Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

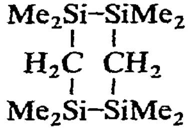
SILICON-CONTAINING HETEROCYCLIC COMPOUNDS
I. PREPARATION AND REACTIONS OF 1,1,2,2-TETRAMETHYL-1,2-DISILACYCLOALKANES, FROM DISILACYCLOPENTANE TO DISILACYCLOOCTANE

MAKOTO KUMADA, KOHEI TAMAO, TADASHI TAKUBO AND MITSUO ISHIKAWA
Department of Synthetic Chemistry, Kyoto University, Kyoto (Japan)

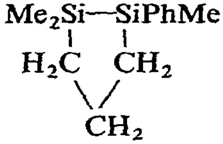
(Received January 2nd, 1967)

INTRODUCTION

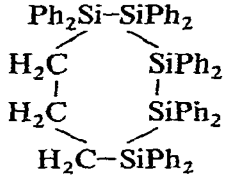
Despite a large number of publications dealing with silacyclohydrocarbons[1], only very little interest has been shown in a class of compounds that contain the silicon–silicon bond in the ring. To our knowledge only a few such cyclic compounds, (I)[2], (II)[3], (III)[4], (IV)[5] and (V)[6], have been described in the literature.



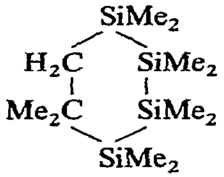
(I)



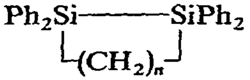
(II)



(III)



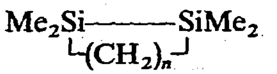
(IV)



$n = 4$ and 5

(V)

As part of a program concerned with the chemistry of organopolysilanes we were interested in preparing 1,1,2,2-tetramethyl-1,2-disilacycloalkanes and studying their chemical behavior, because the silicon–silicon bond in some of these compounds should be more highly strained and hence would be expected to be more reactive than or different in modes of reaction from that in the related open-chain molecules. We report here the preparation of 1,1,2,2-tetramethyl-1,2-disilacyclopentane (VI), -hexane (VII), -heptane (VIII) and -octane (IX), and some of their reactions.

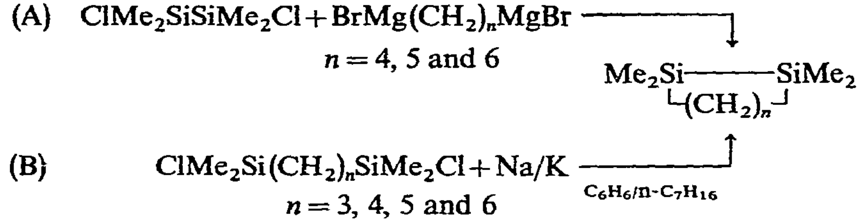


(VI), $n = 3$
(VII), $n = 4$
(VIII), $n = 5$
(IX), $n = 6$

RESULTS AND DISCUSSION

Synthesis

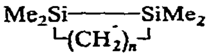
Two types of reaction were utilized to prepare the 1,2-disilacycloalkanes. Method (A) involves the reaction of di-Grignard reagents of the formula $BrMg(CH_2)_nMgBr$, *n* being 4, 5 and 6, with 1,2-dichlorotetramethyldisilane in tetrahydrofuran (THF), while method (B) entails the sodium/potassium condensation of α,ω-bis(chlorodimethylsilyl)alkanes of the formula $ClMe_2Si(CH_2)_nSiMe_2Cl$, where *n* equals 3 through 6, in benzene/n-heptane solution.



Yields of compounds (VI)–(IX) obtained in typical runs by both methods are listed in Table 1, and some physical properties and analytical data in Table 2.

TABLE 1

SYNTHESIS OF 1,1,2,2-TETRAMETHYL-1,2-DISILACYCLOALKANES



Compound		Preparative method[a]	Yield (%)
No.	*n*		
(VI)	3	(B)	45
(VII)	4	(A)	66
		(B)	50
(VIII)	5	(A)	65
		(B)	18
(IX)	6	(A)	<3
		(B)	5

[a] See the text.

TABLE 2

SOME PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR 1,1,2,2-TETRAMETHYL-1,2-DISILACYCLOALKANES

Compound		B.p. (°C/mm)	n_D^{20}	d_4^{20}	MR found (calcd.)	C(%) found (calcd.)	H(%) found (calcd.)
No.	Formula						
(VI)	$C_7H_{18}Si_2$	154–155	1.4708	0.8258	53.59 (53.77)	53.03 (53.08)	11.25 (11.46)
(VII)	$C_8H_{20}Si_2$[a]	174	1.4722	0.8360	57.77 (58.12)	55.52 (55.72)	11.67 (11.69)
(VIII)	$C_9H_{22}Si_2$	76–77/16	1.4811	0.8473	62.90 (63.07)	58.06 (57.98)	11.64 (11.89)
(IX)	$C_{10}H_{24}Si_2$[b]	96/14	1.4882	0.8579	67.35 (67.71)	60.05 (59.91)	12.01 (12.07)

[a] *M.p.* −14 to −12°. [b] *M.p.* 7–9°.

Method (A) gave the disilacyclohexane (VII) and -heptane (VIII) in good and comparable yields. However, this method was found to be far from satisfactory for synthesis of the disilacylcooctane (IX); sometimes only a trace of it could be detected by gas chromatography in the reaction mixture. Almost all the product was a viscous polymeric material.

