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PHOTOLYSIS OF ORGANOPOLYSILANES. SYNTHESIS AND PHOTOCHEMICAL BEHAVIOR OF *Si*-SILYL SUBSTITUTED POLYSILACYCLOALKANES *

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Summary

Four *Si*-silyl substituted polysilacycloalkanes, 2-trimethylsilyl-1,1,2,3,3-pentamethyl-1,2,3-trisilacyclopentane (**1**), 2,3-bis(trimethylsilyl)-1,1,2,3,4,4-hexamethyl-1,2,3,4-tetrasilacyclohexane (**2**), bis(1,1,2,3,3-pentamethyl-1,2,3,-trisilacyclopentyl) (**4**) and 2-trimethylsilyl-1,1,2,3,3-pentamethyl-1,2,3-trisilacyclohexane (**5**) were prepared by co-condensation of 1,2-bis(chlorodimethylsilyl)alkanes and 1,1-dichlorotetramethyldisilane with a lithium dispersion in the presence of a catalytic amount of triphenylsilyllithium in THF. The photochemical behavior of compounds **1**, **2**, **4** and **5** has been investigated in the presence of diethylmethylsilane in cyclohexane. The photolysis of **1** and **5** was found to proceed simultaneously by two different pathways, to give two types of silylene spcies, while compounds **2** and **4** proceeded in a two-step process and expelled a silylene in each step.

Introduction

The generation of silylene species by photolysis of dodecamethylcyclohexasilane was first observed in our laboratory in 1969 [1]. Since that time, considerable attention has been focused on the photochemical formation and reactions of silylene, and many papers dealing with photolysis of cyclic and acyclic polysilanes have been published [2–9]. However, no interest has been shown in the photochemistry of *Si*-silyl substituted polysilacycloalkanes. In this paper, we report the synthesis of this type of polysilacycloalkanes and some aspects of their photochemical behavior, which involves the formation of new types of silylene species.

Results and discussion

Preparation of the Si-silyl substituted polysilacycloalkanes

The co-condensation of 1,2-bis(chlorodimethylsilyl)alkanes and 1,1-dichlorotetra-

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* Dedicated to Professor O.A. Reutov on the occasion of his 65th birthday.

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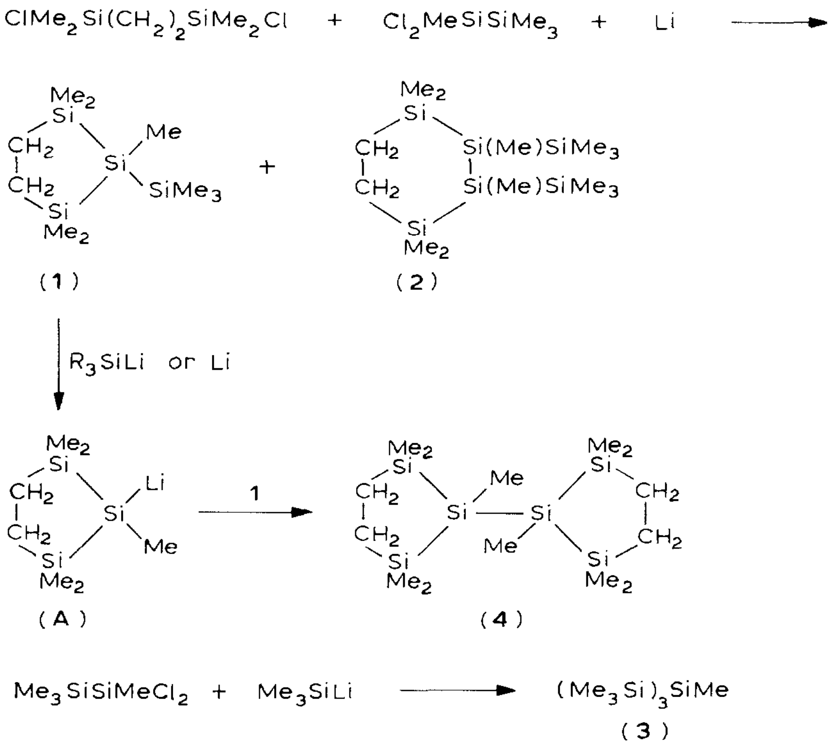
TABLE 1

