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FORMATION OF CYCLIC ORGANOSILICON COMPOUNDS VIA ORGANOPOLYSILYL ANIONS STARTING FROM METHOXYMETHYLDISILANES. A MECHANISTIC STUDY

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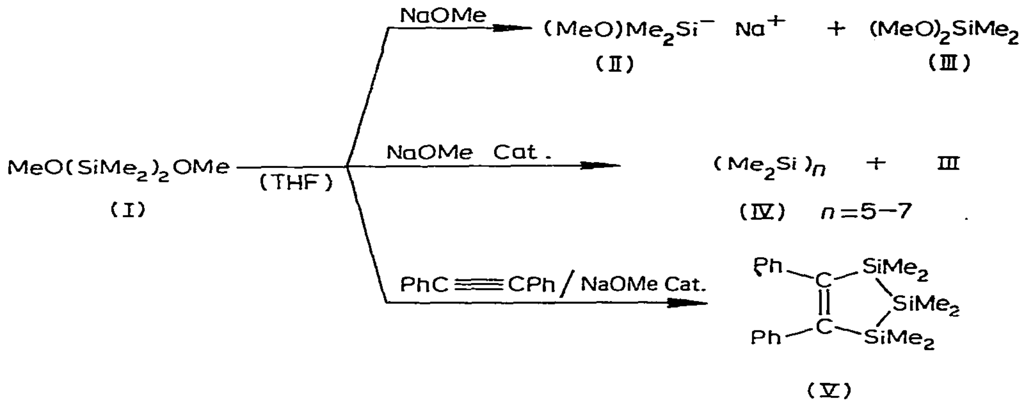
Summary

In the presence of a catalytic amount of sodium methoxide, *sym*-dimethoxytetramethyldisilane was converted into α,ω-dimethoxypermethylpolysilanes, $MeO(SiMe_2)_nOMe$ where $n \geqslant 3$, at room temperature. On the other hand, similar treatment of the disilane in THF solution gave cyclic polysilanes, $(Me_2Si)_n$ where n = 5—7. Decomposition of the disilane in the presence of diphenylacetylene afforded a trisilacyclopentene derivative under similar conditions. This compound was obtained also by the reaction between α,ω-dimethoxypermethylpolysilanes and diphenylacetylene in the presence of sodium methoxide. These cyclic products most likely were formed via permethyl polysilyl anion intermediates derived from α,ω-dimethoxypermethylpolysilanes. Also, the formation of α,ω-dimethoxypermethylpolysilanes could be elucidated in terms of the mechanism involving the base-assisted, concerted nucleophilic substitution or stepwise substitution by silyl anions, rather than the successive dimethylsilylene (Me_2Si:) insertion reaction.

Introduction

Recently we have reported that cleavage of *sym*-dimethoxytetramethyldisilane (I) by a molar equivalent of sodium methoxide in tetrahydrofuran (THF) gives the first functionalized organosilyl anion, monomethoxydimethylsilylsodium (II) (eq. 1) [1]. We reported subsequently that the dimethoxydisilane gives dodecamethylcyclohexasilane (IV, n = 6) in the presence of a catalytic amount of sodium methoxide (eq. 2) [2], and also that the treatment of I with diphenylacetylene under similar conditions furnished a new silicon-containing ring system, a trisilacyclopentene derivative (V) (eq. 3) [3]. This paper deals with the formation of these reaction products from the mechanistic viewpoint.



(1)

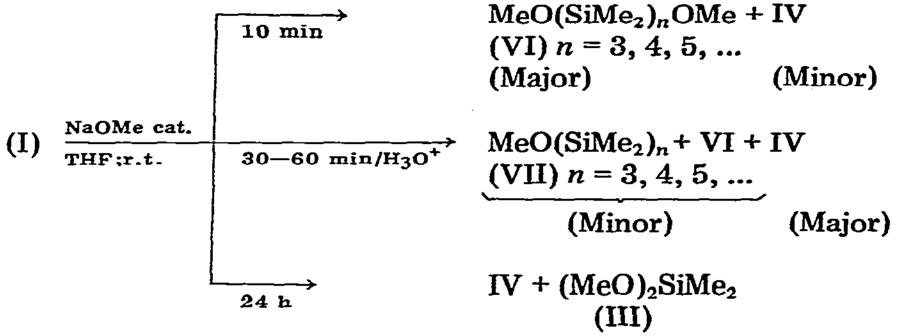
(2)

(3)

Results and discussion

Reaction of I with NaOMe in THF solution

A series of reactions of disilane I with NaOMe gave a variety of products, the formation of which depends upon the conditions employed (eq. 4—6). Stirring a 5 : 1 mixture of the disilane and NaOMe in THF at room temperature under Ar for ca. 10 min afforded a set of α,ω-dimethoxypermethylpolysilanes (VI), $MeO(SiMe_2)_nOMe$ where $n \geqslant 3$, as major products (eq. 4). On the other hand, the same reaction after an extended period of time (24 h) gave mainly cyclic polysilanes (eq. 6). However, the products after a 30—60 min reaction time were found to be mainly cyclic polysilanes (IV); small amounts of α-hydro-ω-methoxypermethylpolysilanes (VII), $MeO(SiMe_2)_nH$ where $n \geqslant 3$, and of compound VI (eq. 5). These results are summarized in Table 1.



