

performing the X-ray analysis of acetate **23**.

Registry No. 1, 41451-75-6; **9a**, 95531-75-2; **9a** (methyl ester), 95531-76-3; **9a** (methyl ester, diethyl ketal), 95531-77-4; **9b**, 95532-00-6; **10a**, 95531-78-5; **10b**, 95532-01-7; **11a**, 95532-02-8; **11b**, 95532-03-9; **12**, 95532-04-0; **13**, 95531-79-6; **14**, 95531-80-9; **16**, 95531-81-0; **17**, 95531-82-1; **18**, 95531-83-2; **19**, 95532-06-2; **20**, 95532-07-3; **21**, 95532-08-4; **22**, 95532-09-5; **23**, 95532-10-8; **24a**, 95531-84-3; **24b**, 95531-85-4; **25a**, 95531-86-5; **25b**, 95531-87-6; **26a**, 95531-88-7; **26b**, 95531-89-8; **27**, 95531-90-1; **28**, 95531-91-2; **29a**, 95531-92-3; **29b**, 95531-93-4; **32**, 95531-94-5; **33a**, 95531-95-6; **33b**, 95531-96-7; **34**,

95531-97-8; $\text{BnO}(\text{CH}_2)_3\text{OH}$, 4799-68-2; $\text{BnO}(\text{CH}_2)_3\text{Br}$, 54314-84-0; $\text{BnO}(\text{CH}_2)_3\text{P}^+(\text{C}_6\text{H}_5)_3\text{Br}^-$, 54314-85-1; (*E*)- $\text{BnO}(\text{CH}_2)_2\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$, 95531-99-0; (*Z*)- $\text{BnO}(\text{CH}_2)_2\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$, 95531-98-9; (*E*)- $\text{BnO}(\text{CH}_2)_2\text{CH}=\text{C}(\text{CH}_3)\text{CHO}$, 95532-05-1; $\text{THPOCH}_2\text{COCH}_3$, 53343-13-8; $\text{CH}_2=\text{C}(\text{Me})\text{CH}_2\text{Br}$, 1458-98-6.

Supplementary Material Available: X-ray positional and thermal parameters and a three-dimensional structure of acetate **23** are provided along with experimental details for the synthesis of compounds **19**, **20**, **21**, **22**, and **23** (10 pages). Ordering information is given on any current masthead page.

Polysilane High Polymers: Mechanism of Photodegradation

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Abstract: Photolysis of the high polymer $(n\text{-C}_6\text{H}_{13}\text{MeSi})_n$ in CCl_4 leads to the formation of C_2Cl_6 , indicating that the photodegradative pathway of these polymers includes the formation of silyl radicals. Photolysis of alkyl-substituted polysilane polymers, $(\text{R}_1\text{R}_2\text{Si})_n$ ($\text{R}_1 = n\text{-hexyl}$, $\text{R}_2 = \text{Me}$; $\text{R}_1 = \text{R}_2 = n\text{-hexyl}$; $\text{R}_1 = \text{cyclohexyl}$, $\text{R}_2 = \text{Me}$), at 254 nm in the presence of triethylsilane gives two major products, $\text{Et}_3\text{Si-R}_1\text{R}_2\text{SiH}$ and $\text{HR}_1\text{R}_2\text{Si-R}_1\text{R}_2\text{SiH}$. Photolysis of $(n\text{-C}_6\text{H}_{13}\text{MeSi})_n$ in the presence of ROH ($\text{R} = \text{Me}$; $\text{R} = n\text{-Pr}$) gives four major products, $n\text{-C}_6\text{H}_{13}(\text{Me})\text{Si}(\text{OH})\text{H}$, $\text{H}(n\text{-C}_6\text{H}_{13})(\text{Me})\text{Si}-(n\text{-C}_6\text{H}_{13})(\text{Me})\text{SiH}$, $\text{H}(n\text{-C}_6\text{H}_{13})(\text{Me})\text{Si}-(n\text{-C}_6\text{H}_{13})(\text{Me})\text{SiOR}$, and $(\text{RO})(n\text{-C}_6\text{H}_{13})(\text{Me})\text{Si}-(n\text{-C}_6\text{H}_{13})(\text{Me})\text{SiOR}$. To explain these results, a photolytic cascade mechanism that involves both the extrusion of silylene units and the formation of silyl radical terminated polymer fragments is proposed. The photochemistry of phenyl-substituted polysilane polymers was examined and found to be considerably more complex than the photochemistry of the alkyl-substituted polymers.

Polysilane polymers, the silicon analogues of saturated linear organic polymers, possess several rather remarkable properties. The polymer backbone acts as an intense UV chromophore, and the position of the absorption maximum and the absorptivity at the absorption maximum are quite dependent upon the polymer chain length. Increasing chain length results in a marked red-shift of the absorption maxima, finally reaching a constant value in high molecular weight polymers at 300–327 nm for polyorganosilanes containing alkyl substituents and 335–360 nm for polyorganosilanes containing aryl substituents.¹ Organosilane polymers are also very photoactive under UV irradiation, with only photolysis processes occurring for alkyl-substituted polymers, and concurrent photolysis and photo-cross-linking processes being observed for polyorganosilanes with aryl and other unsaturated substituents.^{1,2} The quantum efficiencies for these photoreactions in solutions are quite high, between 0.20 and 0.97, depending upon the nature of the organic substituent.^{1a}

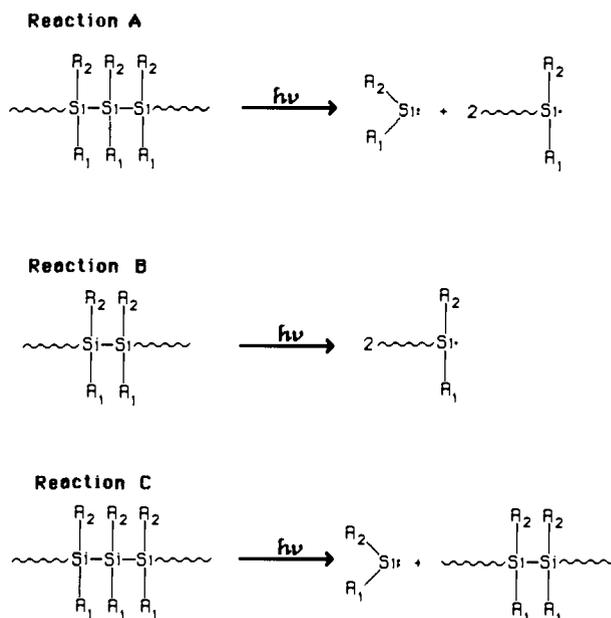
These remarkable properties are currently stimulating intense interest in these organosilane polymers as mid- and deep-UV photoresists,^{2,3} as sensitive photoinitiators for olefin polymerizations,⁴ as photo-cross-linked polymer precursors to $\beta\text{-SiC}$ ceramics,⁵ and in other applications where light sensitivity is required. In view of the unique properties of polyorganosilanes and the current interest in the photoactivity of these polymers, we have investigated the mechanism of photodegradation of polyorganosilanes.