Method (B) afforded the disilacyclopentane (VI) and -hexane (VII) in satisfactory and approximately the same yield. While this method gave the disilacycloheptane (VIII) in much lower yield than did method (A), it gave a somewhat better yield of disilacyclooctane (IX).

As is well known (see *e.g.* ref. 7), the ease of cyclization of a chain depends upon several factors, the most important among them being (*a*) an internal-angle strain of a ring to be formed, (*b*) the interactions between non-vicinal groups attached to the ring, and (*c*) the probability of intramolecular collision of the chain ends bearing the reactive groups. On these bases, the variation in yields obtained by method (B) with the ring size can be accounted for. Thus, a somewhat lower yield of the disilacyclopentane (VI) as compared with the disilacyclohexane (VII) may be attributed to somewhat larger ring strain inherent in the former, whereas the sharp drops in yield with increasing ring size from six through seven to eight are doubtless due to severely increasing repulsions of non-bonded groups attached to the ring, in addition to a lowering of the probability of intramolecular collision of the two reactive atoms at the chain ends. The conventional framework molecular model of the disilacyclooctane (IX) shown in Fig. 1 indicates that a great steric interaction is present among an axial methyl group and three axial hydrogen atoms on either side of the ring.

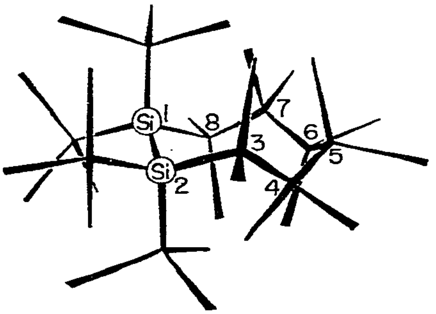
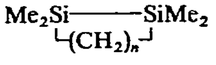


Fig. 1. A framework molecular model of 1,1,2,2-tetramethyl-1,2-disilacyclooctane.

TABLE 3

THE ^{1}H CHEMICAL SHIFTS OF 1,1,2,2-TETRAMETHYL-1,2-DISILACYCLOALKANES



Me_2Si—$SiMe_2$ $\llcorner(CH_2)_n\lrcorner$

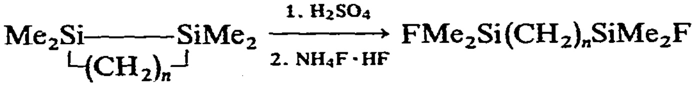
Compound	*Chemical shifts (τ values)*		
(*n*)	*Methyl*	*Methylene α to silicon*	*Methylene β and γ to silicon*
3	9.88	9.25–9.45	8.1–8.6
4	9.95	9.1–9.5	8.3–8.6
5	9.95	9.1–9·6	8.3–8.5
6	9.97	9.1–9.3	8.3–8.8

The proton NMR spectral data, listed in Table 3, confirm the sturcture of each of the disilacycloalkanes.

Reactions with concentrated sulfuric acid

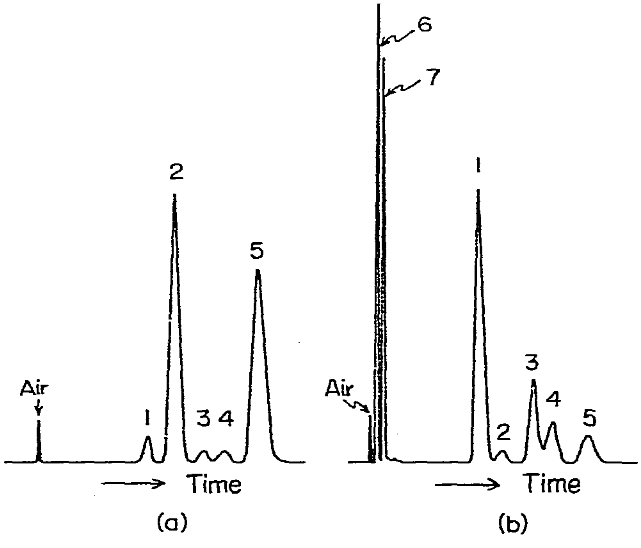
Much work has been done on the demethylation by concentrated sulfuric acid of compounds containing certain trimethylsilyl organic structures[8]. Previously, we described[9] that this process was successfully applied to hexamethyldisilane without being accompanied by significant cleavage of its silicon–silicon bond to give, after treatment with ammonium chloride or fluoride, compounds of the formula $XMe_2SiSiMe_2X$, where X stands for Cl or F, in satisfactory yields. However, 1,1-dimethyl-1-silacyclobutane[10], -pentane[11] and -hexane[12] were reported to undergo the ring opening either exclusively or predominantly rather than the demethylation when treated with concentrated sulfuric acid. It was therefore of considerable interest to examine the behavior of the disilacycloalkanes toward the action of sulfuric acid.

