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## PHOTOLYSIS AT $\lambda$ 185 nm OF HEXAMETHYLDISILOXANE IN THE LIQUID PHASE \*

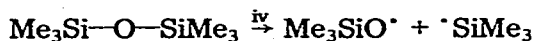
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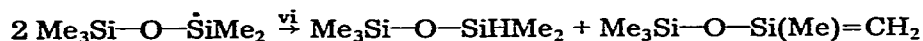
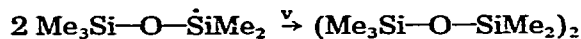
### Summary

Liquid hexamethyldisiloxane has been photolyzed at 15°C with a low pressure Hg arc (effective wavelength 185 nm). 19 products have been identified and their quantum yields determined. The quantum yields of the three main products are  $\phi[\text{CH}_4] = 0.20$ ,  $\phi[\text{C}_2\text{H}_6] = 0.045$ , and  $\phi[(\text{Me}_3\text{Si}-\text{O}-\text{SiMe}_2)_2] = 0.042$ . The main event in this photolysis is the rupture of a Si-C bond, following the homolytic (i) as well as the molecular mode (ii). Process iii occurs to a minor ex-



tent, but iv is not found at all. Cage disproportionation reactions cannot be distinguished from molecular eliminations in these experiments.

The very reactive intermediate species  $\text{Me}_3\text{Si}-\text{O}-\text{Si}(\text{Me})=\text{CH}_2$  interacts with free radicals, with polar compounds such as methanol, and with each other, with the formation of stable compounds. It appears that  $\text{Me}_3\text{Si}-\text{O}-\text{Si}(\text{Me})=\text{CH}_2$  is also formed in a disproportionation reaction (vi).



\* Presented at the IVth International Symposium on Organosilicon Chemistry, Moscow, July 1975 and dedicated to Professor Leonhard Birkofer on the occasion of his 65th birthday.

## Introduction

Whereas the photochemistry of organosilanes and organopolysilanes has received considerable attention [cf. 1–5], much less is known about the photochemical behaviour of organosiloxanes. In the photolysis of organosilanes, “Si=C” systems [6] are often formed which are highly reactive and readily undergo combination or polar addition reactions [1; 6–8]. A major process undergone by organopolysilanes is the photoelimination of diorganosilylene [5]. Polymethylpolyphenylpolysiloxane on photolysis gives rise to methyl radicals as detected by ESR [9]; accordingly organosilyl radicals must be formed as well. While the disproportionation of organosilyl radicals at room temperature has been rejected generally in the past, this reaction has recently been observed between trimethylsilyl radicals ( $k_d/k_c = 0.046$ ) [10]. Hexamethyldisiloxane, unlike Si–Si linked organosilicon compounds [5,11], shows strong absorption only below 200 nm (Fig. 1). In this respect it resembles the saturated aliphatic ethers where the absorption in the first band has been attributed to an  $n \rightarrow \sigma^*$  [12], or an  $n \rightarrow 3s$  transition [11], and it is likely that in the present system too the oxygen lone electron pair acts as the chromophore [11]. The photolysis of saturated ethers at 185 nm has been studied in this laboratory [13–16], among them that of di-*t*-butyl ether [15], the carbon analog of hexamethyldisiloxane. In the series of saturated aliphatic ethers C–O bond rupture predominates among the primary processes.

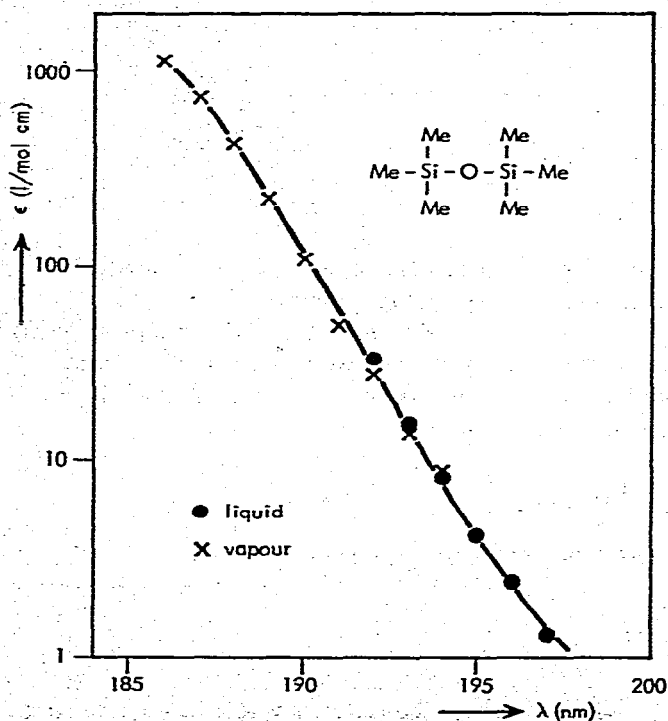


Fig. 1. Molar extinction coefficient of hexamethyldisiloxane between 186 and 197 nm.