The photochemistry of small cyclosilanes $(\text{R}_1\text{R}_2\text{Si})_n$, $n = 4\text{--}6$, has been extensively investigated, and photolysis is believed to result in sequential extrusion of silylene units resulting in the formation of smaller cyclosilanes:⁶



The photochemistry of small linear permethylpolysilanes, Me-

Scheme I. Possible Reactions for the Photodegradation of Polysilane Polymers



$(\text{Me}_2\text{Si})_n\text{Me}$, $n = 4\text{--}8$, has also been studied.^{6a,7} As with cyclosilanes, photolysis results primarily in the extrusion of silylenes,

(1) (a) Trefonas, P., III; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 823. (b) West, R.; David, L. D.; Djurovitch, P. I.; Stearley, K. L.; Srinivasan, K. S. V.; Yu, H. *J. Am. Chem. Soc.* **1981**, *103*, 1352. Zhang, X. H.; West, R. *J. Polym. Sci.* **1984**, *22*, 159. Zhang, X. H.; West, R. *J. Polym. Sci.* **1984**, *22*, 255. Zhang, X. H.; West, R. *J. Polym. Sci.* in press. Zhang, X. H.; West, R. *Polym. Commun. (Peking)*, in press.

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Table I. Product Distribution and Yields from 254-nm Photolysis of High Molecular Weight $(R^1R^2Si)_n$ with Excess Triethylsilane Present as a Chemical Trap

product	$R^1 = n-C_4H_9$ $R^2 = n-C_4H_9$	$R^1 = n-C_6H_{13}$ $R^2 = Me$	$R^1 = c-C_6H_{11}$ $R^2 = Me$
$Et_3Si-R^1R^2SiH$ (1a-c)	59%	70%	71%
$HSiR^1R^2-SiR^1R^2H$ (2a-c)	11%	11%	14%
$Et_3Si-R^1R^2Si-SiEt_3$	a	3%	a
$HSiR^1R^2-O-SiR^1R^2H$	a	a	2%
$Et_3Si-O-SiR^1R^2SiR^1R^2H$	a	a	3%

^aNo attempt was made to identify these and other products whose yields were less than 2%.

which results in chain contraction. Also found were a smaller amount of Si-H-terminated chain fragments, believed to be formed by abstraction of hydrogen radicals by silyl radical products resulting from homolytic scission of silicon-silicon bonds.

In view of these experimental results, three possible reactions, shown in Scheme I, were considered most likely to occur in the photolysis of alkyl-substituted polysilane high polymers. Reaction A should produce both silylene insertion products and silyl radical derived products. Reaction B should give only silyl radical derived products, and C should yield only silylene insertion products. Reaction C cannot be the only one occurring in the photodegradation of peralkyl polysilane polymers, because this mechanism would not result in as rapid a rate of photoscission as observed, and also would not account for the observed random photoscission process.^{1a} Note also that reaction A would give the same products as a combination of B and C, if reactions B and C were occurring concurrently at equal rates. Hence, it might be very difficult to differentiate between A and a combination of B and C.

Results and Discussion

Silyl radicals readily abstract chlorine radicals from chlorinated alkanes;⁸ thus the reaction of silyl radicals with CCl_4 should produce $\cdot CCl_3$ radicals, which can dimerize to form Cl_6C_2 .⁹ In order to test for the formation of silyl radicals in polysilane photolysis, a degassed CCl_4 solution containing dissolved $(n-C_6H_{13}MeSi)_n$, $M_w = 524\,000$, $\lambda_{max} = 306$ nm, was irradiated at 300 nm for 15 h to give the silyl radical derived product Cl_6C_2 in 33% yield based on the number of $n-C_6H_{13}MeSi$ units. In the absence of competing reactions, this would indicate that 66 $\cdot CCl_3$ radicals were formed for every 100 silicon atoms in the polymer backbone. This result confirms the hypothesis that many silyl radicals are formed upon photolysis of polyorganosilanes.¹⁰

Triethylsilane serves as an efficient chemical trap for silylenes, which readily insert into the Si-H bond to form a disilane.¹¹ In

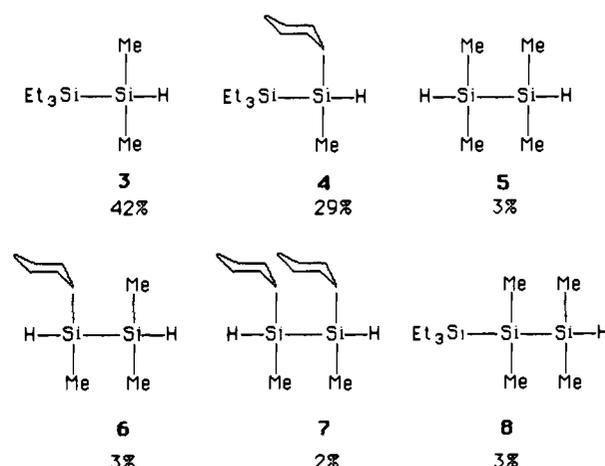
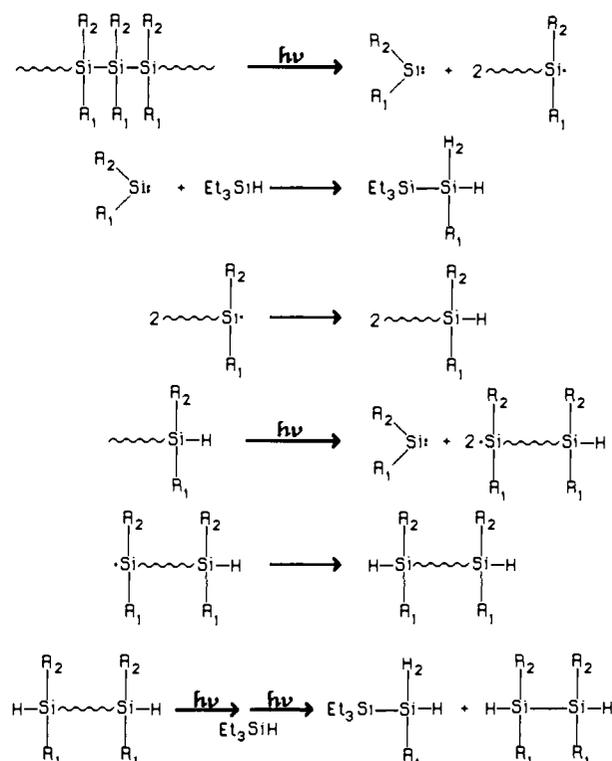


Figure 1. Major products from 254-nm photolysis of high molecular weight $[(Me_2Si)_{1.89}(c-C_6H_{11}MeSi)_{1.6}]_n$ in cyclohexane with excess Et_3SiH present.

Scheme II. Mechanistic Hypothesis for the Photodegradation of Polysilane Polymers



order to test for the formation of silylenes upon photolysis of organosilane polymers, a series of Et_3SiH trapping experiments were carried out on several representative peralkyl polysilane polymers. The polymers were dissolved in a 200-fold excess of

(2) Miller, R. D.; Hofer, D.; Wilson, G.; Trefonas, P.; West, R. In "Materials for Microlithography: Radiation-Sensitive Polymers"; Thompson, L., Willson, C. G., Fréchet, J. M. J., Eds.; American Chemical Society: Washington, DC, 1984.

(3) Trefonas, P.; West, R.; Miller, R. D.; Hofer, D. "Polysilane High Polymers: Synthesis, Properties and Photodegradation", presented at the 17th Organosilicon Symposium, Fargo, ND, June 3, 1983; Hofer, D.; Miller, R. D.; Willson, G. C. *Proc. SPIE Int. Soc. Opt. Eng.* **1984**, *469*, 16. Hofer, D.; Miller, R. D.; Willson, G. C.; Neureuther, A. R. *Ibid.* **1984**, *469*, 108.

