Journal of Organometallic Chemistry, 244 (1983) 329–341
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

REACTIONS OF 1,2-DIMETHOXYTETRAMETHYLDISILANE WITH STYRENES: FORMATION OF A NEW TYPE OF SILACYCLOPENTANES HAVING PHENYL SUBSTITUENTS ON RING CARBONS

HAMAO WATANABE*, JUN INOSE, TSUTOMU MURAOKA, MASAYUKI SAITO and YOICHIRO NAGAI*

Department of Chemistry, Gunma University, Kiryu, Gunma 376 (Japan)

(Received September 6th, 1982; in revised form November 4th, 1982)

Summary

The reaction of 1,2-dimethoxytetramethyldisilane with styrene and α-methylstyrene in the presence of NaOMe catalyst in tetrahydrofuran (THF) gave the new silacyclopentanes 1,1-dimethyl-2,4-diphenyl-1-silacyclopentane (IIIa) and 1,1,2,4-tetramethyl-2,4-diphenyl-1-silacyclopentane (IIIb), respectively. These silacyclopentanes were found to exist as *cis-trans* mixtures. The use of sodium metal in place of NaOMe afforded similar results. Reactions of a polysilane mixture, MeO-$(SiMe_2)_nOMe$ ($n \geq 3$), with the styrenes also gave similar results. In some cases, polysilacycloalkanes such as 1,2,3-trisilacyclopentanes (IV) and 1,2,3,4-tetrasilacyclohexanes (V) were obtained as by-products. A mechanism for the formation of the silacyclopentanes and polysilacycloalkanes is presented. It was found that electron impact decomposition of silacyclopentanes IIIa and IIIb, trisilacycloalkane IV and tetrasilacycloalkane V gave molecular ions corresponding to the silacyclopropane, cyclotrisilane and cyclotetrasilane systems.

Introduction

During the course of our studies of silicon-functional organosilyl anions such as methoxydimethylsilyl and dimethoxymethylsilyl anions [1], we found that, in the presence of a catalytic amount of NaOMe, 1,2-dimethoxytetramethyldisilane (I) gives a series of permethylcyclopolysilanes, $(SiMe_2)_m$ where $m = 5$–7 [2], and a series of α,ω-dimethoxypermethylpolysilanes, $MeO(SiMe_2)_nOMe$ where $n \geq 3$ [2,3].

Recently, we also reported that the reaction of I with diphenylacetylene and stilbene (*cis* and *trans*) using a catalytic amount of NaOMe furnished 1,2,3-trisilacyclo-pentene [3,4] and -pentane [5] systems, respectively.

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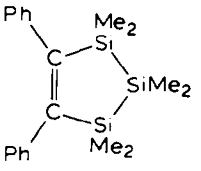
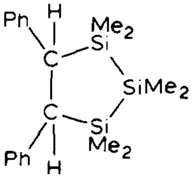
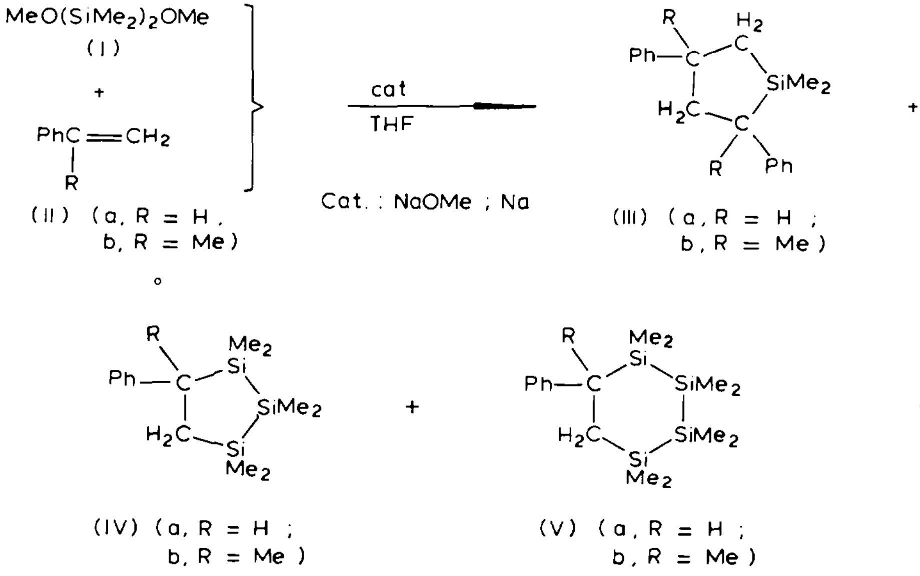




This paper deals with the formation of new silacyclopentane derivatives, 2,4-diphenyl-1,1-dimethyl-1-silacyclopentanes, from the reactions of I with styrene (IIa) and α-methylstyrene (IIb) in the presence of NaOMe or sodium metal. Although several reports on 2,5- and 3,4-diphenyl-1-silacyclopentanes have appeared [6], there are no reports on the formation of 2,4-diphenylsilacyclopentanes. The present reaction provides a simple and convenient method for the selective preparation of these new silacyclopentane derivatives.