## Results and discussion

The photolysis at 185 nm of liquid hexamethyldisiloxane leads to a large number of products, the more important of which have been identified. They are given with their quantum yields in Table 1. Some approximate information about the molecular weights of the various products was initially provided by the gas chromatogram, but full identification of the products was made with the help of reference material and/or by GC-MS. In general, the mass spectra of the products show a simple pattern. Organosilicon compounds as a rule show  $\alpha$ -cleavage leading to alkyl loss [17,18]. In the case of heavily methyl-substituted products  $m/e M - \text{CH}_3$  is almost always important, this enables determination of the molecular weight. Other dealkylations reveal further structural features.  $m/e M - 103(M - \text{CH}_2\text{OSiMe}_3)$  is often prominent,  $m/e 73$ ,  $\text{Si}(\text{CH}_3)_3$ , is fairly common. The mass spectra of some products are shown in Table 2.

The quantitative measurement of the volatile products  $\text{H}_2$ ,  $\text{CH}_4$ , and  $\text{C}_2\text{H}_6$  is straightforward and was done as described previously [19]. Of the organosilicon compounds only pentamethyldisiloxane was available in a quantity and purity sufficient for calibration. In order to determine quantitatively the yields of the remaining siloxanes, the assumption was made that the GC FID response per

TABLE 1

PRODUCTS AND THEIR QUANTUM YIELDS FROM THE 185 nm PHOTOLYSIS OF LIQUID HEXAMETHYLDISILOXANE. Legend: +, compound present; —, compound absent ( $\phi < 5 \times 10^{-4}$ ); no symbol, compound not determined.

No.	Product	(neat)	3% MeOH as scavenger
1	$\text{H}_2$	0.01	
2	$\text{CH}_4$	0.20	
3	$\text{C}_2\text{H}_6$	0.045	
4	$\text{Me}_3\text{SiH}^a$	—	
5	$\text{Me}_4\text{Si}^a$	—	
6	$\text{Me}_3\text{SiOH}^a$	—	+
7	$\text{Me}_3\text{SiOMe}^a$	—	+
8	$\text{Me}_3\text{SiOSiMe}_2\text{H}^{a,b}$	0.020	+
9	$\text{Me}_3\text{SiOSiMe}_2\text{Et}^{a,b}$	0.017	+
10	$\text{Me}_3\text{SiOSiMe}_2\text{OMe}^b$	—	+
11	$\text{Me}_3\text{SiOSiMe}_2\text{OSiMe}_3^{c,d}$	0.018	—
12, 13	$\begin{array}{c} \text{Me} \quad \text{CH}_2 \quad \text{Me} \quad (\text{OSiMe}_3)^b \\ \diagdown \quad \diagup \quad \diagdown \quad \diagup \\ \text{Si} \quad \quad \quad \text{Si} \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \\ \text{Me}_3\text{SiO} \quad \text{CH}_2 \quad \text{OSiMe}_3 \quad (\text{Me}) \end{array}$	0.002 ea.	— ea.
14	$(\text{Me}_3\text{SiOSiMe}_2)_2^{a,b}$	0.042	+
15	$\text{Me}_3\text{SiOSiMeEtSiMe}_2\text{OSiMe}_3^b$	0.011	—
16	$(\text{Me}_3\text{SiOSiMe}_2)_2\text{CH}_2^b$	0.011	
17	$(\text{Me}_3\text{SiOSiMe}_2)_2\text{O}^c$	0.02	—
18	$(\text{Me}_3\text{SiOSiMe}_2\text{CH}_2)_2^{a,b}$	0.004	
19	$\text{Me}_3\text{SiOSiMe}(\text{SiMe}_2\text{OSiMe}_3)\text{CH}_2\text{SiMe}_2\text{OSiMe}_3^b$	0.005	—

<sup>a</sup> Authentic reference material available. <sup>b</sup> Mass spectral details see Table 2. <sup>c</sup> Mass spectrum agrees with that given in [17]. <sup>d</sup> Mass spectrum agrees with that given in [18].