(4) Wolf, A. R.; West, R.; Peterson, D. G. "Polysilanes: A New Class of Vinyl Photoinitiators", presented to 18th Organosilicon Symposium, Schenectady, NY, April 4, 1984.

(5) West, R.; David, L. D.; Djurovich, P. I.; Yu, H. *J. Am. Ceram. Soc.* **1983**, *62*, 899. West, R. In "Ultrastructure Processing of Ceramics, Glasses and Composites"; Hench, L., Ulrich, D. R., Eds.; Wiley: New York, 1984; Chapter 19, Baney, R. H., Chapter 20; Beatty, C. H., Chapter 22.

(6) (a) See, for example: Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981**, *19*, 51 and references within. (b) Helmer, B. J.; West, R. *Organometallics* **1982**, *1*, 1458.

(7) Ishikawa, M.; Takaoka, T.; Kumada, M. *J. Organomet. Chem.* **1972**, *42*, 333.

(8) See, for example: Wilt, J. W. "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum Press: New York, 1983; Vol. 3, Chapter 4 and references within.

(9) Besprozvannyi, M. A.; Konov, N. F.; Kharlamov, V. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1965**, 1345.

(10) Photolysis of a solution of an olefin (e.g., styrene) containing a catalytic amount of polysilane polymer results in rapid photopolymerization of the olefin.⁴ It is likely that the polymerization of the olefin is initiated by photolytically derived silyl radicals.

(11) See, for example: Gaspar, P. P. "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum Press: New York, 1978; Vol. 3, Chapter 7 and references within.

Et₃SiH solvent [for (c-C₆H₁₁MeSi)_n, which is insoluble in Et₃SiH, in cyclohexane solvent containing a 75-fold excess of Et₃SiH], degassed, and photolyzed in a quartz vessel under Ar at 35 °C for 15 h. Two major products were isolated (see Table I), Et₃Si-R¹R²SiH (1) and HR¹R²Si-R¹R²SiH (2), in 59–71% and 11–14% yields, respectively.¹²

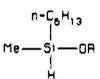
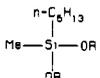
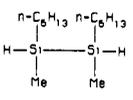
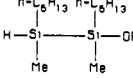
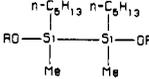
Products 1a–c result from photochemically generated silylene insertion into triethylsilane. The presence of 2a–c are also important to understanding the photochemical degradation mechanism of these polymers. We believe that 2a–c are formed by photochemical “cascade”, in which absorption of a photon results in formation of a silylene and generation of two silyl radical terminated polymer fragments (see mechanism A in Scheme I). The silylene inserts into triethylsilane to form 1, and the silyl radicals abstract hydrogen radicals from the solvent to give two H-terminated polymer fragments (see Scheme II). These photoproducts also absorb UV light at 254 nm and therefore are also potentially photoactive. Subsequent absorption of photons by these hydrogen-terminated polymer fragments will result in the generation of more silylenes, which insert into triethylsilane, and more smaller silyl radical terminated polymer fragments, which again abstract hydrogen atoms to give α,ω-H-terminated polymer fragments. Further photolysis by this same mechanism leads eventually to 2, which does not absorb 254-nm light.¹³

A similar 254-nm photolysis of the soluble random copolymer [(Me₂Si)_{1.89}(c-C₆H₁₁MeSi)_{1.0}]_n dissolved in cyclohexane with a 90-fold excess of triethylsilane present gave the product distribution found in Figure 1. Products 3 and 4 correspond to the expected products of silylene insertion into triethylsilane. Because the copolymer was enriched in the amount of Me₂Si: units relative to c-C₆H₁₁MeSi: units, 3 was formed in greater yield than 4 (although the ratio of 3:4 is less than that of the initial copolymer). Products 5–7 correspond to product 2 in the photochemical cascade mechanism explained above. Product 8 is formed by the insertion of a second Me₂Si: unit into 3.¹⁴ A second identical experiment, in which aliquots were removed throughout the photolysis and analyzed by GLC, was performed in order to determine at which point in the photolysis various products were formed. Initially 3 and 4 are generated in the same relative ratio as found at the end of the photolysis, and several unidentified higher mass products are formed. These higher mass products gradually disappear with the formation of 5–7.

Further evidence for the formation of photochemically generated silylene and silyl radical intermediates during the photodegradation of alkyl-substituted polysilanes can be found in a similar series of photolysis experiments on polymer solutions containing alcohol cosolvents. Alcohols serve as efficient chemical traps for silylenes, with the highly reactive silylene readily inserting into the oxygen–hydrogen bond.¹⁵ Silyl radicals readily abstract both hydrogen radicals and alkoxy radicals from alcohols.¹⁶

Experimental results for the 254-nm photolysis of (n-C₆H₁₃MeSi)_n in degassed solutions containing methanol (60-fold

Table II. Product Distribution and Yields from 254-nm Photolysis of High Molecular Weight (n-C₆H₁₃MeSi)_n in Toluene with Excess MeOH and n-PrOH Present, Respectively

		a, R = Me	b, R = n-Pr
9		65%	39%
10		0%	5%
11		7%	7%
12		15%	20%
13		7%	12%

excess) or n-propanol (over a 150-fold excess) are shown in Table II. In both cases, the major product, 9, results from the trapping of silylene by the alcohol. We believe that the minor products 11–13 are formed by the same photochemical cascade mechanism explained above. In the presence of alcohols, photochemically generated silyl radical-terminated polymer fragments will abstract either hydrogen atoms or alkoxy radicals to give polymer fragments terminated with Si–H or Si–OR groups, respectively. Continued photolysis generates more silylenes and smaller radical terminated polymer fragments, eventually stopping at disilanes, which do not absorb at 254 nm. This will result in three possible disilanes, each containing different combinations of Si–H and Si–OR terminating groups. The yields of 11:12:13 are in an approximate 1:2:1 ratio; statistically, this would be expected if the silyl radicals abstract hydrogen atoms and alkoxy radicals at equal rates.

Other possible explanations for the formation of photoproducts 2 and 9–13 cannot be entirely excluded. Chemical trapping of triplet silylenes could lead to 9 and 10 (assuming the triplet species can abstract either hydrogen atoms or alkoxy radicals), and dimerizing of a triplet species followed by abstraction of hydrogen atoms or alkoxy radicals could lead to 11–13 (or 2). However, if triplet silylenes were present, they should also form the product R₁R₂SiH₂ by the abstraction of two hydrogen atoms; none of this proposed photoproduct was found. It is also improbable that 11–13 (or 2) could be formed by the dimerization of triplet silylene intermediates because of the large excess of chemical trap present and the very low concentration of the highly reactive silylene at any one time.¹⁷

Another possible photoreaction is the direct extrusion of a disilene, R₂Si=SiR₂. Alcohols are known to react with disilenes to give addition products like 12.¹⁸ However, this mechanism would not account for the presence of 11 or 13, and there is no literature precedent for the extrusion of disilene from linear polysilanes.

Finally, we considered the possibility that 12 and 13 are formed by alcoholysis of the Si–H bond during the course of the photolysis experiment. This is unlikely, because such alcoholysis is normally quite slow except in the presence of a base. Nevertheless, we investigated this possibility by subjecting a similar concentration of H-(n-BuMeSi)₂-H (14) to the identical experimental conditions used in the above photolysis. The results establish that alcoholysis

(12) Also isolated was one minor product, Et₃Si-(n-C₆H₁₃)MeSi-SiEt₃, in a yield of 3%, which probably was formed through a radical mechanism. Other oxygen-containing minor products, formed in minute yields, probably result from residual O₂ remaining in the solution after degassing. See Experimental Section for details.