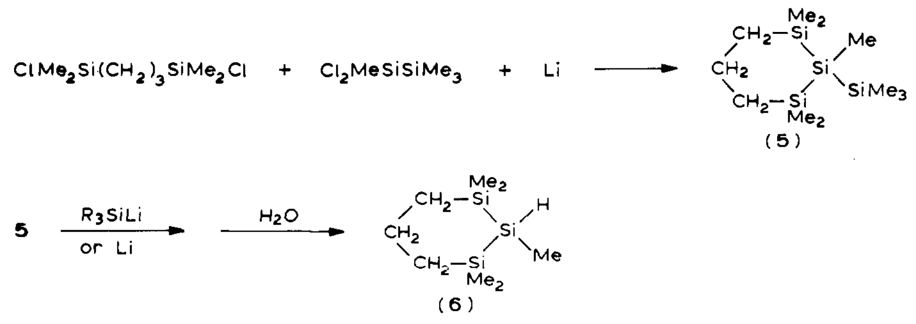
REACTION OF $ClMe_2(CH_2)_nMe_2Cl$ AND $Cl_2MeSiSiMe_3$ WITH Li IN THE PRESENCE OF Ph_3SiLi

$ClMe_2Si(CH_2)_n$-$SiMe_2Cl$ (mol)	Cl_2MeSi-$SiMe_3$ (mol)	Li (mol)	Reaction temperature (°C)	Time (h)	Yield of volatile product (%)	Product and molar ratio (%)			
						1	2	3	4
0.052 ($n = 2$)	0.10	0.43	10	5	51	5	75	20	–
0.10 ($n = 2$)	0.10	0.55	10	5	27	47	42	11	–
0.025 ($n = 2$)	0.025	0.20	15	10	64	16	8	52	24
						5	6	3	
0.018 ($n = 3$)	0.018	0.09	15	5	25	> 95	–	trace	
0.050 ($n = 3$)	0.050	0.40	50-60	7	49	19	62	19	

methyldisilane with a lithium dispersion in the presence of a catalytic amount of triphenylsilyllithium in THF resulted in the formation of *Si*-trimethylsilyl-substituted polysilacycloalkanes. Thus, treatment of a mixture of 0.5 molar equivalent of 1,2-bis(chlorodimethylsilyl)ethane and 1 molar equivalent of 1,1-dichlorotetramethyldisilane with excess of a lithium dispersion in the presence of triphenylsilyllithium at 10°C for 5 h gave volatile products (50% yield) consisting of 2,3-bis(trimethylsilyl)-1,1,2,3,4,4-hexamethyl-1,2,3,4-tetrasilacyclohexane (**2**) and tris(trimethylsil-



SCHEME 1



SCHEME 2

yl)methylsilane (**3**) in a ratio of 3.2/1.0, along with a small amount of 2-trimethylsilyl-1,1,2,3,3-pentamethyl-1,2,3-trisilacyclopentane (**1**). The relative yield of the products is strongly dependent upon the molar ratio of the starting chlorosilanes and the duration of the reaction as shown in Table 1. If equimolar amounts of 1,2-bis(chlorodimethylsilyl)ethane and 1,1-dichlorotetramethyldisilane were treated with a lithium dispersion under the same conditions, an increased yield of **1** was found in the volatile products. The prolonged reaction time resulted in an increased total yield of the volatile products. However, the yield of **1** and **2** decreased, and the amount of the cleavage product **3** increased instead. Moreover, in this reaction, bis(1,1,2,3,3-pentamethyl-1,2,3-trisilacyclopentyl) (**4**) was formed in 24% yield (Scheme 1).

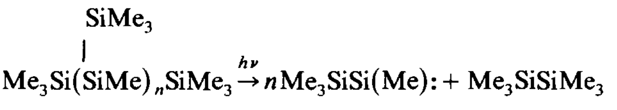
The formation of **4** may be ascribed to the reaction of compound **1** with 2-lithiotrisilacyclopentane (**A**), formed either from lithium/silyl exchange between **1** and the silyllithium species or cleavage of **1** by lithium metal. The structures of compounds **1**–**4** were verified by mass and ^{1}H NMR spectrometry as well as elemental analysis.

