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SOLVOLYSIS OF 1,2-DIMETHYL-1-SILACYCLOBUTANE

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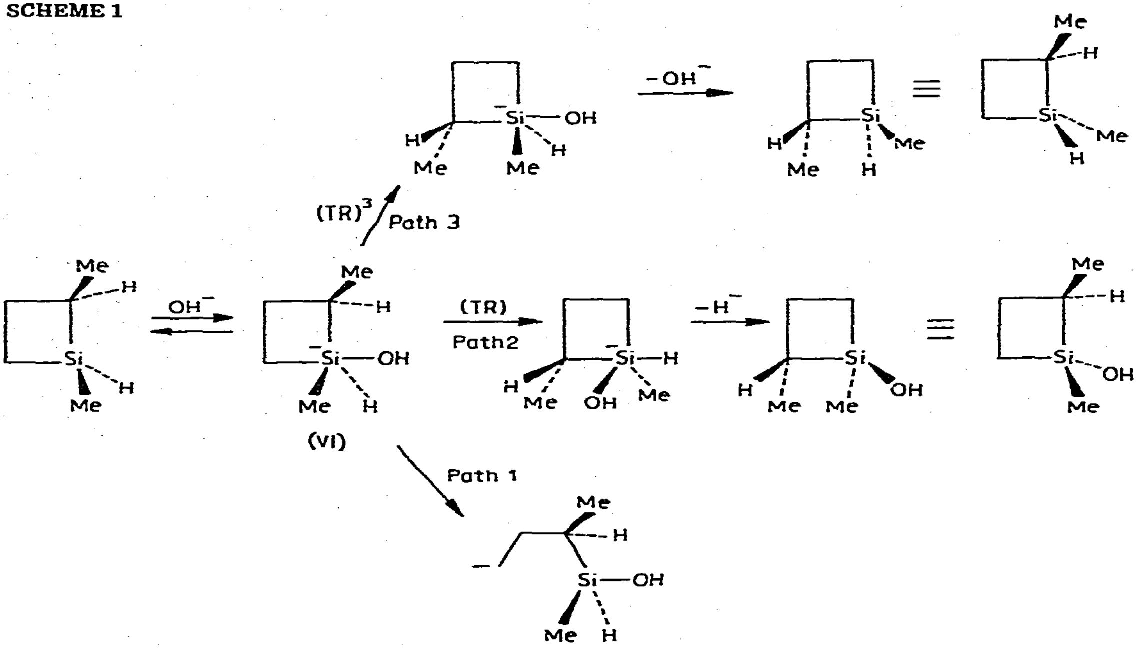
Summary

The geometric isomers of 1,2-dimethyl-1-silacyclobutane (I) have been subjected to solvolysis in alkaline aqueous methanol. Ring-opened products have been isolated, and evidence has been accumulated indicating that ring opening and hydride displacement occur at competitive rates. No epimerization of I occurs during the course of the reaction. Kinetic and stereochemical results are discussed in terms of the mechanism of hydride displacement from the silacyclobutane ring and from acyclic silicon hydrides. A mechanism involving rate-determining formation of a pentacovalent intermediate is preferred for the former. Mass spectral data for a number of the products of solvolysis are discussed.

Some significant mechanistic questions remain unanswered about nucleophilic displacement reactions at silicon. One of the foremost among these is the relationship between stereochemistry of the reactions and their mechanisms. Systems investigated until recently are basically very similar with respect to silane structure and probably have not revealed some perhaps common stereochemical possibilities. Recent investigations with strained ring systems have already shown one such new possibility [1,2]. Furthermore, the question remains whether extracoordinate intermediates are at all common in displacement reactions at silicon [3,4]. Nucleophilic displacements at tetracoordinate phosphorus frequently do proceed through pentacoordinate intermediates which have sufficient lifetime to undergo pseudorotations, and stereochemical results are predictable in terms of the relative stabilities of stereoisomeric trigonal bipyramids [5]. A question of fundamental importance is whether the rationalizations of phosphorus stereochemistry can be generalized to include silicon.

