eq 5). Modification of the catalyst improved the yield

$$(Et_2Si)_4 \; + \; \diagup\!\!\diagdown\!\!\diagup \xrightarrow{\;Pd(PPh_3)_2Cl_2\;}$$

7
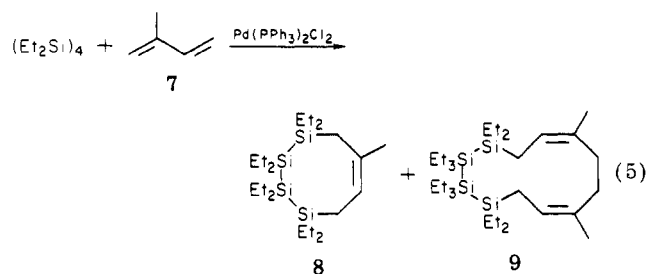
somewhat; an analogous reaction of 1 and with bis(p-methoxybenzonitrile)palladium(II) chloride [Pd(p-MeOC$_6$H$_4$CN)$_2$Cl$_2$], gave 20% 8, 22% 9, and 51% 1. The 1,10-dimethyl isomer was chosen for 9 on the basis of its ^{13}C NMR spectrum, which requires a symmetrical structure, and its ^{1}H NMR spectrum, which shows that the ring methylenes attached to silicon (δ 1.74, the 3- and 8-positions) are coupled to the alkene proton. Other alkenes failed to give addition products when reacted with 1 in benzene using Pd(p-MeOC$_6$H$_4$CN)$_2$Cl$_2$. These included 2,3-dimethylbutadiene, 1,4-diphenylbutadiene, 1-hexene, and cyclopentene.

Oxidation of 1 by MCPBA. Tetrasilane 1 oxidizes slowly in air, forming mainly 2,2,3,3,4,4,5,5-octaethyl-1-oxacyclopentasilane, c-(Et$_2$Si)$_4$O, 10. Oxidation is much more rapid if m-chloroperbenzoic acid (MCPBA) is used as the oxidizing agent. High yields of 10 (87%) are obtained instantly upon addition of 1.0 equiv of MCPBA to solutions of 1 in benzene. Besides 10, 4% unreacted 1 and 3% c-(Et$_2$Si)$_4$O$_2$, 11, are obtained. The high selectivity observed for the oxidation to 10 probably results from strain acceleration of the first step in the oxidation of 1, leading to the relatively unstrained five-membered ring.

Slow dropwise addition of 1, 2, and 3 equiv of MCPBA in benzene to 1 led to mixtures of the oxidation products containing 95% 10, 86% 11, and 65% c-(Et$_2$Si)$_4$O$_3$, 12, respectively. Quantitative yields of c-(Et$_2$Si)$_4$O$_4$, octaethylcyclotetrasiloxane, 13, were obtained when more than 4 equiv of MCPBA were used.

Although 13 has been previously identified,[12] the re-

maining three products derived from 1 are new. All show similar IR and mass spectra. The ^{13}C signals may be assigned to the methylene (2-7 ppm) and methyl (7.5-11 ppm) carbons; the chemical shift in each case depends primarily upon the number and location of the adjacent oxygen and silicon atoms. The proton signals of the ethyl groups, an unresolved multiplet for both 1 and 10, are separated into the expected quartet and triplet in the more highly oxidized products 11-13. The ^{13}C NMR spectrum of 11 showed two isomers, 11a and 11b, to be present, and
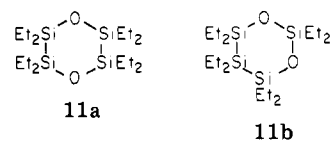
their signals were assigned by reference to pure 11a, made by a different route (vide infra). Analysis of the line intensities showed the ratio of 11a:11b to be 1.0:2.2. This contrasts to the double oxidation product from (t-BuMeSi)$_4$ and MCPBA, which contained only the 1,3-dioxa isomer.[2b] The smaller steric bulk of the ethyl substituents may lead to higher reactivity, and consequently less selectivity, in the oxidation steps.

Ring-Opening Reactions of 1. Cyclotetrasilane 1 undergoes a number of ring-opening reactions, typically forming high yields of 1,4-disubstituted tetrasilanes under mild conditions. The selectivity of these reactions resembles that for (Ph$_2$Si)$_4$[6] and is in both cases a probable consequence of a ring-opening step that is much more facile than subsequent Si-Si bond cleavages in the linear polysilane.[13]

The halogenated tetrasilane, 1,4-dichlorooctaethyltetrasilane, Cl(Et$_2$Si)$_4$Cl, 14, is made in 98% yield by reaction of 1 with 1 equiv of PCl$_5$ in benzene at room temperature. A similar reaction with bromine as the halogenating agent forms Br(Et$_2$Si)$_4$Br (15, 87%). The dibromo derivative is markedly moisture sensitive, though less so than the diiodo derivative I(Et$_2$Si)$_4$I, 16, formed from 1 and iodine in nearly quantitative yields. The 1,4-diiodotetrasilane was also found to undergo facile oxidation and could be isolated only under oxygen-free conditions. All of the halogenation reactions were rapid. Hydrolysis of 15 and 16 gave siloxane 10, the expected condensation product of an intermediate 1,4-dihydroxytetrasilane.

The simplest of the linear derivatives of 1, H(Et$_2$Si)$_4$H, 17, was obtained in 86% yield by direct interaction of excess lithium aluminum hydride and 1 in THF. A small amount of H(Et$_2$Si)$_3$H (13%) was also obtained, providing the only example of additional Si-Si bond cleavage to be observed.[16]

A variety of other hydrosilanes were also prepared from 1. High yields of both H(Et$_2$Si)$_4$Cl (18, 97%) and H-(Et$_2$Si)$_4$Br (19, 92%) could be obtained by shaking a benzene solution of 1 with a concentrated *aqueous* solution of HCl or HBr, respectively; the active reagent in each case was probably the hydrogen halide dissolved in the benzene

(10) An analogous increase in the yield of 4c is not observed in similar attempts using 1 and 2c, perhaps because of a decline in the effectiveness of the catalyst.

(11) The conversion of 3a to 4a also requires addition of a single drop of 1, perhaps in order to generate the reactive intermediates active in the catalysis.