(13) We find that while n-alkyl 2-substituted permethyltrisilanes have absorption maxima at ca. 215 nm, the absorption band tails beyond 240 nm, which is within the output band of our lamps. In a control experiment, a sample of 2-n-butyl-1,1,1,2,3,3,3-heptamethyltrisilane was irradiated under the same conditions as the other experiments to give a sufficient yield of triethyl-n-butylmethylidisilane trapping product to account for the yields of 2a–c and 10a,b–12a,b. Hydrogen substitution onto permethyltrisilanes is reported to cause a slight red-shift in the absorption maximum of the trisilane. The absorption maximum of 1,3-dihydro-1,1,2,2,3,3-hexamethyltrisilane is red-shifted by 2 nm relative to octamethyltrisilane. Pitt, C. G. In “Homocyclic Rings, Chains and Macromolecules of Main Group Elements”; Rheingold, A. L., Ed.; Elsevier Scientific: Amsterdam, 1977.

(14) We have also identified a minor oxygen-containing product in ca. 1.5% yield, possibly the result of a residual amount of oxygen present in the solution prior to photolysis. See Experimental Section for details.

(15) Gu, T. Y. Y.; Weber, W. P. J. *Organomet. Chem.* **1980**, *184*, 7.

(16) Steele, K. P.; Tzeng, D.; Weber, W. P. J. *Organomet. Chem.* **1982**, *231*, 291.

(17) Trefonas, P.; West, R., unpublished results.

(17) Silylenes have only been observed as singlets, and theoretical calculations predict the singlet state to be much more stable than the triplet. See, for example: Gasper, P. R. “Reactive Intermediates”; Abramovich, R. A., Ed.; Plenum Press: New York, 1980; Vol. 2, Chapter 9 and references within. Gordon, M. S. J. *Am. Chem. Soc.* **1984**, *106*, 4054.

(18) West, R.; Fink, M. J.; Michl, J. *Science (Washington, D.C.)* **1981**, *214*, 1343.

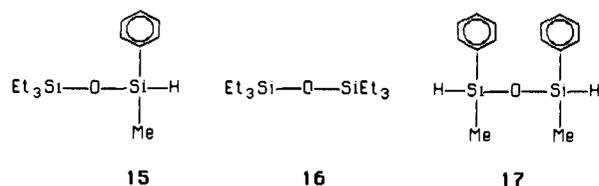


Figure 2. Products identified from 254-nm photolysis of high molecular weight $(\text{PhMeSi})_n$ in THF with 75-fold excess Et_3SiH present.

does not occur at a significant rate under these experimental conditions.

With these experimental results in mind, the mechanistic proposals given earlier in Scheme I will now be examined in greater detail. A single photocission process, such as the one described in mechanism A or B, will yield two silyl radicals, which, in the presence of a hydrogen radical source and the absence of other competing reactions, should result in the formation of two Si-H bonds. The yield of **2**, which contains two Si-H bonds and therefore was originally formed from two silyl radicals, should, in the absence of other competing reactions, be approximately equal to the yield of scission processes (mechanisms A or B). We find a preponderance of **1a-c**, the silylene trapping product, over **2a-c**, the silyl radical trapping product (or in the case of alcohol trapping experiments, the yield of **9** is greater than the sum of the yields of **11-13**). This indicates that either mechanism C is occurring at a significant rate along with mechanism A or B or, more likely, that cage effects allow many of the silyl radical terminated polymer ends to recombine, so that only some of the silyl radicals that are formed become trapped. Some evidence for the occurrence of cage effects is seen in the alcohol trapping experiments. Because 1-propanol is not as poor a solvent as methanol, we were able to use over a 150-fold excess of propanol as a chemical trap, as compared with only a 60-fold excess of methanol. Consequently, with the greater amount of 1-propanol present, radical scavenging should occur much more efficiently and the amount of radical recombination should be significantly reduced. This is reflected in the increased yields of **11b-13b** relative to **11a-13a**.

Photolysis of aryl-substituted polysilane polymers is more complicated than that of alkyl-substituted polysilane polymers, with both photocission and photo-cross-linking processes reported to occur.^{1,2} Photolysis of a high molecular weight $(\text{PhMeSi})_n$ ($M_w = 742000$) at 254 nm in degassed THF (aryl-substituted polysilane polymers are insoluble in all alkyl solvents) with a 70-fold excess of triethylsilane present gave a deep red solution containing brown insolubles which decomposed over a 6-h period at room temperature with the formation of unidentified high-mass products and more insoluble material. From the initial photosylate we were able to isolate a minute yield of four products, three of which were tentatively identified by mass spectroscopy (see Figure 2). The source of oxygen in **15-17** is unknown; there may have been residual oxygen present in the solution despite our best attempts to exclude it, or the oxygen could have been scavenged from the THF solvent through an unknown process.

Photolysis of low molecular weight $(\text{PhMeSi})_n$ ($M_w = 4000$), which contains some oxygen atoms in the polymer backbone, in THF under the same conditions in the presence of triethylsilane gave a stable photosylate. We were able to identify five major products from a complicated product mixture, which also contained a small amount of insoluble material (see Figure 3). Again, the major product, **18**, is formed from the insertion of phenylmethylsilylene into triethylsilane. The trisilane **21** is formed from the sequential insertion of a second silylene into the Si-H bond of **18**. The origin of oxygen-containing products **15** and **20** is unknown, although **15** may be formed by insertion of photochemically extruded phenylmethylsilane into triethylsilane. The origin of **19** is also unknown, but it may arise from a photorearranged silene intermediate.¹⁹ We did not find any evidence of the disilane analogous to **2a-c**, $\text{H}-(\text{PhMeSi})_2-\text{H}$ (**22**).

The differences found in the trapping products from the photolysis of phenyl-substituted and alkyl-substituted polymers are

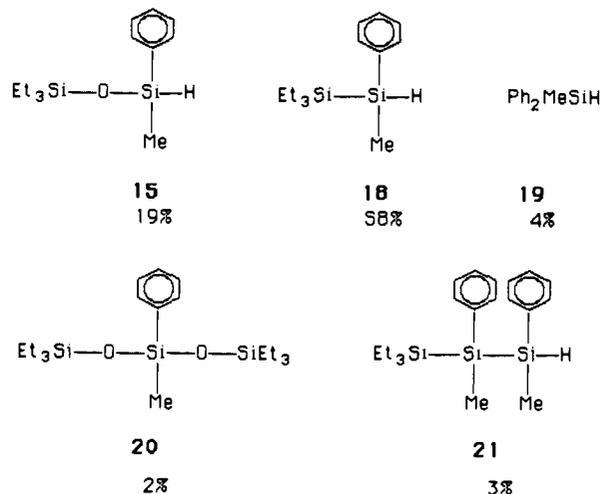


Figure 3. Products identified from 254-nm photolysis of low molecular weight $(\text{PhMeSi})_n$ in THF with 75-fold excess Et_3SiH present. There was also an 8% yield of insoluble material.

not entirely unexpected. Phenyl-substituted trisilanes photolyze to form both silylenes and a photorearranged intermediate ("silene") containing a highly reactive Si-C double bond.^{6a} Phenylpentamethyldisilane also absorbs at 254 nm and photolyzes to form isomerized silene intermediates, phenylmethylsilylene, and phenyltrimethylsilane.¹⁹ Thus one may expect that under prolonged photolysis, the structurally similar $\text{Et}_3\text{Si}-\text{PhMeSi}-\text{H}$ may even be photolabile. The absence of **22** can also be explained. We independently prepared **22** and found that it absorbed at 254 nm. Photolysis of **22** in the presence of triethylsilane under the same conditions as the previous experiments led to several products. Therefore it is likely that as **22** is formed in the course of the photolysis of $(\text{PhMeSi})_n$, it is consumed by further photoreactions, leaving little or no **22** to be found at the end of the experiment.