A promising system in which to gain some new information is the substituted silacyclobutane ring in which geometric isomerism is possible. We [2] and others [6] have reported the preparation and some reactions of 1,2- and 1,3-dimethylsilacyclobutanes. We wish to report now the base-catalyzed hydrolysis of *Z*- and *E*-1,2-dimethyl-1-silacyclobutane (Ia and Ib, respectively). We chose this system in part because the combination of poor leaving group and strained ring should favor formation of a trigonal bipyramidal intermediate if it is ever going to be important in displacement reactions with organosilanes. Further, a number of details concerning the reaction are well established from the work of others [7,8], including previous investigations of 1-methylsilacyclobutane [9]. The possibility for geometric isomerism in I, however, allows studies to be made which were not previously possible. If in the course of hydrolysis of Ia, a pentacoordinate intermediate is formed following the same groundrules which seem to apply for phosphorus compounds [5] (axial entry of hydroxide to form a trigonal bipyramid with one ring bond axial), then several eventual outcomes are possible, including those outlined in Scheme 1. It seemed of paramount interest to us to determine whether path 3 of Scheme 1 were operating, since we believe that *cis—trans* isomerization would require the intervention of an extracoordinate species with sufficient lifetime to undergo pseudorotations. It is possible that Ia could be converted to Ib by ring opening to a carbanion followed by reclosure, but we consider that a highly unlikely process in a protic solvent mixture. A closely related case in which isomerization of a four-membered phosphorus ring occurs with base catalysis is also proposed to result from formation of a trigonal bipyramid and pseudorotation [10].

SCHEME 1

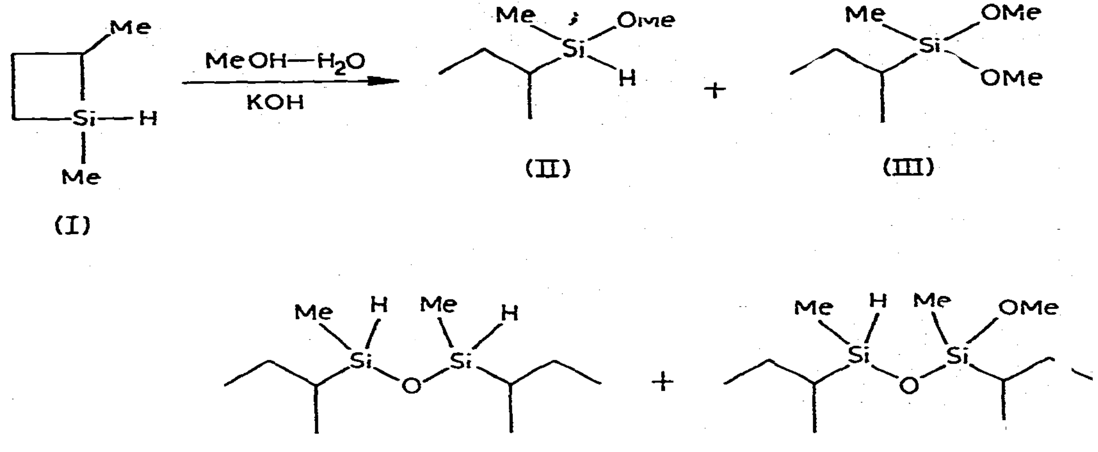


(TR) : turnstile pseudorotation process

(TR)^3 : triple turnstile rotation

The reaction of Ia with 95% (by volume) methanol/water catalyzed by hydroxide ion is complex. At least nine products are formed, but when relatively short reaction times are used (ca. two half lives) four of the products account for greater than 75% of the product mixture. Three of the products shown in Scheme 2, s-butylmethylmethoxysilane (II), s-butylmethyldimethoxysilane (III)

SCHEME 2



(I) (II) (III) (IV) (V)

and 1,3-di(s-butyl)-1,3-dimethyldisiloxane (IV) were identified by comparison of retention times and mass spectra with those of authentic samples prepared as described in the experimental part. The fourth product, 1,3-di(s-butyl)-1,3-dimethyl-1-methoxydisiloxane (V), was identified after isolation from the product mixture by thick layer chromatography. All of the products isolated are ring-opened ones, and perhaps surprisingly, the ring opens in only one direction to give s-butylsilanes and not n-butylsilanes. An authentic sample of 1,3-dibutyl-1,3-dimethyldisiloxane (VII), was prepared and shown not to be the same as any of the hydrolysis products by comparison of GLC retention times and mass spectra.