The products obtained from reaction of compounds (VI), (VII) and (VIII) with 98% sulfuric acid at a temperature of 17–35° followed by treatment with ammonium hydrogen fluoride were analyzed by gas chromatography. It was found that the first two compounds (VI) and (VII) violently reacted with sulfuric acid at 17–20° and exclusively underwent cleavage of the silicon–silicon bond to give α,ω-bis(fluorodimethylsilyl)propane and -butane, respectively, in very high yields.



$$\underbrace{Me_2Si\text{———}SiMe_2}_{(CH_2)_n} \xrightarrow[2.\ NH_4F\cdot HF]{1.\ H_2SO_4} FMe_2Si(CH_2)_nSiMe_2F$$

(VI) $n = 3$; (VII) $n = 4$



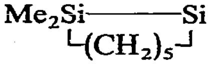
(a) (b)

Fig. 2. Gas chromatograms of the products from reaction of 1,1,2,2-tetramethyl-1,2-disilacycloheptane (VIII) with H_2SO_4 followed by treatment with $NH_4F\cdot HF$. (a) Reaction at 17–18°. (b) Reaction at 17–35°. (1), $F(n\text{-}C_5H_{11})MeSiSiMe_2F$ (XIII); (2), $(n\text{-}C_5H_{11})Me_2SiSiMe_2F$ (X); (3), $FMeSiSiMeF(CH_2)_5$ (XIV); (4), $FMe_2Si(CH_2)_5SiMe_2F$ (XV); (5), $Me_2SiSiMeF(CH_2)_5$ (XI); (6) $FMe_2SiSiMeF_2$ (XVII); (7), $FMe_2SiSiMe_2F$ (XVI).

On the other hand, reaction of the disilacycloheptane (VIII) with sulfuric acid was not so vigorous as that of (VI) and (VII), and gave several products. The reaction that was carried out at a lower temperature (17–18°) and discontinued when the reaction mixture had just become homogeneous gave, after treatment in the usual way with ammonium hydrogen fluoride, two compounds in the ratio of about 1 : 1 as the main products: 1-fluoro-2-n-pentyltetramethyldisilane (X) and 1-fluoro-1,2,2-trimethyl-1,2-disilacycloheptane (XI) (see Fig. 2a). These two new products were isolated in a reasonably pure state by preparative gas chromatography. An authentic sample of (X) was prepared in 60% yield by the reaction of n-pentylmagnesium chloride with 1,2-difluorotetramethyldisilane*. Further proof for structures of (X) and (XI) was afforded by their conversion to n-pentylpentamethyldisilane (XII) and compound (VIII), respectively, through the reaction with methylmagnesium bromide.

$(n\text{-}C_5H_{11})Me_2SiSiMe_2F$

(X)



$\underbrace{Me_2Si\text{———}SiMeF}_{(CH_2)_5}$

(XI)

$(n\text{-}C_5H_{11})Me_2SiSiMe_3$

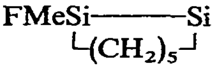
(XII)

In addition to the two principal products, the formation of insignificant quantities of 1,2-difluoro-1-n-pentyltrimethyldisilane (XIII), 1,2-difluoro-1,2-dimethyl-1,2-disilacycloheptane (XIV) and 1,5-bis(fluorodimethylsilyl)pentane (XV) were observed by gas chromatography.

No starting substance was detected.

$F(n\text{-}C_5H_{11})MeSiSiMe_2F$

(XIII)



$\underbrace{FMeSi\text{———}SiMeF}_{(CH_2)_5}$

(XIV)

$FMe_2Si(CH_2)_5SiMe_2F$

(XV)

An authentic sample of compound (XIII) was obtained from the higher temperature reaction that will be described below, while that of compound (XV) was prepared according to the reported procedure[13]. The identification of compound (XIV) was also based on the complete coincidence of its retention time in the gas chromatogram with that of one of the *cis,trans* isomers of 1,2-difluoro-1,2-dimethyl-1,2-disilacycloheptane that was prepared by fluorodephenylation of 1,2-diphenyl-1,2-dimethyl-1,2-disilacycloheptane with sulfuric acid and ammonium hydrogen fluoride in the cold**.

When the reaction was initially carried out by keeping the temperature at 17–18°, later by increasing it gradually up to 35° and holding it at this temperature until gas evolution ceased, the composition of the product mixture was substantially altered. The gas chromatogram reproduced in Fig. 2b indicates that at the cost of a sharp decrease in quantities of the two major products (X) and (XI) in the lower temperature reaction, yields of the two (XIII) and (XIV) of the three compounds that had been minor were increased and also a few other new lower-boiling compounds were formed. In contrast, an increase in yield of compound (XV) was insignificant. From this product mixture we could isolate, by preparative gas chromatography,

---

* Use of n-pentylmagnesium *bromide* instead of chloride gave rise to the formation of considerable amounts of 1-bromo-2-n-pentyltetramethyldisilane (see *Experimental*).

** The preparation and chemistry of 1,2-diphenyl-1,2-dimethyl-1,2-disilacycloalkanes and related compounds will be reported elsewhere.

both 1,2-difluoro-1-n-pentyltrimethyldisilane (XIII) and 1,2-difluorotetramethyldisilane (XVI) in the pure state, and 1,1,2-trifluorotrimethyldisilane (XVII) in a somewhat impure state.

$$\underset{\text{(XVI)}}{\mathrm{FMe_2SiSiMe_2F}} \qquad \underset{\text{(XVII)}}{\mathrm{F_2MeSiSiMe_2F}}$$

As can be seen from Table 4, which summarizes the yields of the silicon–silicon cleavage products from the action of sulfuric acid on compounds (VI)–(VIII), the silicon–silicon bond in the 1,2-disilacycloheptane (VIII) is as stable as that in hexamethyldisilane toward concentrated sulfuric acid. On the other hand, this bond, in the lower members of the homologous series, (VI) and (VII), is extraordinarily susceptible to cleavage by the action of sulfuric acid. Probably, in these smaller ring molecules, an internal-angular strain may be concentrated at the silicon–silicon bond, whereas in molecules with a suitably large ring size, for example, compound (VIII), the strain will be smaller and uniformly distributed all over the ring. In the latter case, therefore, cleavage by sulfuric acid will occur at the silicon–carbon bond according to a mechanism accepted for electrophilic substitutions at a saturated carbon[14].

