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Supplementary Material Available: Details of the crystal data collection and structure refinement, a fully labeled diagram, and tables of crystal data, atomic coordinates, anisotropic thermal parameters, and bond distances and angles for 1 (15 pages); a table of structure factors (34 pages). Ordering information is given on any current masthead page.

Photochemistry of Permethyloligosilanes

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Summary: Primary photochemical pathways have been identified in the irradiation of three oligosilanes at 254 nm. These pathways include a reductive elimination not previously observed in oligosilanes but closely analogous to a chain-scission process that has been observed in polysilane materials.

Investigation of the thermal and photochemical breakdown of polysilanes is of topical interest because of the importance of these compounds as photoresists.[1] To complement work on the photoablation of these materials,[2] we are undertaking separate pyrolysis[3] and photochemical studies on a number of permethyloligosilanes as simple models for polysilanes; we now report preliminary results of our photochemical experiments.

The compounds we have studied so far are 2,3-bis(trimethylsilyl)octamethyltetrasilane (I), $(Me_3Si)_2Si(Me)Si(Me)(Me_3Si)_2$, 2-(trimethylsilyl)heptamethyltrisilane (II), $(Me_3Si)_3SiMe$, and 2,2-diethylhexamethyltrisilane (III), $(Me_3Si)_2SiEt_2$. Ishikawa and Kumada have published a preliminary account[4] of the photochemistry of the branched oligosilanes I and II and a more detailed account[5] of the photochemistry of the series of linear oligosilanes $Me(Me_2Si)_nMe$, where n = 4–8, in cyclohexane solution at 254 nm, using diethylmethylsilane as a silylene trap. They found extrusion of dimethylsilylene, $:SiMe_2$, to be the main primary photochemical pathway, together with some homolytic Si–Si bond rupture; e.g., irradiation of the permethylated tetrasilane gave 84% Me_6Si_3 (the stable product concomitant with extrusion of $:SiMe_2$), with 11% Si–Si bond rupture. Likewise,[6] dimesitylsilylene was formed photochemically from the trisilane $(Me_3Si)_2SiMes_2$, although Wilking and Gaspar recently reported that irradiation at 254 nm of the mesityl-substituted disilane and trisilane $(MesMe_2Si)_2$ and $(MesMe_2Si)_2SiMe_2$ mainly caused Si–Si bond rupture followed by radical reactions.[7]

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(1) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359.
(2) Magnera, T. F.; Balaji, V.; Michl, J.; Miller, R. D.; Sooriyakumaran, R. *Macromolecules* **1989**, *22*, 1624.
(3) Bortolin, B. N.; Davidson, I. M. T.; Lancaster, D.; Simpson, T.; Wild, D. A. *Organometallics* **1990**, *9*, 281.
(4) Ishikawa, M.; Kumada, M. *J. Chem. Soc. D* **1971**, 489.
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(6) West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343.
(7) Wilking, J.; Gaspar, P. P. Presented at the Ninth International Symposium of Organosilicon Chemistry, Edinburgh, U.K., 1990.

Photochemical studies of polysilanes have revealed that three types of simultaneous primary processes may occur:

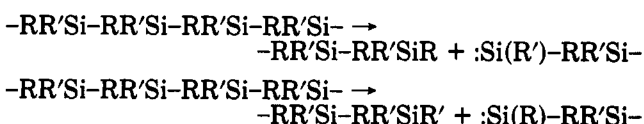
(A) chain scission by homolytic Si–Si bond cleavage[8]

-RR′Si-RR′Si-RR′Si-RR′Si- → -RR′Si-RR′Si• + •RR′Si-RR′Si-

(B) chain abridgement by elimination of a silylene from the polysilane chain[8]

-RR′Si-RR′Si-RR′Si-RR′Si- → -RR′Si-RR′Si-RR′Si- + :SiRR′

(C) chain scission with formation of a silylene on the polysilane chain[9]



-RR′Si-RR′Si-RR′Si-RR′Si- → -RR′Si-RR′SiR + :Si(R′)-RR′Si-

-RR′Si-RR′Si-RR′Si-RR′Si- → -RR′Si-RR′SiR′ + :Si(R)-RR′Si-

Processes B and C occur by reductive elimination. It has been proposed that the silylenes formed in process C readily isomerize to disilenes, e.g. :SiR′-RR′Si-RR′Si- → RR′Si-SiR′=SiRR′, and that these disilenes can then add to polysilyl radicals generated by process A to form new radicals.[9] It has been established[10] that photochemically produced silyl radicals abstract hydrogen originally attached to the α- position of alkyl chains in the polysilane material (presumably in a radical disproportionation process), rather than from the solvent or from silylene traps such as Et_3SiH or Et_3SiD.