No products containing the silacyclobutane ring intact have been isolated, but using an argument previously formulated [9], we infer from relative rates of hydrogen evolution that either or both 1-hydroxy- and 1-methoxy-1,2-dimethyl-1-silacyclobutane must have been present and undergone subsequent rapid ring opening. Rates of hydrogen evolution for Ia and Ib and for the hydride-containing products II and IV, are given in Table 1. When Ia and Ib are hydrolyzed there is an initial period of rapid hydrogen evolution up to approximately 30% reaction, followed by continued but much slower evolution. A reasonable

TABLE 1

RATES OF HYDROGEN EVOLUTION AT 0°

Compound	[KOH], (M)	k' [a] (min^{-1})	k ($M^{-1}\ \text{min}^{-1}$)	k_{rel} [b]	H_2 evolved (% of theory)
Ia	1.5×10^{-4}	0.81	5.4×10^{3}	16000	42
Ib	1.5×10^{-4}	0.33	2.2×10^{3}	7000	23
II	0.201	0.31	1.5	4.6	100
IV	0.815	0.27	0.33	1	100

[a] Pseudo-first order rate constant. [b] Experimental difficulties precluded measurements at identical [KOH]. Salt effects will thus alter the relative rates [7b,d] in the direction of increasing the spread in rates among I, II and IV.

explanation for this phenomenon is that during the initial period hydride displacement from I and ring opening of I are competing, and thereafter slow hydride displacement from the ring-opened products is occurring. Indeed, both II and IV evolve hydrogen at a rate that is slower by a factor of at least 10^3 compared to the initial rate from I. In addition to the kinetic evidence, GLC-mass spectral analysis of the product mixture afforded reasonably good evidence that one of the solvolysis products is 1-(s-butylmethylsiloxy)-1,2-dimethylsilacyclobutane (VIII). This product is present at early stages of the reaction but then disappears as additional V is formed. The mass spectrum of this product is discussed in a later section.

It has been more difficult for us to obtain pure samples of the *trans*-silacyclobutane isomer, Ib, so that kinetic runs have had to be made on small amounts of sample with consequent greater uncertainty. However, without question the *cis* isomer, Ia, gives hydride displacement at a rate about twice that of the *trans* isomer, Ib. It seems most reasonable to us to attribute the rate differential to a steric acceleration. If formation of the intermediate (VI), (Scheme 1) from Ia is the rate determining step, then it is easy to imagine some relief of steric interactions between the *cis* methyl groups which would accelerate the formation of VI relative to the corresponding intermediate from Ib. Of course, arguments of a similar nature could be advanced based on the assumption of a direct displacement mechanism (S_Ni—Si [3b] or S_N2—Si retention [11]).

Reaction of the *cis* isomer, Ia, at 0° for approximately two half lives (based on the initial rapid rate of hydrogen evolution) was followed by quenching with excess HCl. No isomerization of Ia to Ib could be detected by GLC. Control experiments indicated that the method used could have detected as little as 0.5% isomerization. That isomerization fails to occur under these conditions does not, of course, rule out the possibility of an extracoordinate intermediate. A pentacoordinate species could be formed in the rate-determining step, or it could be formed rapidly and reversibly but with the condition that path 3 in Scheme 1 is considerably slower than paths 1 and 2. The latter would not be surprising since $(TR)^3$ processes are reputed to have higher activation energy barriers than a single TR process [12]. Eaborn has recently concluded [8] for acyclic systems that the mechanism of solvolysis is either direct displacement or reversible formation of a pentacoordinate species followed by rate-determining loss of hydride. If acyclic systems react through rapid formation of a pentacoordinate intermediate, then one could reasonably argue that the silacyclobutane ring system ought to react the same way*. On the other hand, given the results for phosphorus compounds [13], it is quite possible to imagine that strained silicon systems react through an extracoordinate intermediate while unstrained systems do not. At present we lean toward the last interpretation on the basis of Sommer's isotope effect data [14], and the *cis/trans* rate ratio and lack of isomerization reported here.