(12) Andrianov, K. A.; Nogaideli, A. I.; Kananashvili, L. M.; Nakaidze, L. I. *Izv. Akad. Nauk SSSR* **1968**, 828 and references cited therein.

(13) The quite different course of ring-opening reactions in larger rings is illustrated by the reaction of (Me$_2$Si)$_6$ with phosphorus pentachloride[14] or chlorine,[15] from which a mixture of α,ω-substituted chlorosilanes, Cl(Me$_2$Si)$_n$Cl, where n = 3, 4, and 6, are obtained. In this case subsequent cleavage of the polysilane chains competes with the initial ring-opening step.

(14) Gilman, H.; Inoue, S. *J. Org. Chem.* **1964**, *29*, 3418.

(15) (a) Wojnowski, W.; Hurt, C. J.; West, R. *J. Organomet. Chem.* **1977**, *124*, 271. (b) Sen, P. K.; Ballard, D.; Gilman, H. *Ibid.* **1968**, *15*, 237.

(16) Although monosilane Et$_2$SiH$_2$ is also an expected product from the cleavage of H(Et$_2$Si)$_4$H (to H(Et$_2$Si)$_3$H), we did not determine if it was present in the volatile fraction from this reaction.

Table I. ^{13}C NMR of Derivatives of 1[a]

compd	δ (no. of ethyl carbons)	other
1	3.64 (8), 11.04 (8)[b]	
3a	3.20 (4), 6.33 (4), 8.54 (4), 10.66 (4)	51.06 (OCH₃), 154.31 (C=C), 170.87 (C=O)
4a	5.37 (4), 7.63 (4)	51.58 (OCH₃), 153.19 (C=C), 168.85 (C=O)
3b	3.04 (2), 3.61 (2), 6.48 (2), 6.96 (2), 8.76 (2), 9.11 (2), 10.88 (2), 10.99 (2)	14.27, 23.03, 32.95, 42.82 (n-Bu), 142.81 (C=CH)[c]
4b-1	4.66 (2), 6.31 (2), 8.01 (2), 8.10 (2)	38.62, 30.91, 23.08, 14.27 (n-Bu), 140.26 (C=CH), 160.88 (C=CC₄H₉)
4b-2	5.76 (4), 8.10 (4)	39.32, 31.04, 23.08, 14.27[d] (n-Bu), 139.72 (C=CH)
5b	1.22 (2), 5.79 (4), 9.00 (2), 9.19 (2), 11.14 (2)	14.30, 22.11, 31.77, 39.36 (n-Bu), 145.56 (C=CH)[c]
3c[e]	2.77 (2), 3.38 (2), 6.45 (2), 6.86 (2), 8.44 (2), 8.64 (2), 10.58 (2), 10.68 (2)	148.46 (C=CH), 164.40 (C=CPh), phenyl, 125.4 (p), 126.59 (m), 127.76 (o), 150.87 (i)
4c-1[e]	3.26 (2), 5.64 (2), 7.44 (2), 10.56 (2)	⎱ 145.02 (C=CH),[f] phenyl, 126.35 (p + m),
4c-2[e]	4.87 (4), 7.78 (4)	⎰ 128.20 (o)[g]
8	4.49 (4), 5.56 (2), 6.83 (2), 8.48 (4), 10.82 (4)	14.91, 18.74 (CH₂C=C), 26.67 (CH₃), 118.78 (C=CCH₃), 130.59 (C=CH)
9	4.74 (4), 6.20 (4), 8.58 (4), 10.87 (4)	14.18, 16.56 (CH₂C=C), 36.30 (CH₃), 121.30 (C=CCH₃), 133.17 (C=CH)
10	2.04 (4), 7.07 (4), 9.50 (4), 10.93 (4)	
11a	6.79 (8), 9.39 (8)	
11b	1.99 (2), 6.85 (6), 8.12 (2), 9.87 (2), 10.71 (2)	
12	6.90 (4), 6.96 (4), 7.82 (4), 9.17 (4)	
13	6.87 (8), 7.71 (8)	
14	4.25 (4), 7.38 (4), 10.44 (4), 10.92 (4)	
15	5.02 (4), 8.54 (4), 10.80 (4), 11.08 (4)	
16	5.39 (4), 9.95 (4), 10.10 (4), 10.49 (4)	
17	3.41 (4), 4.40 (4), 10.75 (8)	
18	3.48 (2), 4.25 (2), 4.58 (2), 7.40 (2), 10.44 (2), 10.66 (4), 10.99 (2)[b]	
19	3.39 (2), 4.36 (2), 4.44 (2), 8.21 (2), 10.42 (2), 10.60 (2), 10.68 (2), 10.75 (2)	
20	3.42 (2), 4.03 (2), 4.53 (2), 7.01 (2), 10.32 (2), 10.77 (6)	
21	3.53 (2), 4.43 (2), 4.58 (2), 7.71 (2), 8.94 (2), 10.76 (6)	18.92, 59.38 (OCH₂CH₃)
22	3.46 (2), 4.23 (2), 4.44 (2), 7.40 (2), 8.49 (2), 10.57 (2), 10.73 (4)	22.27 (OCH₃)[h]
23[e]	3.04 (2), 3.35 (2), 4.12 (2), 4.77 (2), 8.30 (2), 10.38 (2), 10.55 (4)	phenyl, 127.68 (m), 128.19 (p), 134.60 (o), 138.06 (i)
24[e]	4.29 (4), 4.86 (4), 8.30 (4), 10.31 (4)	phenyl, 127.64 (m), 128.12 (p), 134.67 (o)[g]
25	3.00 (2), 6.61 (2), 7.22 (2), 7.35 (2), 10.27 (2), 10.55 (2), 10.64 (4)	

[a] In benzene-d_6 using Me₄Si as the internal standard. [b] Reference 5. [c] The n-Bu-substituted ethylene carbon is not seen. [d] The n-Bu-substituted ethylene carbon is not seen or is coincident with the δ 160.88 signal of 4b-1. [e] In chloroform-d_1. [f] The phenyl-substituted ethylene carbon is not observed. [g] The ipso carbon is not observed. [h] The carbonyl carbon is not observed.

layer. Only minimal hydrolysis was seen; evidently attack on the Si–halogen bond is slow under acidic conditions. The reaction of 1 with HCl under these conditions was complete within 0.5 h; this is much more rapid than similar reactions of (i-Pr₂Si)₄ and (Ph₂Si)₄ with gaseous HCl. The hydroxy derivative H(Et₂Si)₄OH, 20, was prepared by hydrolysis of 18 or 19 in the presence of pyridine as an HX acceptor. Reaction of 1 in neat EtOH or glacial acetic acid produced H(Et₂Si)₄OEt (21, 95%) and H(Et₂Si)₄OAc (22, 99%), respectively. Similar reactions of polysilanes with alcohols or organic acids have not previously been reported.

