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# The Perethylcyclopolysilanes $(Et_2Si)_4$ through $(Et_2Si)_8$

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Diethyldichlorosilane reacts with alkali metals to produce the diethylcyclosilanes $(Et_2Si)_n$, $n = 4$–8. The products obtained from this reaction depend upon the alkali metal and the conditions: with 2.0 equiv of lithium in THF, the major products are $n = 5$ and $n = 7$; with excess potassium in THF, $n = 5$ is formed; and with sodium in toluene, $n = 4$ is the major product. Each of the cyclopolysilanes was characterized by $^1H$, $^{13}C$, and $^{29}Si$ NMR, UV, IR, Raman, and mass spectroscopy. Photolysis of $n = 5$–8 leads to elimination of $Et_2Si$ and formation of the next smaller ring.

## Introduction

Numerous investigations of the permethylcyclopolysilanes have been reported.[1] These substances exhibit unusual properties arising from electron delocalization in the $\sigma$ framework,[2] such as the formation of charge-transfer complexes[3] and delocalized anion[4] and cation radicals.[5] Despite the interest arising from the special electronic features of the alkylcyclopolysilanes, only lately has attention been given to compounds containing substituents other than methyl. The cyclotetrasilane isomers $(t\text{-BuMeSi})_4$ have been investigated,[6,7] and brief reports have appeared on the isolation of cyclopentasilanes $(R_2Si)_5$ (R = Et, $n$-Pr, $n$-Bu, and $i$-Bu)[8] and of $(i\text{-}Pr_2Si)_4$.[9]

In 1980 we communicated the synthesis of diethylcyclosilanes, $(Et_2Si)_n$.[10,11] Although the methyl and ethyl groups are very similar electronically, the steric bulk of the ethyl substituent is significantly greater, leading to differences between the two series of rings, some subtle and some rather marked. Such differences will be addressed in this paper.

## Results and Discussion

The perethylcyclopolysilanes are made by reaction of diethyldichlorosilane, $Et_2SiCl_2$, with an alkali metal (eq 1). The yields and compositions obtained from these

$$Et_2SiCl_2 + 2M \rightarrow (Et_2Si)_n + 2MCl \qquad (1)$$
$$n = 4\text{–}8$$

condensations depend strongly upon the choice of reaction conditions (Table I). The high degree of selectivity in these reactions is unusual; by contrast, $(Me_2Si)_6$ is the major product in all the analogous condensations of $Me_2SiCl_2$. Compounds $(Et_2Si)_4$, **4**, $(Et_2Si)_5$, **5**, and $(Et_2Si)_7$, **7**, may all be synthesized in high yields; $(Et_2Si)_6$, **6**, and $(Et_2Si)_8$, **8**, are obtained only as minor products, but **6** may be made indirectly by photolysis (vide infra).

Table I. Products from the Reactions of $Et_2SiCl_2$

| condtns for $Et_2SiCl_2$ + M | yields (wt %), $(Et_2Si)_n$, $n$ = 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|
| 2.0 equiv of Li, 0 °C, THF | 0 | 10 | 6 | 38 | 6 |
| 2.0 equiv of Li, −40, °C, THF | 0 | 7 | 15 | 33 | 2 |
| 10% excess of Li, 0 °C, THF | 0 | 29 | 4 | 22 | 2 |
| 10% excess of Li, 65 °C,[a] THF | 0 | 49 | 2 | 10 | trace |
| 2.0 equiv of potassium, 65 °C, THF[b] | 32 | 45 | trace | 0 | 0 |
| 10% excess potassium, 65 °C, THF | 0 | 91 | trace | 0 | 0 |
| 10% excess sodium, 110 °C, toluene[c] | 50 | 9 | 00 | 0 | 0 |

[a] Addition at 25 °C and stirred for 15 h at this temperature, and then refluxed 72 h at 65 °C. [b] Also contained a derivative of 4, **10** (8%). [c] Also contained derivatives of 4, **9** (6%) and **10** (5%).

The diethylcyclosilanes are all colorless crystals except for **4**, which is a viscous oil. Compounds **5**–**8** all melt over a broad temperature range and undergo visible-phase transitions below their melting points.[13] The larger cyclics **5**–**8** are inert to oxygen; **4**, a strained cyclotetrasilane, is moderately oxygen sensitive but is indefinitely stable if stored in an inert atmosphere.[14]

**Synthesis.** The reaction of $Et_2SiCl_2$ with greater than 2 equiv of potassium leads to high yields (91%) of the cyclic pentamer **5**. If instead exactly 2 equiv of potassium are used, a mixture of **4** (32%) and **5** (45%) is obtained. Minor products in the latter reaction include two derivatives of **4**: the oxidation product, c-$(Et_2Si)_4O$, **9**, and 1$H$-4-chlorooctaethyltetrasilane, **10**.[16] In order to reconcile these quite different results, the course of the reaction of $Et_2SiCl_2$ and excess potassium in refluxing THF was followed by GLC. Figure 1 shows the observed changes in the concentration of Si–Cl bonds following a very rapid

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(1) For reviews see: (a) West, R. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Chapter 9.4, p 365. (b) West, R.; Carberry, E. *Science (Washington, D.C.)* **1975**, *189*, 179.

(2) West, R. *Pure Appl. Chem.* **1982**, *54*, 1041.

(3) Traven, V. F.; West, R. *J. Am. Chem. Soc.* **1973**, *95*, 6824.

(4) Carberry, E.; West, R.; Glass, G. E. *J. Am. Chem. Soc.* **1969**, *91*, 5446.

(5) Bock, H.; Kaim, W.; Kira, M.; West, R. *J. Am. Chem. Soc.* **1979**, *101*, 7667.

(6) Helmer, B. J.; West, R. *Organometallics* **1982**, *1*, 1458 and references cited therein.

(7) Helmer, B. J.; West, R. *Organometallics* **1982**, *1*, 1463.

(8) Watanabe, H.; Muraoka, T.; Kohara, Y.; Nagai, Y. *Chem. Lett.* **1980**, 735.

(9) Watanabe, H.; Muraoka, T.; Kageyama, M.; Nagai, Y. *J. Organomet. Chem.* **1981**, *216*, C45.

(10) Carlson, C. W.; Matsumura, K.; West, R. *J. Organomet. Chem.* **1980**, *194*, C5.

(11) The synthesis of $(Et_2Si)_6$ has been reported previously.[12] However, there is doubt about the identity of the reported product, as discussed later in this paper.

(12) Bukhtiyarov, V. V.; Solodovnikov, S. P.; Nefedov, O. M.; Shiryaev, V. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1968**, *5*, 1012.

(13) The plastic crystalline behavior of $(Me_2Si)_5$ and $(Me_2Si)_6$ is described in: Larsen, D. W.; Soltz, B. A.; Stary, F. E.; West, R. *J. Phys. Chem.* **1980**, *84*, 1340.