(4)

(5)

(6)

Interestingly, α,ω-dimethoxypermethylpolysilanes VI seem to be the precursors for the cyclic polysilanes IV. In fact, the comparison of the product distribution in Table 1A with that in Table 1B reveals that the longer reaction time resulted in an increased amount of the cyclic polysilanes IV at the expense of α,ω-dimethoxypermethylpolysilanes VI. Accordingly, the formation of cyclic polysilanes can be rationalized in terms of the intervention of straight-chain polysilyl anions (VIII) as shown by Scheme 1.

Since a set of α-hydro-ω-methoxypermethylpolysilanes VII was isolated after hydrolysis of the reaction mixture, it is evident that the polysilyl anions are

TABLE 1

PRODUCT DISTRIBUTION OBTAINED BY THE TREATMENT OF DIMETHOXYDISILANE I WITH SODIUM METHOXIDE CATALYST IN TETRAHYDROFURAN

A. The result after 10 min period of time

GLC peak order	Product	
	Polysilane	Distribution (GLC area, %) [a]
1	$MeO(SiMe_2)_3OMe$	28.0
2	[b]	1.1
3	$MeO(SiMe_2)_4H$	5.7
4	$MeO(SiMe_2)_4OMe$	26.6
5	$(Me_2Si)_5$	2.2
6	$MeO(SiMe_2)_5H$	3.7
7	$MeO(SiMe_2)_5OMe$	18.7
8	$(Me_2Si)_6$	0.9
9	$MeO(SiMe_2)_6H$	2.0
10	$MeO(SiMe_2)_6OMe$	11.3

B. The result after 30 min period of time [c]

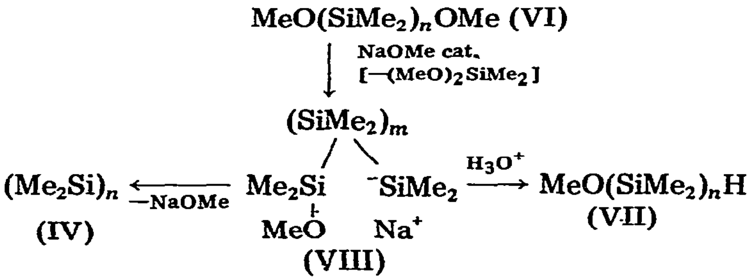
GLC peak order	Polysilane	Distribution (GLC area, %)
1	$MeO(SiMe_2)_3H$	6.8
2	$MeO(SiMe_2)_4H$	[d]
3	$MeO(SiMe_2)_4OMe$	7.8
4	$(Me_2Si)_5$	28.3
5	$MeO(SiMe_2)_5H$	7.8
6	$MeO(SiMe_2)_5OMe$	6.3
7	$(Me_2Si)_6$	40.0
8	$MeO(SiMe_2)_6H$	3.0
9	$MeO(SiMe_2)_6OMe$	[d]
10	$(Me_2Si)_7$	[d]

[a] Silicone SF-96; column temp. 232°C; He flow-rate, 120 ml/min (see Experimental). [b] Not identified. [c] Silicaone SF-96; column temp. 227°C; He flow-rate, 100 ml/min (see Experimental). [d] Only small amount.

formed by Si—Si bond cleavage of VI by NaOMe. In the final stage, the polysilyl anions undergo intramolecular nucleophilic substitution to give the cyclic polysilanes and NaOMe [4].

In order to confirm whether the cyclic polysilanes IV would be formed from the linear polysilanes VI or not, a mixture of α,ω-dimethoxypermethylpolysilanes VI, prepared separately according to the literature method [5], was treated with NaOMe, resulting in the formation of a significant amount of