Acting under the assumption that protic solvent accelerates the loss of hydride from an extracoordinate intermediate, we have sought to slow this down relative to formation of the intermediate by exploring the hydrolysis reaction

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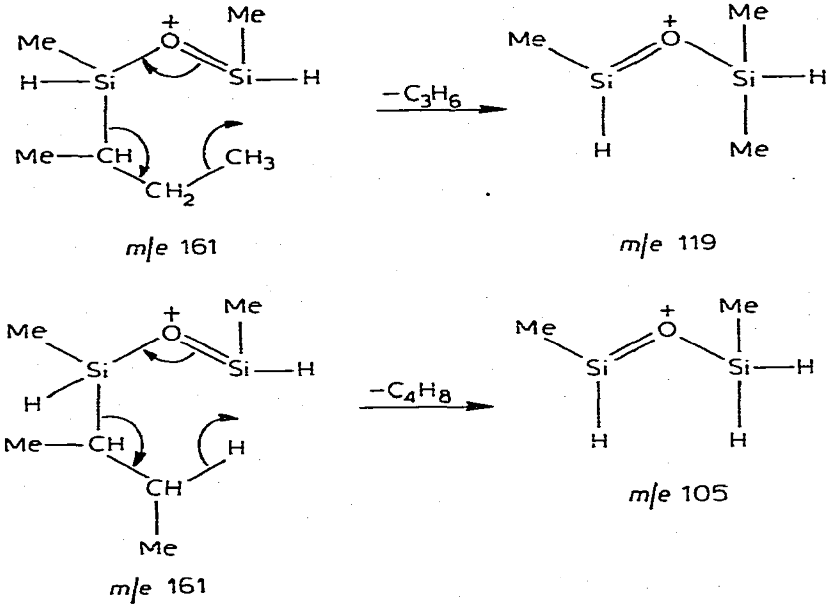
* For a recent summary of arguments concerning the effects of ring strain in phosphorus heterocycles on reactivity in nucleophilic displacement, see [13].

in other media. We have been surprised to find that some isomerization of hydride occurs in dimethyl formamide alone at a slow rate. Unfortunately, the isomerization is accompanied by a complex reaction resulting in loss of the hydride. We are in the process of investigating this isomerization, which appears as if it could be related to previously reported cases of solvent-induced racemization of silyl halides [15] and ozone-catalyzed racemization of a silicon hydride [16].

Mass spectral properties

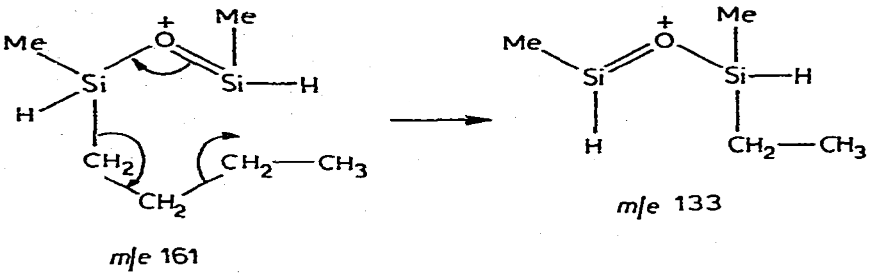
Significant differences in the mass spectra of 1,3-di-s-butyl-1,3-dimethyldisiloxane (IV) and 1,3-di-n-butyl-1,3-dimethyldisiloxane (VII) were observed. Both showed an intense peak at *m/e* 161 formed by loss of C_4H_9 from the parent. Loss of C_3H_6 from *m/e* 161 leading to a fragment of *m/e* 119 is observed only for IV. A metastable ion at *m/e* 88.0 provides evidence in support of this pathway. However, both IV and VII show loss of C_4H_8 from *m/e* 161 leading to *m/e* 105, the base peak for both compounds. This is supported by a metastable ion at *m/e* 68.5 in the spectrum of IV. An acceptable six-membered ring transition state can be written for both rearrangements (Scheme 3). This sort of transition state is supported by a more intense *m/e* 133 in VII than in IV, presumably due to loss of C_2H_4 from *m/e* 161 by a similar transition state (Scheme 4) although no metastable ion was observed to support this. We know of no report of direct analogs of these rearrangements in organosilanes, although numerous reports of silyl-McLafferty-type rearrangements have appeared [17a] and it has been noted [17b] that rearrangement of atoms or groups to the silicon atoms of siliconium ions is a generally favorable process.