(14) The chemistry of **4** is described in the accompanying paper.[15] Compound **4** is less reactive than the hindered cyclotetrasilanes $(t\text{-BuMeSi})_4$ and $(i\text{-}Pr_2Si)_4$, but less so than $(Me_2Si)_4$, which oxidizes rapidly in air and polymerizes slowly at room temperature. See: Ishikawa, M.; Kumada, M. *J. Organomet. Chem.* **1972**, *42*, 325.

(15) Carlson, C. W.; West, R. *Organometallics*, following paper in this issue.

(16) The formation of this tetrasilane results from the hydrolysis of unreacted Si–Cl bonds upon quenching the reaction, forming HCl which reacts with **4** to yield the cleavage product **10**. Further hydrolysis is slow under the (two-phase) conditions of the workup. This reaction is discussed in detail in ref 15.

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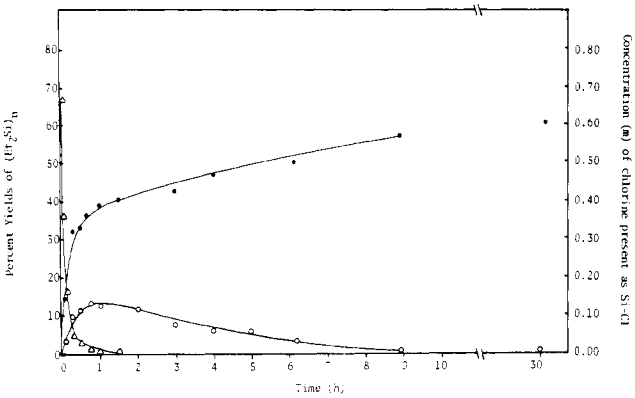

**Figure 1.** Progress of the reaction of $Et_2SiCl_2$ with potassium, showing percent yield of $(Et_2Si)_5$ (●), percent yield of $(Et_2Si)_4$ (○), and concentration of chlorine present as Si–Cl bonds (△).

(<1 min) addition of the chlorosilane. In the early stages of the reaction, the number of Si–Cl bonds is seen to drop rapidly, and both **4** and **5** appear and increase rapidly in yield. After the number of Si–Cl bonds have decreased to nearly zero, the yield of **4** levels off and then begins to fall. The amount of **5**, however, continues to rise. Beyond 10 h following the addition, **5** and a trace of **6** are the only cyclic products.[17]

It appears that **4** is a kinetic product in this reaction; following the disappearance of the Si–Cl bonds, it is equilibrated to the thermodynamically favored ring **5**. Similar ring-to-ring redistribution is well-known for permethylcyclopolysilanes, where equilibrium mixtures containing mainly $(Me_2Si)_6$ are obtained in the presence of sodium–potassium (Na/K) alloy[18] or silyllithium reagents.[19] The preference for the smaller five-membered ring in the perethylcyclosilanes can be attributed to the greater steric bulk of the ethyl groups.[20] In reactions using only 2 equiv (or less) of potassium, the yield of **5** is reduced, and the products are, at least in part, kinetically controlled.

Attempts to produce the equilibrium mixture of $(Et_2Si)_n$ rings by stirring **5** in THF in the presence of K or Na/K were unsuccessful, since equilibration under these conditions was rather slow and occurred at a rate comparable to decomposition of the cyclosilanes. Use of the more reactive **4** in place of **5**, however, led to faster rates of redistribution, permitting equilibrium to be approached. The observed composition at equilibrium, 96% **5**, 2% **4**, and 2% **6** at 30 °C, is similar to the product mixture resulting when $Et_2SiCl_2$ is treated with excess potassium.

The first reported synthesis of a perethylcyclopolysilane was by Nefedov and co-workers, who described **6** as the only product from the condensation of $Et_2SiCl_2$ with Li in THF.[12] However, the data given did not establish that the diethylcyclosilane formed was the hexamer. Our results show that although a small amount of **6** is obtained, the major products are instead **5** and **7**. The reaction of $Et_2SiCl_2$ using exactly 2 equiv of Li was found to give **7** (38%) as the major cyclic product and lesser amounts of **5** (10%), **8** (8%), and **6** (6%) (Table I). Similar results were observed when using a slight deficiency of Li. By contrast, the reaction of $Me_2SiCl_2$ with 2 equiv of Li yields a mixture containing $(Me_2Si)_6$ and $(Me_2Si)_8$ as the major cyclosilanes.[21] The reasons leading the preference for a cyclosilane *two units larger* than the thermodynamic ring size in both cases is not understood, but sterically dependent interactions on the Li surface may be involved.

If an excess of Li is used, the yields of **5** are much higher. Reaction of $Et_2SiCl_2$ with 10% excess Li in THF at 0 °C produced a mixture of **5**–**8**, initially containing **7** as its major component. The amount of each ring increased slowly; after ca. 4–6 h, the yields of the cyclosilanes resembled the product mixture obtained from $Et_2SiCl_2$ and 2.0 equiv of Li. After this, the yields of **6**, **7**, and **8** declined, while the amount of **5** continued to increase. The final product distribution was present after 24 h (Table I). These results show that **7**, **6**, and **8** are kinetic products in the reactions of $Et_2SiCl_2$ and Li; equilibration to **5** occurs upon stirring in the presence of Li. The highest yields of **7** and **8** are obtained if the $Et_2SiCl_2$ is added rapidly (~15 min) to the reaction vessel. If instead the addition of chlorosilane is extended over several hours, the amount of **5** increases, apparently because some equilibration occurs during the addition. The amount of **5** also increased when the reaction was carried out on a larger (0.60-mol) scale, probably because less efficient cooling in the larger reaction volume led to partial equilibration.

The reaction of dichlorosilanes with sodium metal in a nonpolar solvent usually produces polysilane polymers. For example, $Me_2SiCl_2$ reacts with sodium in toluene to give quantitative yields of poly(dimethylsilylene), and cocondensation of $Me_2SiCl_2$ and $MePhSiCl_2$ under similar conditions yields soluble phenylmethyl polysilane polymer.[22] Analogous attempts to produce poly(diethylsilylene) led to rather different results. When $Et_2SiCl_2$ is treated with excess sodium in refluxing toluene, the major product is **4**, typically obtained in 50% yield along with ~10% **5**; the remainder of the reaction product consists of soluble and insoluble polymers. Nearly all of the **4** and **5** (in an approximate 5:1 ratio) appears in the first 24 h of reaction; large numbers of Si–Cl bonds (ca. 15%) remained unreacted at this time. The Si–Cl bonds are reduced nearly to zero after 3–4 days at reflux temperature, coinciding with a small increase in the yield of cyclics. The rather slow disappearance of the chlorine in the later stages of the reaction is probably due to deactivation of the sodium by coatings of polymer and salts. No equilibration of **4** to **5** was observed in any of the reactions using sodium and toluene, most likely because ring-to-ring redistribution is slow in the absence of a strongly coordinating solvent such as THF.