Experimental Section

The synthesis of all of the polymers, except $(n\text{-Bu}_2\text{Si})_n$, have been described elsewhere.²⁰ Proton NMR spectra were determined in CDCl_3 or CD_2Cl_2 on a Bruker WP-200 spectrometer and carbon-13 NMR spectra were determined in C_6D_6 on a JEOL FX-200 spectrometer and are reported in parts per million downfield from Me_4Si . Mass spectra were recorded on a Kratos MS-80 and AEI MS-902 spectrometers at 20 and 30 eV, respectively. All fragments displayed the correct isotope patterns. Infrared spectra were recorded on a Beckman IR4235 spectrometer, and ultraviolet spectra were recorded on an Applied Physics Corporation Cary 14 spectrometer. Polymer molecular weights were determined by gel permeation chromatography using four Microstyrigel columns calibrated by polystyrene standards (porosity ranges 10^3 , 10^4 , 10^5 , and 10^6 Å) with THF as the eluent at a flow rate of 2 mL/min. Triethylsilane and $n\text{-Bu}_2\text{SiCl}_2$ were obtained from Petrarch Chemical Co. and were purified by fractional distillation prior to use. Methanol and 1-propanol were dried by refluxing over Mg. Cyclohexane and THF were dried by refluxing over sodium benzophenone. CCl_4 was dried by refluxing over P_2O_5 . All photoproducts were isolated by preparative gas chromatography on a Gow-Mac Chromatograph fitted with a heated outlet port and a thermal conductivity detector using a 9-ft column containing 10% Dexsil on Chromosorb-W.

$(n\text{-Bu}_2\text{Si})_n$. Sodium dispersion was added to a refluxing solution of $n\text{-Bu}_2\text{SiCl}_2$ in toluene according to the literature method²⁰ to give a 13% yield of $(n\text{-Bu}_2\text{Si})_n$, $M_w = 1480000$, as a nonsticky flexible hard white elastomer soluble in hexane, toluene, chloroform, and THF; ^1H NMR (CDCl_3) δ 0.77-1.02 (br, 10 H, Si- CH_2 and $-\text{CH}_3$), 1.18-1.48 (br, 8 H, CH_2CH_2); ^{13}C NMR (C_6D_6) δ 29.70, 27.42, 14.81, 13.76; IR (film) 2913 (s), 1457 (s), 1407 (m), 1369 (s), 1070 (s), 1012 (m), 860 (m) cm^{-1} ; UV (hexane) $\lambda_{\text{max}} = 314$ nm.

Standard Procedure for Photolyzing Polymers. The molecular weights of the polymers used are as follows: $(n\text{-Bu}_2\text{Si})_n$, $M_w = 1480000$; $(\text{-C}_6\text{H}_{11}\text{MeSi})_n$, $M_w = 804000$; $(n\text{-C}_6\text{H}_{13}\text{MeSi})_n$, $M_w = 524000$; low mo-

(19) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1979**, *173*, 117 and references within.

(20) Trefonas, P., III; Djurovich, P. I.; Zhang, X. H.; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 819. Trefonas, P., III; West, R. *Inorg. Synth.*, in press.

lecular weight (PhMeSi)_n, $\bar{M}_w = 4000$; high molecular weight (PhMeSi)_n, $\bar{M}_w = 742000$. In all cases, oven-dried glassware was used and chemical manipulations were carried out under a dry Ar or N₂ atmosphere. For (*n*-Bu₂Si)_n and (*n*-HexMeSi)_n, approximately 100 mg of polymer was dissolved into 15 mL of Et₃SiH; for (c-C₆H₁₁MeSi)_n and [(Me₂Si)_{1.89}(c-C₆H₁₁MeSi)_{1.0}]_n, which are insoluble in Et₃SiH, 100 mg of the polymers was dissolved into 15 mL of cyclohexane, and 10 mL of Et₃SiH was added. For (PhMeSi)_n, which is insoluble in alkanes, 100 mg of polymer was dissolved into 15 mL of THF, and 7 mL of Et₃SiH was added. In trapping experiments using alcohols, approximately 100 mg of (*n*-C₆H₁₃MeSi)_n was dissolved into 15 mL hexane, to which 2.5 mL of MeOH or 9.5 mL of *n*-PrOH was added. These solutions were placed into a quartz photolysis tube (1-cm o.d.) equipped with a magnetic stir bar and freeze-thaw-degassed 5 times and then photolyzed in a Southern New England Ultraviolet Company RPR-100 Rayonet equipped with 16 low-pressure 254-nm Hg lamps at 35 °C for 15 h. The solvent was stripped off and the photolyte weighed. The photoproducts were isolated by preparative gas chromatography. Photoproduct yields were determined, when possible, relative to C₁₈H₂₀ standards. Otherwise, photoproduct yields were estimated by GLC peak areas; in these cases the weighed crude photoproduct yield agreed to within 8% of the total mass as calculated from the product distribution determined from GLC peak areas.

Photolysis of (*n*-C₆H₁₃MeSi)_n in CCl₄. A solution of 172 mg of (*n*-C₆H₁₃MeSi)_n in CCl₄ in a quartz photolysis tube was degassed and then photolyzed in a rayonet containing 16 300-nm lamps at 35 °C for 15 h to give a deep-red solution. GLC analysis showed one primary product at low retention time plus several minor products at high mass. Evaporation and recrystallization gave a total of 0.104 g of C₂Cl₆: mp 185 °C, with sublimation and bubbling (lit. mp 186.8 °C, triple point); MS, *m/e* (relative intensity) 207 (1.8%), 205 (14), 203 (59), 201 (100%), 199 (57), 170 (1.7), 168 (10), 166 (22), 164 (16), 121 (20.5), 119 (89), 117 (90).

1,1,1-Triethyl-2,2-di-*n*-butyldisilane (1a). (*n*-Bu₂Si)_n was photolyzed under the standard procedure in triethylsilane to give 59% **1a**: clear liquid; ¹H NMR (CDCl₃, 25 °C) δ 0.67 (t + q, SiCH₂, 10 H), 0.95 (t + t, CH₃, 15 H), 1.32 (m, CH₂CH₂, 8H) 3.54 (p, SiH, 1 H); ¹³C NMR (CDCl₃, 25 °C) δ 28.82, 26.31, 13.70, 10.19, 8.27, 4.06; HRMS calcd for C₁₄H₃₃Si₂ (M - 1) 257.2122, found 257.2122.

1,1,2,2-Tetra-*n*-butyldisilane (2a). This compound eluted after **1a** on the GLC in 11% yield: clear liquid; ¹H NMR (CDCl₃, 25 °C) δ 0.69 (m, SiCH₂, 8 H), 0.89 (t, CH₃, 12 H), 1.32 (m, CH₂CH₂, 16 H), 3.49 (m, SiH, 2 H); MS, selected *m/e* (relative intensity) 286 (48%), 258 (11), 229 (7.4), 143 (56), 142 (62), 87 (100%); HRMS calcd for C₁₆H₃₈Si₂ 286.2511, found 286.2511.