TABLE 4

CLEAVAGE OF THE SILICON–SILICON BOND IN 1,1,2,2-TETRAMETHYL-1,2-DISILACYCLOALKANES BY SULFURIC ACID

No. of compound	*Reaction temp.* (°C)	*Cleavage*[a] (%)
(VI)	18–20	>90
(VII)	18–20	>90
(VIII)	17–18	< 7
	17–35	< 7

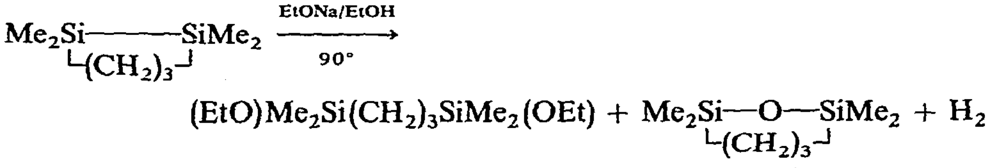
[a] Estimated by gas chromatographical analysis of the products formed on treatment with ammonium hydrogen fluoride.

Reaction with sodium ethoxide in ethanol

Hexaorganodisilanes have long been known to be resistant to alcoholic alkali[15-17]. We have reconfirmed this fact by observing that ethylpentamethyldisilane underwent no change at all after having been refluxed in 0.6 *N* ethanolic solution of sodium ethoxide for many hours.

As regards the behavior of 1,1-dimethyl-1-silacycloalkanes toward alcoholic alkali, the silacyclobutane has been reported by Sommer and Baum[10] to undergo ring opening with considerable heat evolution when treated with 1 *N* potassium hydroxide in ethanol at room temperature.

We, therefore, were much interested to learn how the 1,2-disilacycloalkanes would behave toward this type of reagents, and we found that compound (VI) underwent cleavage exclusively at the silicon–silicon bond with evolution of an almost quantitative volume of hydrogen when heated at 90° with 0.6 *N* sodium ethoxide in ethanol over an 80-h period, giving 1,3-bis(ethoxydimethylsilyl)propane (XVIII) and 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane (XIX), together with a small amount of higher-boiling substance.



$$\underbrace{Me_2Si\text{——}SiMe_2}_{(CH_2)_3} \xrightarrow[90°]{EtONa/EtOH} (EtO)Me_2Si(CH_2)_3SiMe_2(OEt) + \underbrace{Me_2Si\text{—}O\text{—}SiMe_2}_{(CH_2)_3} + H_2$$

(XVIII) (XIX)

In marked contrast, the disilacyclohexane (VII) did not react at all with sodium ethoxide in ethanol under the same conditions as above.

These results indicate that the disilacyclopentane (VI) is much more highly strained than the disilacyclohexane (VII).

Studies on further reactions of the disilacycloalkanes (VI)–(IX) are under way.

EXPERIMENTAL

All organosilicon compounds reported here were fractionally distilled through a 1.0 × 30 cm column packed with glass helices, and were gas chromatographically homogeneous, unless otherwise stated. Boiling points were uncorrected. NMR spectra were obtained in carbon tetrachloride solutions containing cyclohexane as an internal reference (Varian A-60, 60 Mc/sec).

1,2-dichlorotetramethyldisilane was most conveniently prepared by chlorodemethylation of hexamethyldisilane with acetyl chloride in the presence of anhydrous aluminum chloride, as reported recently[18].

1,3-Bis(chlorodimethylsilyl)propane, 1,4-bis(chlorodimethylsilyl)butane, 1,5-bis(chlorodimethylsilyl)pentane and 1,6-bis(chlorodimethylsilyl)hexane were prepared by heating the corresponding α,ω-bis(fluorodimethylsilyl)alkanes[13] with excess trimethylchlorosilane in the presence of anhydrous aluminum chloride[19] in a distillation apparatus fitted with the same column as described above, and by removing trimethylfluorosilane as it was formed. After no appreciable reaction occurred (about

TABLE 5

SOME PHYSICAL PROPERTIES, YIELDS AND ANALYTICAL DATA FOR $ClMe_2Si(CH_2)_nSiMe_2Cl$

n	*b.p. (°C/mm)*	n_D^{20}	d_4^{20}	*MR found (calcd.)*	*Yield (%)*	*C (%) found (calcd.)*	*H (%) found (calcd.)*	*Cl (%) found (calcd.)*
3[a]	103–104/21	1.4497	0.9878	62.35 (62.10)	89	36.80 (36.66)	8.09 (7.91)	30.47 (30.93)
4[b]	123–124/24	1.4509	0.9782	66.70 (66.75)	78	39.32 (39.49)	8.32 (8.28)	29.05 (29.14)
5	132–133/21	1.4537	0.9813	70.98 (71.09)	78	42.17 (42.00)	8.68 (8.62)	27.69 (27.55)
6[c]	113–116/3	1.4538	0.9613	76.42 (76.04)	75	44.36 (44.26)	9.06 (8.91)	25.80 (26.13)

[a] Reported[20]: b.p. 118–119°/41 mm, n_D^{20} 1.4474, d_4^{20} 0.9855. [b] Reported[21]: b.p. 112°/15 mm [c] Reported[22]: b.p. 110°/2 mm.