Careful workup of products from the 0.60-mol scale reaction of $Et_2SiCl_2$ and sodium in toluene leads to isolation of ca. 12–13 g (46–50%) of **4** in purities of 95% or greater. Hence, this synthesis offers a convenient route to a reactive cyclotetrasilane.[23] By contrast, $(Me_2Si)_4$ is obtained in rather low yields from mixtures produced in the photolysis of $(Me_2Si)_6$ or by a difficult two-step procedure starting with $(Ph_2Si)_4$.[26]

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(17) The lower yield of **5**, 60% vs. the normal 75–85%, probably results from introduction of traces of water or other impurities into the reaction during the sampling procedure.

(18) Brough, L. F.; West, R. *J. Organomet. Chem.* **1980**, *194*, 139.

(19) Kumada, M.; Ishikawa, M.; Sakamoto, S.; Maeda, S. *J. Organomet. Chem.* **1969**, *17*, 223. Kumada, M.; Sakamoto, S.; Ishikawa, M. *Ibid.* **1969**, *17*, 231.

(20) The cyclic pentamer is also the most stable ring in the perphenyl series.[21] If larger substituents are present, even smaller rings are favored; for example, equilibration in the $(t\text{-BuMeSi})_n$ series yields only $(t\text{-BuMeSi})_4$.[6]

(21) Gilman, H.; Schwebke, G. L. *J. Am. Chem. Soc.* **1964**, *86*, 2693; Also unpublished studies by S.-M. Chen and R. West. Matsumura, K.; Brough, L. F.; West, R. *J. Chem. Soc., Chem. Commun.* **1978**, 1092.

(22) West, R.; David, L. D.; Djurovich, P. I.; Stearley, K. L.; Srinivasan, K. S. V.; Yu, H. *J. Am. Chem. Soc.* **1981**, *103*, 7352. West, R.; David, L. D.; Djurovich, P. I.; Yu, H.; Sinclair, R. *Am. Ceram. Soc. Bull.* **1983**, *62*, 899.

(23) Recent work in our laboratories has shown that other small-ring cyclosilanes, $(EtMeSi)_4$[24] and $[(CH_2)_5Si]_4$,[25] can be similarly be prepared.

(24) Carlson, C. W.; Katti, A.; West, R., unpublished work.

(25) Carlson, C. W.; Zhang, X.-H.; West, R. *Organometallics* **1983**, *2*, 453 and unpublished studies.

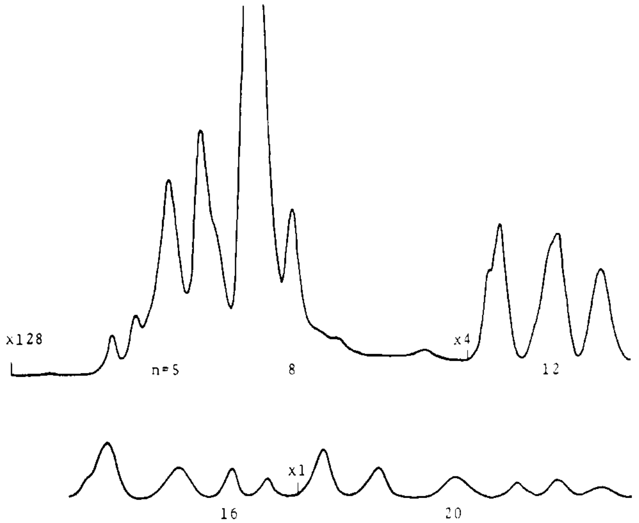

**Figure 2.** High-pressure liquid chromatogram of the products from the reaction of $Et_2SiCl_2$ and Li in THF at -40 °C, showing possible formation of cyclosilanes from $(Et_2Si)_5$ to $(Et_2Si)_{23}$.

Table II. NMR Data for the Perethylcyclopolysilanes

| $(Et_2Si)_n$, $n$ = | $^1H$,[a-c] ppm | $^{13}C$,[a,d] ppm | $^{29}Si$,[a] ppm |
|---|---|---|---|
| 4 | 1.117<br>0.914 | 11.04<br>3.64 | -16.04 |
| 5 | 1.134<br>0.893 | 10.82<br>3.81 | -30.36 |
| 6 | 1.167<br>1.017 | 10.88<br>5.47 | -30.49 |
| 7 | 1.179<br>1.107 | 10.82<br>5.69 | -30.03 |
| 8 | 1.194<br>1.104 | 10.88<br>6.35 | -27.70 |

[a] In $C_6D_6$; relative to internal $Me_4Si$. [b] 270 MHz. [c] Each shows non-first-order coupling with $J \simeq 7$ Hz. The downfield multiplet in each pair is an approximate triplet (3 H), and the upfield multiplet is an approximate quartet (2 H). [d] The intensity ratio for each pair is 1:1.

Nonequilibrium condensations of $Me_2SiCl_2$[27] or $(CH_2)_4SiCl_2$[25] have been shown to produce mixtures containing very large rings, but analogous attempts with $Et_2SiCl_2$ generally did not lead to similar products. However, when $Et_2SiCl_2$ was condensed with 2.0 equiv of Li at -40 °C, HPLC of the products indicated that larger rings were formed, up to $n = 23$ (Figure 2). Estimated yields were 0.1% for rings from $n = 9$ to $n = 14$, with gradually declining yields for still larger rings. These conditions also produce **6** in larger than usual amounts (Table I).

One possible explanation for the scarcity of large $(Et_2Si)_n$ rings is simply that the bulkiness of the ethyl groups inhibits ring closure in the medium-ring region, where destabilizing dihedral interactions (nonclassical strain) become important.[28] In the extended series of methylcyclosilanes $(Me_2Si)_n$ ($n$ = 5-35), sharply lowered yields are observed for $n$ = 7-10; it is suggested that this results primarily from the effects of nonclassical strain.[27] Such a strain effect may explain the abrupt drop from the usual 8% for $(Et_2Si)_8$ to the zero or near zero yields of $(Et_2Si)_9$.