1,1,1-Triethyl-2-*n*-hexyl-2-methyldisilane (1b). (*n*-C₆H₁₃MeSi)_n was photolyzed under the standard procedure in triethylsilane to give 70% **1b**: clear liquid; ¹H NMR (CDCl₃, 25 °C) δ 0.11 (d, SiCH₃, 3H), 0.63 (t + q, SiCH₂, 8 H), 0.95 (t, CH₃, 12 H), 1.26 (m, CH₂, 8 H), 3.50 (p, SiH, 1 H); MS, selected *m/e* (relative intensity) 244 (18%), 229 (0.1), 215 (3.3), 187 (0.2), 159 (0.9), 131 (11), 129 (1.3), 115 (100%); HRMS calcd for C₁₃H₃₂Si₂ 242.2042, found 242.2042.

1,2-Di-*n*-hexyl-1,2-dimethyldisilane (2b). This compound eluted after **2a** on the GLC in 11% yield: clear liquid; ¹H NMR (CDCl₃, 25 °C) δ 0.13 (d, SiCH₃, 6 H), 0.65 (t of d, SiCH₂, 4 H), 0.88 (t, CH₃, 6 H), 1.28 (m, CH₂, 16 H), 3.53 (m, SiH, 2 H); MS, selected *m/e* (relative intensity) 258 (9.1%), 257 (28), 256 (100%), 173 (24), 172 (19), 143 (15), 133 (11), 129 (2.8); HRMS calcd for C₁₃H₃₂Si₂ 258.2190, found 258.2198.

1,1,1,3,3,3-Hexaethyl-2-*n*-hexyl-2-methyltrisilane. This compound eluted after **2b** on the GLC in 3% yield: clear liquid; ¹H NMR (CDCl₃, 25 °C) δ 0.17 (s, SiCH₃, 3 H), 0.39 (t, SiCH₂CH₂, 12 H), 0.62 (t, SiCH₂, 2 H), 0.88 (t + t, CH₃, 21 H), 1.26 (m, CH₂, 8 H); MS, selected *m/e* (relative intensity) 358 (3.4%), 329 (1.1), 273 (100%), 243 (82), 128 (2.7), 115 (7.4); HRMS calcd for C₁₉H₄₆Si₃ 358.2908, found 358.2895.

Another minor product (4%) is tentatively identified by ¹H NMR (which is quite complex, but consistent) and MS to be Et₃SiO-(*n*-C₆H₁₃MeSi)₂-H: clear liquid; MS, selected *m/e* (relative intensity) 388 (4.5%), 359 (0.3), 303 (0.3), 288 (0.7), 273 (10.1), 259 (45.6), 219 (5.2), 203 (1.4), 175 (100%), 129 (9.4), 115 (4.6).

1,1,1-Triethyl-2-cyclohexyl-2-methyldisilane (1c). (c-C₆H₁₁MeSi)_n was photolyzed under the standard procedure in cyclohexane/triethylsilane to give 71% **1c**: clear liquid; ¹H NMR (CDCl₃, 25 °C) δ 0.07 (d, SiCH₃, 3 H), 0.64 (q of d, SiCH₂, 6 H), 0.97 (t, CH₃, 9 H), 1.19 and 1.69 (m, c-C₆H₁₁, 11 H), 3.47 (p, SiH, 1 H); MS, selected *m/e* (relative intensity) 242 (27%), 213 (3.6), 159 (0.6), 131 (15), 115 (100%); HRMS calcd for C₁₃H₃₀Si₂ 242.1878, found 242.1887.

1,2-Dicyclohexyl-1,2-dimethyldisilane (2c). This compound eluted after **1c** on the GLC in 14% yield: clear liquid; ¹H NMR (CDCl₃, 25 °C) δ 0.11 (d, SiCH₃, 6 H), 0.86 (m, SiCH, 2 H), 1.17 and 1.69 (m,

c-C₆H₁₁, 22 H), 3.48 (m, SiH, 2 H); MS, selected *m/e* (relative intensity) 254 (58%), 127 (18), 126 (100%), 99 (10), 89 (24.3); HRMS calcd for C₁₄H₃₀Si₂ 254.1878, found 254.1887.

1,3-Dicyclohexyl-1,3-dimethyldisiloxane. This product was isolated by preparative GLC from the photolysis of (c-C₆H₁₁MeSi)_n in triethylsilane in 2% yield: clear liquid; ¹H NMR (CDCl₃, 25 °C) δ 0.10 (d, SiCH₃, 6 H), 0.90 (m, SiCH, 2 H), 1.22 and 1.71 (m, c-C₆H₁₁, 22 H), 3.46 (m, SiH, 2 H); MS selected *m/e* (relative intensity) 270 (4.2%), 269 (22), 255 (6.2), 187 (100%), 143 (4.9), 105 (56), 89 (5.1); HRMS calcd for C₁₄H₃₀O₁Si₂ 270.1835, found 270.1835.

1,2-Dicyclohexyl-1,2-dimethyl-1-(triethylsiloxy)disilane. This product was isolated by preparative GLC from the photolysis of (c-C₆H₁₁MeSi)_n in triethylsilane in 3% yield: clear liquid; ¹H NMR was highly complex, but consistent with structure; MS, selected *m/e* (relative intensity) 384 (9.2%), 355 (0.4), 301 (3.1), 257 (34), 219 (14), 175 (100%), 131 (1.0), 115 (3.0), we found no *m/e* 241; HRMS calcd for C₂₀H₄₄O₁Si₃ 384.2699, found 384.2699.

Photolysis of [(Me₂Si)_{1.89}(c-C₆H₁₁MeSi)_{1.0}]_n in Triethylsilane. Photolysis under standard procedure gave 1,1,1-triethyl-2,2-dimethyl-disilane (**3**) in 42% yield and 1,1,2,2-tetramethyldisilane (**5**) in approximately 3% yield (the yield of **5** was estimated because its GLC elution peak overlapped significantly with cyclohexane). The ¹H NMR and MS for **3** and **5** agreed with literature data.²¹ We also found 1,1,1-triethyl-2-cyclohexyl-2-methyldisilane (**4**), in 29% yield and 1,2-dicyclohexyl-1,2-dimethyldisilane (**7**) in 2% yield. The ¹H NMR and MS for **4** and **7** were identical with those of **1c** and **2c**.

1,1,2-Trimethyl-2-cyclohexyldisilane (6). This compound was isolated in 3% yield by preparative GLC from the photolysis of [(Me₂Si)_{1.89}(c-C₆H₁₁MeSi)_{1.0}]_n: MS, selected *m/e* (relative intensity) 186 (26%), 126 (34), 103 (33), 88 (5.2), 73 (40), 59 (100%); HRMS calcd for C₉H₂₂Si₂ 186.1260, found 186.1260.

1,1,1-Triethyl-2,2,3,3-tetramethyltrisilane (8). This compound was isolated in 3% yield by preparative GLC from the photolysis of [(Me₂Si)_{1.89}(c-C₆H₁₁MeSi)_{1.0}]_n: MS selected, *m/e* (relative intensity) 232 (7.2%), 217 (34), 189 (11), 175 (3.5), 173 (1.7), 161 (12), 147 (4.7), 133 (4.9), 118 (6.2), 117 (26), 116 (100%), 115 (13); HRMS calcd for C₁₀H₂₆Si₃ 232.1491, found 232.1475.