A similar reaction of an equimolar amount of 1,3-bis(chlorodimethylsilyl)propane and 1,1-dichlorotetramethyldisilane with a lithium dispersion in the presence of triphenylsilyllithium in THF at ca. 15°C gave a single product, which was identified as 2-trimethylsilyl-1,1,2,3,3-penta-methyl-1,2,3-trisilacyclohexane (**5**), by mass and ^{1}H NMR spectroscopic analysis. Nonvolatile substances were also produced. At higher temperatures, however, **5** underwent further reaction to give 2-hydro-1,1,2,3,3-pentamethyl-1,2,3-trisilacyclohexane (**6**) (Scheme 2).

Some physical constants and analytical results, and ^{1}H NMR and UV data are summarized in Tables 2 and 3.

Photolysis of branched polysilacycloalkanes

In our previous paper, it was shown that the photolysis of branched-chain polysilanes such as 1,1,2,2-tetrakis(trimethylsilyl)dimethyl disilane proceeds with generation of a divalent silicon intermediate, (trimethylsilyl)methylsilylene, which readily inserts into an Si–H bond [10].



$$\mathrm{Me_3Si(\overset{\overset{SiMe_3}{|}}{SiMe})_nSiMe_3 \xrightarrow{h\nu} n\,Me_3SiSi(Me){:} + Me_3SiSiMe_3}$$

$(n = 1$ and $2)$

TABLE 2

PHYSICAL AND ANALYTICAL DATA FOR THE SILYL-SUBSTITUTED POLYSILACYCLOALKANES

Compound	B.p. (°C/mmHg) or m.p. (°C)	n_D^{20}	M^+ (Mol.wt.)	Analyses (Found (calcd.)(%))	
				C	H
1 ($C_{10}H_{28}Si_4$)	110–113/18	1.5084	260 (260.68)	46.38 (46.08)	11.10 (10.85)
2 ($C_{14}H_{40}Si_4$)	99–100	–	376 (376.99)	45.07 (44.85)	10.33 (10.22)
4 ($C_{14}H_{38}Si_6$)	105	–	374 (374.98)	44.98 (44.89)	10.83 (10.21)
5 ($C_{11}H_{30}Si_3$)	–	1.5073	274 (274.71)	48.33 (48.10)	11.18 (11.01)
6 ($C_8H_{22}Si_3$)	–	1.4529	202 (202.52)	47.65 (47.84)	10.71 (10.95)

The *Si*-trimethylsilyl-substituted polysilacycloalkanes discussed in this paper also undergo photolysis upon irradiation with a low-pressure mercury lamp, to afford (trimethylsilyl)methylsilylene.

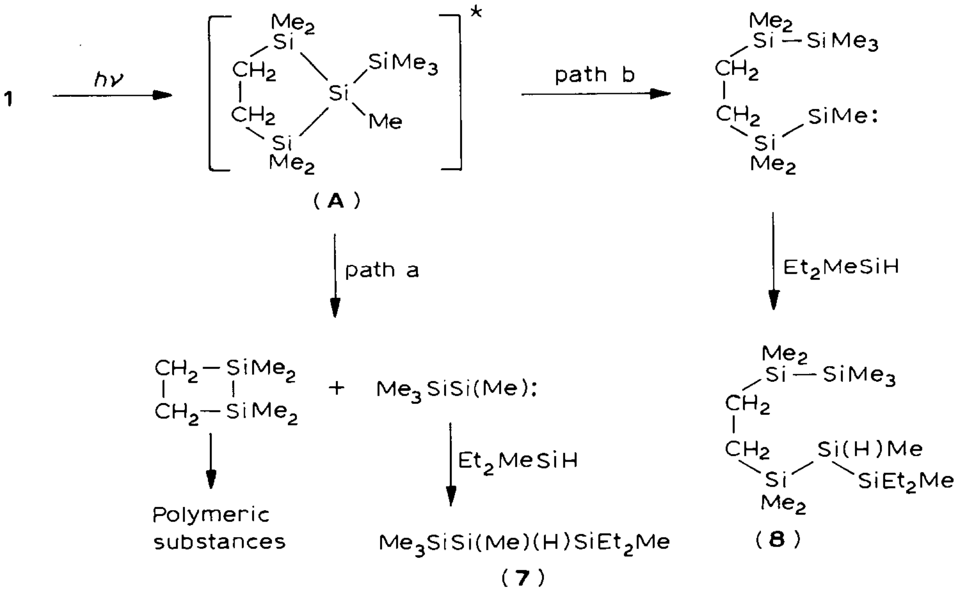
In the present system, however, appreciable amounts of another silylene species were formed. Thus, the photolysis of **1** in the presence of diethylmethylsilane in cyclohexane at room temperature gave 1,1-diethyl-1,2,3,3,3-pentamethyltrisilane (**7**) and an unexpected compound, 3-ethyl-3,4,5,5,8,8,9,9-octamethyl-3,4,5,8,9-pentasiladecane (**8**) in 60 and 22% yield, respectively. All spectra data for **7** were identical with those of an authentic sample [10]. Compound **8** was identified by mass and ^1H NMR spectrometry and elemental analysis.