SCHEME 1



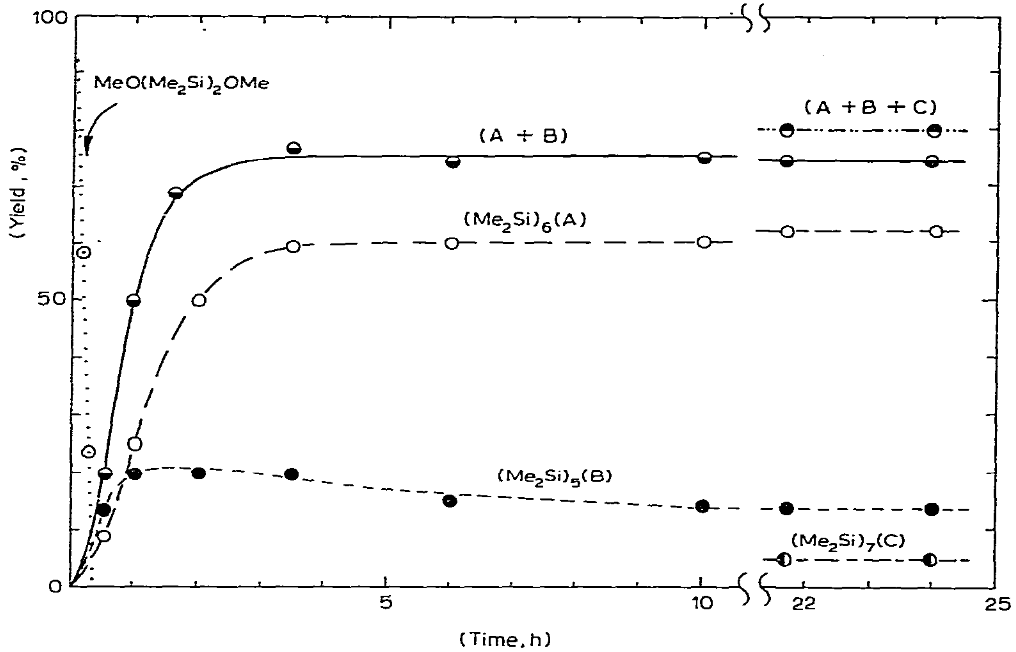


Fig. 1. Profile for the formation of cyclic polysilanes IV vs. reaction time. The yields (GLC) were calculated on the basis of the starting disilane used (an internal standard was employed; see Experimental).

cyclic polysilanes IV. To monitor the formation of the cyclic polysilanes IV, the progress of the reaction was followed by GLC using n-hexadecane as an internal standard. Figure 1 shows the profiles for the formation of cyclopolysilanes $(Me_2Si)_n$, where $n = 5$ and 6, vs. time. It will be seen from Fig. 1 that the formation of $(Me_2Si)_5$ occurs somewhat faster than that of $(Me_2Si)_6$ in the early stages of the reaction and that the yield of $(Me_2Si)_5$ reaches a maximum value after 1 h and then decreases gradually to attain a constant value of ca. 12%. On the other hand, the formation of $(Me_2Si)_6$ occurs rapidly in the early stages of the reaction within 2 h and the yield reached to ca. 50% and then continues to increase gradually up to about 60%. After a 4 h reaction period, the combined yield of the two cyclic polysilanes remained almost constant, and the total yield of the cyclic polysilanes, including $(Me_2Si)_7$, at the final stage was about 82% based on the disilane I used. Thus, the product yields of permethylcyclo-penta-, hexa- and hepta-silane were approximately 13, 63 and 6%, respectively. These findings clearly indicate that the cyclopentasilane is a kinetically controlled product, whereas the cyclohexasilane is a thermodynamically controlled product. This conclusion is in accord with the results observed recently by West and coworkers who found that in the equilibria between the three cyclic polysilanes, cyclohexasilane exists in preference to other two cyclopolysilanes [4b,6].

Previously, we first isolated a new trisilacyclopentene system, 1,1,2,2,3,3-hexamethyl-4,5-diphenyl-1,2,3-trisilacyclopent-4-ene (V) [3] *. This compound

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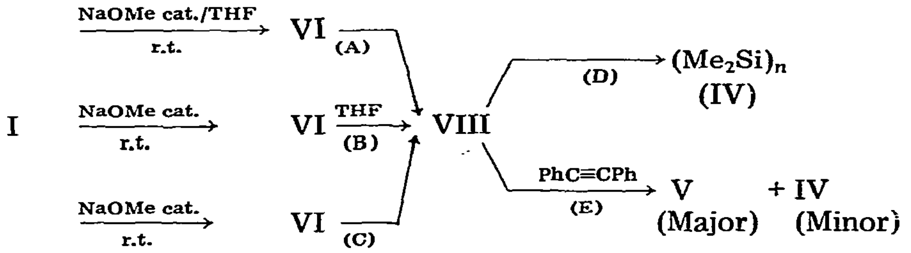
* Sakurai et al. reported that this compound also was obtained from the reaction of 1,1,2,2-tetramethyl-3,4-diphenyl-1,2-disilacyclobut-3-ene with dimethylsilylene at 350°C [see ref. 7].

was obtained by the reaction between dimethoxydisilanes I and diphenylacetylene in the presence of NaOMe catalyst in 47% yield. Also, the treatment of a mixture of α,ω-dimethoxypermethylpolysilanes VI with diphenylacetylene and NaOMe in THF gave the trisilacyclopentene V (eq. 7). The results suggest that

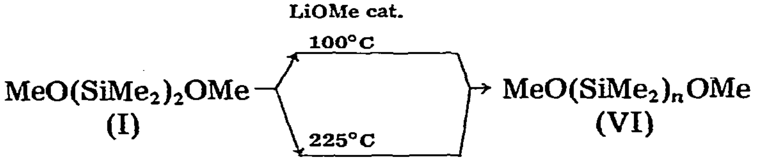
$$\underset{(I)}{MeO(SiMe_2)_2OMe} \xrightarrow[\text{THF; r.t.}]{\text{PhC≡CPh/NaOMe cat.}} V \xleftarrow[\text{THF; r.t.}]{\text{PhC≡CPh/NaOMe cat.}} \underset{(VI)}{MeO(SiMe_2)_nOMe} \quad (7)$$

formation of compound V in both reactions occurred from the identical precursors, methoxypermethylpolysilyl anions (VIII), generated by the cleavage of α,ω-dimethoxypermethylpolysilanes VI by NaOMe, as shown in Scheme 1 (eq. 8).