The cleavage of 1 by excess phenyllithium in diethyl ether was very slow. Following 6 days of reflux and quenching by acid hydrolysis, the products were 27% H(Et₂Si)₄Ph, 23, 27% Ph(Et₂Si)₄Ph, 24, and 26% unreacted 1; numerous compounds in minor yield were present as well.

Attempted chlorination of 1 using the organic halides carbon tetrachloride or sym-tetrachloroethane produced only low yields of the 1,4-dichlorotetrasilane. Instead, the major product, as shown by its IR and NMR spectra (Table I), is a mixed functional linear polysilane, 1,5-dichloro-1,1,3,3,4,4,5,5-octaethyl-2-oxapentasilane, ClEt₂SiO(Et₂Si)₃Cl, 25. This compound forms rapidly in

solutions of 1 and oxygen-saturated CCl₄ but more slowly in partially degassed solutions. A typical yield of 25 from this reaction is 82%; smaller amounts of products arising from oxidation of 1 [(Et₂Si)₄O, 10] and hydrolysis and condensation of 25 [(Et₂Si)₄O₂, 11b] are also seen. Solutions of 10 in CCl₄ and of 14 in oxygen-saturated benzene or CCl₄, both failed to form any of dichlorosiloxane 25, suggesting that neither is an intermediate in the reaction. Further proof for its structure was obtained by hydrolyzing dilute solutions of 25: the expected condensation product 11b is obtained in 60% yield. A second product (39%) appears to be HOEt₂SiO(Et₂Si)₃OH (26), the uncondensed compound corresponding to 11b.

Each of the linear derivatives of 1 was characterized spectroscopically. The ^{13}C NMR (Table I) again showed two sets of resonances in the Si–Et region, assignable to the methylene and methyl groups. The observed chemical shifts depended on the substituents present; relative to unsubstituted 17, addition of an electronegative substituent generally led to deshielding of the methylene carbons and shielding of the methyl carbons. Halo-substituted tetrasilanes gave characteristic mass spectral fragmentation patterns in which [c-(Et₂Si)₃X]⁺ was often the base peak, much as has been previously observed for chloro- and

bromo-substituted permethyl polysilanes.[17]

Experimental Section

Methods. Tetrasilane $(Et_2Si)_4$, **1**, was prepared by reaction of Et_2SiCl_2 with sodium in toluene as previously described.[5] The purity of **1** used for reactions was at least 95%, the remainder consisting of 1–2% **10** and 2–3% $(Et_2Si)_5$. Benzene was predried over molecular sieves and distilled from sodium benzophenone ketyl. Catalysts $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$, and $Pd(PhCN)_2Cl$ were obtained from Aldrich Chemical Co., while $Pd(p-MeOC_6H_4CN)_2Cl_2$ was made from $PdCl_2$ and p-methoxybenzonitrile by analogy to the literature methods.[18] Alkenes and alkynes were reagent grade from Aldrich Chemical Co. and were used without further purification. The MCPBA was technical grade (85%) from Aldrich Chemical Co. All reactions were carried out by using oven-dried glassware under an atmosphere of dry nitrogen or argon. Syringe and Schlenk techniques were used for handling oxygen- and moisture-sensitive compounds. Solvents were generally degassed before use to prevent oxidation of **1**.

Chromatograph and Spectroscopy. Analytical scale GLC was done with a Hewlett-Packard 5720A gas chromatograph equipped with a flame ionization detector, using 3 ft × $^1/_8$ in. Dexsil (5% on Chromosorb W) or 6 ft × $^1/_8$ in. SE-30 (20% on Chromosorb W) columns. Preparative scale GLC was carried out by using a Varian Model 90-P gas chromatograph containing a thermal conductivity detector and using a 6 ft × $^3/_8$ in. SE-30 column (20% on Chromosorb W). Separation of **3a** was completed by using an HPLC system consisting of a Waters 6000A LC pump, a Whatman M-9 ODS-2 reverse-phase column, and an Altex UV detector; a mixture of 95% MeOH and 5% THF was used as the eluent.

NMR spectra were determined by using Me_4Si as the internal standard and benzene-d_6 as the solvent, except as otherwise noted. The ^1H NMR spectra were recorded on a JEOL MH-100 spectrometer, while ^{13}C NMR spectra were determined on a JEOL FX-200 spectrometer operating at 50.10 MHz. Mass spectra were obtained on a Kratos MS902C mass spectrometer, usually at 70 eV. IR spectra were recorded by using a Beckman 4250 spectrophotometer, generally using neat films of the samples on CsI plates.

Double Silylation of Alkynes by 1. 1. With Dimethyl Acetylenedicarboxylate, 2a. In a typical reaction, 172 mg (0.50 mmol) of **1**, 71 mg (0.8 mmol) of **2a**, and 17 mg (3 mol %) of $Pd(PPh_3)_4$ were dissolved in 10 mL in a flask equipped with magnetic stirring, a water condenser, and a nitrogen inlet. The reaction was refluxed for 4 h, during which the solution became a characteristic deep brown color. The benzene was removed under reduced pressure, and the mixture was distilled by Kugelrohr distillation (120 °C (0.1 torr)), to give 300 mg of product containing, from GLC analysis, 73% **3a**, 16% **4a** (based on 1.0-mmol theoretical yield), and small amounts of other products, including PPh₃. Disilacyclohexadiene **4a** was isolated as pure colorless crystals (70 mg, 6%) from the product by recrystallization from hexane. Tetrasilacyclohexene **3a**, which is apparently thermally unstable and was decomposed upon attempted isolation by preparative GLC, could be obtained as a greasy crystalline solid by using HPLC.