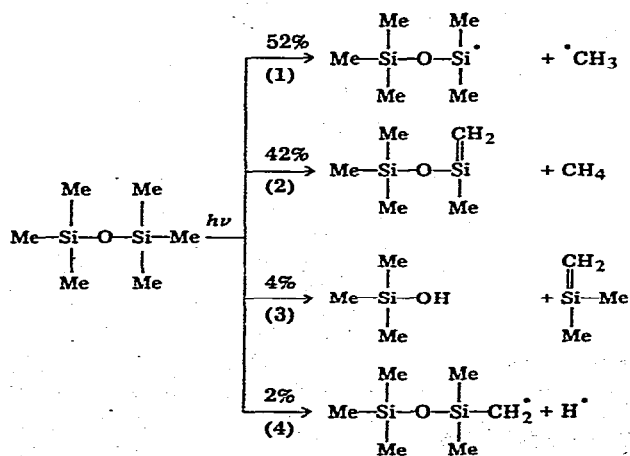
TABLE 2  
MASS SPECTRAL DETAILS OF SOME PRODUCTS

8	<i>m/e</i> 133 ( <i>M</i> - CH <sub>3</sub> , 100%); 73 (Si(CH <sub>3</sub> ) <sub>3</sub> , 20%); 147 ( <i>M</i> - H, 8%)
9	<i>m/e</i> 147 ( <i>M</i> - C <sub>2</sub> H <sub>5</sub> , 100%); 59 (75%); 133 (65%); 73 (55%); 45 (35%); 66 (30%); 161 ( <i>M</i> - CH <sub>3</sub> , 15%)
10	<i>m/e</i> 163 ( <i>M</i> - CH <sub>3</sub> , 100%); 133 (90%); 59 (20%); 73 (15%)
12	<i>m/e</i> 277 ( <i>M</i> - CH <sub>3</sub> , 100%); 73 (60%); 189 ( <i>M</i> - CH <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>3</sub> , 20%); 59 (10%); 45 (8%); 292 ( <i>M</i> , 4%)
13	<i>m/e</i> 73 (100%), 277 ( <i>M</i> - CH <sub>3</sub> , 85%); 189 ( <i>M</i> - CH <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>3</sub> , 25%); 59 (15%); 45 (14%); 131 (8%); 292 ( <i>M</i> , 2%)
14	<i>m/e</i> 147 ( <i>M</i> /2, 100%); 73 (75%); 221 ( <i>M</i> - Si(CH <sub>3</sub> ) <sub>3</sub> , 70%); 191 ( <i>M</i> - CH <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>3</sub> , 23%); 117 (20%); 45 (8%); 279 ( <i>M</i> - CH <sub>3</sub> , 5%)
15	<i>m/e</i> 235 ( <i>M</i> - Si(CH <sub>3</sub> ) <sub>3</sub> , 100%); 133 (70%); 73 (65%); 147 (Si(CH <sub>3</sub> ) <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>3</sub> , 55%); 191 ( <i>M</i> - CH <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>3</sub> , 35%); 161 (Si(CH <sub>3</sub> )(C <sub>2</sub> H <sub>5</sub> )OSi(CH <sub>3</sub> ) <sub>3</sub> , 20%); 117 (20%); 59 (15%); 205 (10%); 293 ( <i>M</i> - CH <sub>3</sub> , 7%); 279 ( <i>M</i> - C <sub>2</sub> H <sub>5</sub> , 3%)
16	<i>m/e</i> 73 (100%); 205 ( <i>M</i> - CH <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>3</sub> , 90%); 293 ( <i>M</i> - CH <sub>3</sub> , 30%); 147 (Si(CH <sub>3</sub> ) <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>3</sub> ; 15%); 59 (8%); 45 (7%)
18	<i>m/e</i> 147 (Si(CH <sub>3</sub> ) <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>3</sub> , 100%); 73 (25%); 160 (10%); 219 ( <i>M</i> - CH <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>3</sub> , 6%); 307 ( <i>M</i> - CH <sub>3</sub> , 5%); 322 ( <i>M</i> , 1%)
19	<i>m/e</i> 73 (100%); 205 (50%); 293 ( <i>M</i> - Si(CH <sub>3</sub> ) <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>3</sub> , 30%); 147 (Si(CH <sub>3</sub> ) <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>3</sub> , 12%); 425 ( <i>M</i> - CH <sub>3</sub> , 1%); 337 ( <i>M</i> - CH <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>3</sub> , 0.5%)

siloxane molecule is proportional to its carbon number. This assumption was tested and verified when pentamethylidisiloxane and hexamethylidisiloxane were compared. The sensitivity-per-molecule ratio of hexamethylidisiloxane to pentamethylidisiloxane was  $1.25 \pm 0.10$ ; the carbon-per-molecule ratio is 1.20. There remain several unidentified minor products. None of them is expected to have a quantum yield of much above  $3 \times 10^{-3}$  as judged by GC peak size.