(8)

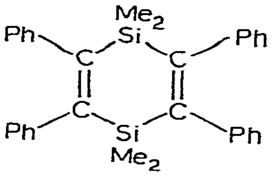
In order to elucidate the role of solvent, the reaction of disilane I with NaOMe was conducted in the absence of the solvent (THF). Thus, the treatment of disilane I with a catalytic amount of NaOMe afforded α,ω-dimethoxypermethylpolysilanes VI and dimethoxydimethylsilane II. In this case, the cyclic polysilanes IV were not detected to any measurable extent. The present base-catalyzed reaction of disilane I giving VI is reminiscent of the reported decomposition of I catalyzed by LiOMe at 100°C [8] and of the high temperature decomposition (225–250°C) of disilane I [5]. But, it should be emphasized that the formation of α,ω-dimethoxypermethylpolysilanes (VI) in the NaOMe-catalyzed reaction can be accomplished quite smoothly under milder conditions than in the case of the reported reactions. Therefore, it is apparent that the present reaction provides a simple and convenient method for the room-temperature preparation of α,ω-dimethoxypermethylpolysilanes VI.



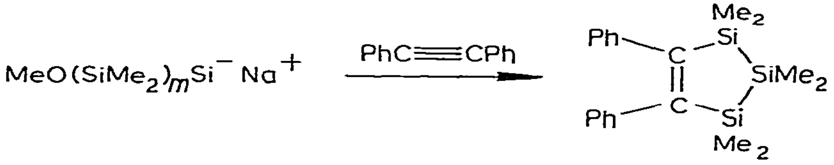
Interestingly, on addition of THF to the reaction mixture, the α,ω-dimethoxypermethylpolysilanes VI thus formed were converted to cyclic polysilanes IV as expected (eq. 8BD). This furnishes supporting evidence for the proposed mechanism that compounds IV are derived from methoxypermethylpolysilyl anions VIII (see also Scheme 1).

Similarly, on addition of PhC≡CPh and THF to the reaction mixture, polysilanes VI gave rise to compound V in good yield along with small amounts of cyclic polysilanes IV (eq. 8BE). Furthermore, the treatment of disilane I with

PhC≡CPh in the absence of the solvent gave α,ω-dimethoxypermethylpolysilanes VI and dimethoxydimethylsilane III mainly; only a small amount of trisilacyclopentene V was formed (eq. 8CE). However, a silylene trapping product, such as 1,4-disilacyclohexadiene (IX) or cyclic polysilane IV, could not be detected. When THF was added to the reaction mixture, the polysilanes formed were converted into the trisilacyclopentene derivative V which was the main product. These results can be explained well by the hypothesis that trisilacyclopentene derivative V is formed by the reaction of methoxypermethylpolysilyl anions VIII with PhC≡CPh (eq. 9) and not by the reaction of dimethylsilylene (Me_2Si:) with PhC≡CPh (eq. 10). On the other hand, it has been documented that the reaction of diphenylacetylene with an alkylmetal such as RLi in ether gives the corresponding *cis*-adducts, metalated olefins (X), which were carbonated to yield substituted acrylic acids (XI) (eq. 11) [9]. Although the mechanism for the reaction of the intermediate polysilyl anions VIII with diphenylacetylene is not fully understood, the reaction might involve the following processes in analogy with eq. 11. In the cyclization reaction, there is a possibility



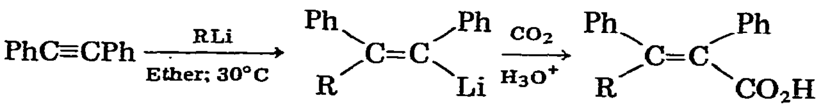
(IX)



(V)

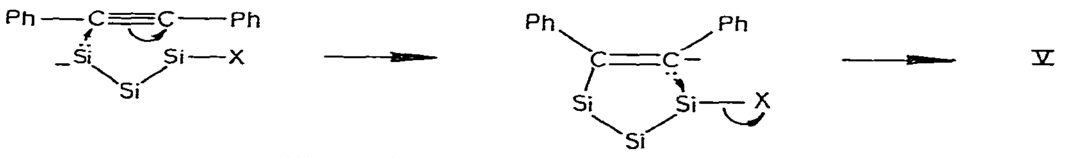
(9)

$$PhC\equiv CPh + Me_2Si: \longrightarrow \longrightarrow \not\longrightarrow V \qquad (10)$$