The formation of **7** can best be undertood in terms of insertion of (trimethylsilyl)methylsilylene into the Si–H bond of diethylmethylsilane. Compound **8** may be rationalized by the production of another silylene arising from isomerization of a photo-excited molecule of **1**, which involves a 1,2-trimethylsilyl shift, followed by

TABLE 3

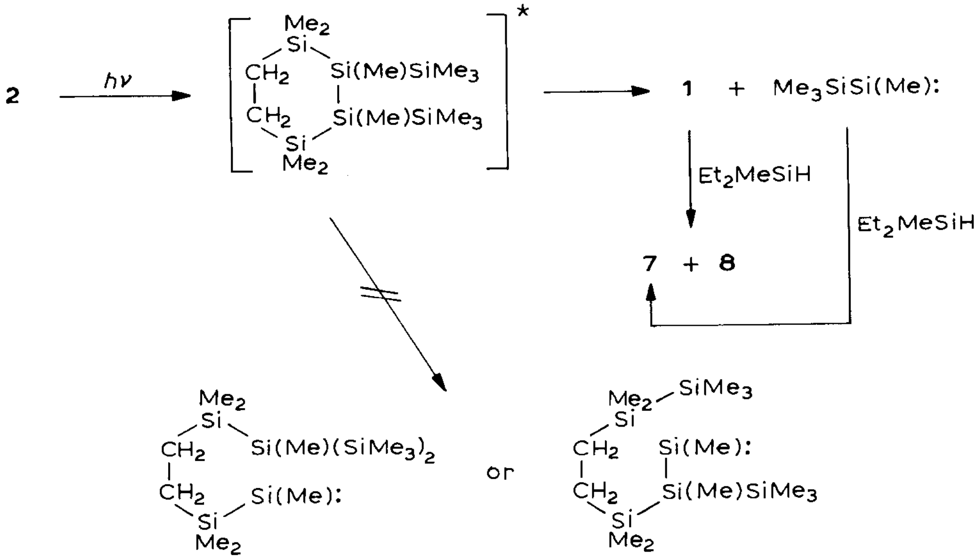
^1H NMR AND UV DATA FOR SILYL-SUBSTITUTED POLYSILACYCLOALKANES

Compound	Chemical shifts δ(ppm)	λ_{max} (nm)[ε]
1	0.02(s, 3H, MeSi), 0.14(s, 6H, MeSi), 0.16(s, 9H, Me_3Si), 0.17(s, 6H, MeSi), 0.71(s, 4H, CH_2)	250[1100]
2	0.07(s, 6H, MeSi), 0.13(s, 30H, Me_2Si, Me_3Si), 0.85(s, 4H, CH_2)	224[8700] 258[3900]
4	0.10(s, 6H, MeSi), 0.11(s, 9H, MeSi), 0.82(s, 4H, CH_2)	235[7000] 264[900]
5	0.04(s, 3H, MeSi), 0.10(s, 6H, MeSi), 0.12(s, 6H, MeSi), 0.14(s, 9H, Me_3Si), 0.53–0.83(m, 4H, CH_2), 1.34–1.65(m, 2H, CH_2)	240[1800]