When photolysis was carried out in the presence of 3% methanol three new products, 6, 7, and 10, appeared, whereas the formation of 11–13, 15, 17 and 19 was suppressed (Table 1). These results are explained on the basis of the primary processes 1–4 given in Scheme 1 and a series of free radical processes,

SCHEME 1. Primary processes in the 185 nm photolysis of hexamethylidisiloxane.  $\Phi$  (Primary processes)  $\approx 0.4$ .



as well as combination and polar addition reactions of Si=C intermediates.

Hydrogen atoms (from reaction 4) and methyl radicals (from reaction 1) are reactive radicals and undergo hydrogen abstraction reactions. Molecular hydrogen, methane, and  $\text{Me}_3\text{SiOSiMe}_2\text{CH}_2$  radicals result. Whereas the reactive hydrogen atom is thought mostly to be consumed in this reaction and is not believed to undergo combination reactions with other radicals in this system to any large extent, the less reactive methyl radical undergoes both abstraction and combination reactions. This is evidenced by the formation of ethane 3 and a number of products containing a methyl unit in excess, such as 9 and 15.

#### "Si=C" intermediates

Molecular processes such as reactions 2 and 3 in Scheme 1 usually play a significant role in saturated systems if the energy of the photolyzing light is not too high. Cage disproportionation reactions cannot be recognized as such in these experiments [13–16]. In organosilicon chemistry the nature of Si=C systems is not yet well established; the possibility of their biradical character has been discussed [6,10] but evidence for dipolar character is at least equally convincing [7]. The chemistry of these systems appears to be somewhat better established. They can be generated either by thermolysis [6,7,20,21] or photolysis [2,6,22,23], are known to dimerize giving four-membered ring systems [7], and are readily scavenged by polar species such as alcohols and carbonyl compounds [6,7,21–23].

In the present case, the intermediate formation of Si=C systems according to reactions 2 and 3 in Scheme 1 is evidenced by the formation of 7 and 10 in the presence of methanol. In its absence the chemistry becomes more complex since the reactivity of these Si=C systems towards free radicals appears to be much higher than that of the corresponding C=C analogs. Under these experimental conditions the Si=C systems compete for free radicals. A similar difficulty was not encountered with the olefinic products from the photolysis of saturated aliphatic ethers [13–16]. The Si=C systems thus give rise to products with molecular weights higher than that of the dehydrodimer 18 (e.g. 19). The adducts of radicals to an Si=C bond undergo further radical reactions. GC showed the formation of products besides 19 with even higher molecular weights, although at comparatively lower yields. These products, except 19, were not identified. Likewise, the formation of trisilanes and higher polysilanes was observed in the Hg-sensitized photolysis of trimethylsilane and other partially methyl-substituted silanes [24].

As has been pointed out Si=C systems are highly susceptible to polar addition reactions. Methanol has been shown to be a good reactant and  $\text{Me}_3\text{SiOH}$  probably also reacts. Traces of moisture also scavenge efficiently. Thus Si=C systems generated in reactions 2 and 3 in the absence of methanol are expected to be converted to Si—OH derivatives by moisture which could not be removed completely from the substrate. These silanol derivatives on further reaction with Si=C systems form stable products such as 11 and 17.

Dimerization of the Si=C intermediates leads to four-membered ring systems, such as products 12 and 13. The similarity of their mass spectra suggests that both are stereoisomeric 1,3-disilacylobutane derivatives (*cis* and *trans*). Their yield is comparatively small. The Si=C system from reaction 3 is generated in

a much lower yield. Hence four-membered rings containing this unit would be expected in correspondingly small yields. They might account for some of the unidentified minor peaks in the gas chromatogram.

#### *Formation of pentamethyldisiloxane*

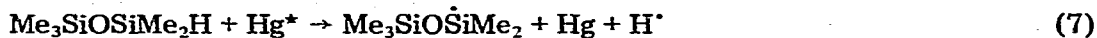
A very interesting product of this photolysis is pentamethyldisiloxane **8**. Carbene elimination from hexamethyldisiloxane does not occur here (see below). H abstraction reactions by organosilyl radicals from silicon-bound methyl groups are endothermic [25] and are not expected to take place near room temperature. Indeed, when the light intensity was decreased by a factor of about 30 the increase of the ratio  $\phi(8)/\phi(14)$  was at most 20%. Nevertheless, thermalized silyl free radicals for the most part must be the precursors of **8** since after oxygen saturation **8** is quenched to less than 5% (**14**, to less than 1%) of the O<sub>2</sub>-free case. Similarly, strong quenching of these products is also observed after ethylene saturation.