Our experiments were carried out in rigorously purified n-hexane solution with concentrations of oligosilanes in the range of 0.02–0.05 mol dm^{-3}; most irradiations were carried out with a low-pressure mercury lamp at 254 nm, but some were with a cadmium lamp at 228 nm. Products were separated and identified by GC/mass spectrometry. Information about the nature of the intermediates produced was obtained by irradiating solutions of oligosilane in 1:1 n-hexane–triethylsilane; silylenes insert into the Si–H bond in Et_3SiH to form photochemically stable hydridodisilanes, while characteristic products are also

(8) Trefonas, P.; West, R.; Miller, R. D. *J. Am. Chem. Soc.* **1985**, *107*, 2737.
(9) McKinley, A. J.; Karatsu, T.; Wallraff, G. M.; Miller, R. D.; Sooriyakumaran, R.; Michl, J. *Organometallics* **1988**, *7*, 2567. McKinley, A. J.; Karatsu, T.; Wallraff, G. M.; Thompson, D. P.; Miller, R. D.; Michl, J. *J. Am. Chem. Soc.*, in press.
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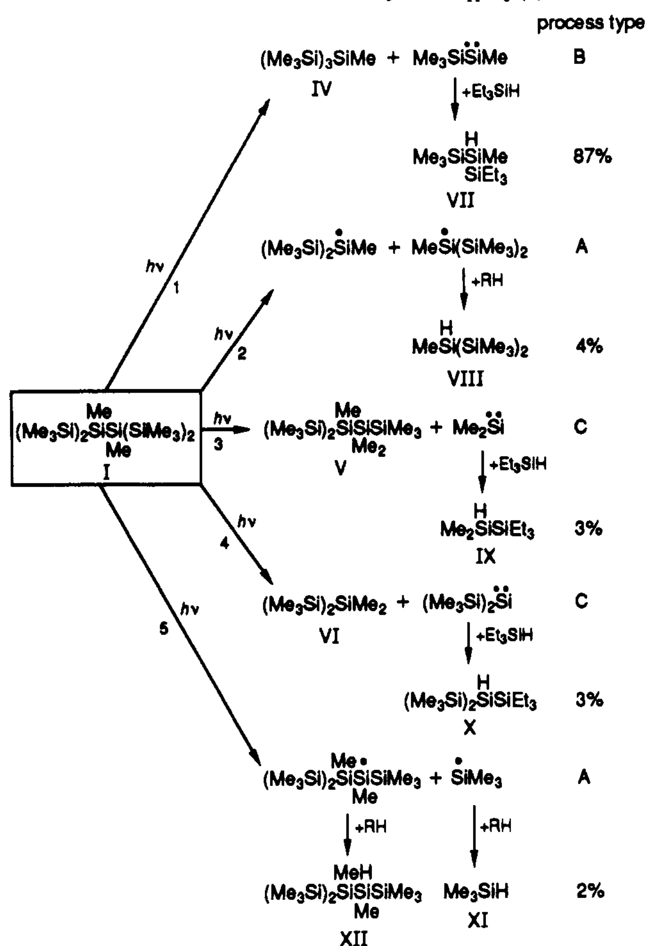
Scheme I. Photochemistry of $Me_{14}Si_6$ (I)

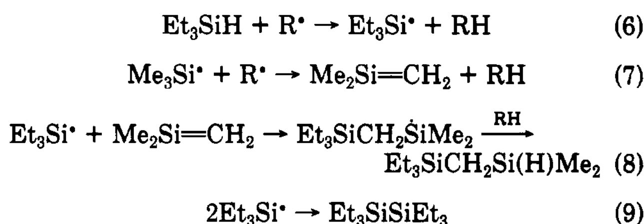


formed from radicals by hydrogen abstraction from the Si–H bond of Et_3SiH.

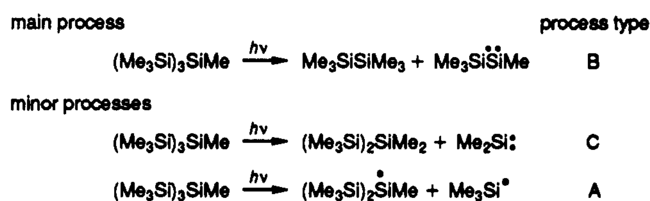
Irradiation of I at 254 nm gave the products shown in Scheme I. Experiments without Et_3SiH gave IV–VI, VIII, XI, and XII, with IV by far the major product. In addition, another major product VII and minor products IX and X were formed in the experiments with Et_3SiH. All of these products may reasonably be accounted for by the reactions in Scheme I.[11] Progress curves were plotted for the formation of products in irradiations in the presence of Et_3SiH. These curves were linear, indicating that all products were formed in primary photochemical processes; in contrast, progress curves showed maxima in similar experiments at 228 nm, indicating that the primary products absorbed light at this wavelength to undergo further photoreactions. The types of primary processes thus identified are listed in Scheme I.