SCHEME 3



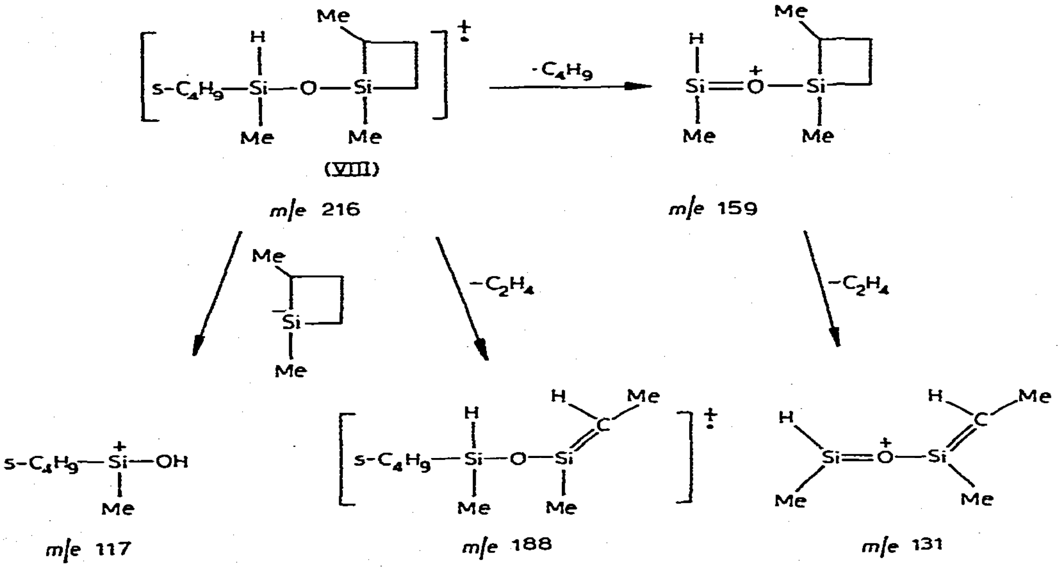
The fragmentation pattern of the transient product VIII, shown in Scheme 5, provides evidence for its suggested structure. The parent ion, *m/e* 216, shows loss of CH_3 leading to *m/e* 201 and loss of C_4H_9 leading to *m/e* 159, the base

SCHEME 4



peak. The presence of two silicon atoms in m/e 159 is confirmed by the relative intensities of m/e 160 and 161. The presence of the silacyclobutane ring is indicated both by loss of C_2H_4 from the parent ion leading to m/e 188 and from m/e 159 to give m/e 131. The latter is supported by a metastable peak at m/e 108. Loss of C_2H_4 from silacyclobutanes has previously been observed [18], and was the predominant fragmentation pathway for I although loss of C_3H_6 was also observed for I to a much lesser extent [19]. No cleavage of a silicon—oxygen bond was observed in the disiloxanes IV or VII. However, VIII showed loss of $C_5H_{11}Si$ leading to m/e 117.

SCHEME 5



Experimental

General

All Grignard reactions were run in three-neck flasks equipped with a magnetic stirrer, reflux condenser, and addition funnel. All distillations were through a 7 cm Vigreux column. Pentane and quinoline were dried over calcium hydride

TABLE 2

NMR SPECTRA

Compound	Si—Me	Si—H	δ(Si—OMe)	δ(s-C_4H_9—Si)
II[a]	0.02d	4.35	3.37s	0.43—1.80
III[a]	—0.08s		3.41s	0.62—1.90
IV[a]	0.12d	4.50		0.78—1.95
V[b]	0.00s; 0.14d	4.55	3.42s	0.47—1.66
VI[a]	0.39d	4.62		0.62—1.88

[a] Values are in ppm measured at 60 MHz, external TMS as reference. [b] Values are in ppm measured at 100 MHz, internal benzene as reference.

and distilled. Methanol was dried over 3 Å molecular sieves. Where mixed solvents were used, the percent composition quoted is volume percent. NMR spectra were obtained routinely on a Varian A60A or Varian HA100, and IR spectra were recorded using a Perkin—Elmer 137. A Perkin—Elmer Model 900 was used for routine GLC. GLC-mass spectra were obtained on a Perkin—Elmer 990 GLC interfaced through a Biemann—Watson separator to a Hitachi—Perkin—Elmer RMS-4 Mass Spectrometer. Mass spectra were taken at 70 eV and are reported as *m/e* (relative abundance).