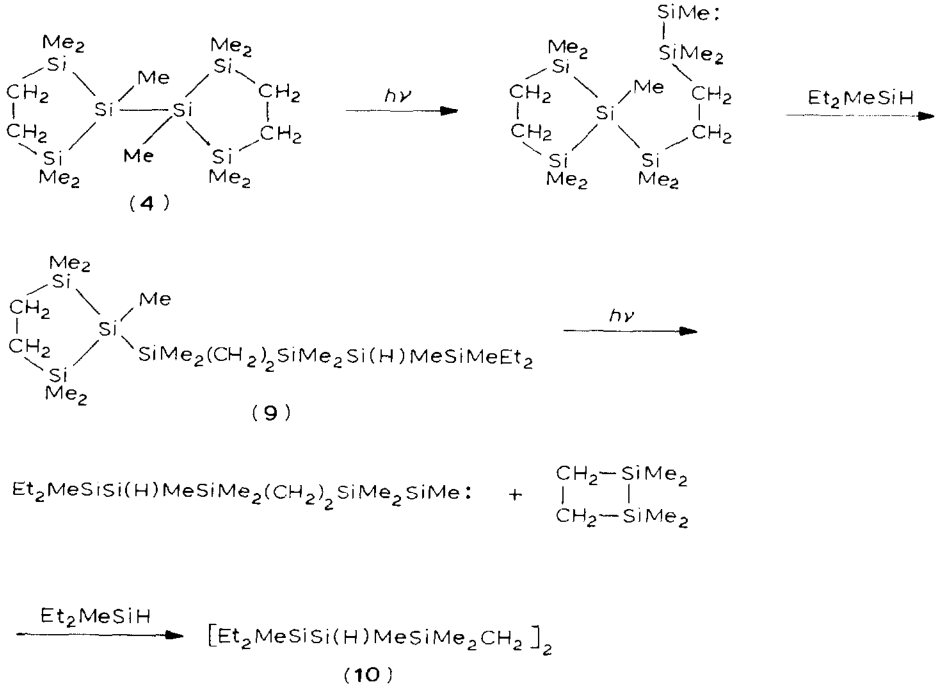


SCHEME 3

subsequent insertion into diethylmethylsilane. These results indicate that the photochemical degradation of **1** proceeds simultaneously in two different pathways, a and b, giving two types of silylene species (Scheme 3). 1,1,2,2-Tetramethyl-1,2-disilacyclobutane which is thought to be formed according to path a would be transformed



SCHEME 4



SCHEME 5

into nonvolatile substances. It is well known that the 1,2-disilacyclobutane is thermally unstable and readily undergoes polymerization to give nonvolatile substances at room temperature [11].

Interestingly, the photochemical degradation of **2** in the presence of diethylmethylsilane was found to proceed in a two-step process. At the initial step, compounds **1** and **7** were produced. The fact that no compound having a longer retention time than that of the starting compound **2** on GLC was detected during the photochemical reaction, indicates that the production of **1** with extrusion of (trimethylsilyl)methylsilylene is a predominant pathway in the initial step. Compound **1** thus formed is photolyzed to give **7** and **8** in the second stage (Scheme 4). In this photolysis, compounds **7** and **8** were obtained in 50 and 21% yields, respectively.

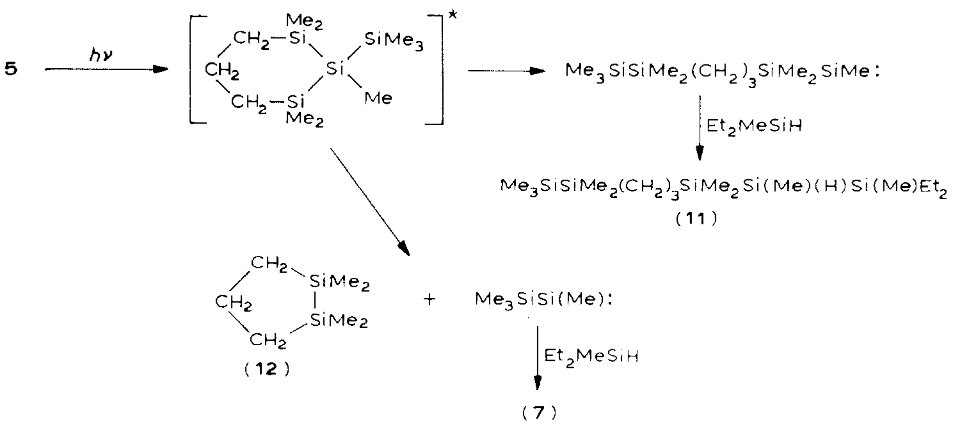
Photolysis of **4** under the same conditions revealed that the silylene is expelled in two consecutive steps. In contrast to the photolysis of **1**, in which two different types of silylene species were produced simultaneously, photolysis of compound **4** proceeded to afford only one kind of silylene in each step. In the first step, a compound (**9**) was produced as the sole product whose formation is ascribed to insertion of the silylene resulting from rearrangement of **4** into diethylmethylsilane (Scheme 5). Compoud **9** thus formed underwent further photolysis yielding another type of silylene species in the second step, which readily reacted with diethylmethylsilane to give 3,10-diethyl-4,9-dihydro-3,4,5,5,8,8,9,10-octamethyl-3,4,5,8,9,10-hexasiladodecane (**10**) (Scheme 5).

