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PHOTOLYSIS OF PERMETHYLATED LINEAR POLYSILANES

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SUMMARY

The UV photolysis of the permethylated linear polysilanes $Me(Me_2Si)_nMe$ (I), with $n=4$ to 8, in cyclohexane at, or a little above, room temperature has been found to proceed simultaneously by two different routes, one of these involves contraction of the chain with loss of dimethylsilylene species to produce octamethyltrisilane which was usually very resistant to the photolysis), while the other comprises homolytic scission of the silicon–silicon bond followed by abstraction of hydrogen atoms by the resultant silyl radicals to form 1*H*-polymethylpolysilanes. From the photolysis of (I) in diethylmethylsilane, it has been shown that the extent of homolysis increases with increasing chain length of (I), whereas the effective yield of dimethylsilylene species is almost constant regardless of this chain length. No evidence could be obtained for insertion of the photochemically generated dimethylsilylene into a silicon–silicon bond.

INTRODUCTION

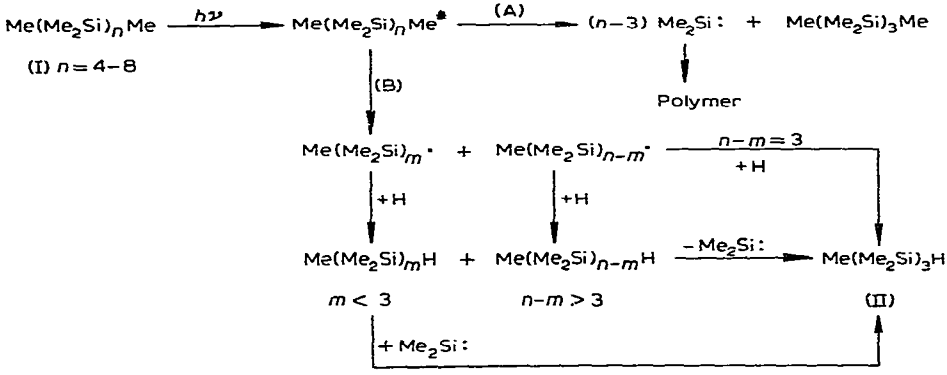
In the preceding paper[1] it was shown that dodecamethylcyclohexasilane undergoes photochemical degradation to produce mainly two of the lower homologs of the permethylated cyclopolysilanes, *viz.* the cyclotetra- and cyclopentasilane, with simultaneous generation of dimethylsilylene species, Me_2Si:. We have also found[2] that the photolytic generation of silylene species is quite a general reaction for acyclic permethylated polysilanes and offers a novel and convenient route to divalent silicon intermediates such as Me_2Si: and $Me_3SiSi(Me)$:. As part of a continuing investigation of the photolysis of organometalloidal catenate and related compounds, we have now examined in more detail the photochemical behavior of certain lower members of the permethylated linear polysilanes (I)[3], with $n=3$–8.

$$Me(Me_2Si)_nMe \quad (I)$$

RESULTS AND DISCUSSION

In some preliminary experiments we found that when any one of the linear polysilanes (I) with $n=4$–8 was photolyzed by irradiation with ultraviolet light (2537 Å) in cyclohexane at ca. 45° under bubbling dry nitrogen, octamethyltrisilane (I, $n=3$)[3a,4] was always formed as the major volatile product, with 1*H*-heptamethyltrisilane, $Me(Me_2Si)_3H$ (II)[5] as a minor product, together with a significant quantity of polymeric material.

The contraction of the silicon–silicon chain of a higher polysilane molecule to give the trisilane can be explained as a result of loss of dimethylsilylene species* (Path A). However, the formation of 1*H*-polysilanes, such as (II), with skeletal chains shorter than that of the starting polysilane, must be ascribed to homolytic scission of the silicon–silicon bond to produce silyl radicals, which immediately abstract hydrogen atoms from solvent molecules or other available sources (Path B)**. If the number of silicon atoms in the thus formed 1*H*-silanes is larger than three, they will undergo further photolysis. On the other hand, the fate of hydrosilanes containing less than three silicon atoms may be dependent upon whether or not a silylene-trapping agent has been added to the reaction system, since it has conclusively been shown recently that the dimethylsilylene species can readily insert into a silicon–hydrogen bond. In the absence of an added silylene-trapping agent, such hydrosilanes will undergo insertion of the dimethylsilylene species to give (II), while in the presence of a large quantity of, say, diethylmethylsilane as the silylene quencher they will survive almost entirely, because such lowest members are themselves highly resistant towards UV photolysis. The pathways leading to the observed compounds may thus be represented schematically as follows:



Photolysis of (*I*) *in diethylmethylsilane*

In order to obtain further insight into the process of photochemical degradation of the linear polysilanes (I), we made use of the silylene-trapping technique. Thus, a solution of a weighed sample of (I) (around 0.3 g) and a given quantity of n-decane (around 1.5 g, as an internal standard for GLC analysis) in diethylmethylsilane (10 ml) contained in a closed quartz tube was irradiated externally for 40 h at room tempera-

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* For dimethylsilylene, see preceding paper[1] and references cited therein.