Results

Reactions of 1,2-dimethoxytetramethyldisilane (I) with styrenes (IIa and IIb) in THF proceeded smoothly at room or refluxing temperatures in the presence of NaOMe, giving 1,1-dimethyl-2,4-diphenyl-1-silacyclopentanes (IIIa and IIIb) in 38–65% yields. In addition, 1,1,2,2,3,3,4-heptamethyl-4-phenyl-1,2,3-trisilacyclopentane (IVb) and 1,1,2,2,3,3,4,4-octamethyl-5-phenyl-1,2,3,4-tetrasilacyclohexane (Va) were isolated in small amounts from the reactions with IIb and with IIa, respectively. An attempt to isolate the structurally closely related by-products such as IVa and Vb was not successful. Similar results were obtained with the use of a catalytic amount of sodium metal in place of sodium methoxide (eq. 1).



(1)

Interestingly, the reactions of a set of α,ω-dimethoxypermethylpolysilanes (I′), MeO(SiMe$_2$)$_n$OMe where $n \geq 3$, prepared by the method previously reported [3], with styrenes also gave rise to IIIa and IIIb in ca. 60% yields (eq. 2). Table 1 lists the

$$\mathrm{I} \xrightarrow{\text{NaOMe cat.}} \underset{(\mathrm{I'})\ (n \geqq 3)}{\mathrm{MeO(SiMe_2)}_n\mathrm{OMe}} \xrightarrow[\mathrm{THF}]{\mathrm{II}} \underset{(\text{Major})}{\mathrm{III}} + \mathrm{IVb} + \underset{(\text{Minor})}{\mathrm{Va}} \qquad (2)$$

reaction conditions and yields of the major products. It is seen from the Table that the yields of III in preparative scale syntheses (Runs 2 and 6) were somewhat lower than in analytical experiments, but a sizable amount of the main products could be isolated by simple vacuum distillation.

Structures IIIa and IIIb were assigned from their ^{13}C NMR, ^{1}H NMR, IR and mass spectra properties as well as elemental analysis. The NMR data were used for the determination of the positions of the two phenyl substituents in III and of the geometrical configurations. Thus, the ^{13}C NMR spectrum of each isomer of IIIa and IIIb showed four different carbon signals for the five-membered ring structure, while that of each isomer of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentane which was obtained by the literature method [6d] exhibited only two carbon signals (Table 2). These observations are in good agreement with the 2,4-disposition of two phenyl groups in the ring system. On the other hand, the ^{1}H NMR spectrum of IIIa showed three different Si–Me singlets at δ −0.25, −0.15 and 0.28 ppm, compatible with a *cis-trans* mixture of IIIa. An assignment was made such that the first singlet is due to the *cis* isomer, the second due to the *trans* isomer, and the last due to both the *cis* and *trans* isomer. This interpretation seems consistent with the structural assignment made by Gilman and Atwell [6c] and also by Weyenberg and coworkers [6d] for *cis*- and *trans*-1,1-dimethyl-2,5-diphenyl-1-silacyclopentane. They found in the ^{1}H NMR spectrum SiMe singlets at δ −0.64 and 0.29 ppm for the *cis* isomer and −0.14 ppm for the *trans* isomer. A similar interpretation applies in the case of the *cis-trans* mixture of IIIb which showed in the ^{1}H NMR singlets at δ −0.32 and 0.37 ppm for

TABLE 1

REACTION OF 1,2-DIMETHOXYTETRAMETHYLDISILANE AND POLYSILANES WITH STYRENES IN THE PRESENCE OF NaOMe OR SODIUM TO FORM MONO-SILACYCLOPENTANES (IIIa and IIIb)

Run	Substrate		Catalyst [a]	Conditions	Product and yield (%) [b]
	Disilane (mmol)	Ph(R)C=CH$_2$ (mmol)			
1	5.6	R = H, 5.6	NaOMe	reflux; 3 h	IIIa 64
2	56	R = H, 112	NaOMe	reflux; 3 h	IIIa 38 [c]
3 [d]	11.2	R = H, 9.6	NaOMe	r.t; 15 h	IIIa 56
4	5.6	R = H, 11.2	Na [e]	r.t.; 15 h	IIIa 48
5	11.2	R = Me, 11.2	NaOMe	reflux; 3 h	IIIb 64
6	56	R = Me, 112	NaOMe	reflux; 3 h	IIIb 46 [c]
7 [d]	11.2	R = Me, 9.6	NaOMe	r.t.; 20 h	IIIb 65
8	5.6	R = Me, 11.2	Na [e]	r.t.; 6 h	IIIb 67

[a] Ca. 15 mol% relative to the substrate of which least was used. [b] GLC yield. [c] Isolated yield by distillation. [d] Polysilane method in eq. 2: a polysilane mixture was mixed with a solution of styrene in THF, and the mixture was allowed to react under the conditions indicated. [e] Sodium sand.

TABLE 2

CHARACTERISTIC ^{13}C NMR SIGNALS FOR 2,4- AND 2,5-DIPHENYL-1-SILACYCLOPENTANES

Compound		Chemical shifts (CDCl$_3$, TMS) (δ, ppm) (Off-res.)[a]						
		C(2)	C(3)	C(4)	C(5)	C(2)–Me	C(4)–Me	Si–Me
IIIa (2,4-)	*trans*	37.46(d)	40.69(t)	44.35(d)	22.40(t)			−1.61(q) −3.35(q)
	cis	37.24(d)	41.10(t)	44.13(d)	21.64(t)			−0.17(q) −3.13(q)
IIIb (2,4-)	*trans*	34.58(s)	53.06(t)	44.92(s)	27.20(t)	28.41(q)	36.70(q)	−0.35(q) −2.42(q)
	cis	34.00(s)	55.25(t)	45.11(s)	28.41(t)	33.73(g)	36.70(q)	−0.42(q) −2.20(q)
(2,5-)	*trans*[b]	37.23(d)	31.61(t)	31.61(t)	37.23(d)			−3.78(q)
	cis[b]	35.60(d)	31.97(t)	31.97(d)	35.60(d)			−2.02(q) −5.97