The NMR data of compounds II—VI are reported in Table 2.

The preparation of *Z*- and *E*-1,2-dimethyl-1-silacyclobutane [2,6] and methyltrimethoxysilane [20] have previously been reported. 1,3-Dibutyl-1,3-dimethyldisiloxane (VII), was prepared by the method of Liu [21], and obtained in 18% yield, b.p. 77-78° (9-10 mm) (lit. [21]: b.p. 99-100° (22 mm)). (Found: C, 54.84; H, 11.95; Si, 25.66. $C_{10}H_{26}OSi_2$ calcd.: C, 54.97; H, 11.99; Si, 25.71%.) Mass spectrum: *m/e* 218(3), 216(11), 161(70), 159(14), 147(17), 133(2), 119(3), 105(100), 103(9), 91(15), and metastable at 68.5.

s-Butylmethylchlorosilane

To a solution of 26.0 g (0.226 mol) of methyldichlorosilane in 50 ml of dry ether under a nitrogen atmosphere was added with stirring a solution of s-butylmagnesium bromide obtained from 27.4 g (0.200 mol) of 2-bromobutane and 7.0 g (0.29 mol) of magnesium powder in 320 ml of dry ether. After stirring 20 h under reflux the mixture was filtered under nitrogen, the residue washed once with dry ether and the filtrate distilled yielding a fraction (12.7 g, 47%) b.p. 119-125°. The material was used in subsequent reactions without further purification.

s-Butylmethylmethoxysilane (II)

To a solution of 2.00 ml (49.5 mmol) of methanol and 6.00 ml (50.9 mmol) of quinoline in 40 ml of pentane held in an ice bath was added under nitrogen with stirring a solution of 6.21 g (45.5 mmol) of s-butylmethylchlorosilane in 20 ml of pentane. After addition was complete the ice bath was removed and stirring continued 2 h. The quinoline hydrochloride was removed by filtration. Distillation of the filtrate yielded a fraction (4.0 g, 67%) b.p. 64-65° (144-145 mm). (Found: C, 54.70; H, 12.30. $C_6H_{16}OSi$ calcd.: C, 54.48; H, 12.10%.) IR (film): 2900s, 2080s, 1440m, 1360w, 1230m, 1180w, 1080s, 860s, and 745m cm^{-1}. Mass spectrum: *m/e* 132(1), 131(9), 77(10), 75(100), 74(14), 61(14), and 45(13).

s-Butylmethyldimethoxysilane (III)

To a solution of 20.0 g (0.147 mol) of methyltrimethoxysilane in 50 ml of dry ether was added under nitrogen with stirring a solution of s-butylmagnesium bromide obtained from 20.1 g (0.147 mol) of 2-bromobutane and 5.0 g (0.21 mol) of magnesium turnings in 300 ml dry ether. After refluxing and stirring 2 h the mixture was filtered under nitrogen. The filtrate was distilled yielding a fraction, b.p. 54-58° (28 mm), which was redistilled to yield a fraction (2.42 g, 10%) b.p.75-76° (65-66 mm) (lit. [22]: b.p. 49-50°/24 mm). (Found: C, 51.62; H, 11.14; Si, 17.42. $C_7H_{18}O_2Si$ calcd.: C, 51.80; H, 11.18; Si, 17.31%.) IR (film): 1460s, 1375m, 1250s, 1210m, 1180s, 1090s, 1000m, and 970w cm^{-1}. Mass spectrum: *m/e* 162(1), 105(100), 75(27), 59(7), 45(5), and metastables at 53.6 and 68.0.