20 h), the residue was flash-distilled *in vacuo*, and the catalyst-free distillate was redistilled in the column. Table 5 lists some physical properties, yields and analytical data for the α,ω-bis(chlorodimethylsilyl)alkanes obtained.

1,1,2,2-*Tetramethyl*-1,2-*disilacyclopentane* (*VI*)

Method (*B*). An alloy was prepared from 6.0 g (0.26 g-atom) of sodium and 51 g (1.3 g-atom) of potassium in 150 ml of n-heptane. To the stirred mixture was added dropwise 150 g (0.65 mole) of 1,3-bis(chlorodimethylsilyl)propane diluted with 700 ml of benzene under gentle reflux over a 3-h period. The reaction mixture was then kept under reflux for an additional 30 h with stirring. At this point it was decomposed in the cold by adding successively 200 ml of an ethanol/acetic acid mixture (1 : 1), 400 ml of absolute ethanol, 200 ml of 50% aqueous ethanol and 800 ml of water. The organic layer was separated, combined with ether extracts from the aqueous phase, washed with sodium bicarbonate solution to neutral, dried over calcium chloride and distilled initially through a Widmer column for the purpose of removing most of the solvents but later in the packed column to give 74 g of a fraction boiling over the range of 149–154° and 38 g of residue. Since the distillate was found to contain a relatively large amount of a siloxane derivative, it was treated with sulfuric acid in the cold. The acid-insoluble upper layer was separated, washed to neutral, dried and finally redistilled to give 47 g (45% yield) of compound (VI), b.p. 154–155°, in the pure state.

1,1,2,2-*Tetramethyl*-1,2-*disilacyclohexane* (*VII*)

Method (*A*). In a 500-ml three-necked flask there was prepared in the usual way a Grignard solution from 58 g (0.27 mole) of 1,4-dibromobutane and 13 g (0.52 g-atom) of magnesium in 250 ml of tetrahydrofuran (THF). To the stirred solution was added dropwise and with cooling 40 g (0.21 mole) of 1,2-dichlorotetramethyldisilane diluted with 100 ml of THF over a 15 min period. The mixture was then refluxed for 6 h with continuous stirring. At this point, about 150 ml of THF was distilled off from the mixture, and the residue was decomposed with saturated solution of ammonium chloride. The resulting organic layer and ether extracts from the aqueous phase were combined, washed with water, dried over potassium carbonate, and distilled to give 21 g of a liquid boiling over the range of 70–110°/30 mm and 13 g of residue. Redistillation of the distillate through the column gave 19 g (52% yield) of compound (VII) in the pure state.

A second run was carried out by using about 2.5 times as large quantities of materials as before and in essentially the same way but by spending 2 h in addition of the chlorosilane. The yield of compound (VII) was increased to 66%.

Method (*B*). 1,4-Bis(chlorodimethylsilyl)butane (36.5 g, 0.15 mole) diluted with 200 ml of benzene was allowed to react with sodium (2.3 g, 0.10 g-atom)/potassium (11.7 g, 0.30 g-atom) alloy dispersed in 50 ml of n-heptane. The reaction mixture was worked up in the same manner as described in the preparation of compound (VI) to give 13 g (50% yield) of compound (VII) which was slightly contaminated by a siloxane compound.

1,1,2,2-*Tetramethyl*-1,2-*disilacycloheptane* (*VIII*)

Method (*A*). To a Grignard solution prepared from 157 g (0.68 mole) of 1,5-

dibromopentane and 32 g (1.32 g-atom) of magnesium in 500 ml of THF was added 102 g (0.545 mole) of 1,2-dichlorotetramethyldisilane diluted with 200 ml of THF over a 50-min period. After a work-up similar to that described in the preparation of compound (VII), there was obtained 42 g (41 % yield) of compound (VIII) in the pure state. A second run carried out by using identical quantities of materials but by spending 3 h in addition of the chlorosilane gave compound (VIII) in 65% yield.

Method (*B*). The procedures and quantities of materials used were the same as those for the preparation of compound (VII) except that 38.5 g (0.15 mole) of 1,5-bis(chlorodimethylsilyl)pentane was employed in place of 1,4-bis(chlorodimethylsilyl)butane. There was obtained 5 g (18% yield) of compound (VIII), along with 18 g of residue. In a second run, to an alloy prepared from 0.6 g (0.025 g-atom) of sodium and 5.3 g (0.14 g-atom) of potassium in 20 ml of n-heptane was added 16 g (0.062 mole) of 1,5-bis(chlorodimethylsilyl)pentane diluted with 650 ml of benzene under gentle reflux with vigorous stirring over an 18-h period. After the addition was completed, the mixture was refluxed with stirring for an additional 40 h. It was then worked up as above to give 3.2 g of impure compound (VIII). Its purity was estimated at about 70% by gas chromatography, hence the yield corresponded to 19%. Residue weighed 9.5 g. The results of these two runs thus indicate that method (B) is unfavorable for synthesis of compound (VIII), regardless the extent of dilution.

1,1,2,2-*Tetramethyl*-1,2-*disilacyclooctane* (*IX*)

Method (*A*). To a Grignard solution prepared from 24.5 g (0.1 mole) of 1,6-dibromohexane and 4.9 g (0.2 g-atom) of magnesium in 300 ml of THF was added 19 g (0.1 mole) of 1,2-dichlorotetramethyldisilane diluted with 500 ml of THF over an 8.5-h period. After 16-h reflux and then a work-up in the usual way, 1.3 g of a distillate boiling over the range of 70–130°/25 mm was obtained, along with 18 g of residue. Gas chromatographic analysis indicated that the distillate contained about 0.6 g (3% yield) of compound (IX).