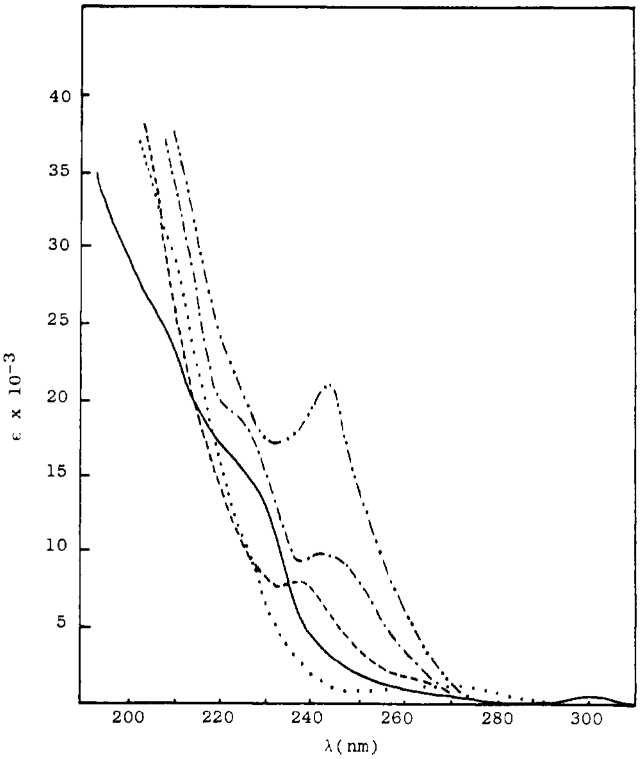

**Figure 3.** Ultraviolet absorption spectra of $(Et_2Si)_n$, $n$ = 4-8 (4, —; 5, ···; 6, - - -; 7, -·-; 8, -···).

Table III. Ultraviolet Spectral Data for $(Et_2Si)_n$, $n$ = 4-8

| $n$ | $\lambda_{max}$, nm ($\epsilon$)[a] |
|---|---|
| 4 | 304 sh (180), 228 sh (14 000), 211 sh (23 000) |
| 5 | 266 (1100),[b] 225 sh (11000), 210 sh (30 000) |
| 6 | 259 sh (1900), 237 (8000),[c] 205 sh (40 000)[c] |
| 7 | 257 sh (4400), 244 (9900),[c] 227 sh (18 000), 200 sh (60 000) |
| 8 | ~260 sh (6100), 244 (21 000), 221 sh (24 000), 196 sh (82 000) |

[a] In 2,2,4-trimethylpentane. [b] Probable doublet. [c] Replaces value given in ref 10.

**Spectroscopy.** The NMR chemical shifts for the perethylcyclopolysilanes are listed in Table II. The proton NMR is resolved, roughly, into an upfield quartet (the methylene group) and a downfield triplet (the methyl group) at 270 MHz. The observed coupling is not first order; the spectra closely resemble those of known $A_2B_3$ compounds such as diethyl sulfide. The $^{13}C$ spectrum of each ring consists of two lines in 1:1 ratio. Because the shielding effect of silicon should be greatest at the $\alpha$-position, the upfield line is assigned to the methylene carbon. The larger changes in chemical shift observed for the upfield resonances (as the ring size increases from four to eight) also support this assignment, since the $\alpha$-carbons are expected to be more sensitive than the $\beta$-carbons to changes in the ring environment. The chemical shift becomes more positive from $n = 6$ to $n = 8$; a similar trend was found in $\delta(^{29}Si)$ for the permethylcyclosilanes.[27] In **4** $\delta$ is shifted downfield to -16.04 ppm, perhaps due to the effect of ring strain on the Si-Si bonding in this molecule.

The ultraviolet spectra of **4**-**8** are shown in Figure 3 and their absorption maxima are listed in Table III. These compounds all have absorptions in the near-UV which are attributed to electronic transitions of the Si-Si $\sigma$ framework, probably involving excitation from delocalized $\sigma_{Si-Si}$ orbitals to an unfilled orbital with $\sigma^*$ or $\pi^*$ character. The number and positions of the $\lambda_{max}$ in the perethylcyclopolysilanes are similar, but not identical, to those of the

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[26] Hengge, E.; Schuster, H. G.; Peter, W. *J. Organomet. Chem.* **1980**, *186*, C45.

[27] Brough, L. F.; West, R. *J. Am. Chem. Soc.* **1981**, *103*, 3049.

[28] Such interactions account for the "medium-ring effect" observed in carbocyclic systems; for example, see: Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. "Conformational Analysis"; Wiley; New York; 1965; Chapter 4.

Table IV. Vibrational Spectra (100-500 $cm^{-1}$) for $(Et_2Si)_n$, $n = 4-8$

| 4 | | 5 | | 6 | | 7 | | 8 | |
|---|---|---|---|---|---|---|---|---|---|
| IR | Raman | IR | Raman | Ir | Raman | IR | Raman | IR | Raman |
| 479 w | | 496 vw | 491 w | | 473 w | | 464 w | | 479 w |
| 450 m, br | | | 464 w, br | 412 w | 400 m | | 458 m | | 439 w |
| 426 w | 432 m, sh, br | 448 w, br | | | | 410 w | | 413 vw | 411 m |
| 410 w, sh | 406 sh | | 395 m | 361 vw | | 392 w | | 346 m, br | |
| | | 338 m, br | | 434 w | | 381 vw | 384 m | | 306 w |
| 352 m | | | 252 w | 318 w | | | | | 253 w |
| 335 m | | | 224 m | | 300, w, br | 357 w | | | ~216 w, sh |
| 329 m, sh | | | 182 w, sh | | 273 w | 349 w, sh | | | 172 w, sh |
| | 282 m | | 136 m | | 234 s | 320 w | | | 141 m |
| | 225 m | | | | 156 m | | 269 w, sh | | 105 w |
| | 135 m | | | | 131 m | | 236 w | | |
| | | | | | 122 m | | 193 w | | |
| | | | | | | | 171 w | | |
| | | | | | | | 120 w | | |

analogous permethyl compounds,[27] as expected from the similar electronic nature of the ethyl and methyl groups. The small differences between the methyl and ethyl compounds may arise from conformational changes that result from the rather different steric effects of the two substituents. The long wavelength band for **4** at 304 nm is slightly lower in energy than the corresponding absorptions for $(t\text{-BuMeSi})_4$ (300 nm)[6] and $(i\text{-Pr}_2\text{Si})_4$ (290 nm).[9]

The infrared and Raman spectra of each of the perethylcyclosilanes were quite similar above 500 $cm^{-1}$, showing C–H, C–C, and C–Si modes. Below 500 $cm^{-1}$, the vibrational absorptions of each ring are rather different (Table IV). The long wavelength vibrational spectra are complex, containing Si–Si stretching bands (300–500 $cm^{-1}$), ring deformations (below 300 $cm^{-1}$), and $SiC_2$ modes.[29]

**Photolysis.** Photolysis of the perethylcyclopolysilanes at 254 nm leads to ring contraction and concurrent elimination of diethylsilylene, $Et_2Si$, much as has previously been observed for the permethyl compounds.[14] The photolysis proceeds in a stepwise fashion, leading to mixtures of the cyclosilanes down to $n = 4$ in size. For example, irradiation of a cyclohexane solution of **7** led to 14% **4**, 32% **5**, 22% **6**, and 25% recovered **7** after 15 min. Photolysis appears to occur most rapidly for the larger rings. The presence of diethylsilylene was confirmed by photolysis of **7** in the presence of $Et_3SiH$, to give the trapped product pentaethyldisilane (68%), **11**. A second product, 1,1,1,2,2,3,3-heptaethyltrisilane (24%), **12**, was also formed, apparently by insertion of a second diethylsilylane into **11**.