3a: mass spectrum, selected m/e (relative intensity) 486 (8.7, M⁺), 471 (0.4, M – CH_3), 457 (4.2, M – C_2H_5), 443 (8.1, M – C_2H_5 – CH_3), 427 (2.3, M – CO_2CH_3), 400 (51.6), 289 (21.3), 117 (52.1, Et_2MeSiO), 87 (89.8, Et_2SiH), 59 (100, $EtSiH_2$ or CO_2CH_3); exact mass, calcd 486.2460, measd 486.2472, dev 2.5 ppm; ^1H NMR δ 3.43 (s, 6 H), 0.80–1.20 (m, 40 H); IR (cm⁻¹) 1725 (vs, br), 1718 (s, sh, C=O), 1534 (m, C=C), 1212 (vs, br, C–O). Anal. Calcd for $C_{22}H_{46}Si_4O_4$: C, 54.27; H, 9.52. Found: C, 54.31; H, 9.70.

4a: mp 110 °C; mass spectrum, selected m/e (relative intensity) 456 (4.8, M⁺), 441 (3.0), 427 (4.9), 425 (9.4), 399 (5.5), 397 (19.3), 314 (28.1), 231 (12.7), 117 (58.5), 89 (100, $HEtSiOCH_3$); exact mass, calcd 456.1626, measd 456.1635, dev 1.9 ppm; ^1H NMR 3.45 (s, 12 H), 1.16 (s, 20 H); IR (cm⁻¹) 1720 (vs, br), 1710 (s, sh, C=O),

(17) Middlecamp, C. H.; Wojnowski, W.; West, R. *J. Organomet. Chem.* **1977**, *140*, 133.

(18) Kharasch, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882.

1555 (m, C=C), 1234 (s), 1215 (s, C–O). Anal. Calcd for $C_{20}H_{32}O_8Si_2$: C, 52.61; H, 7.06. Found: C, 52.72; H, 7.00.

A reaction of **1** (0.5 mmol) and **2a** (1.2 mmol) in 10 mL of benzene by the procedure described above but using 18 mg (5 mol%) of $Pd(PPh_3)_2Cl_2$ gave 10% **1**, 83% **3a**, and 4% **4a** after 4 h of reflux. The yield of **4a** was increased by a large excess of **2a** and by longer reaction times. A silylation reaction of **2a** (2.0 mmol) and **1** (0.5 mol) in 10 mL of benzene in the presence of 5 mol % $Pd(PPh_3)_2Cl_2$ gave 320 mg of product containing **3a** (74%), **4a** (23%), and unreacted **1** (4%), following 4 h of reflux. An identical reaction, but where the reaction time was 62 h, gave 19% **3a** and 72% **4a**.

The conversion of **3a** to **4a** was attempted by refluxing a benzene solution of **3a** (50 mg, 0.1 mmol), **2a** (1.0 mmol), and a catalytic amount of $Pd(PPh_3)_2Cl_2$. After 48 h, GLC analysis showed no change had occurred. However, addition of a single drop of **1** (<<0.1 mmol) led to a noticeable darkening of the reaction solution, and 70% **4a** and 29% **3a** were present after a further 48 h of reflux.

2. With 1-Hexyne, 2b. Reactions of **1** and **2b** were carried out analogously to those of **1** and **2a**. Refluxing a solution of **1** (0.5 mmol), **2b** (50 mg, 0.6 mmol), and $Pd(PPh_3)_4$ (25 mg, 4 mol %) for 4 h yielded 210 mg of an oily mixture following Kugelrohr distillation. The products were **3b** (50%), **4b** (8%), **5b** (4%), **6** (2%), and unreacted **1** (7%) (GLC analysis). A number of minor products were also observed. A second attempt also produced **3b** (44%), **4b** (15%), **5b** (4%), and **6** (2%). A reaction (2.0-mmol scale) using 5 mol % $Pd(PPh_3)_2Cl_2$ led to a mixture of the cyclic compounds, forming, after 15 h of reflux, 30% **3b**, 9% **4b**, 6% **5b**, and 20% **1**. From the latter reaction, the silylation products were isolated as colorless oils by preparative GLC. While **5b** was obtained pure for mass spectroscopy, NMR and IR samples contained a 1:1 mixture of **5b** and **10**. Compound **6**, with empirical formula corresponding to $(Et_2Si)_3(HC=CC_4H_9)_2$, was identified only by its mass spectrum.

3b: mass spectrum, selected m/e (relative intensity) 426 (52.0, M⁺), 397 (5.2), 311 (100, $Et_5Si_3(C_2C_4H_9)$), 281 (12.8), 172 (6.1), 115 (22.8), 87 (63.4), 57 (32.1, C_4H_9); exact mass, calcd 426.2976, measd 426.2988, dev 2.8 ppm; ^1H NMR δ 6.66 (s, 1 H), 2.42 (t, $J = 6$ Hz, 2 H), 1.5–1.7 (m, 6 H), 0.7–1.4 (m, 40 H).

4b: mass spectrum, selected m/e (relative intensity) 336 (4.3, M⁺), 307 (100, M – C_2H_5), 279 (2.3), 141 (1.8), 115 (2.1), 87 (9.8), 59 (11.5); exact mass, calcd 336.2658, measd 336.2663, dev 1.5 ppm; ^1H NMR δ 6.62 (s, 0.66 H), 6.52 (s, 0.33 H), 2.05–2.15 (m, 2 H), 1.20–1.60 (m, 3 H), 0.50–1.20 (m, 14 H); IR (cm⁻¹) 1555 (m), 1570 (m, sh, C=C).

5b: mass spectrum, selected m/e (relative intensity 340 (36.4, M⁺), 311 (36.0), 283 (6.0), 273 (7.3), 115 (18.1), 87 (78.1), 59 (100, C_4H_9); exact mass, calcd 340.2427, measd 340.2437, dev 2.9 ppm; ^1H NMR δ 6.86 (s, 1 H), 2.20–2.40 (m, 2 H), 1.25–1.60 (m, 3 H), 0.60–1.25 (m, contains resonances from compound **10**); IR (cm⁻¹) 1561 (w, C=C).

6: mass spectrum, selected m/e (relative intensity) 422 (28.6, M⁺), 393 (10.1), 365 (1.0), 335 (4.1), 307 (100, $Et_3Si_2(C_2C_4H_9)_2$), 225 (1.4), 87 (13.0), 59 (11.4); exact mass, calcd 422.3207, measd 422.3219, dev 2.8 ppm.