[a] Signals by off-resonance method; d: doublet, q: quartet, s: singlet, t: triplet. [b] Tentatively assigned.

the *cis* isomer and −0.17 and 0.23 ppm for the *trans* isomer. The chemical shifts for the SiMe absorptions exhibited by these compounds and also by 1,1-dimethyl-3,4-diphenyl-1-silacyclopentanes for reference are shown in Fig. 1. From peak intensities for the SiMe signals we estimate the *cis/trans* ratio for IIIa to fall in the range of 10–20/80–90 and for IIIb in the range of 30–40/60–70.

Discussion

Mechanistic considerations

A previous study [4] has shown that reactions of the disilane I and an α,ω-dimethoxypermethylpolysilane mixture (I′) with diphenylacetylene using NaOMe catalyst gave a common product, 4,5-diphenyl-1,2,3-trisilacyclopent-4-ene. It has been suggested that polysilyl anions derived from the dimethoxypolysilanes play an important role in the formation of the trisilacyclopentene. Since the present reaction employs similar conditions, the mechanism through which it proceeds probably involves similar polysilyl anions as key intermediates. Taking this view in mind, the processes leading to IIIa and IIIb are shown in Scheme 1.

Thus, ω-methoxypermethylpolysilyl anions (A) can be formed by the reaction of I′ with sodium methoxide and then react with styrenes at the methylene carbon to give the carbanion B. The carbanion B will next pickup a second molecule of styrene and nucleophilic attack on the terminal carbon will result in the formation of the dimeric carbanion C. The structures of B and C are expected because of resonance stabilization by the phenyl ring and also by steric requirements [7]. Finally, cyclization leading to the silacyclopentanes, IIIa and IIIb, can be achieved via intramolecular nucleophilic attack of the anionic carbon in C at the δ-silicon which bears a methoxy or a polysilyl substituent as a leaving group. The 2,4-disposition of two phenyl groups in the silacyclopentane system can now be accommodated within this scheme, but factors determining *cis-trans* stereochemistry are not clear at the present time.