2-Cyclohexyl-1,1,2-trimethyl-1-(triethylsiloxy)disilane. This compound was isolated in 1.5% yield by preparative GLC from the photolysis of [(Me₂Si)_{1.89}(CyclohexylMeSi)_{1.0}]_n: clear liquid; ¹H NMR was highly complex, but consistent with structure; MS, selected *m/e* (relative intensity) 316 (19%), 288 (45), 257 (20), 233 (4), 201 (0.7), 189 (100%), 173 (17), 144 (17), 115 (36); HRMS calcd for C₁₅H₃₀O₁Si₃ 316.2074, found 316.2074.

***n*-Hexylmethylmethoxydisilane (9a).** (*n*-C₆H₁₃MeSi)_n was photolyzed under standard procedure in hexane/MeOH to give 65% **9a**: clear liquid, ¹H NMR (CDCl₃, 25 °C) δ 0.17 (d, SiCH₃, 3 H), 0.62 (m, SiCH₂, 2 H), 0.86 (t, CH₃, 3 H), 1.28 (m, CH₂, 8 H), 3.45 (s, OCH₃, 3 H), 4.50 (q, SiH, 1 H); MS, selected *m/e* (relative intensity) 160 (1.0%), 159 (6.7), 130 (3.5), 103 (18), 75 (100%), 8.7 (61), 59 (13); HRMS calcd for M - 1, C₈H₁₉O₁Si₁, 159.1204, found 159.1204.

11a and 11b had identical ¹H NMR and MS with **2b** and both were found in 7% yields.

1,2-Di-*n*-hexyl-1,2-dimethyl-2-methoxydisilane (12a). This compound eluted after **11a** on the GLC in 15% yield: clear liquid, ¹H NMR (CDCl₃, 25 °C) δ 0.13 (d, SiCH₃, 3 H), 0.20 (s, SiCH₃, 3 H), 0.72 (m, SiCH₂, 4 H), 0.88 (t + t, CH₃, 6 H), 1.27 (m, CH₂, 16 H), 3.41 (s, OCH₃, 3 H), 3.61 (q, SiH, 1 H); MS, selected *m/e* (relative intensity) 288 (5.0%), 273 (4.0), 203 (9.4), 189 (60), 159 (53), 128 (14), 75 (100%); HRMS calcd for M, C₁₃H₃₆O₁Si₂, 288.2295, found 288.2307.

1,2-Di-*n*-hexyl-1,2-dimethyl-1,2-dimethoxydisilane (13a). This compound eluted after **12a** on the GLC in 7% yield: clear liquid; ¹H NMR (CDCl₃, 25 °C) δ 0.22 (s, SiCH₃, 6 H), 0.74 (m, SiCH₂, 4 H), 0.87 (t + t, CH₃, 6 H), 1.28 (m, CH₂, 16 H), 3.43 (s, OCH₃, 6 H); MS, selected *m/e* (relative intensity) 318 (14%), 303 (33), 233 (18), 219 (42), 159 (59), 135 (91), 75 (100%); HRMS calcd for M, C₁₆H₃₈O₂Si₂, 318.2400, found 318.2409.

***n*-Hexyl-*n*-propoxymethylsilane (9b).** (*n*-C₆H₁₃MeSi)_n was photolyzed under standard procedure in hexane/*n*-PrOH to give 65% **9b**: clear liquid; ¹H NMR (CDCl₃, 25 °C) δ 0.13 (d, SiCH₃, 3 H), 0.64 (m, SiCH₂, 2 H), 0.90 (t + t, CH₃, 6 H), 1.28 (m, CH₂, 8 H), 1.54 (m, OCH₂CH₂, 2 H), 3.57 (t, OCH₂, 2 H), 4.51 (m, SiH, 1 H); MS, selected *m/e* (relative intensity) 188 (2.0%), 187 (10), 173 (13), 145 (0.4), 103 (100%), 89 (3.3), 75 (11); HRMS calcd for C₁₀H₂₄O₁Si₁, 188.1590, found 188.1596.

***n*-Hexyldi-*n*-propoxymethylsilane (10b).** This compound eluted after **9b** on the GLC in 5% yield: clear liquid; ¹H NMR (CDCl₃, 25 °C) δ 0.08

(s, SiCH₃, 3 H), 0.60 (m, SiCH₂, 2 H), 0.88 (t + t, CH₃, 9 H), 1.25 (m, CH₂, 8 H), 1.53 (m, OCH₂CH₂, 4 H), 3.60 (t, OCH₂, 4 H); MS, selected *m/e* (relative intensity) 231 (M - CH₃, 8.5%), 187 (2.6), 161 (100%), 119 (13), 103 (12), 77 (29), 43 (15); HRMS calcd for M - CH₃, C₁₂H₂₇O₂Si₁, 231.1773, found 231.1771.

1,2-Di-*n*-hexyl-1,2-dimethyl-2-propoxydisilane (12b). This compound eluted after **11b** on the GLC in 20% yield: clear liquid; ¹H NMR (CDCl₃, 25 °C) δ 0.12 (d, SiCH₃, 3 H), 0.20 (s, SiCH₃, 3 H), 0.68 (m, SiCH₂, 4 H), 0.87 (t + t + t, CH₃, 9 H), 1.27 (m, CH₂, 16 H), 1.54 (m, OCH₂CH₂, 2 H), 3.51 (t, OCH₂, 2 H), 3.60 (q, SiH, 1 H); MS, selected *m/e* (relative intensity) 316 (16%), 315 (12), 301 (4.4), 273 (38), 189 (100%), 187 (54), 129 (85); HRMS calcd for M - C₃H₇, C₁₄H₃₃O₁Si₂, 273.2061, found 273.2013.

1,2-Di-*n*-hexyl-1,2-dimethyl-1,2-dipropoxydisilane (13b). This compound eluted after **12b** on the GLC in 12% yield: clear liquid; ¹H NMR (CDCl₃, 25 °C) δ 0.19 (s, SiCH₃, 6 H), 0.69 (m, SiCH₂, 4 H), 0.85 (t + t, CH₃, 12 H), 1.27 (m, CH₂, 16 H), 1.52 (m, OCH₂CH₂, 4 H), 3.52 (t, OCH₂, 4 H); MS, selected *m/e* (relative intensity) 331 (M - C₃H₇, 76%), 315 (4.4), 289 (23), 247 (70), 205 (100%), 187 (94); HRMS calcd for M - C₃H₇, C₁₇H₃₉O₂Si₂, 331.2478, found 331.2486.

1,1,1-Triethyl-3-phenyl-3-methylsilofoxane (15). This compound was found in minute yield from photolysis of high molecular weight (PhMeSi)_{*n*} in THF/triethylsilane under standard conditions. Photolysis of low molecular weight (PhMeSi)_{*n*} under the same conditions gave a 19% yield of **15**: clear liquid; ¹H NMR (CD₂Cl₂, 25 °C) δ 0.42 (d, SiCH₃, 3 H), 0.57 (q, SiCH₂, 6 H), 0.93 (t, CH₃, 9 H), 5.11 (q, SiH, 1 H), 7.40 and 7.59 (m, PhH, 5 H); MS, selected *m/e* (relative intensity) 252 (0.3%), 237 (1.1), 224 (14.4), 223 (100%), 195 (9.1), 167 (4.7), 121 (1.0).

Hexaethylsilofoxane (16). This compound was found in minute yield from photolysis of high molecular weight (PhMeSi)_{*n*} in THF/triethylsilane under standard conditions. MS, selected *m/e* (relative intensity) 217 (M - C₂H₅, 41%), 189 (18), 161 (17), 133 (7.8), 116 (100%), 115 (14).