Extended reaction of mixtures containing **1**, **2b**, and $Pd(PPh_3)_2Cl_2$ led to increased yields of **4b**. In one instance, 25% **4b** and 42% **3b** were obtained as the major products following 22 h of reflux.

3. With Phenylacetylene, 2c. If **2c** was reacted with **1** in the presence of a palladium catalyst as described for **1** and **2a**, a mixture of cyclic products was again formed. When a solution of **1** (2.0 mmol), **2c** (224 mg, 2.2 mmol), and 25 mL of benzene was refluxed for 9 h with $Pd(PPh_3)_2Cl_2$ (2.5 mol %) and the resulting mixture distilled by the Kugelrohr method, 840 mg of an oily product was collected. The yields were 71% **3c**, 7% **4c**, and 3% **5c** (GLC analysis), and only minor amounts of other products were present. A similar reaction using 5 mol % $Pd(PPh_3)_4$ gave 73% **3c**, 4% **4c**, and 6% **5c**. Attempts carried out in evacuated sealed tubes at 120 °C produced slightly higher yields of **4c**. With $Pd(PPh_3)_2Cl_2$ (5 mol %) as the catalyst, **1** and **2c** formed 46% **3c**, 17% **4c**, 5% **5c**, and 22% unreacted **1** after 3 h at 120 °C. With use of $Pd(PPh_3)_4$ (5 mol %), reaction of **1** and **2c** at 120 °C led to 72% **3c**, 16% **4c**, and 1% unreacted **1**, also after 3 h. Heating a solution of **1** and **2c** in benzene under these

conditions in the absence of a catalyst gave no reaction.

Separation using preparative GLC gave the three products as colorless oils. Compound **5c** was identified only by its mass spectrum.

3c: mass spectrum, selected m/e (relative intensity) 446 (63.8, M$^+$), 417 (5.0), 331 (78.1, Et$_5$Si$_3$(PhC$_2$H)), 172 (23.0), 115 (18.5), 87 (89.6), 59 (100, Et$_2$SiH$_2$); exact mass, calcd 446.2664, measd 446.2677, dev 2.9 ppm; ^{1}H NMR (chloroform-d_1) δ 7.0–7.35 (m, 5 H), 6.52 (s, 1 H), 0.6–1.1 (m, 40 H); IR (cm^{-1}) 3080–3020 (w, C=C*H*), 1600 (m), 1577 (m), 1488 (m, C=C).

4c: mass spectrum, selected m/e (relative intensity) 376 (27.0, M$^+$), 347 (100, M – C$_2$H$_5$), 319 (18.5), 217 (6.1), 131 (50.5), 107 (13.0, PhSiH$_2$), 87 (10.3); exact mass, calcd 376.2034, measd 376.2043, dev 2.4 ppm; ^{1}H NMR (chloroform-d_1) 7.15–7.35 (m, 10 H), 6.78 (s, 0.66 H), 6.75 (s, 0.33 H), 0.55–1.1 (m, 20 H); IR (cm^{-1}) 3020–3080 (w, C–CH), 1599 (m), 1487 (m, C=C).

5c: mass spectrum, selected m/e (relative intensity) 360 (100, M$^+$), 331 (63.9), 202 (22.1), 172 (21.6), 115 (6.7), 87 (66.5); exact mass, calcd 360.2115, measd 360.2126, dev 3.1 ppm.

The use of a large excess of **2c** and long reaction times failed to improve the yield of **4c**. The usual proportions of **3c** (ca. 70%) and **4c** (ca. 10%) were instead obtained in every attempt, and these products were observed to be unchanged, even after 5 days of reflux in benzene.

Double Silylation of Isoprene, 7, by 1. In a typical reaction, 345 mg of **1** (1.0 mmol), 1680 mg (10.0 mmol) of **7**, and 20 mg (5 mol %) of Pd(*p*-MeOPhCN)$_2$Cl$_2$ were dissolved in 5 mL of benzene and sealed in an evacuated thick-walled tube. The mixture was heated at 120 °C for 72 h, and then the products (400 mg) were collected by Kugelrohr distillation (110 °C (0.1 torr)). In addition to unreacted **1** (51%), **8** (20%) and **9** (22%) were present, as shown by GLC analysis. An analogous reaction on a 0.5-mmol scale with Pd(PhCN)$_2$Cl$_2$ (10 mg, 5 mol %) resulted in 10% **8**, 13% **9**, and 73% **1** after 4 days at 120 °C. If **1** (0.5 mmol) and **7** (5.0 mmol) were reacted in 5 mL of benzene using Pd(PPh$_3$)$_2$Cl$_2$ as the catalyst, then 9% **8** and 6% **9** formed: the remaining product included 71% unreacted **1** and a number of minor products, including PPh$_3$. Cyclic products **8** and **9** were purified by preparative GLC as colorless oils.

8: mass spectrum, selected m/e (relative intensity) 412 (6.5, M$^+$), 383 (14.7), 331 (15.4), 259 (8.1), 172 (48.1), 115 (39.9), 87 (100, Et$_2$SiH); exact mass, calcd 412.2820, measd 412.2833, dev 3.2 ppm; ^{1}H NMR δ 5.11 (t, J = 8 Hz, 1 H), 1.77 (s, 3 H), 1.71 (s, 2 H), 1.63 (d, J = 8 Hz, 2 H), 0.6–1.2 (m, 40 H); IR (cm^{-1}) 1649 (vw, C=C).

9: mass spectrum, selected m/e (relative intensity) 480 (5.7, M$^+$), 297 (5.5), 231 (1.2), 172 (33.3), 115 (18.9), 87 (42.5), 69 (100, C$_6$H$_9$); exact mass, calcd 480.3444, measd 480.3458, dev 2.9 ppm; ^{1}H NMR δ 5.37 (m, 2 H), 2.20 (s, 4 H), 1.74 (d, J = 7 Hz, 4 H), 1.64 (s, 6 H), 0.60–1.20 (m, 40 H); IR (cm^{-1}) 1655 (w, C=C).