In principle, intramolecular attack of the anionic carbon in C is possible at

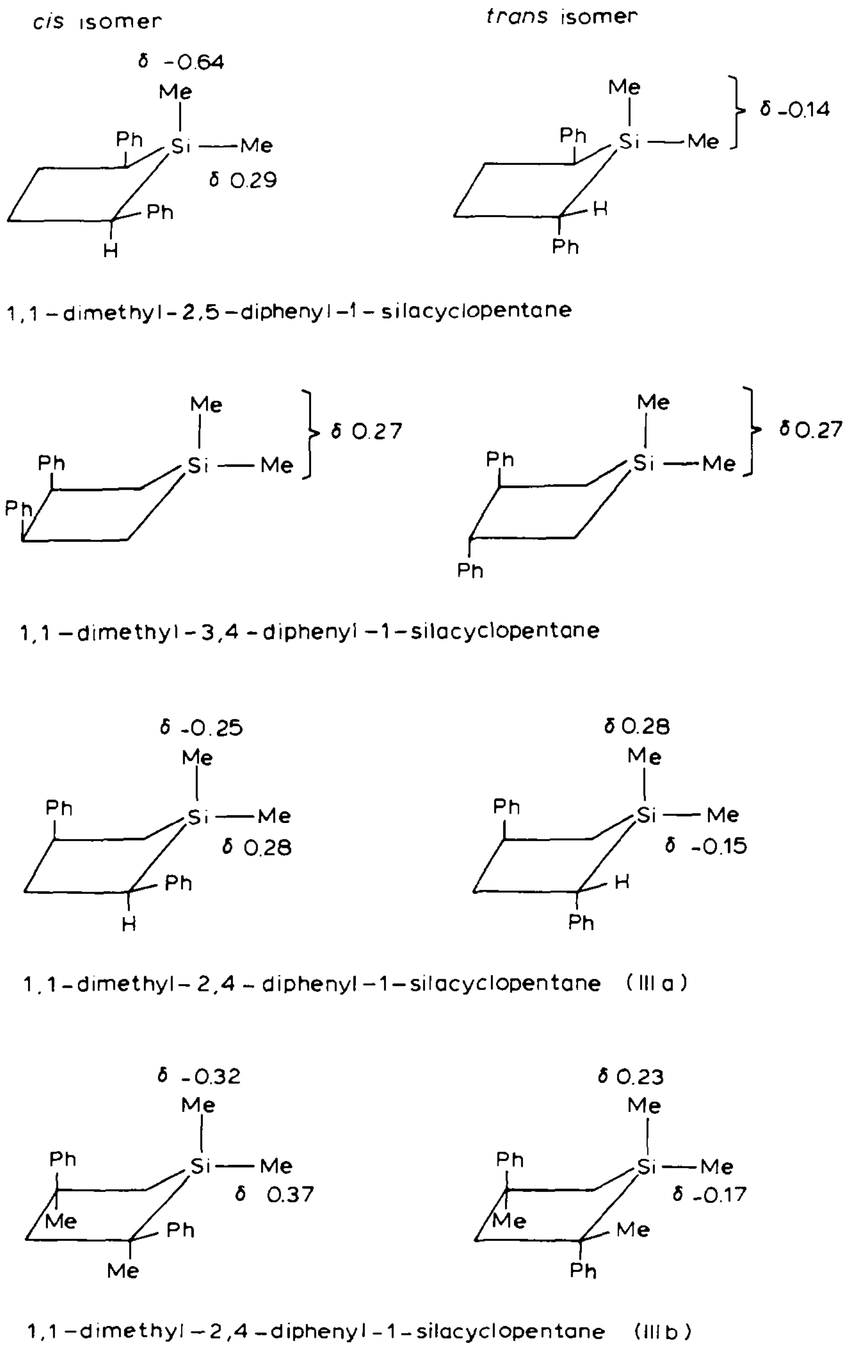


Fig. 1. Chemical shifts for the Si–Me protons of silacyclopentanes.

silicons located on various positions other than δ leading to larger ring systems such as 1,2-disilacyclohexanes, 1,2,3-trisilacycloheptanes and so on. In fact, the reaction of I with styrene gave a trace amount of a compound the mass spectrum of which exhibited *m/e* 324 [*M*], 220 [*M* – 104], 162 [*M* – 162], 147 [*M* – 177] and 116 [$Me_2Si{=}SiMe_2$] (see also Experimental). The structure of 1,1,2,2-tetramethyl-4,6-diphenyl-1,2-disilacyclohexane (VI) can be deduced from the data, but the insufficiency of the isolated sample precluded further confirmation of the structure by other means.

The carbanion B is capable of undergoing cyclization to give IVb and Va via the nucleophilic displacement at silicon at a relevant position if the chain length permits the reaction to take place. These processes are essentially the same as those proposed previously for the formation of 4,5-diphenyl-1,2,3-trisilacyclopent-4-ene from the reaction of diphenylacetylene with I in the presence of sodium methoxide [4]. Compounds such as IVa and Vb would have been produced as well, but efforts to isolate these or other ~~related~~ compounds were discarded because good yields are hardly expected. Furthermore, larger ring systems such as cyclic C_2Si_5, C_2Si_6, etc. were also possibly formed, but isolation and characterization of these compounds were felt to be the subject of future investigations.

Interestingly, the reactions using sodium metal as an initiator (18% or less relative to the disilane used) furnished almost identical product mixtures in comparable yields to the NaOMe-catalyzed reactions. This fact might suggest that the Si–Si bond cleavage of I by sodium occurred initially to give methoxydimethylsilyl sodium which is the active species postulated in the NaOMe-catalyzed reactions. The cleavage of I by sodium metal (eq. 3) is not entirely surprising, since the similar

$$MeO(SiMe_2)_2OMe + 2Na \rightarrow 2(MeO)Me_2SiNa \qquad (3)$$

cleavage of disilanes containing aryl groups is known [8]. However, the cleavage of the Si–OMe bond (eq. 4) is another possibility which must be taken into account. The formation of $Ph_2SiClLi$ has been postulated from the reaction of diphenyl-

$$MeO(SiMe_2)_2OMe + 2Na \rightarrow MeO(SiMe_2)_2Na + NaOMe \qquad (4)$$

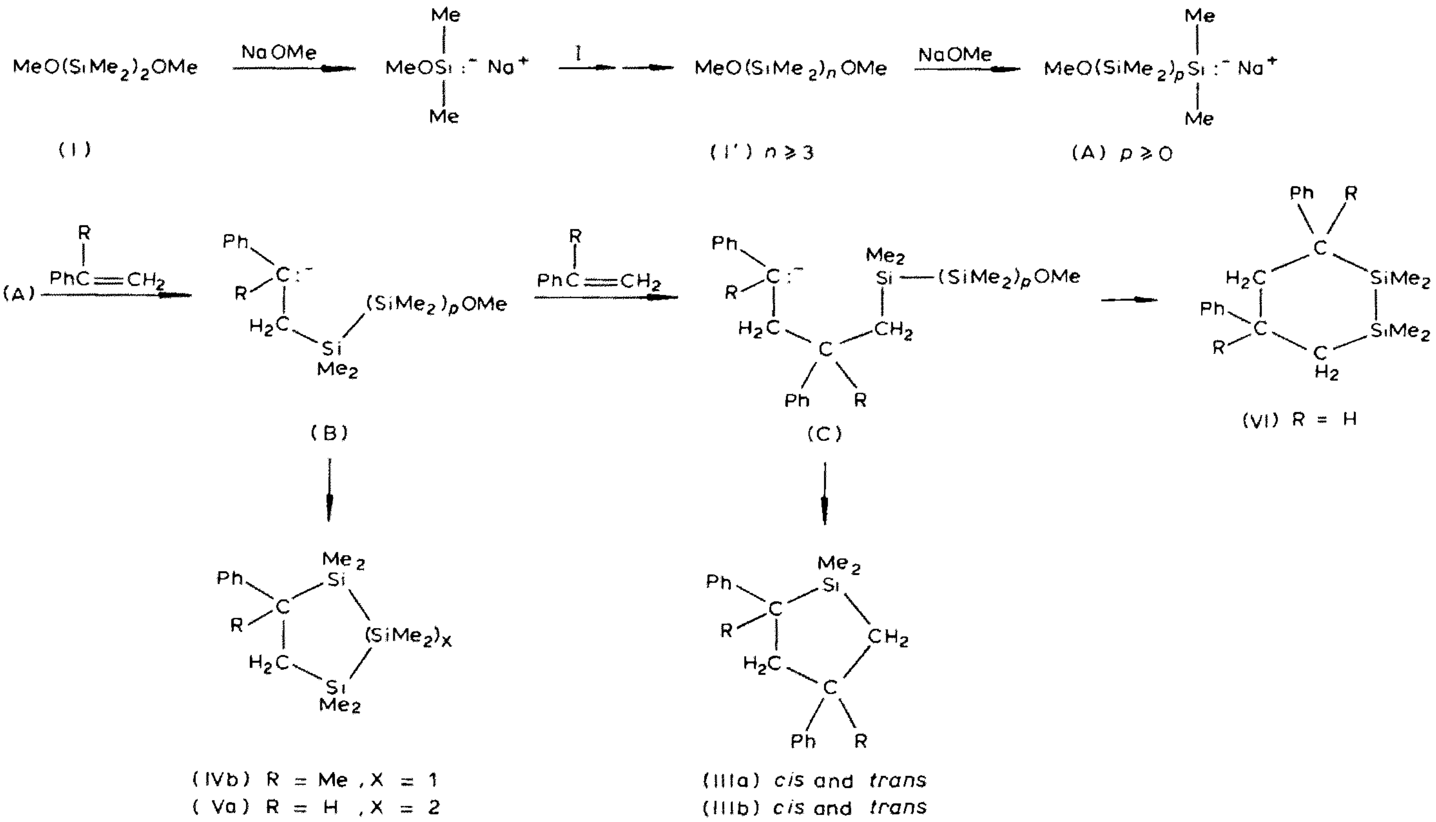
dichlorosilane with lithium metal leading to octaphenylcyclotetrasilane [8]. Whatever the mechanism may be, the formation of silyl anions from the reaction of I with sodium metal was now verified by the fact that treatment of I with a catalytic amount of sodium metal in THF at room temperature for 22 h afforded dodecamethylcyclohexasilane in 48% yield (eq. 5). The formation of the cyclohexasilane in