Irradiation of an isooctane solution of **4** in the presence of $Et_3SiH$ for 16 h led to high yields of **11** and **12** and lower yields of 1,1,2,2,3,3-hexaethyltrisilane (31%), **13**. Trisilane **13** perhaps results from elimination of $Et_2Si$ from **4**, giving the unstable hexaethylcyclotrisilane. Subsequent ring opening to a 1,3 diradical and hydrogen abstraction would then form **13**. Other routes, including generation of the diradical directly without formation of the intermediate cyclotrisilane, are also possible. Photolysis of $(Me_2Si)_6$ leads initially to $(Me_2Si)_5$ and $(Me_2Si)_4$; continued irradiation then gives $H(Me_2Si)_4H$, ascribed to an analogous ring opening by $(Me_2Si)_4$.[7] By contrast, no $H(Et_2Si)_4H$ was observed in the photolysis of **4**.

Photolysis of samples rich in **7** offers a convenient route to cyclosilane **6**, otherwise available only in low yields from reactions of $Et_2SiCl_2$ and Li. Mixtures suitable for preparative HPLC and containing up to 25% **6** may be obtained in this fashion.

## Experimental Section

**Methods.** Diethyldichlorosilane is commercially available and was distilled before use. Tetrahydrofuran (THF) was predried over KOH and distilled from lithium aluminum hydride. Toluene and xylene were refluxed over sodium for 12–24 h and then distilled. Diethyl ether was distilled from lithium aluminum hydride, and benzene was predried over molecular sieves and distilled from sodium benzophenone. Preformed Na/K alloy (78% potassium by weight) was obtained from Callery Chemical Co. Elemental analyses were done by Galbraith Laboratories, Knoxville, TN. All reactions were carried out by using oven-dried glassware under at atmosphere of dry nitrogen or argon. Syringe and Schlenk techniques were used in the handling of moisture- or oxygen-sensitive compounds. Aliquots from reaction mixtures were withdrawn by syringe; for reactions of potassium or Na/K, the syringe was equipped with a glass wool filter.

Yields were determined by analytical GLC using $C_{28}H_{58}$ as an internal standard, and the values were corrected for different responses of the cyclosilanes and the standard on the detector. To analyze solutions for the concentration of chlorine present as Si–Cl, 4 mL of the sample was added to an equivalent volume of water; the resulting solution was then titrated by using a standardized sodium hydroxide solution to phenolphthalein end point.

**Chromatography.** Analytical scale GLC analyses were done on a Hewlett-Packard 5720A gas chromatograph equipped with a flame-ionization detector. A 2.5 ft × $^1/_8$ in. Dexsil column (5% on Chromosorb W) was used to observe the perethylcyclopolysilanes, while more volatile compounds were analyzed with a longer (6 or 20 ft) SE-30 column (20% on Chromosorb W). Preparative GLC was carried out with a Varian Model 90-P chromatograph equipped with a thermal conductivity detector using a 5 ft × $^3/_8$ in. Dexsil column (5% on Chromosorb W) or a 6 ft × $^3/_8$ in. SE-30 column (20% on Chromosorb W). HPLC separations were done with a Waters Associates 6000 LC pump equipped with a Whatman M-9 ODS-9 semipreparative column and an Altex Model 153 UV detector. The mobile phase for HPLC consisted of MeOH and THF mixtures of various compositions, usually 65% MeOH and 35% THF.

**Spectroscopy.** NMR spectra were determined in benzene-$d_6$ by using $Me_4Si$ as an internal standard. $^1H$ NMR spectra were obtained by using either a JEOL MH-100 or a Brüker 270-MHz spectrometer. $^{13}C$ NMR were collected on a JEOL FX-60 spectrometer operating at 15.04 MHz, and $^{29}Si$ NMR were run on a JEOL FX-200 operating at 39.60 MHz. The $^{29}Si$ spectra were obtained by using the INEPT method with $\Delta = 25.7$ ms and $\tau = 38.5$ ms.[30]

Mass spectra were obtained at 70 eV with a Kratos MS902C mass spectrometer. Ultraviolet spectra were recorded on a Cary 118 spectrophotometer using spectrograde isooctane. IR spectra were recorded with a Perkin-Elmer 457 spectrometer. NaCl liquid IR cells were used above 600 $cm^{-1}$ using both $CHCl_3$ and $CS_2$ as solvents; spectra below 600 $cm^{-1}$ were obtained by using a Nujol mull on CsI plates. Raman spectra were measured in the range

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(29) Detailed studies of the vibrational spectra of cyclopolysilanes can be found in the following: (a) Hofler, F.; Bauer, G.; Hengge, E. *Spectrochim. Acta, Part A*, **1976**, *32A*, 1435. (b) Hassler, K.; Hengge, E.; Kovar, D. *Ibid.* **1978**, *34A*, 1193. (c) Hengge, E.; Lunzer, F. *Monatsch. Chem.* **1976**, *107*, 371.

(30) Helmer, B. J.; West, R. *Organometallics* **1982**, *1*, 877.

100–3500 cm$^{-1}$ on a Spex Ramalog-4 laser spectrometer, using neat samples contained in glass capillaries.

**Synthesis. 1. Reaction of $Et_2SiCl_2$ with Potassium.** Small chunks of potassium (8.60 g, 0.22 mol) were added to 300 mL of dry THF contained in a 1-L flask equipped with a mechanical stirrer, a condenser, and a $N_2$ inlet. The reaction was stirred at reflux until the potassium had melted and dispersed into small beads. Then $Et_2SiCl_2$ (15.7 g, 0.10 mol) was added over 3 h. The solution slowly turned blue upon addition of the chlorosilane and eventually became a deep blue-green. The reaction mixture was stirred at reflux for an additional 15.5 h and then was allowed to cool. Hexane (200 mL) was added, and the potassium was quenched by *very slow dropwise* addition of water. The solution initially became quite viscous, but continued addition of water gradually reduced the viscosity. After 100 mL of water had been added, the solution was stirred for 0.5 h and filtered and the organic layer was washed with water and dried over $MgSO_4$. Evaporation of the solvent then gave 8.70 g of a clear viscous oil. GLC analysis showed the products to be 91% **5** and 6% cyclo-$(Et_2Si)_5O$; a trace of **6** was also observed. Additional runs showed that **5** could consistently be obtained in 75–85% yields by this procedure. Preparative HPLC, or careful Kugelrohr distillation (120 °C (1 torr)), gave pure **5**, a greasy colorless solid: mp 151–155 °C; mass spectrum, selected *m/e* (relative intensity) 432 (15.5), 431 (32.7), 430 (75.7, $M^+$), 401 (3.4, $M - C_2H_5$), 287 (15.4, $Si_3Et_7$), 259 (7.0, $Si_3Et_6H$), 173 (10.5, $Si_2Et_4H$), 171 (6.7), 115 (21.5, $Et_3Si$), 87 (100, $Et_2SiH$); exact mass measd 430.2757, calcd 430.2745, dev 1.9 ppm. Anal. Calcd for $C_{20}H_{50}Si_5$: C, 55.73; H, 11.69; Si, 32.58. Found: C, 55.73; H, 11.80; Si, 32.29.

c-$(Et_2Si)_5O$ was isolated by GLC as a colorless oil and identified by its mass spectrum: selected *m/e* (relative intensity) 448 (10.6), 447 (23.4), 446 (59.2, $M^+$), 417 (100, $M - C_2H_5$), 389 (4.8, $M - C_2H_5 - C_2H_4$), 331 (16.5, $Si_4Et_7O$), 217 (7.4, $HSi_3Et_4O$), 173 (25.5, $HSi_2Et_4$).