Method (*B*). To an alloy prepared from 0.9 g (0.04 g-atom) of sodium and 8.2 g (0.21 g-atom) of potassium in 70 ml of n-heptane was added a solution of 27.1 g (0.10 mole) of 1,6-bis(chlorodimethylsilyl)hexane in 1.2 l of benzene under gentle reflux with stirring over a 30-h period. The reaction mixture was heated to reflux for an additional 30 h, and then worked up as described in the preparation of compound (VI). Distillation of the resulting organic layer gave 2.5 g of a fraction boiling over the range of 80–143°/10 mm and 18 g of residue. Five runs were carried out under the same conditions. All the distillates were combined and treated with 150 g of concentrated sulfuric acid at 4° for the purpose of removing a slight amount of any silicon–hydrogen compound (detected by IR). The acid-insoluble layer was washed, dried and distilled to give 5.0 g (5% yield) of compound (IX) in the pure state.

Reaction of (*VI*) *with* H_2SO_4

The techniques for reaction of 1,2-disilacycloalkanes (VI)–(VIII) with concentrated sulfuric acid followed by treatment with ammonium hydrogen fluoride were essentially the same as described previously[9].

A mixture of 30 g (0.19 mole) of compound (VI) and 240 g of concentrated sulfuric acid was stirred vigorously at 18–20°. Gas evolution took place rapidly and ceased when approximately equimolar amount of the gas was collected (*ca.* 30 min) and the reaction mixture became homogeneous. The mixture was then treated with 31 g (0.54 mole) of ammonium hydrogen fluoride in the cold. The resulting organic layer (34.5 g, 90% yield) was found to be gas-chromatographically homogeneous. Distillation gave 33.5 g of 1,3-bis(fluorodimethylsilyl)propane, b.p. 61°/26 mm, n_D^{20} 1.3931, d_4^{20} 0.9147, *MR* 51.25 (calcd. 51.28); reported[13] b.p. 156°, n_D^{20} 1.3926, d_4^{20} 0.9137. (Found: F, 19.46. $C_7H_{18}F_2Si_2$ calcd.: F, 19.35%.)

Reaction of (VII) with H_2SO_4

The reaction of 28 g (0.16 mole) of compound (VII) with 200 g of concentrated sulfuric acid at 18–20°, followed by treatment with 26 g (0.46 mole) of ammonium hydrogen fluoride gave 29 g (90% yield) of 1,4-bis(fluorodimethylsilyl)butane, b.p. 176°, n_D^{20} 1.3984, d_4^{20} 0.9095, *MR* 55.89 (calcd. 55.93); reported[21] b.p. 176°. (Found: F, 17.71. $C_6H_{20}F_2Si_2$ calcd.: F, 18.06%.) A negative result to the bromine test on the sample indicated complete disappearance of the silicon–silicon bond.

1-Fluoro-2-n-pentyltetramethyldisilane (X) and 1-bromo-2-n-pentyltetramethyldisilane

(*a*) *From n-pentylmagnesium chloride.* To a stirred mixture of 15.4 g (0.10 mole) of 1,2-difluorotetramethyldisilane diluted with 20 ml of ether was gradually added with cooling a solution of n-pentylmagnesium chloride, prepared from 14.8 g (0.14 mole) of n-pentyl chloride and 2.9 g (0.12 g-atom) of magnesium in 80 ml of ether. After being stirred at room temperature for 4 h and then heated to reflux for 5 h, the mixture was filtered. Fractional distillation of the filtrate gave 12.5 g (60% yield) of 1-fluoro-2-n-pentyltetramethyldisilane, b.p. 67°/15 mm, n_D^{20} 1.4278, d_4^{20} 0.8341, *MR* 63.66 (calcd. 63.67). (Found: F, 9.11. $C_9H_{23}FSi_2$ calcd.: F, 9.20%.)

(*b*) *From n-pentylmagnesium bromide.* A second run was carried out in essentially the same way and by using identical quantities of materials except for use of n-pentyl bromide (18.1 g, 0.12 mole) in place of the chloride. Fractionation gave 4.0 g (19% yield) of about 97% pure 1-fluoro-2-n-pentyltetramethyldisilane (X) and 12.5 g (47% yield) of 1-bromo-2-n-pentyltetramethyldisilane, b.p. 110°/24 mm, n_D^{20} 1.4725, d_4^{20} 1.0342, *MR* 72.46 (calcd. 72.30). (Found: Br, 29.92. $C_9H_{23}BrSi_2$ calcd.: Br, 29.89%.)

Reaction of (VIII) with H_2SO_4

(*a*) *At* 17–18°. A mixture of 18.6 g (0.10 mole) of compound (VIII) and 128 g of concentrated sulfuric acid was stirred at 17–18°. When gas evolution (*ca.* 2 l) ceased, the mixture became completely homogeneous. It was treated with 19 g (0.33 mole) of ammonium hydrogen fluoride in the cold. The resulting organic layer (19 g) was separated and distilled to give 0.8 g of a lower-boiling material and 16 g of a fraction boiling over the range of 70–88°/25 mm, which was found to consist of two major products and three minor ones by gas chromatography (see Fig. 2a). One of the major products was isolated by preparative gas chromatography (column, Silicone-DC 550; temperature, 132°; He velocity, 30 cc/min) and identified as 1-fluoro-2-n-pentyltetramethyldisilane (X), while another major product was also isolated by gas chromatography and identified as about 90% pure 1-fluoro-1,2,2-trimethyl-1,2-disilacycloheptane (XI), n_D^{20} 1.4627, d_4^{20} 0.9331, *MR* 56.18 (calcd. 56.97). (Found: C, 49.47; H, 10.31; F, 10.46. $C_6H_{19}FSi_2$ calcd.: C, 49.54; H, 10.06; F, 9.98%.) Samples of both compounds reacted with bromine violently in the cold, which affords evidence for the presence of the silicon–silicon bond.