(X) (XI)

(11)



(X = Si_nOMe ; OMe)

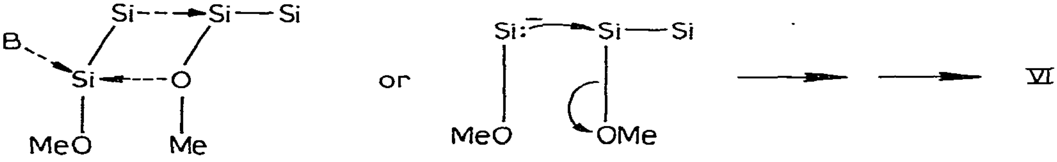
of the formation of larger ring compounds such as tetrasilacyclohexene derivative and so on, although attempts to detect them by the GLC technique were unsuccessful.

Previously, Atwell and coworkers reported that compound IX was not formed when disilane I was heated (100°C) in the presence of PhC≡CPh and a catalytic amount of lithium methoxide, and that the only products formed were polysilanes (VI, n = 3 and 4) and compound III [5b]; the formation of trisilacyclopentene V was not reported at all. Thus, it appears that the present reaction, catalyzed by NaOMe under mild conditions, is considerably different from the LiOMe-catalyzed reaction.

Finally, it should be noted that the action of the solvent (THF) in the present systems resulted in the dramatic changes of the product formation as above.

Mechanistic consideration of the formation of α,ω-dimethoxypermethylpolysilanes VI from disilanes I

Concerning the formation of permethylpolysilanes VI from disilane I catalyzed by sodium methoxide without the solvent, our results also are consistent with a mechanism involving the concerted nucleophilic substitution with base-assistance or stepwise substitution by silyl anion, as has been proposed by Atwell and Weyenberg for the LiOMe-catalyzed redistribution of disilane I (eq. 12) [8]:



(12)

It is of interest to consider the present reaction from the viewpoint of the silylene mechanism leading to the formation of polysilanes VI (eq. 13). The above

$$\mathrm{I} \rightarrow \mathrm{II} \rightarrow \mathrm{Me_2Si\colon} \xrightarrow{\mathrm{I}} \mathrm{MeO(SiMe_2)_3OMe} \rightarrow \rightarrow \mathrm{VI} \qquad (13)$$

results disclosed that in the reaction catalyzed by NaOMe under the mild conditions, the starting disilane I was completely consumed to form dimethoxydimethylsilane III and linear polysilanes VI (and/or cyclic polysilanes IV). Generally, dimethoxydimethylsilane is well recognized to be a good silylene trapping reagent under mild conditions [5e,10]. Therefore, this compound, which could be formed in considerable amount in the present systems, should react with dimethylsilylene ($Me_2Si\colon$), if the latter were formed, to give disilane I, since it would be expected that the reactivity of disilane I is comparable to the higher polysilanes. Thus, as a result, disilane I should have been detected in the final reaction mixture. The treatment of a set of α,ω-dimethoxypermethylpolysilanes VI with a catalytic amount of NaOMe gave a mixture with a composition different to the original one and a small amount of dimethoxydimethylsilane III. However, disilane I could not be detected. During the treatment, the amount of the lower molecular weight polysilanes decreased, while that of those of higher molecular weight increased. These results suggest that the α,ω-dimethoxypermethylpolysilanes VI were converted into a set of higher molecular weight polysilanes, accompanied by the formation of dimethoxydimethylsilane III. Therefore, it is not unreasonable to conclude that α,ω-dimethoxypermethylpolysilanes VI did not liberate dimethylsilylene (Me_2Si:) under the present conditions.

Furthermore, in order to investigate the possibility of the silylene mechanism in the presence of the solvent, disilane I was treated with "silylene trapping reagents" [5e,11] such as triethylsilane, 2,3-dimethylbuta-1,3-diene, triethyl-i-propoxysilane, hexamethyldisiloxane and diphenylacetylene. None of these reagents afforded the expected silylene insertion products. Thus, the silylene mechanism appears not to be compatible with the present observations.

Consequently, the results described above are in favor of the mechanism involving base-assisted, concerted nucleophilic substitution or stepwise substitution by the silyl anion as above, although the silylene mechanism could not be excluded conclusively.

Experimental

All boiling and melting points are uncorrected and the latter was measured in a sealed capillary. The reactions were carried out under an atmosphere of argon. IR spectra were recorded using neat liquid films with a Hitachi EPI-G3 spectrometer, and NMR spectra were measured in CCl_4 solution using a Varian A-60D spectrometer. Mass spectral analyses were conducted using JEOL Model JMS-07 and JMS-D 300 spectrometers, and the latter was operated in connection with a JEOL Model JGC 20-KP gas chromatograph. GLC analyses were conducted using Ohkura Model 802 and 1700 gas chromatographs. Throughout the experiments, gas chromatographies were done under the conditions: Silicone SF-96 20% on Celite 545; 2 m × 4 mm Teflon or stainless-steel column; temp. 150—250°C; He carrier. Unless otherwise specified, thermal conductivity correction using an external standard (n-alkanes selected from C_{12}—C_{18} hydrocarbons) was made for the product yields.