When the reaction of potassium and THF was carried out as described above, but with only 2.00 equiv of potassium (7.8 g, 0.20 mol), a blue (rather than a blue-green) color was formed. After a 2-h addition of $Et_2SiCl_2$, the solution was refluxed for an additional 18 h and 8.9 g of product was obtained after the usual workup. By GLC analysis, the product consisted of 14% **4**, 31% **5**, 2% **6**, and 1% **7**, as well as two derivatives of **4**: **9** (1%) and **10** (8%). A second attempt using 31.4 g (0.20 mol) of $Et_2SiCl_2$, 15.6 g (0.40 mol) of potassium, and 500 mL of THF resulted in 32% **4**, 45% **5**, 8% **10**, and no **6**, **7**, or **9**. Preparative GLC, or preparative HPLC using carefully degassed solvents, led to pure **4**, a colorless oil: mass spectrum, selected *m/e* (relative intensity) 346 (13.2), 345 (30.0), 344 (100, $M^+$), 316 (13.4), 287 (10.5), 228 (22.5), 200 (33.6), 173 (12.8), 171 (21.7), 115 (21.7), 87 (57.4); exact mass, measd 344.2207, calcd 344.2196, dev 3.2 ppm. Anal. Calcd for $C_{16}H_{40}Si_4$: C, 55.73; H, 11.69; Si, 32.58. Found: C, 55.53; H, 11.82; Si, 32.27.

Tetrasilane **10** was obtained from the above reaction mixture by preparative GLC as a colorless oil: mass spectrum, selected *m/e* (relative intensity) 382 (0.2), 381 (0.3), 380 (0.4, $M^+$), 351 (1.8), 323 (0.6), 296 (12.2), 295 (55.2), 294 (30.3), 293 (100, $Si_3Et_6Cl$), 265 (14.6), 259 (8.2), 207 (1.4), 172 (82.0), 144 (10.8); $^{13}C$ NMR ($C_6D_6$) $\delta$ (number of carbons) 10.99 (2), 10.66 (4), 10.44 (2), 7.40 (2), 4.58 (2), 4.25 (2), 3.48 (2); $^1H$ NMR ($C_6H_6$) $\delta$ 3.88 (quintet, $J = 3.5$ Hz, 1 H), 0.6–1.6 (m, 40 H); IR (cm$^{-1}$; in $CHCl_3$) 2080 (Si–H). Shaking a toluene solution of **4** with concentrated aqueous HCl led to quantitative yields of a product whose properties were identical with those of **10**.

When THF solutions of **4** were exposed to air, oxidation occurred, and pure **9** was subsequently obtained by preparative GLC as a colorless oil: mass spectrum, selected *m/e* (relative intensity) 363 (1.4), 362 (8.1), 361 (20.5), 360 (60.0, $M^+$), 331 (91.3, $M - C_2H_5$), 303 (24.7, $M - C_2H_5 - C_2H_4$), 273 (47.9), 245 (20.6), 215 (19.5), 187 (13.3), 159 (24.1), 87 (93.6, $HSiEt_2$), 59 (100, $H_2SiEt$); exact mass, measd 360.2146, calcd 360.2145, dev 0.3 ppm; $^{13}C$ NMR ($C_6D_6$) $\delta$ (number of carbons) 10.93 (4, $O-Si-SiCH_2CH_3$), 9.50 (4, $O-SiCH_2CH_3$), 7.07 (4, $O-SiCH_2CH_3$), 2.04 (4, $O-Si-SiCH_2CH_3$); $^1H$ NMR ($C_6D_6$) $\delta$ 0.60–1.20 (m); IR (cm$^{-1}$, neat) 1000–1050 (Si–O).

When the reaction of potassium (0.22 mol) and $Et_2SiCl_2$ (0.1 mol) was carried out in benzene or toluene, very complex product mixtures were obtained. Analysis by GLC showed >50 products to be present. A control experiment in which potassium alone was stirred in toluene for several days led to a slight discoloration of the solvent, but no change was detectable by GLC. If heptane was used as the solvent, low yields of **4** (11%) and **5** (4%) resulted. Insoluble and soluble polymers accounted for much of the remaining yield in this reaction. A further modification that was attempted was the "slow addition" method (useful for formation of very large rings[27]). This reaction was carried out as described above, except that the chlorosilane was added over 7.5 h and then the reaction was quenched after being stirred only an additional 0.5 h. The product contained 17% **4**, 45% **5**, 1% **6**, and 7% **10**, and HPLC analysis showed that no large rings were present.

If 7.3 g of Na/K alloy (78% potassium by weight, 0.22 mol) in 300 mL of THF was reacted with $Et_2SiCl_2$ (0.10 mol) and quenched (after 16 h of reflux) as described above for potassium, workup (including passage through a short alumina column) yielded 6.2 g of a white oil. Analysis of the mixture by GLC showed only low yields of **5** (25%) and **6** (1%) and no other volatile products. A precipitate, possibly a polymer, was observed in hexane solutions of the product but was not investigated closely. An identical reaction, but refluxing for 6 days, increased the yield of **5** slightly, to 35%. The best yields of **5** resulted when the reaction of Na/K and $Et_2SiCl_2$ was attempted at 25 °C: 59% **5**, 2% **6**, and 3% **7** were obtained after 21 h of stirring.

**2. Reaction of $Et_2SiCl_2$ with Lithium.** Into a 1-L flask equipped with a mechanical stirrer and an $N_2$ inlet were added 600 mL of dry THF and 2.0 equiv (2.78 g, 0.4 mol) of Li wire. Then $Et_2SiCl_2$ (31.4 g, 0.2 mol) was added dropwise with stirring over 15 min during which the temperature was maintained at 0 °C. The mixture was stirred an additional 20.5 h at 0 °C, and the resulting colorless solution was filtered. Approximately 300 mL of hexane was added, and the solution was washed with water, dried over anhydrous $MgSO_4$, concentrated, and passed through a short alumina column, giving 15.5 g of a white, waxy solid. GLC analysis showed the yields to be 10% **5**, 6% **6**, 38% **7**, and 6% **8**; small amounts (ca. 10%) of noncyclic products were also observed. Preparative HPLC of the product mixture led to the isolation of **6**, **7**, and **8**.

**6**: colorless crystals; mp, preshrinkage 206 °C, cloudy melt 207–209 °C, clear melt 212–215 °C; mass spectrum, selected *m/e* (relative intensity) 520 (1.7), 519 (6.3), 518 (19.0), 517 (33.5), 516 (66.2, $M^+$), 487 (2.5), 371 (23.5), 345 (4.3), 173 (11.3), 145 (10.5), 115 (34.3), 87 (100); exact mass, measd 516.3309, calcd 516.3294, dev 2.9 ppm. Anal. Calcd for $C_{24}H_{60}Si_6$: C, 55.73; H, 11.69; Si, 32.58. Found: C, 55.47, H, 11.86, Si, 32.50.