Further evidence for the structure of (X) and (XI) was obtained as follows. To 8 g (Found: F, *ca.* 10%) of the fraction boiling at 70–88°/25 mm was added 0.09 mole of methylmagnesium bromide in 70 ml of ether. The mixture was then heated over a 32-h period. Hydrolysis followed by distillation gave 7 g of a liquid boiling over the range of 100–105°/36 mm, and consisting of two principal components in the ratio of *ca.* 1 : 1 and one component in an insignificant quantity. The first two products could be isolated in the reasonably pure state by gas chromatography. One was identified as n-pentylpentamethyldisilane (XII), n_D^{20} 1.4442, d_4^{20} 0.7705, *MR* 69.77. (calcd. 69.47) (Found: C, 59.23; H, 12.79. $C_{10}H_{26}Si_2$ calcd.: C, 59.31; H, 12.94%), and the other as compound (VIII) by gas chromatographic and IR spectroscopic analyses. The last minor product proved to be 1,5-bis(trimethylsilyl)pentane.

(*b*) *At* 17–35°. A mixture of the same quantities of materials was stirred vigorously at 17–18° as described in (*a*). Since when 2 l of gas was evolved the reaction appeared not to proceed further, the reaction temperature was increased gradually to 35° and maintained there. Gas evolution took place until about 3.3 l of gas was collected. At this point the reaction mixture was treated with 19 g (0.33 mole) of ammonium hydrogen fluoride and worked up in the usual way, giving 18.5 g of an organic layer. Its gas chromatogram is reproduced in Fig. 2b. Simple distillation gave two fractions: (1), 3.0 g, boiling over the range of 65–110°, and (2), 12.5 g, boiling mostly at 172–184°. Fraction (1) consisted mainly of two compounds in the ratio of about 1 : 1. Preparative gas chromatography gave 1,1,2-trifluorotrimethyldisilane (XVII) in an impure state (Found: F, 33.85. $C_3H_9F_3Si_2$ calcd.: F, 36.01%.) and 1,2-difluorotetramethyldisilane (XVI) in the pure state, its retention time in the gas chromatogram being superimposable with that of an authentic sample[9]. (Found: F, 24.38. $C_4H_{12}F_2Si_2$ calcd.: F, 24.62%.) Both compounds reacted with bromine energetically. Fraction (2) was composed of five compounds, from which we could isolate 1,2-difluoro-1-n-pentyltrimethyldisilane (XIII), b.p. 59–60°/18 mm, n_D^{20} 1.4113, d_4^{20} 0.9128, *MR* 57.27 (calcd. 58.07). (Found: F, 17.91. $C_8H_{20}F_2Si_2$ calcd.: F, 18.06%.) Other four products were identified by gas chromatography as shown in Fig. 2b. A colorless liquid (0.5 g) was collected during the reaction in a Dry Ice/acetone trap connected to the reaction flask via the reflux condenser. It was identified as n-pentane.

Reaction of (VI) with EtONa/EtOH

In a 100-ml Erlenmeyer flask fitted with a reflux condenser that was connected to an apparatus for collecting gas was placed a mixture of 4.8 g (0.03 mole) of compound (VI) and 10 ml of 0.6 *N* sodium ethoxide in ethanol. The mixture was maintained at a temperature of 90 ± 5° by means of a silicone-oil thermostat and agitated vigorously with a magnetically operated stirrer. After 80-h reaction, 0.63 l (*ca.* 90% of theory) of hydrogen was collected and only a trace of the starting substance (VI) was detected by gas chromatography. Distillation of the flask content under reduced pressure gave the following three fractions: (1) 0.5 g, b.p. 55–116°/33 mm, consisting of *ca.* 20% of 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane (XIX)[23] and *ca.* 80% of 1,3-bis(ethoxydimethylsilyl)propane (XVIII); (2) 2.8 g of compound (XVIII), b.p. 118°/33 mm, n_D^{20} 1.4231, d_4^{20} 0.8555, *MR* 73.98 (calcd. 73.91) (Found: C, 53.37; H, 11.49. $C_{11}H_{28}O_2Si_2$ calcd.: C, 53.16; H, 11.36%.) and (3) 0.7 g, boiling over the range of 80–120°/2 mm, n_D^{20} 1.4422, d_4^{20} 0.8832, and being gas chromatographically almost homogeneous.

Attempted reaction of (VII) with EtONa/EtOH

A similar reaction to that above with the exception of use of 5.2 g (0.03 mole) of compound (VII) in place of compound (VI) was attempted. However, no gas evolution occurred after 75 h, and all the starting substance was recovered unchanged.

Ethylpentamethyldisilane

To 0.08 mole of ethylmagnesium bromide in 100 ml of ether was added 11.7 g (0.07 mole) of chloropentamethyldisilane[9]. After a work-up in the usual way, 6.0 g (54% yield) of ethylpentamethyldisilane, b.p. 137–138°, n_D^{20} 1.4361, d_4^{20} 0.7512, *MR* 55.85 (calcd. 55.83) was obtained. (Found: C, 52.93; H, 12.64. $C_7H_{20}Si_2$ calcd.: C, 52.41; H, 12.57%.)