Attempted Silylations Using 1. Reactions of diphenylacetylene, bis(trimethylsilyl)acetylene, 2-hexyne, and 3-hexyne with **1** in refluxing benzene using both Pd(PPh$_3$)$_4$ and Pd-(PPh$_3$)$_2$Cl$_2$ as catalysts gave only unchanged **1** and traces of PPh$_3$ in each case, even after prolonged reflux (7 days). Reactions of olefins other than **7** were unsuccessful: no insertion products were observed from the reaction of **1** and 2,3-dimethylbutadiene, 1,4-diphenylbutadiene, 1-hexene, or cyclopentene in the presence of Pd(*p*-MeOPhCN)$_2$Cl$_2$ in sealed tubes at 120 °C. The reaction of **1** (0.5 mmol) and Et$_3$SiH (1.0 mmol) in refluxing benzene, using as catalysts either Pd(PPh$_3$)$_4$ or Pt(PPh$_3$)$_4$, produced only unreacted **1**.

Reaction of 1 and MCPBA. In a typical reaction, 173 mg (0.50 mmol) of **1** was dissolved in 10 mL of benzene and 110 mg (0.5 mmol) of MCPBA (of ca. 85% purity) was added in small portions with stirring. The reaction was observed to be exothermic. After 15 min, the solution was washed three times with saturated sodium bicarbonate and dried over MgSO$_4$; after evaporation of the solvent, the products were distilled by Kugelrohr distillation (100 °C (0.1 torr)) to give 170 mg of an oily mixture containing 87% **10**, 3% **11**, and 4% **1** (GLC analysis). A fourth product, which appears to be *m*-chlorobenzoic acid, was also observed. Separation by preparative GLC yielded pure **10**, a colorless oil: mass spectrum, selected m/e (relative intensity) 360 (66.0, M$^+$, 331 (91.3, M – C$_2$H$_5$), 303 (24.7, M – C$_2$H$_5$ – C$_2$H$_4$), 245 (20.6, Et$_5$Si$_3$O), 189 (10.8, HEt$_4$Si$_2$O), 172 (10.3, Si$_2$C$_5$H$_{20}$), 115 (26.4, Et$_3$Si), 87 (93.6, Et$_2$SiH), 59 (100, EtSiH$_2$); exact mass,

calcd 360.2145, measd 360.2146, dev 0.3 ppm; ^{1}H NMR δ 0.60–1.20 (m); IR (cm^{-1}) 1100–1000 (vs, br, Si–O).

When the MCPBA (0.5 mmol) was dissolved in 5.0 mL of benzene and added dropwise to a solution of **1** (0.5 mmol) in an equivalent volume of benzene, then 95% **10**, 1% **11**, and 4% **1** was formed. A similar reaction using 0.5 mmol of **1** and 1.0 mmol of MCPBA yielded 86% **11**, 9% **10**, and 5% **12**, while the same reaction but using 1.5 mmol of MCPBA gave 65% **12**, 25% **11**, and 10% **13**. Cyclotetrasiloxane **13** was the only oxidation product observed in the reaction of 0.5 mmol of **1** and 2.5 mmol of MCPBA.

Following workup of the appropriate reaction mixture, each of the cyclosiloxanes (Et$_2$Si)$_4$O$_n$, where n = 2–4, was obtained as a colorless oil by preparative-scale GLC. They all gave mass spectra and IR spectra similar to those of **10** but showed different ^{13}C (Table I) and ^{1}H NMR spectra. Dioxide **11** contained two isomers, **11a** and **11b**.

11: exact mass, calcd 376.2094, measd 376.2105, dev 2.9 ppm; ^{1}H NMR δ 1.09 (t, J = 7 Hz, 3 H), 0.87 (q, J = 7 Hz, 2 H).

12: exact mass, calcd 392.2043, measd 392.2053, dev 2.5 ppm; ^{1}H NMR δ 1.09 (t, J = 7 Hz, 3 H), 0.76 (q, J = 7 Hz, 2 H).

13: exact mass, calcd 379.1602, measd 379.1611, dev 2.4 ppm; ^{1}H NMR δ 1.10 (t, J = 7 Hz, 3 H), 0.64 (q, J = 7 Hz, 2 H).

Ring-Opening Reactions of 1. All reactions were carried out by using 172 mg of **1** (0.5-mmol scale). An inert atmosphere, typically N$_2$, was used in each case. The products, mainly colorless oils, were collected by Kugelrohr distillation (100–120 °C (0.1 torr)) and the yields then determined by GLC analysis.

1. Cl(Et$_2$Si)$_4$Cl, 14. Tetrasilane **1** was dissolved in 10 mL of benzene and 115 mg (0.55 mmol) of PCl$_5$ was added to the stirred solution. After 15 min, an aliquot was removed from the solution; GLC showed the reaction to be complete. Distillation yielded 203 mg (98%) of **14**: mass spectrum, selected m/e (relative intensity) 416 (0.1), 414 (0.1, M$^+$), 385 (0.3, M – C$_2$H$_5$), 379 (0.3, M – Cl), 295 (57.7), 293 (100, c-(Et$_2$Si)$_3$Cl), 265 (7.9, c-(Et$_2$Si)$_2$-(HEtSi)Cl), 179 (6.4, HEtSiEt$_2$SiCl), 172 (16.9, C$_8$H$_{20}$Si$_2$), 87 (14.8, Et$_2$SiH); exact mass, calcd 385.1184, measd 385.1191, dev 1.8 ppm; ^{1}H NMR δ 0.70–1.40 (m); IR bands (cm^{-1}) in the Si–Cl region were 502 (s), 465 (m), and 435 (w). Addition of water to a benzene solution of **14** produced **10** as the only product.

2. Br(Et$_2$Si)$_4$Br, 15. To **1** in 5 mL of benzene was added dropwise a mixture of 160 mg (0.5 mmol) of bromine and 5 mL of benzene. The bromine was observed to be decolorized instantly by the stirred solution of **1**. After the addition was completed, 245 mg of product was collected by distillation and found to contain 87% **15** and 4% **19** as well as several minor products thought to arise from hydrolysis. Tetrasilane **15** was isolated by GLC: mass spectrum, selected m/e (relative intensity) 477 (0.2), 475 (0.3), 473 (0.1, M – C$_2$H$_5$), 339 (100), 337 (86, c-(Et$_2$Si)$_3$Br), 311 (4.7), 283 (2.3), 172 (28.3), 87 (30.5); exact mass, calcd 477.0134, measd 477.0143, dev 1.9 ppm; ^{1}H NMR δ 0.90–1.10 (m); IR bands (cm^{-1}) in the Si–Br region were 460 (m), 398 (m), and 366 (s). Hydrolysis of **15** with moist THF led to high yields of the condensed product **10**.