1,3-Di(s-butyl)-1,3-dimethyldisiloxane (IV)

To 25 ml of water containing 3.5 g of sodium bicarbonate was added 6.4 g (47 mmol) of s-butylmethylchlorosilane in 50 ml of ether. After shaking 10 min the aqueous layer was removed, the ether layer washed once with dilute (ca. 0.02 *M*) hydrochloric acid, once with water, and dried over magnesium sulfate. Distillation gave a fraction, b.p.85-88° (27-28 mm), which was redistilled to yield pure product (1.68 g, 33%), b.p. 87-89° (30-31 mm) (Found: C, 54.80; H, 11.96; Si, 25.96. $C_{10}H_{26}OSi_2$ calcd.: C, 54.97; H, 11.99; Si, 25.71%.) IR (film): 2110s, 1460m, 1375w, 1250s, 1210w, 1065s, 885s, and 850s cm^{-1}. Mass spectrum: *m/e* 218(2), 161(49), 147(3), 133(6), 119(63), 105(100), 103(11), 91(6), and metastables at 88.0 and 68.5.

1,3-Di(s-butyl)-1,3-dimethyl-1-methoxydisiloxane (V)

To 15 ml of a 1.8×10^{-2} *M* solution of potassium hydroxide in 95% aqueous methanol held in an ice bath was added 0.78 g of 1,2-dimethyl-1-silacyclobutane. When the evolution of hydrogen had ceased 20 ml of ether was added and all solvent removed under reduced pressure. The remaining oil was dissolved in ether and dried over magnesium sulfate. Removal of the solvent gave an oil which was purified by elution with hexane on a silica gel thick layer chromatographic plate. The component with R_f 0.50 was extracted with ether, the solvent removed and the remaining liquid distilled by molecular distillation, 115° (18-19 mm), to yield ca. 0.15 g of product. (Found: C, 53.36; H, 11.38; Si, 22.57. $C_{11}H_{28}O_2Si$ calcd.: C, 53.16; H, 11.36; Si, 22.60%.) IR (film): 2100s, 1450s, 1400w, 1360m, 1330w, 1250s, and 1060s cm^{-1}. Mass spectrum: *m/e* 248 (<1), 233(2), 191(89), 135(100), 119(19), 105(22), 59(13), and metastables at 95.5 and 82.0.

Attempted isomerization of Z-1,2-dimethyl-1-silacyclobutane (Ia)

To 1.0 ml of 95% aqueous methanol was added 0.10 ml of 99% isomerically pure Ia and 5 μl of toluene as an internal standard. To this stirred solution held in an ice bath was added 1.0 ml of 3.2×10^{-4} *M* potassium hydroxide in

95% aqueous methanol. After 60 s the reaction was stopped by acidifying with 0.25 ml of 3.2×10^{-3} *M* hydrochloric acid in 95% aqueous methanol. GLC analysis (16′ × $\frac{1}{8}$″ column of 15% Apiezon L on 60-80 mesh chromosorb W; 90° to 125° at 10°/min, initial time of 3 min) showed that 75% of Ia had reacted (2 half-lives) and that ca. 35% of the original very small amount of Ib had also reacted. Solutions of a 60/40 mixture of Ia and Ib, respectively, in 95% aqueous methanol and in acidified 95% aqueous methanol showed no reaction of either isomer over a 14 h period. GLC analysis (on the column described above; 90° to 180° at 20°/min) showed nine products were formed in the reaction. Their retention times (min) are: 3.5, 4.8, 8.4, 9.3, 9.6, 11.1, 12.4, 13.0, and 15.4. By GLC mass spectral analysis and comparison of reaction times the products with retention times of 3.5, 4.8, 8.4, and 11.1 min were identified as II, III, IV, and V respectively. The product with retention time 9.3 min has tentatively been identified as VIII. Mass spectrum: *m/e* 216 (<1), 201(1), 188(3), 161(10), 160(18), 159(100), 145(5), 133(9), 132(9), 131(20), 119(19), 117(36), 105(12), 103(15), and a metastable at 108.

Kinetic measurements

The apparatus used for kinetics measurements was an 8 ml vial equipped with magnetic stirrer and septum and connected to a gas buret by use of thick wall tubing and 15 gauge needle. The vial was held in an ice bath at 0° and the hydrogen evolved was collected over water at 25°. In a typical determination 1.90 ml of a solution of potassium hydroxide in 95% aqueous methanol and 0.100 ml of silane were used, the neat silane being added via syringe. At least 20 points were determined per run. The original concentration of silane was determined from the total quantity of hydrogen evolved after about 10 half-lives. All reactions showed good pseudo-first order kinetics. Values in Table 1 are averages of two runs.

Acknowledgement

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