Attempted reaction of ethylpentamethyldisilane with EtONa/EtOH

A mixture of 3.2 g (0.02 mole) of $EtMe_2SiSiMe_3$ and 6.7 ml of 0.6 *N* EtONa in ethanol was stirred under the same conditions as above. No gas evolution was observed at all, and gas chromatography revealed that no compounds were present other than the starting substance.

ACKNOWLEDGEMENT

This research was supported by Tokyo-Shibaura Electric Co., Ltd. and Nitto Electric Industrial Co., Ltd., to which the authors' thanks are due. The authors are also grateful to Nitto Chemical Industrial Co., Ltd. for the carbon and hydrogen analysis.

SUMMARY

Four 1,2-disilacycloalkanes of the formula $\overline{Me_2SiSiMe_2{-}(CH_2)_n}$, where *n* equals 3, 4, 5 and 6, have been prepared by two methods: one involves reaction of $ClMe_2SiSiMe_2Cl$ with $BrMg(CH_2)_n MgBr$, the other comprises sodium/potassium condensation of $ClMe_2Si(CH_2)_nSiMe_2Cl$. It has been found that both the disilacyclopentane and -hexane exclusively undergo cleavage of the silicon–silicon bond when treated with concentrated sulfuric acid, whereas the disilacycloheptane gives several products in which the silicon–silicon bond has not been cleaved. The disilacyclopentane undergoes cleavage of the silicon–silicon bond when heated with 0.6 *N* sodium ethoxide in ethanol at 90°, while the disilacyclohexane is quite stable under the same conditions.

REFERENCES

1 C. Eaborn, *Organosilicon Compounds*, Butterworths, London, 1960, Chapter 13; G. Fritz, J. Grobe and D. Kummer, in H. J. Emeleus and A. G. Sharpe, *Advances in Inorganic Chemistry and Radiochemistry* Vol. 7, Academic Press, New York, 1965, p. 349.
2 H. A. Clark, *U.S. Patent* 2,563,004 (1949); *Chem. Abstr.*, 45 (1951) 10676.
3 Chi-Tao Wang, Hsiu-Chung Chou and Man-Shui Hung, *Hua Hsueh Hsueh Pao*, 30 (1964) 91; *Chem. Abstr.*, 61 (1964) 1888.
4 H. Gilman and S. Inoue, *Chem. Ind. (London)*, (1964) 74.

5 O. M. Nefedov and M. N. Manakov, *Angew. Chem.*, 76 (1964) 270.
6 H. Gilman and W. H. Atwell, unpublished material quoted in H. Gilman, W. H. Atwell and F. K. Cartledge, in F. G. A. Stone and R. West, *Advances in Organometallic Chemistry*, Vol. 4, Academic Press, New York, 1966, p. 18.
7 E. L. Eliel, *Stereochemistry of Carbon Compounds*, McGraw-Hill, New York, 1962, pp. 198–202.
8 L. H. Sommer, N. S. Marans, G. M. Goldberg, J. Rockett and R. P. Pioch, *J. Am. Chem. Soc.*, 73 (1951) 882, and subsequent papers.
9 M. Kumada, M. Yamaguchi, Y. Yamamoto, J. Nakajima and K. Shiina, *J. Org. Chem.*, 21 (1956) 1264.
10 L. H. Sommer and G. A. Baum, *J. Am. Chem. Soc.*, 76 (1954) 5002.
11 V. M. Vdovin, N. S. Nametkin, K. S. Pushchevaya and A. V. Topchiev, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1963) 274; *Chem. Abstr.*, 58 (1963) 13980.
12 A. F. Plate, N. A. Berikova and Yu. P. Egorov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1956) 1085; *Chem. Abstr.*, 51 (1957) 5085.
13 M. Kumada, K. Naka and Y. Yamamoto, *Bull. Chem. Soc. Japan*, 37 (1964) 871.
14 L. M. Shorr, H. Freiser and J. L. Speier, *J. Am. Chem. Soc.*, 77 (1955) 547; G. Kobrich, *Angew. Chem.*, 74 (1962) 453.
15 A. Martin, *Ber.*, 46 (1913) 3294.
16 F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, 119 (1921) 849.
17 A. Taketa, M. Kumada and K. Tarama, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 60 (1957) 201; *Chem. Abstr.*, 53 (1959) 6065.
18 H. Sakurai, K. Tominaga, T. Watanabe and M. Kumada, *Tetrahedron Letters*, (1966) 5493.
19 B. A. Bluestein, *J. Am. Chem. Soc.*, 70 (1948) 3068.
20 K. A. Andrianov, N. V. Delasari, L. M. Volkova and N. A. Chumaevskii, *Dokl. Akad. Nauk SSSR*, 160 (1965) 1307; *Chem. Abstr.*, 62 (1965) 14718.
21 L. H. Sommer and G. R. Ansul, *J. Am. Chem. Soc.*, 77 (1955) 2482.
22 P. G. Campbell, Thesis, Pennsylvania State Univ., *Chem. Abstr.*, 52 (1958) 4532.
23 M. Kumada and A. Habuchi, *J. Inst. Polytech. Osaka City Univ., Ser. C*, 3 (1952) 65; *Chem. Abstr.*, 48 (1954) 9907.