** Recently. Narula[7] has briefly reported that irradiation of hexamethyldisilane with ultraviolet light (236 nm) gives rise to trimethylsilyl radicals. For the photochemical homolysis of silicon–silicon bonds, see also ref. 1.

ture with ultraviolet light through a Vycor filter (2537 Å). Table 1 lists the yields of all the observed products expressed in terms of the molar ratio of each product to the internal standard, values for the effective yield of dimethylsilylene as indicated by the yield of its insertion product (Et$_2$MeSiSiMe$_2$H) divided by $n-3$, and the approximate extent of homolytic silicon–silicon scission estimated from the total yield of Me(Me$_2$Si)$_n$H (with $n=2$ and 3) divided by two.

TABLE 1

PHOTOLYSIS OF Me(Me$_2$Si)$_n$Me (I) IN DIETHYLMETHYLSILANE[a]

Compound n in (I)	*Yields of products (%)*				*Et$_2$MeSiSiMe$_2$H/ $n-3$*	*Homolytic scission (%)*
	Me(Me$_2$Si)$_2$H	*Me(Me$_2$Si)$_3$H*	*Et$_2$MeSiSiMe$_2$H*	*Me(Me$_2$Si)$_3$Me*		
3	Trace	Trace	Trace	97		Trace
4	18	3	58	84	58	11
5	20	22	115	57	58	21
6	29	29	171	51	57	29
7	29	37	224	47	56	33
8	32	40	296	39	59	36
4[b]	Trace	15		83		
5[b]	Trace	22		54		

[a] The reaction mixture contained in a closed quartz tube was irradiated externally at room temperature for 40 h. [b] Photolysis in cyclohexane in the absence of Et$_2$MeSiH.

Trimethylsilane also was detected in the reaction product but the yields were always less than 3%. This suggests that the scission at the terminal silicon–silicon bond is less favored relative to that at an internal one. No Et$_2$MeSi(SiMe$_2$)$_n$H with $n \geq 2$ appeared to be formed under the conditions used.

An attempt to photolyze octamethyltrisilane (I, $n=3$) resulted in a recovery of more than 97% of the starting substance, indicating that this trisilane, once it has been formed as a result of photolysis of the higher homologs will largely remain unchanged, although possibly a very small proportion of it undergoes degradation by the attack of free radicals. (However, under different conditions, in which a sample was irradiated internally with a mercury lamp for a prolonged period ($\approx$60 h), the trisilane also underwent skeletal contraction to hexamethyldisilane with loss of dimethylsilylene up to ca. 20%.)

As shown in Table 1, the "extent of homolytic scission" of the silicon–silicon bond increased with increasing chain length of the starting polysilane, although the poorer material balance observed with the higher homologs suggests that the fate of silyl radicals must be much more complicated than indicated by the figures. On the other hand, the values of the effective yields of dimethylsilylene were practically constant for all the starting polysilanes (I). On an assumption that dimethylsilylene is generated in 84% yield from the photolysis of decamethyltetrasilane (I, $n=4$), the ability of diethylmethylsilane to trap the silylene is thought to be about 69% at a conservative estimate.

Photolysis of (I) in cyclohexane in the absence of the quenching agent produced (I, $n=3$) and (II), but only traces of pentamethyldisilane. Presumably this compound was consumed by its reaction with dimethylsilylene during photolysis, giving (II) along with higher homologs of $Me(Me_2Si)_nH$ which could not be detected by GLC.

Isolation of reaction products

For the purpose of isolating products, photolysis of (I) on a larger scale was carried out with a low-pressure mercury lamp with a Vycor filter inserted into the reaction mixture. Table 2 shows the relative amounts of the distillable products determined by GLC. Each product with the exception of 1*H*-nonamethyltetrasilane was isolated by preparative GLC and identified by mass and ^1H NMR spectroscopic studies. The 1*H*-tetrasilane was identified by comparison of its GLC retention time with that of an authentic sample[7]. ^1H NMR data for (II) and two of the insertion products $Et_2MeSi(SiMe_2)_nH$ ($n=1$ and 2) are listed in Table 3.

TABLE 2

PHOTOLYSIS OF $Me(Me_2Si)_nMe$ (I) IN THE PRESENCE OF DIETHYLMETHYLSILANE IN CYCLOHEXANE[a]

Compound n in (I)	*Volatile product (g)*	*Relative yields[b]*				
		$Me(Me_2Si)_3Me$	*$Me(Me_2Si)_3H$*	*$Et_2MeSiSiMe_2H$*	*$Et_2MeSi(Me_2Si)_2H$*	*$Me(Me_2Si)_4H$*
4	3.1	1.00	0.05	0.80	0.02	
5	3.1	1.00	0.44	1.96	0.13	0.08
6	3.9	1.00	0.56	3.24	0.36	0.18

[a] Each 3.0 g of (I) in the presence of 30 g of Et_2MeSiH in 200 ml of cyclohexane was irradiated at room temperature for 20 h. [b] Molar ratios of 1*H*-polysilanes to octamethyltrisilane in the distillate are given.