1,3-Diphenyl-1,3-dimethyldisiloxane (17). This compound was found in minute yield from photolysis of high molecular weight (PhMeSi)_{*n*} in THF/triethylsilane under standard conditions. MS, selected *m/e* (relative intensity) 258 (M, 27%), 243 (26), 181 (21), 180 (91), 179 (81), 165 (100%), 121 (23), 78 (8.3).

1,1,1-Triethyl-2-phenyl-2-methyldisilane (18). This compound was found in 58% yield from photolysis of low molecular weight (PhMeSi)_{*n*} in THF/triethylsilane under standard conditions: clear liquid; ¹H NMR (CD₂Cl₂, 25 °C) δ 0.46 (d, SiCH₃, 3 H), 0.67 (q of d, SiCH₂, 6 H), 0.94 (t, CH₃, 9 H), 4.29 (q, SiH, 1 H), 7.21 and 7.52 (m, PhH, 5 H); MS, selected *m/e* (relative intensity) 236 (39%), 207 (7.7), 179 (9.3), 158 (1.4), 121 (22), 115 (100%); HRMS calcd for C₁₃H₂₄Si₂, 236.1410, found 236.1394.

Diphenylmethylsilane (19). This compound eluted just after **18** on the GLC with a significant amount of peak overlap. The yield of **19** is estimated to be 4%. MS, selected *m/e* (relative intensity) 198 (56%), 183 (40), 121 (100%); HRMS calcd for C₁₃H₁₄Si₁, 198.0859, found 198.0845.

1,1,1,5,5,5-Hexaethyl-3-phenyl-3-methyltrisiloxane (20). This compound eluted after **19** on the GLC in 2% yield: clear liquid; ¹H NMR (CD₂Cl₂, 25 °C) δ 0.32 (s, SiCH₃, 3 H), 0.57 (q, SiCH₂, 12 H), 0.93 (t, CH₃, 18 H), 7.40 and 7.60 (m, PhH, 5 H); MS, selected *m/e* (relative intensity) 367 (0.4%), 353 (M - C₂H₅, 100%), 325 (7.3), 297 (0.5), 269 (0.2), 267 (0.8), 251 (1.9), 115 (1.0); HRMS calcd for (M - C₂H₅),

C₁₇H₃₃O₂Si₃, 353.1787, found 353.1787.

1,1,1-Triethyl-2,3-diphenyl-2,3-dimethyltrisilane (21). This compound eluted after **20** on the GLC in 3% yield: clear liquid; ¹H NMR (CD₂Cl₂, 25 °C) δ 0.05 (s, SiCH₃, 3 H), 0.09 (d, SiCH₃, 3 H), 0.56 (q, SiCH₂, 6 H), 0.90 (t, CH₃, 9 H), 5.18 (m, SiH, 1 H), 7.35 and 7.52 (m, PhH, 10 H); MS, selected *m/e* (relative intensity) 356 (2.0%), 337 (0.2), 299 (100%), 271 (6.0), 241 (3.0), 121 (1.2), 115 (0.3); HRMS calcd for C₂₀H₃₂Si₃, 356.1812, found 356.1812.

***n*-Butylmethylchlorosilane (23).** This compound was prepared by the reaction of *n*-BuLi with MeHSiCl₂. MeHSiCl₂, 15 mL, and dry hexane, 20 mL, were placed into an oven-dried 250-mL flask fitted with a condenser, pressure equalized addition funnel containing 99 mL of 1.45 M *n*-BuLi, gas inlet, and magnetic stirring bar and cooled in an ice bath. The *n*-BuLi was then added *very slowly*, and the solution was allowed to warm to 25 °C for 12 h. The solution was filtered through an enclosed medium frit to remove LiCl, and fractionally distilled (127 °C) to yield 6.37 g of **23** (32%): clear liquid; ¹H NMR (CDCl₃, 25 °C) δ 0.47 (d, SiCH₃, 3 H), 0.90 (m, SiCH₂ + CH₃, 5 H), 1.31 (m, CH₂, 4 H), 4.80 (q, SiH, 1 H).

Remaining in the pot after distilling off **23** was nearly pure **di-*n*-butylmethylsilane**, 12 g (53%): clear liquid; ¹H NMR (CDCl₃, 25 °C) δ 0.02 (d, SiCH₃, 3 H), 0.58 (m, SiCH₂, 4 H), 0.87 (t, CH₃, 6 H), 1.20 (m, CH₂, 8 H), 3.75 (q, SiH, 1 H).

1,2-Di-*n*-butyl-1,2-dimethyldisilane (14). This compound was prepared by the reaction of **23** with Na metal.²² Dry toluene, 40 mL, and 0.67 g of shiny Na were placed into a 100-mL flask fitted with a condenser, gas inlet, magnetic stirring bar, and a pressure-equalized addition funnel containing 4.01 g of **23**. The reaction was brought to reflux and **23** was slowly added. After 5 h the reaction turned purple. After 12 h, the reflux was stopped and the mixture filtered to remove NaCl. Fractional vacuum distillation (0.2 mm, 40 °C) yielded 5.04 g of **14** (85%): clear liquid; ¹H NMR (CDCl₃, 25 °C) δ 0.15 (d of d, SiCH₃, 6 H), 0.69 (m, SiCH₂, 4 H), 0.88 (t, CH₃, 6 H), 1.33 (m, CH₂, 8 H), 3.63 (m, SiH, 2 H); MS, selected *m/e* (relative intensity) 202 (16%), 101 (31), 100 (45), 89 (32), 71 (100%); HRMS calcd for C₁₀H₂₆Si₂, 202.1566, found 202.1576.

Photolysis of 14. A solution of 45 mg of **14** in hexane/MeOH was photolyzed under standard conditions for 15 h. Examination of the photosylate by GLC and ¹H NMR showed that the starting material had not reacted and was still present in 95% yield.

1,1,1,2,3,3,3-Heptamethyl-2-*n*-butyltrisilane (24). This compound was prepared by reacting 1,1,1,2,3,3,3-heptamethyl-2-chlorotrisilane (**25**)²³ with *n*-BuLi. **25**, 2.38 g, was placed in a 25-mL flask fitted with a condenser, gas inlet, and magnetic stirring bar. *n*-BuLi (8 mL, 1.36 M) was syringed into this solution at reflux, and then the solution was refluxed for 24 h. The LiCl precipitate was filtered off and **24** was isolated by preparative GLC (70% yield): clear liquid; ¹H NMR (CDCl₃, 25 °C) δ 0.03 (s, SiCH₃, 3 H), 0.09 (d, Si(CH₃)₃, 18 H), 0.67 (t, SiCH₂, 2 H), 0.87 (t, CH₃, 3 H), 1.30 (m, CH₂, 4 H); HRMS calcd for C₁₁H₃₀Si₃, 246.1655, found 246.1655; UV λ_{max}, in spectrograde pentane and N₂ atmosphere, 213 nm (ε 9200), tailing to ca. 245 nm.

1,2-Diphenyl-1,2-dimethyldisilane (22). This compound was prepared according to literature methods.²²

(22) Gerval, P.; Frainet, E.; Lain, G.; Moulines, F. *Bull. Soc. Chem. Fr.* **1974**, 1554.

(23) Gilman, H.; Smith, C. L. *J. Organomet. Chem.* **1967**, *8*, 245.