3. I(Et$_2$Si)$_4$I, 16. The 1,4-diiodo derivative oxidizes rapidly, requiring that the reaction be carried out with degassed solvents under oxygen-free conditions. Pure **16** was obtained by adding a solution of 127 mg (0.5 mmol) iodine in 2 mL of benzene dropwise to a stirred solution of **1**, also in 2 mL of benzene. The deep purple color of the iodine solution was decolorized instantly by **1**. After the addition, the benzene was pumped off under vacuum and the product was redissolved in benzene-d_6 and transferred to an NMR tube. The ^{13}C NMR showed only the four resonances expected for **16**, and only ethyl resonances (δ 0.7–1.2, a multiplet) were seen by ^{1}H NMR. Extensive oxidation occurred during attempted mass spectral analysis, although a characteristic fragment, [c-(Et$_2$Si)$_3$I]$^+$ (exact mass, calcd 385.0694, measd 385.0700, dev 1.6 ppm), was present in low intensity. Addition of moist THF to samples of **16** formed mainly **10**.

4. H(Et$_2$Si)$_4$H, 17. Compound **1** was dissolved in 10 mL of THF, and several small scoops of LiAlH$_4$ were added. The mixture was stirred for 3 h and then quenched with dilute HCl. Following extraction with hexane, the organic layer was dried over MgSO$_4$ and then evaporated; distillation yielded 170 mg of product containing **17** (86%) and H(Et$_2$Si)$_3$H (13%). The two ethyl silanes were isolated by GLC. The properties of H(Et$_2$Si)$_3$H were

identical with those previously described.[5]

17: mass spectrum, selected m/e (relative intensity) 346 (4.4, M[+]), 317 (2.1), 259 (68.8, (Et$_2$Si)$_3$H), 231 (15.8), 203 (10.8), 172 (100, Si$_2$C$_8$H$_{20}$), 115 (20.9), 87 (36.5); exact mass, calcd 346.2352, measd 346.2365, dev 3.5 ppm; ^{1}H NMR (benzene-d_6) δ 3.99 (quintet, J = 3 Hz, 2 H), 0.70–1.30 (m, 40 H); IR (cm^{-1}) 2075 (s, Si–H).

5. H(Et$_2$Si)$_4$Cl, 18. A solution of 1 in 10 mL of benzene was shaken vigorously with an equivalent volume of concentrated, aqueous HCl (38%) at 5-min intervals and the progress of the reaction monitored by GLC. After 30 min, all of the 1 had reacted, and the organic layer was separated and dried briefly over MgSO$_4$. Filtration, followed by distillation, gave 185 mg (97%) of pure **18**, whose properties have previously been reported.[5]

6. H(Et$_2$Si)$_4$Br, 19. By a reaction analogous to that described for **18**, but using 48% aqueous HBr, 220 mg of product was obtained after a 30-min reaction and subsequent workup. The yield of **19** was 92%, and several minor products that appeared to arise from hydrolysis also formed. The tetrasilane was isolated pure by using preparative-scale GLC: mass spectrum, selected m/e (relative intensity) 426 (0.1), 424 (0.1, M[+]), 397 (1.6), 395 (1.4), 339 (100), 337 (90.1, c-(Et$_2$Si)$_3$Br), 311 (5.7), 259 (10.0), 172 (54.3), 87 (49.2); ^{1}H NMR δ 4.01 (quintet, J = 4 Hz, 1 H), 0.70–1.50 (m, 40 H); IR (cm^{-1}) 2080 (s, Si–H), bands in the Si–Br region were 360 (s), 399 (w), and 449 (w).

7. H(Et$_2$Si)$_4$OH, 20. To a solution of 190 mg (0.5 mmol) of **18** in 5 mL of THF was added 1 mL of water and several drops of pyridine. Extraction of the products with hexane, followed by distillation, gave essentially quantitative yields of **20**: mass spectrum, selected m/e (relative intensity) 333 (1.3, M – C$_2$H$_5$), 275 (100, (SiEt$_2$)$_3$OH), 247 (1.6), 189 (1.7), 172 (3.9), 87 (13.8); ^{1}H NMR δ 3.90 (quintet, J = 4 Hz, 1 H), 0.60–1.20 (m, 40 H); IR (cm^{-1}) 3670 (m, O–H), 3078 (s, Si–H), 700–800 (s, Si–O). An analogous reaction of **19** with water and pyridine also gave high yields of **20**.

8. H(Et$_2$Si)$_4$OEt, 21. A solution of 1 in 10 mL of absolute EtOH was refluxed for 48 h. Distillation then gave 186 mg (95%) of pure **21**: mass spectrum, selected m/e (relative intensity) 390 (0.1, M[+]), 361 (2.3), 303 (100, (EtSi)$_3$OEt), 275 (2.8), 217 (2.7), 189 (3.7), 87 (12.6); exact mass, calcd 390.2613, measd 390.2627, dev 3.6 ppm; ^{1}H NMR δ 3.91 (quintet, J = 4 Hz, 1 H), 3.58 (q, J = 7.2 Hz, 2 H), 0.70–1.30 (m, 40 H); IR (cm^{-1}) 2081 (s, Si–H), 1108 (s), 1080 (s, C–O), 960 (s, br, Si–O). Anal. Calcd for C$_{18}$H$_{46}$Si$_4$O: C, 55.31; H, 11.86. Found: C, 55.19; H, 12.06.