There seem to be left two hypotheses on how pentamethyldisiloxane is formed in this system. It is conceivable that combination of free H atoms with silyl radicals might successfully compete with the H abstraction reaction from the substrate if the latter reaction were very slow, but this is unlikely in view of the fact that  $k(\text{SiMe}_3 + \text{H})$  has been found at  $(2.3 \pm 1.5) \times 10^6 \text{ l mol}^{-1} \text{ sec}^{-1}$  at room temperature [26].

The other hypothesis is an unorthodox one. While disproportionation reactions of carbon free radicals are common, they have been excluded in the past for organosilyl radicals at room temperature [6,27,28]. Recently though, evidence has been obtained that Si-centered radicals do undergo such reactions [10a], with  $k_d/k_c = 0.046$  for trimethylsilyl. The admission of this hypothesis means that there is considerable disproportionation according to reaction 5 which competes with the combination reaction 6. Work on the photolysis of tetramethylsilane is now in progress in these laboratories. The results so far obtained also point toward such a disproportionation reaction [29].



In order to explore further the scope of reaction 5, pentamethyldisiloxane saturated with mercury was photolyzed at 254 nm. In the Hg-sensitized reac-



tion 7, as in 1 (see Scheme), the pentamethyldisiloxanyl radical is generated, and reaction of the hydrogen atom with pentamethyldisiloxane furnishes another such radical. In the presence of moisture or methanol reactions 5 and 6 eventually lead to **14** and **17**, or **14** and **10**, respectively. Similarly, the 254 nm photolysis of a mixture of pentamethyldisiloxane, methanol, and di-*t*-butylperoxide yielded **14** and **10**, among other products.

The possibility of carbene elimination from hexamethyldisiloxane has been examined and excluded on the basis of the following experiment: It is known that carbene inserts easily into the Si-H and C-H bonds of pentamethyldisiloxane, leading to  $\text{Me}_3\text{SiOSiMe}_3$ ,  $\text{Me}_3\text{SiOSiH(Me)Et}$ , and  $\text{EtMe}_2\text{SiOSiHMe}_2$  in

the ratios 4/3/6 [30] (see Experimental).  $\text{CD}_2$  reacts likewise. A mixture of hexamethyldisiloxane- $d_{18}$  and pentamethyldisiloxane (1/3) was photolyzed at 185 nm and the products analyzed under conditions permitting the resolution of the variously deuterated hexamethyldisiloxanes (retention times decrease with increasing deuterium content). If carbene elimination from hexamethyldisiloxane- $d_{18}$  occurred one would expect the formation of carbene insertion products from pentamethyldisiloxane as above but such products were absent. Instead,  $\text{Me}_3\text{SiOSiMe}_2\text{CD}_3$  was formed, again proving that methyl radicals are indeed mechanistically important in this system. Thus, in the 185 nm photolysis of hexamethyldisiloxane, ethylpentamethyldisiloxane 9 is formed by the combination of a methyl radical with the radical  $\text{Me}_3\text{SiOSiMe}_2\dot{\text{C}}\text{H}_2$ , and not via carbene insertion. This is further supported by the near congruence of the measured value with the value estimated on the basis of encounter probabilities of these two non-disproportionating radicals ( $a^2 + 2ab + b^2$ ,  $a^2 \cong 3$ ,  $ab \cong 9$ ,  $b^2 \cong 18$ ;  $a$ ,  $b$ : steady-state radical concentrations), assuming, for simplicity, equal reaction cross sections.

#### Scission of the Si—O bond

The nonoccurrence of the homolytic scission of the Si—O bond is in contrast with the prominence of the corresponding reaction, C—O bond scission, in all saturated ethers. Trimethylsilyl radicals from this reaction, if it occurred, should react under the present conditions with the readily available methyl radicals and give tetramethylsilane 5 which, however, is absent.

#### Quantitative aspects

The material balance in this system is somewhat unsatisfactory (viz.  $\phi[\dot{\text{C}}\text{H}_3 + \text{CH}_4] = 0.3$  vs.  $\phi[\text{Me}_3\text{SiOSiMe}_2 + \text{Me}_3\text{SiOSi}(\text{Me})=\text{CH}_2] = 0.2$ ). This is mainly due to a deficit (with respect to the easily measurable  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ ) in various products of higher molecular weight generated by radical addition to the Si=C systems, which because of their smallness escaped identification and measurement. The accuracy of the calculation of the relative importance of the primary processes in Scheme 1 suffers from this fact. The scheme has been drawn up with the assumption that reactions between radicals and hydrogen atoms are negligible.