**7**: colorless crystals; mp, preshrinkage 224 °C, cloudy melt 226–228 °C, clear melt 239–245 °C; mass spectrum, selected *m/e* (relative intensity) 605 (3.2), 604 (8.6), 603 (13.8), 602 (20.6, $M^+$), 487 (1.2), 401 (30.3), 373 (18.6), 372 (16.4), 371 (28.0), 345 (11.7), 343 (11.2), 287 (36.5), 259 (19.9), 173 (27.6), 145 (29.0), 115 (58.5), 87 (100); exact mass, measd 602.3864, calcd 602.3843, dev 3.5 ppm. Anal. Calcd for $C_{28}H_{70}Si_7$: C, 55.73; H, 11.69; Si, 32.58. Found: C, 55.38; H, 11.62; Si, 32.38.

**8**: colorless crystals; mp, preshrinkage at 235–236 °C, cloudy melt 238–239 °C, clear melt 246–254 °C; mass spectrum, selected *m/e* (relative intensity) 692 (1.4), 690 (10.8), 689 (17.2), 688 (23.6, $M^+$), 602 (4.9), 487 (16.9), 401 (47.2), 373 (27.2), 372 (27.4), 371 (33.7), 345 (7.6), 287 (79.7), 259 (12.4), 173 (20.7), 145 (25.0), 115 (65.1), 87 (100); exact mass, measd 688.4416, calcd 688.4392, dev 3.5 ppm. Anal. Calcd for $C_{32}H_{80}Si_8$: C, 55.73; H, 11.69; Si, 32.58. Found: C, 55.71; H, 11.98; Si, 32.88.

When the reaction was carried out by using a 10% deficiency of Li, a similar kinetic product distribution was obtained. A large-scale reaction (0.60 mol of $Et_2SiCl_2$, 1.20 mol of Li, 1.5 L of THF) led to a mixture containing 25% **5**, 6% **6**, 26% **2**, and 8% **8**. Carrying out the reaction at −40 °C increased the yield of **6** (see Table I). Reactions with 10% excess Li led to larger amounts of **5**. The amounts of **5** were also increased either by carrying out the reaction at higher temperatures (25 °C) or by adding di-*tert*-butylbiphenyl as an electron-transfer catalyst. Attempts to condense $Et_2SiCl_2$ with Li in diethyl ether gave no reaction either at 0 °C or a reflux temperature.

No insoluble polymer was isolated from these reactions. However, a white, slightly soluble material, presumably low molecular weight poly(diethylsilylene) polymer, was present. This polymer could be obtained as a precipitate by addition of 2-propanol to a solution of the reaction product in THF, or a as a residue upon exhaustive sublimation, and resembled the polymer formed during the photolysis of perethylcyclopolysilanes. It was not detectable by GLC or HPLC. Passage through a short chromatography column was effective in removing most, but not all, of the polymer.

**3. Reaction of $Et_2SiCl_2$ and Sodium.** In a typical reaction, 300 mL of dry toluene was placed in a 1-L flask equipped with a mechanical stirrer, condenser, and positive pressure of argon. Excess sodium (5.52 g, 0.24 mol) was added and the solution was refluxed, causing the sodium to melt and disperse. To the stirred, refluxing solution was added $Et_2SiCl_2$ (15.7 g, 0.10 mol) dropwise over 2 h. The reaction became a deep purple color. The solution was stirred at reflux for 3 h and then was cooled and quenched by dropwise addition of water. Filtration gave 0.55 g (6%) of white, insoluble polymer. The organic layer was separated and concentrated, giving 7.95 g of a white viscous oil containing the cyclosilanes; GLC showed 50% **4**, 9% **5**, trace **6**, 5% **9**, and 6% **10**. A small amount (ca. 15–20%) of toluene-soluble polymer was also present; like the polymer from Li reactions, it can be observed by precipitation or as a residue upon sublimation.

Modification of the workup in the following fashion minimized the formation of **9** and **10**: at regular intervals, the solution was cooled and the solids were allowed to settle. A 2-mL aliquot was withdrawn by syringe, and the sample was examined by GLC before and after being shaken with several milliliters of water. Conversion of **4** to **10** showed that reactive Si–Cl bonds were present in the solution.[16] When little or no conversion was detected (usually after ca. 72 h of reflux), then the solution was cannulated through a glass wool filter into a separate flask while the argon atmosphere was carefully maintained. The toluene was now removed by distillation at reduced pressure and the product distilled by the Kugelrohr method (100 °C (0.1 torr)). Reaction of 0.60 mol of $Et_2SiCl_2$ with 0.70 mol of Na followed by workup by this modified procedure gave 12.6 of clear oil, containing 95% **4**, 3% **5**, and 2% **9** (net yield of 47% **4**). Numerous runs showed that **4** could be consistently obtained in yields up to 50% in purities of ~95% by this simple procedure.

Attempted condensation of $Et_2SiCl_2$ (0.10 mol) and sodium dispersion (0.22 mol) in 300 mL of THF led to slow reaction and only traces of cyclosilanes. A reaction of $Et_2SiCl_2$ (0.10 mol) and sodium (0.22 mol) in 30 mL of refluxing xylene yielded 1.24 g (14%) of white, powdery, insoluble polymer. GLC analysis of the soluble fraction showed that **4** and **5** were present in yields of 35% and 7%, respectively. A second trial gave similar yields of **4** and **5**, but formed 22% insoluble polymer.

**Equilibration of $(Et_2Si)_n$.** Typically, 172 mg (0.5 mmol) of **4** was dissolved in 10 mL of dry THF, and the solution was degassed by the freeze–pump–thaw method. About 10 thinly sliced pieces of potassium were added, and the solution was stirred under $N_2$ at 30 °C. The progress of the reaction was monitored by GLC. Rearrangement to **5** was observed to begin immediately, and the solution gradually became light yellow. When small aliquots of the solution were exposed to air, this yellow color disappeared, suggesting that unstable species (such as polysilane anion radicals) were present. After 10 h, there was present a mixture of 96% **5**, 2% **4**, and 2% **6** which remained largely unchanged for an additional 14 h. After 24 h, a second yellow color appeared which was not quenched by air. This was coincident with the disappearance of **4** and the appearance of new, noncyclic, peaks on the GLC. Similar results were obtained by using Na/K alloy.

When **5** was used as the starting material in the equilibration with potassium (THF, 60 °C), small amounts of **4** and **6** appeared slowly and reached a maximum after about 12 h. When **7** and potassium (THF, 60 °C) were used, the disappearance of **7**, the formation of **5**, and the formation of accompanying traces of **4** and **6** were complete after 21 h. In solutions of both **5** and **7**, the onset of decomposition was observed before a constant composition of cyclosilanes was attained.