$$MeO(SiMe_2)_2OMe \xrightarrow[\text{THF; r.t.}]{\text{Na cat.}} 1/6(Me_2Si)_6 + Me_2Si(OMe)_2 \qquad (5)$$

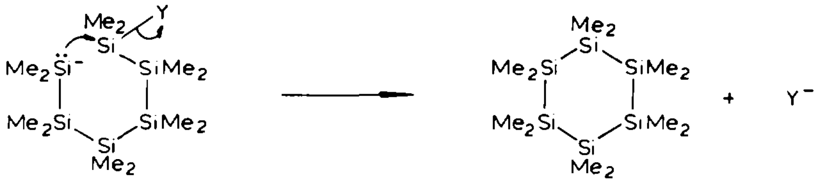
this reaction is well explained in terms of an intramolecular nucleophilic attack of silicon anion center in A at a silicon atom [3] (Scheme 2).

It seemed necessary to consider the present reaction from the viewpoint of a radical anion mechanism involving electron transfer processes from silyl anion A to styrenes, since the triorganosilyl anion, e.g. trimethylsilyl anion, has been shown to be an excellent electron donor [9]. Weyenberg et al. have previously reported that the reactions of dimethyldichlorosilane with styrene and α-methylstyrene in the presence of alkali metals (Li and Na) gave 1,1-dimethyl-2,5- or 3,4-diphenyl-1-silacyclopentanes depending upon the conditions employed [6d]. For the formation of the

SCHEME 1


MeO(SiMe2)2OMe
NaOMe
MeOSi:⁻ Na⁺
Me
Me
I
MeO(SiMe2)nOMe
NaOMe
MeO(SiMe2)pSi:⁻ Na⁺
(I)
(I') n ≥ 3
(A) p ≥ 0
(A)
PhC(R)=CH2
(B)
PhC(R)=CH2
(C)
(VI) R = H
(IVb) R = Me, X = 1
(Va) R = H, X = 2
(IIIa) cis and trans
(IIIb) cis and trans

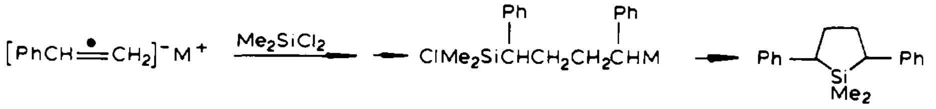
SCHEME 2



(A)

$[Y = (SiMe_2)_nOMe;\ n \geq 0]$

2,5-diphenylsilacyclopentane, they proposed a mechanism involving electron transfer processes from the metals to the substrate, e.g. styrene (eq. 6). Thus, the structures of dimeric anionic species formed should contain a 1,4-diphenylbutylene unit and are