A lower limit for reaction 1 is given by the sum of all products formed by participation of methyl radicals except for methane which is also formed via reaction 2 ( $\phi(\dot{\text{C}}\text{H}_3) > 2\phi(3) + \phi(9) + \phi(15) = 0.12$ ). As mentioned above, some methane is expected to be formed from methyl radicals by hydrogen abstraction from the substrate. The quantum yield of methyl radicals reacting by hydrogen abstraction can be roughly estimated starting with a count of all products containing the  $\text{Me}_3\text{SiOSiMe}_2\text{CH}_2$  unit ( $\phi(9) + \phi(16) + \phi(17) + 2\phi(18) = 0.04$ ). The quantum yield of these radicals from reaction 4 and the subsequent hydrogen abstraction reaction by the hydrogen atom is 0.02, thus leaving  $\phi = 0.02$  for the abstracting methyl radicals. The real yield is probably somewhat higher bearing in mind the deficit of higher molecular weight products. Finally in the  $\phi(\text{CH}_3)$  estimate one must take into account the back reaction, reaction -1, as it were. Its contribution excluding cage recombination and disregarding

disproportionation reactions of  $\text{Me}_3\text{SiOSiMe}_2$ , can be estimated from the yield of 3 and 14, again using the formula for radical combination reactions at random encounter. With  $a^2 = \phi(3)$  and  $b^2 = \phi(14)$ ,  $2ab = \phi$  (hexamethyldisiloxane) can be calculated at 0.09. Although this value is only approximate it shows that this reaction must not be neglected here in the estimate of the quantum yields of the primary processes. In total, a quantum yield of 0.22 can be attributed to reaction 1.  $\phi$  (reaction 2) is easily estimated at 0.18 as  $\phi(\text{CH}_4, \text{molecular}) = \phi(\text{CH}_4, \text{total}) - \phi(\text{CH}_4, \text{radical})$ . The quantum yield of reaction 3 is estimated on the basis of product 11;  $\phi(11) = 0.018$ . Reaction 4 is given by the hydrogen yield;  $\phi(1) = 0.01$ . The sum of all primary processes is then calculated at around 0.4.

In Scheme 1 the participation of each primary process is given as a percentage. The photolysis is largely governed by the homolytic scission of the Si—C bond and the elimination of molecular methane. Together they account for ~94% of the primary events. C—H bond scission (2%) is marginal, similar to saturated ethers. Si—O bond cleavage (4%) is only observed as a molecular process (reaction 3), and homolytic scission is negligible.

## Experimental

Hexamethyldisiloxane (Bayer) was purified by preparative GC and subsequent distillation. It showed a GC purity of 99.98% or better by flame ionization detection, but contained traces of moisture. Samples of neat hexamethyldisiloxane in a Suprasil QS optical cell were deaerated by purging with Ar for 20 min, or in vacuo by the freeze-pump-thaw technique. The samples were then photolyzed in the manner described before [13–15], conversions not exceeding 0.5%. A few runs were carried out with methanol-saturated hexamethyldisiloxane (~3% methanol). These had to be degassed in vacuo because purging led to methanol depletion. The light source was a low pressure Hg arc lamp (Graentzel, Karlsruhe) used without filter. The distance between the cell and the lamp was about 1 mm. 185 nm light intensities were determined with the ethanol actinometer [31] at  $0.30 \times 10^{18}$  quanta/min per 2.0 ml sample. There was no need to remove  $\lambda$  254 nm since it is photochemically inactive in this system.

The molar extinction coefficient of hexamethyldisiloxane (liquid and vapour) was determined between 186 and 197 nm (Fig. 1). The procedure has been described previously [14]. For hexamethyldisiloxane vapour pressure data see [32].

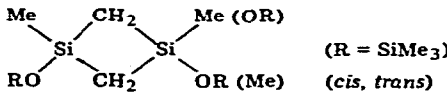
Product analysis and identification was by gas chromatography (see Table 3) and mass spectrometry. Analytical procedures were similar to those previously used [13–16]. The deuterium-labeled material from the experiments testing the involvement of carbene in these photolyses was analyzed on a squalane glass capillary column [30]. Some analytical details are summarized in Table 3.