**Photolysis of $(Et_2Si)_n$.** A solution containing 21 mg (0.035 mmol) of **7**, 3.0 mL of spectrograde cyclohexane, and $C_{28}H_{58}$ as an internal standard was degassed and photolyzed in a quartz tube at 254 nm by using a Rayonet photochemical reactor. The progress of the reaction was monitored by GLC, and yields were determined by GLC analysis. After 15 min, 14% **4**, 32% **5**, 22% **6**, and 25% unphotolyzed **7** were present. Continued photolysis further decreased the yields of the larger rings and led to the formation of a polymeric precipitate, which was believed to be poly(diethylsilyene). There was 40% **4**, 22% **5**, and 1% **6** present after 45 min. A similar photolysis of **5** (16.5 mg, 0.038 mmol) in 3.0 mL of cyclohexane was observed to proceed with slower disappearance of the starting material and gave 31% **4** and 16% **5** after 40 min. Polymer and minor yields of volatile products were present as well. A trapping experiment using a degassed solution of 21 mg (0.035 mmol) of **7**, 35 mg (9.3 mmol) of distilled triethylsilane ($Et_3SiH$), and 3.0 mL of spectrograde cyclohexane led to yields of 68% $Et_3SiEt_2SiH$, **11**, and 24% $Et_3SiEt_2SiEt_2SiH$, **12** (based on elimination of four $Et_2Si$ units/molecule of **7**) after 1 h of photolysis. The mixture also contained 8% **5**, 28% **4**, and several minor products. Evaporation of the solvent followed by preparative GLC allowed the isolation of **11** and **12**.

**11**: colorless oil; mass spectrum, selected *m*/*e* (relative intensity) 204 (1.0), 203 (3.7), 202 (27.4, $M^+$), 173 (11.5, $M - C_2H_5$), 145 (20.2, $M - C_2H_5 - C_2H_4$), 117 (32.5, $Et_2Si_2H_3$), 115 (100, $Et_3Si$), 87 (75.3, $Et_2SiH$), 59 (58.7, $EtSiH_2$); exact mass measd 202.1573, calcd 202.1566, dev 3.5 ppm; $^{13}C$ NMR ($C_6D_6$) $\delta$ (number of carbons) 10.47 (2, $Si(Et)(H)(CH_2\mathit{C}H_3)$), 8.57 (3, $Si{-}SiEt_2CH_2\mathit{C}H_3$), 4.41 (3, $Si{-}SiEt_2\mathit{C}H_2CH_3$), 2.66 (2, $H{-}Si{-}\mathit{C}H_2CH_3$); $^1H$ NMR ($C_6D_6$) $\delta$ 3.83 (quintet, $J = 3.5$ Hz, 1 H, Si–H), 1.04 (t, $J = 6$ Hz, 15 H, $CH_3$), 0.70–0.86 (m, 10 H, $CH_2$); IR ($cm^{-1}$, neat) 2079 (vs, (Si–H).

**12**: colorless oil; mass spectrum, selected *m*/*e* (relative intensity) 289 (1.3), 288 (4.9, $M^+$), 259 (2.1, $M - C_2H_5$), 231 (1.2, $M - C_2H_5 - C_2H_4$), 172 (100, $C_8H_{20}Si_2$), 145 (14 (14.0, $Et_3Si_2H_2$), 117 (11.6, $Et_2Si_2H_3$), 115 (24.2, $Et_3Si$), 87 (40.9, $Et_2SiH$), 59 (45.5, $EtSiH_2$); exact mass for $M^+$, measd 288.2124, calcd 288.2115, dev 3.1 ppm; for $M - C_2H_5$, measd 259.1732, calcd 259.1725, dev 2.7 ppm; $^{13}C$ NMR ($C_6D_6$) $\delta$ (number of carbons) 10.68 (4), 8.74 (3), 4.95 (3), 3.81 (2), 3.31 (2); $^1H$ NMR ($C_6D_6$) $\delta$ 3.94 (m, 1 H, Si–H), 1.05 (t, $J = 6$ Hz, 21 H, $CH_3$), 9.65–0.95 (m, 14 H, $CH_2$); IR ($cm^{-1}$, (neat) 2080 (vs, Si–H).

When **4** (172 mg, 0.50 mmol) was photolyzed in 8.0 mL of degassed, spectrograde isooctane in a quartz tube at 254 nm in the presence of $Et_3SiH$ (580 mg, 5 mmol) for 15 h, five major products were obtained: **4** (12 mg, 7%); $H(SiEt_2)_3H$ (40 mg, 31%), **13**; silylene adducts **11** (186 mg) and **12** (52 mg) (62% and 24%, respectively, based on two units of $Et_2Si$ lost/molecule of **4**); and $Et_3SiSiEt_3$ (37 mg). The yields were determined by GLC analysis. No polymeric precipitate was observed, and except for the above compounds, only minor products were observed to elute after $Et_3SiH$ on the GLC. The solution was concentrated and the major products were isolated by GLC; **13** and $Et_3SiSiEt_3$ were identified by their mass spectra and NMR spectra. **13**: a colorless oil; mass spectrum, selected *m*/*e* (relative intensity) 261 (2.5), 260 (8.7, $M^+$), 231 (3.7, $M - C_2H_5$), 203 (1.4, $M - C_2H_5 - C_2H_4$), 172 (100, $C_8H_{20}Si_2$), 145 (34.4, $Et_3Si_2H_2$), 117 (27.6, $Et_2Si_2H_3$), 115 (13.1, $Et_3Si$), 87 (37.4, $Et_2SiH$), 59 ($EtSiH_2$); exact mass, measd 260.1812, calcd 260.1803, dev 3.5 ppm; $^{13}C$ NMR ($C_6D_6$) $\delta$ (number of carbons) 10.54 (6, $CH_3$), 3.71 (2, $(Et_2HSi)_2Si\mathit{C}H_2CH_3$), 3.14 (4, $Si{-}Si(H)(Et)\mathit{C}H_2CH_3$); $^1H$ NMR ($C_6D_6$) $\delta$ 3.94 (quintet, $J = 3.5$ Hz, 1 H, Si–H), 1.13 (t, $J = 6$ Hz, 18 H, $CH_3$), 0.70–0.92 (m, 12 H, $CH_2$); IR ($cm^{-1}$, neat) 2080 (vs, Si–H). The mass spectrum and $^1H$ NMR of $Et_3SiSiEt_3$ has previously been reported;[30] its $^{13}C$ NMR consisted of two lines, at $\delta$ 8.66 and 4.45, in 1:1 ratio.

Photolysis was used to increase the yields of **6** prior to its isolation by HPLC. Typically, 1.60 g of a mixture of cyclosilanes (consisting of 22% **5**, 6% **6**, and 72% **7**) was photolyzed in 75 mL of distilled, degassed cyclohexane in a quartz vessel at 254 nm. After 175 min the solvent was evaporated to give 1.55 g of an oily solid now containing 6% **4**, 25% **5**, 25% **6**, and 24% **7**.

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