Using the GLC technique, the decrease of **4** and the growth of **9** and **10** could be followed. The results indicate that **9** initially was formed faster than **10**. The amount

TABLE 4

REFLECTIVE INDICES, ^{1}H NMR AND ANALYTICAL DATA FOR INSERTION PRODUCTS

Compound	n_D^{20}	Chemical shifts δ(ppm) in C_6D_6	M^+ (Mol. wt.)	Analysis (Found (calcd.)(%))	
				C	H
7 ($C_9H_{26}Si_3$)	1.4750	0.08(s, 3H, MeSi), 0.13(d, 3H, MeSi, $J = 5$ Hz), 0.15(s, 9H, Me_3Si), 0.56–1.15(m, 10H, C_2H_5), 3.32(q, 1H, HSi, $J = 5$ Hz)	218 (218.57)	49.46 (49.45)	11.96 (11.99)
8 ($C_{15}H_{42}Si_5$)	1.4670	0.16(s, 6H, Me_2Si), 0.18(s, 9H, Me_3Si), 0.19(s, 3H, MeSi), 0.26 (d, 3H, MeSi, $J = 5$ Hz), 0.27(s, 6H, Me_2Si), 0.63–1.10(m, 10H, C_2H_5), 3.55(q, 1H, HSi, $J = 5$ Hz)	362 (362.94)	49.65 (49.69)	11.22 (11.58)
9 ($C_{17}H_{52}Si_7$)	1.5244	0.20(s, 3H, MeSi), 0.22(s, 3H, MeSi), 0.26(s, 6H, MeSi), 0.27(d, 3H, MeSi, $J = 5$ Hz), 0.28(s, 6H, Me_2Si), 0.29(s, 6H, Me_2Si), 0.32(s, 6H, MeSi), 0.62–1.04(m, 10H, C_2H_5), 3.53(q, 1H, HSi, $J = 5$ Hz)	476 (477.24)	48.07 (47.82)	10.96 (10.98)
10 ($C_{18}H_{50}Si_6$)	1.5015	0.21(s, 6H, MeSi), 0.27(d, 6H, MeSi, $J = 5$ Hz), 0.28(s, 12H, Me_2Si), 0.40–1.06(m, 24H, CH_2, C_2H_5), 3.33(q, 2H, HSi, $J = 5$ Hz)	434 (435.14)	49.66 (49.69)	10.90 (11.58)
11 ($C_{16}H_{44}Si_5$)	–	0.04(s, 6H, Me_2Si), 0.07(s, 12H, MeSi and Me_3Si), 0.13(d, 3H, MeSi, $J = 5$ Hz), 0.14(s, 6H, Me_2Si), 9.01–8.56(m, 6H, $CH_2CH_2CH_2$), 3.43(q, 1H, HSi, $J = 5$ Hz)	376 (376.96)	50.69 (50.98)	11.55 (11.77)



SCHEME 6

of **9** was fixed after about 3 h under our conditions, while the amount of **10** continued to increase. After 10 h, the starting compound **4** was almost completely consumed, and products **2** and **10** were produced in 12 and 54% yields, respectively.