Materials

sym-Dimethoxytetramethyldisilane (I) was prepared by methoxylation of the corresponding dichlorodisilane according to the method described previously [12]. Triethylsilane was made as described previously [13]. Sodium methoxide was obtained by the reaction of sodium with absolute methanol in anhydrous ether. Tetrahydrofuran (THF) was freshly distilled from lithium aluminum hydride before use. Triethyl-i-propoxysilane was prepared by the dehydrogenative condensation of triethylsilane with i-propyl alcohol in the presence of $RhCl(PPh_3)_3$ catalyst [14]. Other materials were commercially available.

Treatment of disilane I with catalytic amount of sodium methoxide in THF

A. Formation of α,ω-dimethoxypermethylpolysilanes (VI) (Table 1A). To a solution of NaOMe (0.5 g, 9.3 mmol) in THF (30 ml) was added *sym*-dimethoxytetramethyldisilane (I) (9.0 g, 50.4 mmol) over a period of 4 min with magnetic stirring. After 10 min stirring, the resulting mixture was neutralized with aqueous, saturated NH_4Cl solution and extracted with ether. The ethereal solution gave, on workup, a colorless liquid. GLC analysis of the resulting liquid exhibited the presence of at least ten products and the liquid was distilled to afford a fraction (3.5 g) boiling at 130°C/25 mmHg —170°C/2 mmHg and a residue (0.8 g).

From the above fraction, almost all the products corresponding to the each GLC peak were separated by preparative GLC. Structure assignment and identification of the products were accomplished in the usual manner (NMR, IR and MS, and the comparison of these spectra with those of the literature values). Table 1A shows a set of the product distribution in the above reaction mixture. The main products thus obtained were α,ω-dimethoxypermethylpolysilanes (VI), $MeO(SiMe_2)_nOMe$, and cyclic polysilanes (IV), $(Me_2Si)_n$ (see below: Section C).

B. Formation of α-hydro-ω-methoxypermethylpolysilanes (VII) (Table 1B). In a similar manner to the above, a mixture of NaOMe (40 mmol) and disilane I (200 mmol) in THF (80 ml) was allowed to react for 60 min and worked up to give a liquid product mixture which was subjected to GLC analysis. Table 1B shows a set of the reaction products and their distribution by the GLC analysis. The mixture also was distilled to give a fraction (10.5 g) boiling at 130°C/60 mmHg —215°C/20 mmHg and a residue (4.6 g). The products corresponding to the each GLC peak in the above fraction were isolated by preparative GLC and identified. There were obtained α-hydro-ω-methoxypermethylpolysilanes (VII) $MeO(SiMe_2)_nH$, and cyclic polysilanes IV along with a small amount of α,ω-dimethoxypermethylpolysilanes VI.

On the other hand, the IR spectrum for the above distillation residue showed the presence of Si—H, Si—Me and Si—OMe bonds. Therefore, the residue was thought to be a mixture of higher molecular weight silicon compounds bearing these bonds.

Pertinent physical data for the products obtained in the two reactions, A and B, were summarized in Table 2.

C. Action of NaOMe on disilane I to form cyclic polysilanes VI (Fig. 1). In a 100 ml three-necked flask, previously flushed with argon, sealed with a serum cap and fitted with a condenser, were placed NaOMe (0.5167 g, 9.57 mmol), n-hexadecane (0.7477 g, as the internal standard) and THF (40 ml). The solution was stirred magnetically at room temperature under argon and disilane I (8.3493 g, 46.796 mmol) was added through the serum cap with a hypodermic syringe. At suitable time intervals, small aliquots of the solution were extracted through the serum cap by means of a syringe and analyzed by GLC (Fig. 1). The yields of $(Me_2Si)_5$, $(Me_2Si)_6$ and $(Me_2Si)_7$, after 24 h reaction period, were 13, 63 and 6%, respectively.

At the end of this time, the resulting solution was neutralized with saturated aqueous NH_4Cl solution and extracted with ether. Work-up gave a colorless liquid which was concentrated under reduced pressure to give a product mixture. From the mixture thus obtained, $(Me_2Si)_7$ was isolated by the preparative GLC and identified in the usual manner (see the previous section).