Samples of products were collected from a preparative-scale experiment, thereby enabling the GC to be calibrated for each product and a quantitative assessment of the relative importance of each primary process to be made, also listed in Scheme I.

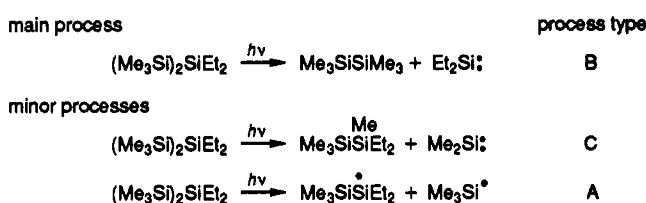
Scheme II. Formation of $Et_3SiCH_2Si(H)Me_2$



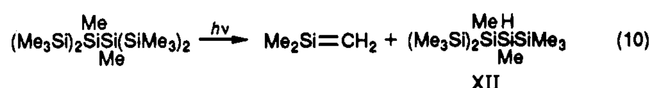
Scheme III. Primary Processes in the Photochemistry of $Me_{10}Si_4$ (II)



Scheme IV. Primary Processes in the Photochemistry of $Et_2Me_6Si_3$ (III)



Two further minor products in experiments with Et_3SiH were $Et_3SiCH_2Si(H)Me_2$ and Et_6Si_2. As shown in Scheme II, the former was very probably formed by attack of $Et_3Si^\bullet$ radicals on $Me_2Si{=}CH_2$, while the latter confirms the involvement of $Et_3Si^\bullet$ radicals. $Me_2Si{=}CH_2$ might also be formed directly by reaction 10, analogous to a prominent pathway in the photochemistry of Me_6Si_2 at 206 nm in the gas phase,[12] but that is unlikely. Such a reaction probably



requires the high-energy, low-pressure conditions of the gas-phase experiment,[12] whereas reaction 7 would be a more probable source of $Me_2Si{=}CH_2$ in solution at 254 nm. Similar experiments were undertaken with the oligosilanes II and III, but with approximate measurements of the relative importance of primary processes. The results are summarized in Schemes III and IV.

Thus, all the primary steps in the photochemistry of the oligosilanes I–III have precedents or counterparts in the processes A–C in the photochemistry of polysilanes.[8-10] Process B is by far the major one in the photochemistry of I–III; this was also found to be the major process in the photochemistry of linear permethylated oligosilanes[5] but not necessarily in the photochemistry of mesityl-substituted oligosilanes, where Si–Si bond rupture predominated in some cases.[7] Our observation of process C, not detected in previous work on oligosilanes,[4-7] is of particular interest. The results for III suggest strongly that even in permethylated linear oligosilanes the photoproduction of $:SiMe_2$ is more complicated than originally assumed; while most of it is due to the chain abridgement process B, in which an internal silicon atom is lost, some of it is due to

(11) A reviewer has reasonably suggested that analysis by GC/mass spectrometry leaves some doubt about the identification of products VII and VIII; the former could be $H–Me_2Si–SiMe_2–SiEt_3$ (VIIa), while the latter could be $H–Me_2Si–SiMe_2–SiMe_3$ (VIIIa). We separated a mixture of IV and VII by preparative GC and measured ^1H and ^{13}C NMR spectra at 300 MHz. The features of the ^{13}C spectra associated with VII were readily distinguished from those for IV and tallied with our assignment rather than VIIa; the ^1H spectrum supported that conclusion. We were only able to obtain a ^1H 300-MHz NMR spectrum of VIII, which was more consistent with our assignment than with VIIIa. However, we have GC/MS data for a sample of VIIIa; the mass spectrum is significantly different from that of VIII. We conclude that the assignments in Scheme I are correct.

(12) Brix, Th.; Bastian, E.; Potzinger, P. *J. Photochem. Photobiol., A* 1989, *49*, 287.

a process of type C, in which a terminal silicon atom is lost. For reasons not yet established, not all possible examples of processes forming silylenes were observed; thus, hexamethyldisilane was not a product of the irradiation of I.

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