The photochemical behavior of **5** is similar to that of **1**. Irradiation of a cyclohexane solution of **5** in the presence of diethylmethylsilane gave **7** and 3-ethyl-4-hydro-3,4,5,5,9,9,10,10-octamethyl-3,4,5,9,10-pentasilaundecane (**11**) in 73 and 13% yields, respectively, in addition to 64% yield of 1,1,2,2,-tetramethyl-1,2-disilacyclopentane (**12**) [12] (Scheme 6).

Reflective indices, ^{1}H NMR data and elemental analysis for the insertion products **7**–**11**, are shown in Table 4.

Experimental

General procedure

All reactions were carried out under an atmosphere of dry nitrogen. Photolysis was carried out using a 10-W immersion low-pressure mercury lamp bearing a Vycor filter. All photolyses were followed by GLC analysis using a 3 m × 0.5 cm stainless columm with 20% Silicone DC oil. An Aerograph Model 920 gas chromatograph with a thermal conductivity detector was used for separating the photolysis products. Most of the products were easily separated by using a 3/8 in. × 20 ft. column containing SE-30 (30%) on Chromosorb W.

Materials

1,2-Bis(chlorodimethylsilyl)ethane [13], 1,3-bis(chlorodimethylsilyl)propane [13], 1,1-dichlorotetramethyldisilane [14] and diethylmethylsilane [15] were prepared by methods described in the literature.

Preparation of the Si-silyl substituted polysilacycloalkanes

The following experiment is typical of the procedures used. A mixture of 11.0 g (0.052 mol) of 1,2-bis(chlorodimethylsilyl)ethane and 18.5 g (0.10 mol) of 1,1-dichlorotetramethyldisilane was added slowly to 3.0 g (0.43 g-atom) of a lithium dispersion in the presence of 5×10^{-3} mol of triphenylsilyllithium in 300 ml of THF at ca.

10°C over a period of 4 h. The mixture was hydrolyzed in the usual manner. The solvent was evaporated, and the residue in the flask was distilled under reduced pressure to give 9.7 g of volatile products boiling over a range of 60–140°C/2 Torr. The pure products, **1**, **2** and **3** were isolated by preparative GLC.

Isolation of 7, 8 and 10

In a 100-ml reaction vessel, fitted with a low-pressure mercury immersion lamp bearing a Vycor filter, a solution of 3.0 g of a 1/1 mixture of **2** and **4**, and 20 g (0.20 mol) of diethylmethylsilane in 80 ml of dry cyclohexane was photolyzed for 20 h. The solvent and diethylmethylsilane were evaporated, and the residue was distilled under reduced pressure to give 2.9 g of a colorless liquid (b.p. ~ 190°C/1 Torr). GLC analysis of the distillate showed three peaks corresponding to **7**, **8** and **10** in a ratio of 2.1/0.4/1.1. The pure compounds **7**, **8** and **10** were isolated by preparative GLC.

Isolation of 9

A solution of 1.5 g (4 mmol) of **4** was photolyzed in the presence of 20 g (0.20 mol) of diethylmethylsilane in 80 ml of cyclohexane for 5 h. After evaporation of the solvent and diethylmethylsilane, the residue was distilled under reduced pressure to give 1.2 g of a colorless liquid. GLC analysis of the distillate showed the presence of the starting **4** and **9** in a ratio of 1/1. Pure **9** was isolated by preparative GLC.

Photolysis of Si-silyl substituted polysilacycloalkanes in the presence of diethylmethylsilane

In a 10-ml quartz tube was placed a solution of an exactly weighed sample of a silyl-polysilacycloalkane and a known quantity of an internal stardard in a mixture of 2 ml of diethylmethylsilane and 7 ml of dry cyclohexane. The tube was flushed with dry nitrogen and sealed with a rubber septum. This was irradiated externally with a low-pressure mercury lamp at room temperature. The reaction mixture was analyzed by GLC.

Photolysis of 5 in the presence of diethylmethylsilane

A mixture of 2.5 g (9.1 mmol) of **5** and 20 ml of diethylmethylsilane in 80 ml of dry cyclohexane was photolyszed for 15 h at room temperature. The solvent and diethylmethylsilane were distilled off, and the residue was then analyzed by GLC as being **7** (73% yield) and **11** (13% yield). Pure **11** was isolated by preparative GLC.

Acknowledgement

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