Preparation of α,ω-dimethoxypermethylpolysilanes VI

According to the literature method [5], disilane I (9.7 g, 54 mmol) was

TABLE 2

PRODUCTS AND PHYSICAL DATA

Compound	n_D^{26}	m.p.[a] (°C)	M.w.[b]	IR (neat; cm^{-1})[c]	NMR (CCl_4; δ, TMS)
$MeO(SiMe_2)_3OMe$[d]	1.4561 (1.4569)[e]		221[f] (236)		[e]
$MeO(SiMe_2)_4OMe$	1.4799 (1.3809)[e]		279[f] (294)		[e]
$MeO(SiMe_3)_5OMe$	1.4983 (1.4974)[e]		337[f] (352)		[e]
$MeO(SiMe_2)_6OMe$			395[f] (410)		[e]
$MeO(SiMe_2)_nOMe$ (n = 8 or 9)				1260; 1248 (SiMe), 1085 1085 (SiOC)	3.36 (SiO*Me*, s, 6H), 0.22 (Si*Me*, s); 0.17 (SiMe, s) (51H)
$MeO(SiMe_2)_3H$			206[g] (206)	2100 (SiH), 1261; 1245 (SiMe), 1085 (SiOC)	
$MeO(SiMe_2)_4H$			264[g] (264)	2100 (SiH), 1261; 1250 (SiMe), 1075 (SiOC)	
$MeO(SiMe_2)_5H$[h]			322[g] (322)	2093 (SiH), 1263; 1250 (SiMe), 1089 (SiOC)	4.07 (SiH, m, 1H), 3.30 (SiO*Me*, d, 3H), 0.27 (SiMe, m, 30H)
$MeO(SiMe_2)_6H$			380[g] (380)		
$(Me_2Si)_5$		183–186 (186–189)[i]	290[f] (290)	[i]	[i]
$(Me_2Si)_6$[j]		249–251 (252–255)[i]	348[f] (348)	[i]	[i]
$(Me_2Si)_7$		220–225 (228–232)[i]	406[f] (406)	[i]	[i]

[a] In a sealed capillary. [b] By mass spectrum; Calculated value is given in parenthesis. [c] Sandwich. [d] Analysis, Found: C, 40.59; H, 10.09. Calcd. for $C_8H_{24}Si_3O_2$: C 40.62; H, 10.23%. [e] See ref. 7. [f] Ionization potential, 70 eV; No molecular peak appeared; m/e, $M^+ - 15$ peak. [g] Ionization potential, 20 eV. [h] λ_{max} 251 nm ($c\text{-}C_6H_{12}$). [i] See ref. 15. [j] λ_{max} 230 nm ($c\text{-}C_6H_{12}$) (lit., 230.5 nm; see ref. 15).

heated, in a sealed stainless-steel vessel, at 280—300°C for 16 h under argon to give a dark-green liquid (9.35 g), for which GLC analysis exhibited that all of the disilane used was consumed. After stripping of low boiling materials (up to 80°C at 9 mmHg; bath temp. 104°C), a dark-brown liquid (4.2 g; 43% yield) remained. It was found by GLC and mass analyses that the liquid consisted of α,ω-dimethoxypermethylpolysilanes, $MeO(SiMe_2)_nOMe$ where n = 3—7.

Treatment of α,ω-dimethoxypermethylpolysilanes VI with NaOMe in THF

In a dry flask, the dimethoxypermethylpolysilane mixture (1.0 g) in 3 ml of THF was added to a mixture of NaOMe (70 mg) and 5 ml of THF under argon. The mixture was stirred for 24 h at room temperature. Work-up, after treatment with solid NH_4Cl, gave 0.7 g of a semi-solid from which dodecamethylcyclohexasilane (0.3 g, m.p. 226—246°C) and solid mixture of cyclic polysilanes $(Me_2Si)_n$ (n = 5 and 7) (0.3 g) were obtained.

Treatment of α,ω-dimethoxypermethylpolysilanes VI with PhC≡CPh and catalytic amount of NaOMe in THF

In a manner similar to that above, a solution of the polysilane mixture (1.0 g) in 3 ml of THF was added to a mixture of PhC≡CPh (1.0 g), NaOMe (0.1 g) and THF (5 ml) under argon. The mixture was stirred at room temperature for 20 h, during which time polysilanes were consumed gradually with an increase of a new product peak (by GLC) corresponding to trisilacyclopentene V. Upon treatment with NH_4Cl and filtration, the resulting mixture gave an orange liquid which was concentrated to give a solid material. It afforded, on trituration with warm methanol, colorless crystals of compound V (0.4 g; 20% based on the acetylene; m.p. 162—164°C). From the methanol solution after the separation of this product, a mixture containing the unreacted acetylene and small amount of compound V was recovered.

Treatment of disilane I with NaOMe in the absence of THF and subsequent reaction in the presence of THF to form various products

A. Formation of α,ω-dimethoxypermethylpolysilanes VI. A mixture of disilane I (3.85 g, 21.6 mmol) and NaOMe (0.3 g, 5.6 mmol) was magnetically stirred under argon at room temperature for 2 h. The reaction mixture was subjected to GLC analysis which showed that α,ω-dimethoxypermethylpolysilanes VI ($n \geqslant 3$) and dimethoxydimethylsilane III were formed, and that no starting disilane I remained. After treatment with solid NH_4Cl (0.3 g), the mixture was filtered. The filtrate gave yellow liquid (0.65 g), on stripping the low boiling materials under reduced pressure up to 10 mmHg at 54°C (0.3 g). GLC and mass analyses for the yellow liquid showed that it consists of a mixture of α,ω-dimethoxypermethylpolysilanes VI, $MeO(SiMe_2)_nOMe$ where n = 4—7. The low boiling fraction also was found to be a mixture of polysilanes (n = 3 and 4). From the dry-ice acetone trap, dimethoxydimethylsilane (1.35 g) was obtained.