*Pentamethyldisiloxane* (8). Under vigorous stirring and exclusion of moisture, 18.35 g (0.203 mol) of trimethylsilanol [33] were added dropwise to 13.90 g (0.1045 mol) of tetramethyldisilazane (Serva, Heidelberg) which was cooled by crushed ice. Ammonia was liberated immediately. After stirring 5 h at room temperature, the reaction mixture which contained 94% of 8 (determined by GC), was distilled in a concentric tube column (Fischer Labortechnik, Bad Godesberg,



TABLE 3

DETAILS ON THE GC ANALYSIS OF HEXAMETHYLDISILOXANE PHOTOLYSIS PRODUCTS AND SOURCES OF REFERENCE COMPOUNDS

Product	Relative retention times			Source
H <sub>2</sub>	2.5 <sup>a</sup>			
CH <sub>4</sub>	1.4 <sup>b</sup>			
C <sub>2</sub> H <sub>6</sub>	3.0 <sup>b</sup>			
Me <sub>3</sub> SiH		0.14 <sup>c</sup>		PCR
Me <sub>4</sub> Si		0.40 <sup>c</sup>		Merck
Me <sub>3</sub> SiOSiMe <sub>2</sub> H	0.29 <sup>d</sup>	1.00 <sup>c</sup>	0.38 <sup>e</sup>	<i>g, h</i>
(Me <sub>3</sub> SiOSiMe <sub>3</sub> )	0.57 <sup>d</sup>	0.29 <sup>f</sup>		Bayer
Me <sub>3</sub> SiOMe		0.31 <sup>f</sup>		<i>g, i</i>
Me <sub>3</sub> SiOSiMe <sub>2</sub> Et	1.00 <sup>d</sup>	3.5 <sup>c</sup>	1.00 <sup>e</sup>	<i>g, h</i>
Me <sub>3</sub> SiOSiMe <sub>2</sub> OMe	1.15 <sup>d</sup>	1.00 <sup>f</sup>		<i>g</i>
Me <sub>3</sub> SiOSiMe <sub>2</sub> OSiMe <sub>3</sub> (MeOH)	2.06 <sup>d</sup>			<i>g</i>
(Me <sub>3</sub> SiOSiMe <sub>2</sub> ) <sub>2</sub> O	0.11 <sup>d</sup>	2.0 <sup>f</sup>		
(Me <sub>3</sub> SiOSiMe <sub>2</sub> ) <sub>2</sub>	5.8 <sup>d</sup>		5.3 <sup>e</sup>	<i>g</i>
Me <sub>3</sub> SiOH	6.6 <sup>d</sup>	3.8 <sup>f</sup>	6.7 <sup>e</sup>	<i>g, h</i>
	8.0 <sup>d</sup>	4.0 <sup>f</sup>	1.70 <sup>e</sup>	<i>g, j</i>
RO-Si(CH <sub>2</sub> ) <sub>2</sub> -Si(OR)(Me) <sub>2</sub>	8.3 <sup>d</sup>			<i>g</i>
(Me <sub>3</sub> SiOSiMe <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub>	8.5 <sup>d</sup>			<i>g</i>
Me <sub>3</sub> SiOSiMe(Et)SiMe <sub>2</sub> OSiMe <sub>3</sub>	8.6 <sup>d</sup>			<i>g</i>
(Me <sub>3</sub> SiOSiMe <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub>	9.5 <sup>d</sup>			<i>g, h</i>
Me <sub>3</sub> SiOSiMe(SiMe <sub>2</sub> OSiMe <sub>3</sub> )CH <sub>2</sub> SiMe <sub>2</sub> OSiMe <sub>3</sub>	15.9 <sup>d</sup>			<i>g</i>
(CH <sub>3</sub> ) <sub>3</sub> SiOSiH(CH <sub>3</sub> ) <sub>2</sub>	11.9 <sup>k</sup>			<i>h</i>
(CD <sub>3</sub> ) <sub>3</sub> SiOSi(CD <sub>3</sub> ) <sub>3</sub>	14.00 <sup>k</sup>			<i>h</i>
(CH <sub>3</sub> ) <sub>3</sub> SiOSi(CH <sub>3</sub> ) <sub>2</sub> CD <sub>3</sub>	14.60 <sup>k</sup>			<i>l</i>
(CH <sub>3</sub> ) <sub>3</sub> SiOSi(CH <sub>3</sub> ) <sub>2</sub> CD <sub>2</sub> H	14.65 <sup>k</sup>			<i>m</i>
(CH <sub>3</sub> ) <sub>3</sub> SiOSi(CH <sub>3</sub> ) <sub>3</sub>	14.70 <sup>k</sup>			<i>m</i>
(CH <sub>3</sub> ) <sub>3</sub> SiOSiH(CH <sub>3</sub> )(CH <sub>2</sub> CD <sub>2</sub> H)	21.80 <sup>k</sup>			<i>m</i>
(CH <sub>3</sub> ) <sub>3</sub> SiOSiH(CH <sub>3</sub> )(C <sub>2</sub> H <sub>5</sub> )	22.05 <sup>k</sup>			<i>m</i>
(CD <sub>2</sub> HCH <sub>2</sub> )(CH <sub>3</sub> ) <sub>2</sub> SiOSiH(CH <sub>3</sub> ) <sub>2</sub>	22.40 <sup>k</sup>			<i>m</i>
(C <sub>2</sub> H <sub>5</sub> )(CH <sub>3</sub> ) <sub>2</sub> SiOSiH(CH <sub>3</sub> ) <sub>2</sub>	22.65 <sup>k</sup>			<i>m</i>