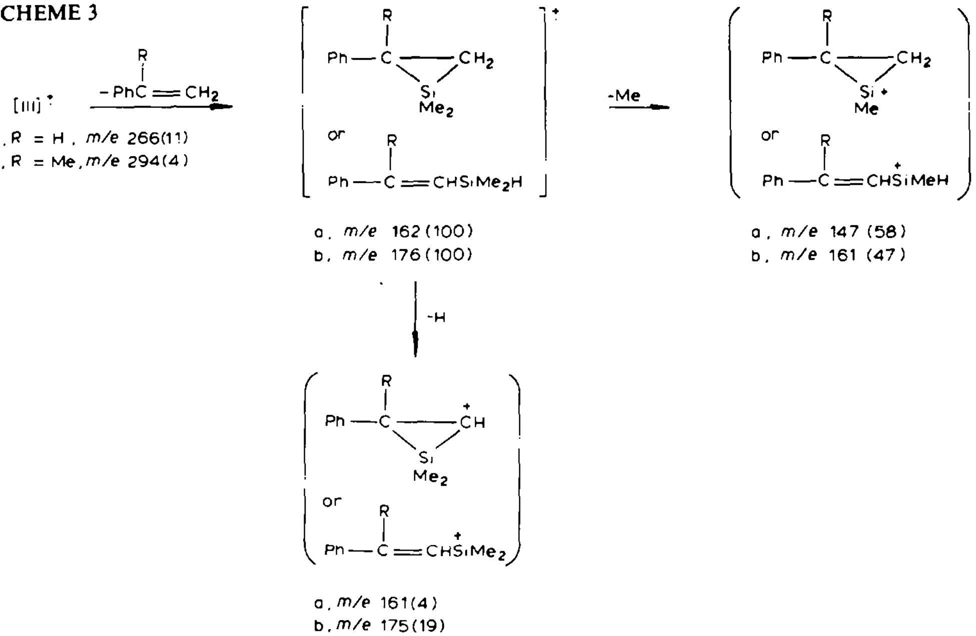
(6)

not in accord with the 2,4-diphenyl disposition in the silacyclopentanes obtained in the present study. In addition, the structures of IV, V and VI are consistent with the radical anion mechanism, but they are equally consistent with the silyl anion mechanism. Isolation of these compounds in only very small amounts does not support the former pathway.

Mass spectral behavior of IIIa, IIIb, IVb and Va

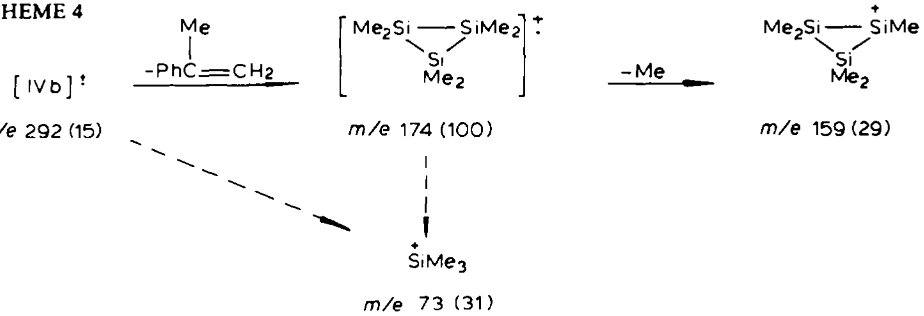
It is of interest to investigate the mass spectral behavior of the silicon-containing ring compounds obtained, since it discloses the nature of the compounds and provides further information about the structures. The mass spectra of IIIa, IIIb, IVb and Va gave the corresponding parent ion peaks with varying intensities. The electron impact fragmentation of these compounds appears to have a common feature in the decomposition mode. Thus, it was found that the dominant fragmentation route of IIIa and IIIb was the abstraction of a styrene and an α-methylstyrene molecule with the formation of molecular silacyclopropane ions or alkenyl hydrosilane ions which are the base peaks, *m/e* 162 $[M-104]^+$ and *m/e* 176, $[M-118]^+$, respectively (Scheme 3). These fragments subsequently eliminated a methyl group, forming the corresponding three-membered ring siliconium ions or alkenyl siliconium ions, *m/e* 147, $[M-119]^+$ and *m/e* 161, $[M-133]^+$, respectively. It should be noted that the fragmentation of IIIa was partly different from that of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentane, for which the base peak was the ion of *m/e* 117, $[M-149]^+$, as has been shown by Maruca et al. [10]. Similarly, in IVb and Va, the dominant fragmentation was the elimination of an α-methylstyrene and a styrene molecule with the formation of ions of the corresponding small ring polysilanes such as the cyclotrisilane *m/e* 174, $[M-118]^+$ and the cyclotetrasilane *m/e* 232, $[M-104]^+$ (Schemes 4 and 5). The loss of a methyl group then followed. Such a decomposition mode is in agreement with those of polysilacycloalkanes such as 4,5-diphenyl-1,2,3-trisilacyclopentane and 5,6-diphenyl-1,2,3,4-tetrasilacyclohexene

SCHEME 3

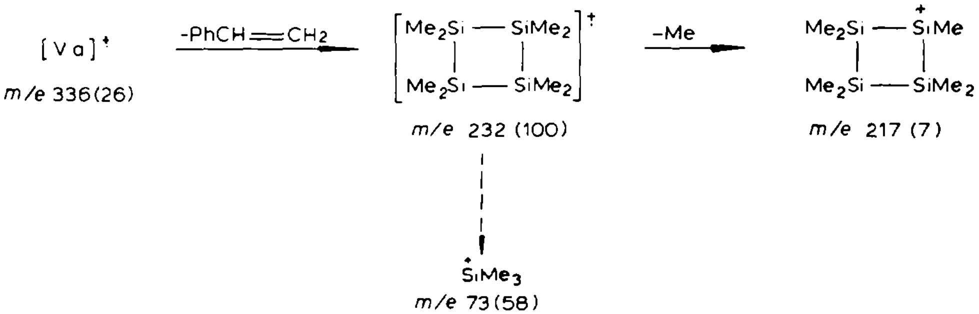


[5]. It is noteworthy that this is the first example of the formation of small ring and strained cyclopolysilanes such as permethylcyclotrisilane during electron impact dissociation, although the first synthesis of a cyclotrisilane bearing sterically crowded substituents has been achieved quite recently by Masamune et al. [11].