9. H(Et$_2$Si)$_4$OAc, 22. Cyclotetrasilane 1 was dissolved in 10 mL of glacial acetic acid and the solution refluxed. The reaction was followed by GLC and found to be complete after 2 h. Distillation provided **22** in ca. 99% yield: mass spectrum, selected m/e (relative intensity) 375 (0.4, M – C$_2$H$_5$), 360 (2.3), 317 (41.0), 275 (41.6), 231 (100, Et$_5$Si$_3$H$_2$), 145 (11.3, Et$_2$SiOCOCH$_3$), 87 (14.3), 43 (73.0, C$_2$H$_3$O); exact mass for M – C$_2$H$_5$, calcd 375.2016, measd 375.2028, dev 3.2 ppm; ^{1}H NMR (benzene-d_6) δ 3.92 (quintet, J = 4 Hz, 1 H), 1.82 (s, 3 H), 0.75–1.30 (m, 40 H); IR (cm^{-1}) 2081 (s, Si–H), 1720 (s, C=C), 960 (s), 930 (s, Si–O).

10. H(Et$_2$Si)$_4$Ph, 23, and Ph(Et$_2$Si)$_4$Ph, 24. A solution of ca. 2 mmol of PhLi in 15 mL of diethyl ether was freshly prepared from Li and bromobenzene;[19] then cyclosilane 1 was added and the solution refluxed. The reaction, as shown by GLC, was observed to be slow. After 6 days the mixture was quenched by slow addition of a dilute HCl solution and the organic layer was washed with water, dried over MgSO$_4$, and filtered. The products were distilled to yield 370 mg of the polysilanes, consisting of 27% **23**, 27% **24**, and 26% unreacted 1 as well as numerous minor products. The two tetrasilanes were isolated by preparative GLC of the mixture.

23: mass spectrum, selected m/e (relative intensity) 422 (3.3, M[+]), 335 (20.1, (Et$_2$Si)$_3$Ph), 259 (40.0), 249 (14.0, (Et$_2$Si)$_2$Ph), 172 (51.7), 163 (25.9, PhEt$_2$Si), 135 (100, PhEtSiH), 107 (29.4, PhSiH$_2$), 87 (31.2); exact mass, calcd 422.2664, measd 422.2677, dev 3.1 ppm;

^{1}H NMR (chloroform-d_1) δ 7.25–7.45 (m, 5 H), 3.60 (quintet, J = 4 Hz, 1 H), 0.60–1.20 (m, 40 H); IR (cm^{-1}) 3030–3080 (w, C=CH), 2080 (s, Si–H), 1575 (w), 1430 (m, C=C).

24: mass spectrum, selected m/e (relative intensity) 498 (5.6, M[+]), 335 (100, (Et$_2$Si)$_3$Ph), 307 (8.5, HEt$_5$Si$_3$Ph), 279 (2.6), 249 (18.2), 221 (16.8), 163 (6.7), 135 (17.2), 107 (19.1); exact mass, calcd 498.2976, measd 498.2991, dev 3.0 ppm; ^{1}H NMR (chloroform-d_1) δ 7.20–7.40 (m, 10 H), 0.50–1.00 (m, 40 H); IR (cm^{-1}) 3030–3080 (w, C=CH), 1580 (w), 1432 (m, C=C).

11. Reaction of 1 in CCl$_4$. When a mixture of 1 and 10 mL of undegassed CCl$_4$ were stirred at 25 °C for 24 h, the products (as shown by GLC) consisted of unreacted 1 (49%), **25** (38%), and **14** (6%). Reaction upon continued stirring was markedly slower, and 23% 1, 46% **25**, 11% **14**, and 4% **11** were present after 14 days. Similar results were observed for 1 in s-C$_2$H$_2$Cl$_4$.

Further investigation of the reaction of 1 in CCl$_4$ showed that degassing the solution (by several cycles of the freeze–pump–thaw method) inhibited the formation of **25**, although slow chlorination to **14** continued to be observed. If oxygen was bubbled through the solution, then the conversion of 1 to **25** was complete after 10 min; after evaporation of the solvent, there was obtained 210 mg of a mixture of products, consisting of 82% **25**, 6% **11**, and 6% **10**, from which the dichlorosiloxane **25** was obtained by preparative GLC. The mass spectrum showed contamination by the hydrolysis product from **25**, **11**, but a satisfactory peak match was obtained.

25: 430 (0.1, M[+]), 401 (1.4, M – C$_2$H$_5$), 376 (38.9, (Et$_2$Si)$_4$O$_2$), 347 (100, (Et$_2$Si)$_4$O$_2$ – C$_2$H$_5$), 311 (22.1), 309 (58.5, Et$_6$Si$_3$OCl), 172 (64.7), 87 (10.8); exact mass, calcd 430.1523, measd 430.1531, dev 1.9 ppm; ^{1}H NMR δ 0.80–1.40 (m); IR (cm^{-1}) 1070 (s, br, Si–O), bands in the Si–Cl region were 564 (m), 510 (m), and 481 (m).

No observable yield of **25** could be produced by stirring **10** in CCl$_4$ for 24 h or by stirring **14** in solutions of oxygen-saturated CCl$_4$ or benzene for identical lengths of time.

Hydrolysis of ca. 170 mg (0.40 mol) of **25** in 10 mL of CCl$_4$ using 1 mL of H$_2$O and several drops of pyridine formed **11b** (60%) and **26** (39%). From this mixture **11b** was isolated pure by preparative GLC. Its spectral properties, other than the ^{13}C NMR, did not vary noticeably from those of the mixed isomers of **11** obtained from MCPBA.

Dihydroxy compound **26** was obtained as a 1:2 mixture of **11b**–**26** by preparative-scale GLC. The ^{13}C NMR of this mixture contained peaks for **11b** plus the following resonances [δ (number of carbons)] 3.07 (2), 7.14 (4), 7.75 (2), 10.07 (2), 10.36 (2), 10.73 (4)]. The ^{1}H NMR of the mixture showed δ 0.50–1.30 (m, 60 H) and 5.05 (br s, ~1 H). Bands on the IR (cm^{-1}) were 3250 (s, br, O–H) and 1100–1000 (vs, Si–O). Mass spectra of the mixture gave only peaks assignable to **11**.

12. Other Attempts. No cleavage products derived from 1 were observed in reactions with Et$_2$NH (56 °C), H$_2$O (100 °C), MeLi in diethyl ether (35 °C), or Li powder in THF (25 °C). Reaction of 1 with a concentrated (triphenylsilyl)lithium solution gave only equilibration to the cyclopentasilane (Et$_2$Si)$_5$.

(19) Jones, R. G.; Gilman, H. *Org. React. (N.Y.)* **1951**, *6*, 339.