<sup>a</sup> Elution time, minutes. Column: active coal, 4 m, i.d. 5 mm, 23° C, 28 ml Ar/min. <sup>b</sup> Elution time, minutes. Column: Porapak Q 100–120 mesh, 2.3 m, i.d. 2.2 mm, 110° C, 13 ml Ar/min. <sup>c</sup> Capillary column: Perkin–Elmer 7G 3 (polypropylene/glycol) 100 m stainless steel, i.d. 0.5 mm, 40° C, 2 ml N<sub>2</sub>/min. <sup>d</sup> Capillary column: OV 101, 50 m glass, i.d. 0.27 mm, temperature programmed 4 min isothermal at 70°, 70° to 250° at 8°/min, carrier gas N<sub>2</sub> 1.35 at across column. <sup>e</sup> Column temperature 90° C, otherwise as c. <sup>f</sup> Capillary column: Carbowax 20M, 80 m glass, i.d. 0.27 mm, temperature programmed 60 to 160° C at 2°/min, carrier gas N<sub>2</sub> 1.3 at across column. <sup>g</sup> Identification through GC-MS analysis. <sup>h</sup> GC peak assignment by means of reference material synthesized as described in the text. <sup>i</sup> Synthesized according to [37]. <sup>j</sup> Synthesized according to [33]. <sup>k</sup> Elution time, minutes. Capillary column: squalane, 120 m glass, i.d. 0.25 mm, 35° C, carrier gas N<sub>2</sub> 1.75 at across column. <sup>l</sup> Product of the co-photolysis of pentamethyldisiloxane and hexamethyldisiloxane-*d*<sub>18</sub>. <sup>m</sup> Synthesized through carbene insertion using diazomethane-*d*<sub>2</sub>, similar to the preparation of ethylpentamethyldisiloxane described in the text.

length 500 mm). 16.3 g (0.11 mol) of a fraction was collected with b.p. 85°C/760 Torr [34] and a purity of 99.5%. Yield: 54.02% (based on trimethylsilanol).

**Ethylpentamethyldisiloxane (9).** Gaseous diazomethane was bubbled into a sample of hexamethyldisiloxane in a glass vessel using argon as a carrier gas. As

soon as a yellow color persisted, the stream of argon/diazomethane was stopped and the reaction mixture UV-irradiated until the yellow color had disappeared. Identification of **9** was by mass spectroscopy.

**2,2,4,4,5,5,7,7-Octamethyl-2,4,5,7-tetrasilolane-3,6-dioxaoctane (14)**. In a 2-necked flask, a solution of 1.28 g (6.845 mmol) 1,1,2,2-tetramethyl-1,2-dichlorodisilane [**35**] (purity 78%) and 3.5 ml of dry benzene was cooled to 0°C under exclusion of moisture. 1.08 g (9.64 mmol) of sodium trimethylsilanolate (prepared by adding the stoichiometric amount of sodium hydride to a benzene solution of trimethylsilanol), dissolved in a few ml of benzene, were added over 30 min. After refluxing for 1 h, sodium chloride was filtered off and the solvent removed in vacuo. The residue contained 22.8% **14** according to GC. Identification was performed by mass spectroscopy.

**2,2,4,4,7,7,9,9-Octamethyl-3,8-dioxo-2,4,7,9-tetrasiladecane (18)**. By analogy to the procedure for preparing vinyl-diethylmethylsilane [**36**], 100 ml of dry tetrahydrofuran were placed in a small 3-necked flask which was fitted with a dry ice cooled reflux condenser, a dropping funnel, and a gas inlet tube. After adding 100 mg of 5% platinum on charcoal and heating the contents of the flask to reflux temperature, a vigorous stream of acetylene (free of acetone) and 7 g (0.047 mol) of pentamethyldisiloxane, by dropwise addition, were introduced. By stripping off the solvent and unreacted starting material over a spinning band column at 28–30°C/200 Torr, an oily residue was obtained which contained 59.4% of **18** according to GC. Micropreparative GC was used to isolate a sample for analysis. Found: C, 45.2; H, 10.8. Mol. wt. by MS 322.  $C_{12}H_{34}O_2Si_4$  C, 44.7; H, 10.6%. Mol. wt. 322.8.

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