SCHEME 4



SCHEME 5



Experimental

All boiling points are uncorrected. All the reactions were carried out under an atmosphere of argon. IR spectra were recorded using neat liquid films with a JASCO A-102 spectrometer. ^1H NMR spectra were recorded at 60 MHz using a Varian EM-360A spectrometer in CCl_4 with TMS as an internal standard. ^{13}C NMR spectra were measured at 20.0 MHz using Varian FT-80A and at 22.5 MHz using JEOL JNM-FX90Q spectrometers in $CDCl_3$ with TMS as standard. Mass spectral analyses were conducted at 20 eV (ionization potential) using a JEOL JMS-07 spectrometer. GLC analyses were performed using Ohkura Model GC-103 and 802 instruments equipped with a 1 or 2 m × 4 mm Teflon or stainless-steel column packed with Silicone SE-30 or Apiezon L (5-19%) on Celite 545-AW (60–80 mesh) (column temp. 80–300°C; He carrier). Thermal conductivity correction using an external standard (n-alkanes selected from C_{20}–C_{25} hydrocarbons) was made for the GLC product yields.

Materials

1,2-Dimethoxytetramethyldisilane (I) was prepared by methoxylation of the corresponding dichlorosilane according to the method described previously [12]. 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. Other materials were commercially available and were used without purification.

Reaction of disilane I with styrenes in the presence of NaOMe

To a suspension of NaOMe (0.06 g, 1.2 mmol) in THF (2 ml) was added with stirring a solution of 1,2-dimethoxytetramethyldisilane (I) (2.0 g, 11.2 mmol) and styrene (1.0 g, 5.6 mmol) in THF (5 ml). The mixture was refluxed for 3 h. The course of the reaction was monitered by GLC. After addition of NH_4Cl (0.5 g) and stirring for a night, the mixture was filtered to give a pale yellow solution which was concentrated. The resulting viscous liquid was subjected to GLC analysis. It was shown that three products were formed.

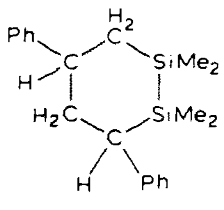
The first product eluted (liquid) was isolated in a very small amount and identified as 1,1,2,2,3,3,4,4-octamethyl-5-phenyl-1,2,3,4-tetrasilacyclohexane (Va). This compound showed the following spectral properties: ^1H NMR (δ, ppm), 7.38–6.63 (m, 5H, Ph), 2.18 (mc, 1H, CH), 1.64–0.65 (m, 2H, CH_2), 0.20, 0.13, 0.07, -0.10, -0.23 (five singlets, 24H, SiMe); IR (neat) (cm^{-1}), 3080, 3065, 3030 (CH of Ph), 1260(sh), 1246(SiMe); MS, m/e (intensity), 336[M](26), 234(18), 233(30), 232[$M-104$](100), 217(7), 174(11), 173(13), 160(14), 159(23), 158(48), 157(11), 145(11), 143(15), 116(18), 73(58). Analysis, Found: C, 57.33; H, 9.31. Calcd. for $C_{16}H_{32}Si_4$: C, 57,04; H, 9.58%.

The second major eluted product (liquid) was isolated (GLC) and identified as 1,1-dimethyl-2,4-diphenyl-1-silacyclopentane (IIIa); n_D^{20} 1.5700; 60% yield (GLC) based on the styrene used. The compound exhibited the following spectral properties: ^1H NMR (δ, ppm) 7.32, 7.17(two singlets, 10H, Ph), 3.60–1.80(m), 1.63–0.50(m) (6H, CH_2 and CH), 0.28(s) and -0.25(s) (*cis*-SiMe), 0.28(s) and -0.15(s) (*trans*-SiMe) (6H) [the intensity ratio of the signals at -0.25 (*cis*) and at -0.15 (*trans*) was 10 : 90]; IR (neat) (cm^{-1}), 3080, 3060, 3025(CH of Ph), 1255(sh), 1248(SiMe);

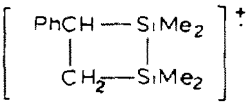
MS, *m/e* (intensity), 266[*M*](11), 163(16), 162[*M* – 104] (100), 148(10), 147(58). Analysis, Found: C, 81.09; H, 7.98. Calcd. for $C_{18}H_{22}Si$: C, 81.14; H, 8.32%.

The third product eluted was isolated in only very small amounts. But the product was assumed by the fragmentation pattern of its mass spectrum to be 1,1,2,2-tetramethyl-3,5-diphenyl-1,2-disilacyclohexane (VI). The mass spectrum for the compound was as follows: *m/e* (intensity), 324[*M*] (12), 220[*M* – 104] (43), 162[*M* – 162] (64), 161(38), 147[*M* – 177] (75), 145(32), 135(44), 117(28), 116[*M* – 208] (100), 91(28), 73[*M* – 251] (60), 59[*M* – 265] (38).

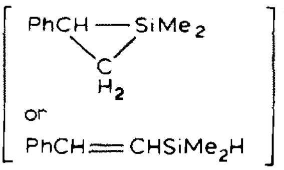
In a larger preparative scale reaction using I (56 mmol), styrene (112 mmol) and NaOMe (8.4 mmol) in THF (30 ml) (reflux for 3 h; NH_4Cl 5 g), there was obtained IIIa, 5.7 g (38%) as a fraction boiling at 151–155°C/1 mmHg; n_D^{20} 1.5713. The residue in the distillation was solidified.