B. Formation of α,ω-dimethoxypermethylpolysilanes and the subsequent formation of cyclic polysilane $(Me_2Si)_n$. Disilane I (4.0 g, 22.4 mmol) was treated with NaOMe (0.3 g, 5.6 mmol) at room temperature 3.5 h with stirring to give α,ω-dimethoxypermethylpolysilanes VI, $MeO(SiMe_2)_nOMe$ ($n \geqslant 3$). To this was added THF (11 ml). The resulting mixture was stirred for 20 h and then treated with solid NH_4Cl (0.3 g). GLC analysis for the mixture showed that it contained cyclopolysilanes $(Me_2Si)_n$ where n = 5—7. Work-up gave dodecamethylcyclohexasilane (0.43 g; 34% based on I; m.p. 218—230°C). From the filtrate after the separation of the product, additional crystals (0.07 g; an equimolar mixture of cyclopolysilanes (n = 5—7)) were obtained (eq. 8BD).

C. Formation of α,ω-dimethoxypermethylpolysilanes and the subsequent treatment with PhC≡CPh to form trisilacyclopentene derivative V. A light yellow mixture of disilane I (2.0 g, 11.2 mmol) and NaOMe (125 mg, 2.3 mmol) was stirred at room temperature for 3 h to give α,ω-dimethoxypermethylpolysilanes VI, $MeO(SiMe_2)_nOMe$ ($n \geqslant 3$). To this was added a solution of PhC≡CPh (1.8 g, 9.6 mmol) in THF (9 ml). The resulting solution was stirred for 27 h at room temperature and treated with solid NH_4Cl (0.3 g). On work-up and trituration with warm methanol crude colorless crystals of trisilacyclopentene V (0.55 g; 41% based on the disilane; m.p. 160—165.5°C; recrystallization from a EtOH/THF mixture gave a pure sample, m.p. 165.5—167.5°C) and the unreacted diphenylacetylene (0.7 g) were obtained. The analytical and spectral data of compound V are as follows: Found: C, 67.85; H, 7.82. Calcd. for $C_{20}H_{28}Si_3$; C, 68.11; H, 8.00%; NMR (CCl_4, TMS) (δ, ppm): 7.15—6.50 (m, phenyl proton, 10 H), 0.30 (s, SiMe, 6 H), 0.14 (s, SiMe, 12 H); IR (KBr pellet) (cm^{-1}) 3060m; 3010w (aromatic CH), 2950m, 2880w, 1595s; 1570w; 1480s (Ph), 1403w, 1243s (SiMe), 1180m, 1063s (Ph), 1032m, 990w, 979m, 855—640 (w to s, thirteen peaks), 610w, 570m, 515s; Mass spectrum (70 eV) (m/e) 352 (M^+; Calcd. 352).

Similarly, a mixture of disilane I (1.2 g, 6.5 mmol), PhC≡CPh (1.0 g, 5.6 mmol) and NaOMe (90 mg, 1.63 mmol) was allowed to react for 47 h at room temperature. GLC analysis for the resulting mixture showed that α,ω-dimethoxypermethylpolysilanes VI and trisilacyclopentene V were formed and no starting disilane remained. The reaction mixture thus obtained was added with THF (5 ml), giving a dark-red clear solution which was stirred for 7 h at room temperature and treated with solid NH_4Cl (0.2 g). Work-up afforded colorless crystals of trisilacyclopentene V (0.25 g; 38% m.p. 157—162°C) and the recovered acetylene (0.7 g).

Attempted reactions of disilane I with "silylene trapping reagents", Et_3SiH, Et_3SiOPr^i, $CH_2{=}CMeMeC{=}CH_2$ and $Me_3SiOSiMe_3$, in the presence of NaOMe

In order to examine the reproducibility for each reaction, several runs were carried out by "in situ" and "anion" methods. The "in situ" method was as follows: To a mixture of NaOMe and THF were added at one time all of the substrates. The "anion" method involved the following: To a silyl anion solution, prepared previously from I and NaOMe in THF, was added a solution of the silylene trapping reagents in THF.

Thus, the reactions were carried out using a 1—3 : 1 : 0.2—1.0 molar ratio of the reagent, disilane and NaOMe in THF solution at room temperature for 6—48 h with stirring. However, none of these reagents gave the corresponding silylene insertion products. Instead, the only products formed were cyclic polysilanes, $(Me_2Si)_n$ (n = 5—7), in which dodecamethylcyclohexasilane was the main product.

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