TABLE 3

^1H NMR DATA FOR 1*H*-ORGANOPOLYSILANES

Compound	*Chemical shift (τ)*					
	H^a	*H^b*	*H^c*	*H^d*	*H^e*	*H^f*
$(CH_3^a)_3Si–Si(CH_3^b)_2–Si(CH_3^c)_2H^d$	9.89	9.95	9.83[a]	6.27[b]		
$(C_2H_5^e)_2CH_3^fSi–Si(CH_3^c)_2H^d$			9.89[a]	6.32[b]	9.58–8.81	9.99
$(C_2H_5^e)_2CH_3^fSi–Si(CH_3^b)_2–Si(CH_3^c)_2H^d$		9.79	9.80[a]	5.97[b]	9.52–8.84	9.91

[a] The center of a doublet. [b] The center of a septet.

Attempted insertion of dimethylsilylene into Si–Si bonds

In order to learn whether or not dimethylsilylene could insert into a silicon–silicon bond, we carried out the photolysis of permethylated tetrasilane (I, $n=4$) in 1,2-diethyltetramethyldisilane. GLC analysis of the reaction mixture revealed that octamethyltrisilane (I, $n=3$) was produced in 80% yield. However, no 1,3-diethylhexamethyltrisilane, which would arise from insertion of dimethylsilylene into the silicon–silicon bond, was detected.

$$Me_2Si: + EtMe_2Si{-}SiMe_2Et \not\rightarrow EtMe_2SiSi(Me_2)SiMe_2Et$$

This is consistent with the observation made by Atwell and coworkers that methoxymethylsilylene, (MeO)MeSi: generated by thermolysis of *sym*-tetramethoxydimethyldisilane, did not insert into the silicon–silicon bond[8], although several papers which have appeared recently suggest the possible occurrence of such an insertion in the case of silylene (H_2Si:) itself.

EXPERIMENTAL

Molecular weights were determined by mass spectrometry. GLC analysis and separation were carried out as described in the preceding paper[1]. All of the permethylated linear polysilanes are known compounds, and were prepared by established methods[3,4].

Photolysis of (I) in diethylmethylsilane

In a carefully dried ca. 10 ml quartz test-tube was placed a solution of an exactly weighed sample of a polysilane (I) and a known quantity of n-decane (as internal standard) in 10 ml of diethylmethylsilane. The following are the quantities (g) used of the polysilanes (I) and n-decane (shown in parentheses): for (I, $n=4$) 0.3047 (0.1803); for (I, $n=5$) 0.3401 (0.1702); for (I, $n=6$) 0.3001 (0.1425); for (I, $n=7$) 0.1425 (0.3427); and for (I, $n=8$) 0.2241 (0.1626). The solution was purged with dry nitrogen and the tube was sealed with a serum cap. It was then irradiated externally with a low-pressure mercury lamp with a Vycor filter at room temperature for 40 h. The reaction product was analyzed by GLC. The results are given in Table 1.

Isolation of products

In a reaction vessel, fitted internally with a low-pressure mercury lamp having a Vycor filter, a solution of a sample of (I) and diethylmethylsilane in dry cyclohexane was photolyzed under bubbling nitrogen (see Table 2). The solvent cyclohexane and

TABLE 4

REFRACTIVE INDICES AND ANALYTICAL DATA FOR ISOLATED COMPOUNDS

Compound	*Formula*	n_D^{20} *found (reported)*	*Mol. wt. found (calcd.)*	*C (%) found (calcd.)*	*H (%) found (calcd.)*
Octamethyltrisilane	$C_8H_{24}Si_3$	1.4608 (1.4610)[a]	204 (204.54)		
1*H*-Heptamethyltrisilane	$C_7H_{22}Si_3$	1.4624 (1.4637)[b]	190 (190.52)		
1*H*-2,2-Diethyltrimethyldisilane	$C_7H_{20}Si_2$	1.4493	160 (160.41)	52.11 (52.41)	12.81 (12.57)
1*H*-3,3-Diethylpentamethyltrisilane	$C_9H_{26}Si_3$	1.4771	218 (218.57)	49.31 (49.45)	11.37 (11.99)

[a] Ref. 3a. [b] Ref. 3b.

unchanged diethylmethylsilane were evaporated, and the residue was distilled under reduced pressure. The distillate was analyzed by GLC and individual products were separated by preparative GLC. The refractive indices, molecular weights, and elemental analyses for the isolated products are given in Table 4.

Attempted insertion of Me_2Si: species into Si–Si bond

In a similar quartz tube to that used above was placed a mixture of 0.2563 g of decamethyltetrasilane and 0.1803 g of n-decane dissolved in 10 ml of 1,2-diethyltetramethyldisilane. The mixture was irradiated externally with ultraviolet light at room temperature for 40 h. The mixture was then analyzed by GLC to reveal the formation of 80% of octamethyltrisilane (I, $n=3$). However, no 1,3-diethylhexamethyltrisilane or its higher homologs could be detected in spite of the use of several different columns for GLC analysis.

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