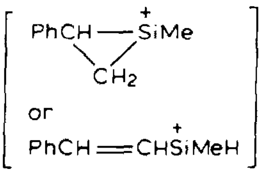
(VI)



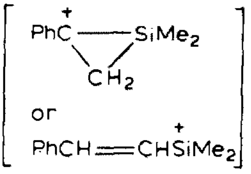
m/e 220 (43)



m/e 162 (64)



m/e 147 (75)



m/e 161 (38)

$[Me_2Si{=}SiMe_2]^{+\cdot}$

m/e 116 (100)

$\overset{+}{Si}Me_3$

m/e 73 (60)

Similarly, I (56 mmol) was treated with α-methylstyrene (112 mmol) in the presence of NaOMe (8.4 mmol) in THF (30 ml) to give, on work-up, 7.5 g (46%) of 1,1,2,4-tetramethyl-2,4-diphenyl-1-silacyclopentane (IIIb), b.p. 145–155°C/0.4 mmHg; n_D^{20} 1.5703. The compound exhibited the following spectral properties: ^1H NMR (δ, ppm), 7.67–6.75 (m, 10H, Ph), 2.90–1.90 (m, 2H, CH_2), 1.86–0.70 (m, $SiCH_2$), 1.38 (s, C–C*Me*–C), 0.93 (s, Si–C*Me*) (8H), 0.37(s) and –0.32(s) (*cis*-SiMe), 0.23(s) and –0.17(s) (*trans*-SiMe) (6H) (the intensity ratio of the signals for the *cis* and *trans* was 30 : 70); IR (neat) (cm^{-1}), 3038, 3055, 3020 (CH of Ph), 1250 (SiMe); MS, *m/e* (intensity), 294 [*M*](4), 177(19), 176 [*M* – 118](100), 175(19), 174(25), 162(8), 161(47), 159(8). Analysis, Found: C, 81.13; H, 8.68. Calcd. for $C_{20}H_{26}Si$: C, 81.56; H, 8.90%.

The residue (1.2 g) after separation of IIIb was semi-solid upon cooling.

Reaction of disilane I with styrenes in the presence of Na

The reaction of α-methylstyrene is representative. A mixture of I (5.6 mmol) and α-methylstyrene (11.2 mmol) in THF (5 ml) was allowed to react in the presence of sodium sand (0.6 mg.-atom) at room temperature for 6 h. Work-up afforded a product mixture, GLC analysis of which showed that there were obtained IIIb (GLC yield, 67%) and 1,1,2,2,3,3,4-heptamethyl-4-phenyl-1,2,3-trisilacyclopentane (IVb) in a small amount. The spectral data for IVb are as follows: ^{1}H NMR (δ, ppm), 7.13 (mc, 5H, Ph), 1.62–0.64(m, CH_2Si), 1.29(s, C–Me)(5H), 0.67 ~ −0.58(m, 18H, SiMe); IR (neat) (cm^{-1}), 3080, 3050, 3025, 3010(CH of Ph), 1245(SiMe); MS, m/e (intensity), 292[M](15), 176(14), 175(33), 174[$M-118$](100), 159[$M-133$](29), 129(16), 117(18), 116(11), 73(31). Analysis, Found: C, 61.28; H, 9.10. Calcd. for $C_{15}H_{28}Si_3$: C, 61.56; H, 9.64%.

Reaction of α,ω-dimethoxypermethylpolysilanes (I′) with styrenes in the presence of NaOMe

A typical method is given for the reaction of permethylpolysilanes with α-methylstyrene. To obtain α,ω-dimethoxypermethylpolysilanes (I′), $MeO(SiMe_2)_nOMe$ ($n \geq 3$), a mixture of I (2.0 g, 11.2 mmol) and NaOMe (0.06 g, 1.2 mmol) was stirred at room temperature for 24 h. To the polysilane mixture [3] was added a solution of α-methylstyrene (1.1 g, 9.6 mmol) in THF (5 ml). After stirring for 20 h at room temperature, work-up gave a viscous liquid which was subjected to GLC analysis. Two products, which were isolated by preparative GLC, were formed. The main product was IIIb (GLC yield, 65% based on the disilane used). The minor product was IVb, the yield of which was not determined but was estimated to be very low.

Treatment of disilane I with Na

Disilane I (1.0 g, 5.6 mmol) was treated with sodium sand (23 mg, 1.0 mg.-atom) in THF (3 ml) at room temperature with stirring for 22 h, during which time the reaction was monitored by GLC. At the end of this time, no increase of the main product peak was observed. After treatment with solid NH_4Cl (0.1 g), the mixture was filtered. On concentration, the filtrate gave a pale yellow liquid, GLC analysis of which showed that three products were formed. The main product was isolated and identified as dodecamethylcyclohexasilane, $(Me_2Si)_6$, (GLC yield, 48%). The minor products were other cyclopolysilanes, $(Me_2Si)_5$ and $(Me_2Si)_7$, and their yields were not determined. On the other hand, GLC analysis for the above distillate separated from the reaction mixture showed that it contained a small amount of dimethoxydimethylsilane, $Me_2Si(OMe)_2$.

Acknowledgement

The author (H.W.) is grateful to the Ministry of Education of Japan for support of this work through a Grant-in-Aid for Scientific Research, No. 56540290.

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