teristics of the sulfur-containing species present in solutions of $\mathrm{K_2S}$ and $\mathrm{H_2S}$. The data suggest that the species in $\mathrm{H_2S}$ solutions which absorbs at 270 $\mathrm{m}\mu$ is probably a sulfide ion hydrogen bonded to an ammonium ion, *i.e.*, $\mathrm{S^{2-}\cdots HNH_3^+}$. However, this species probably would not be distinguishable from a hydrosulfide ion hydrogen bonded to ammonia, $\mathrm{SH^-\cdots NH_3}$, and the species at equilibrium in solutions of hydrogen sulfide are related through equilibrium 4 which is related to eq 2.

$$\mathrm{H_2S + 2NH_3 \rightleftharpoons [SHNH_3]^- + NH_4^+} \tag{4}$$

In contrast, the sulfur-containing species in solutions of $\mathrm{K_2S}$ can only be hydrogen bonded to solvent molecules, since the sulfide ion is apparently not a sufficiently strong base to remove successfully a proton from the solvent (*cf.* the absence of an $\mathrm{NH_2^-}$ band in these solutions).

The negative deviation of solutions containing $\mathrm{H_2S}$ from Beer's law would be expected if the species in eq 4 are at equilibrium. Under these conditions, an increase in the formal concentration of hydrogen sulfide would cause the point of equilibrium in eq 4 to shift toward the products with a corresponding decrease in the fraction of sulfur in the form of $\mathrm{[SHNH_3]^-}$. Using the extrapolated value of the molar extinction coefficient for the sulfide ion at the band maximum (ϵ 9.14 $\times 10^3$) to estimate the fraction of sulfur in the $\mathrm{[SHNH_3]^-}$ form and assuming that concentrations can be substituted for activities in dilute solution, the equilibrium constant for eq 4 at $-77°$, expressed in the standard manner, can be estimated from the data in Figure 3 as $(1.04 \pm 0.19) \times 10^{-2}$. In aqueous solutions the first and second ionization constants for $\mathrm{H_2S}$ are 9.5×10^{-8} (25°) and 1.0×10^{-14} (20°), respectively,[1c] and an increase in the value of K_1 in liquid ammonia would be expected on the basis of an increase in the basicity of the solvent.

The apparent anomaly of solvated electrons being less reactive than amide ions with respect to the "second hydrogen ion" in $\mathrm{H_2S}$ is probably related to the fact that the solvated amide ion is more similar structurally to the solvent than is the solvated electron and therefore does not require a reorganization of its solvent sphere before reacting with the species $\mathrm{S^{2-}\cdots HNH_3^+}$.

Acknowledgment.—We wish to thank the Robert A. Welch Foundation and the National Science Foundation for financial support.

CONTRIBUTION FROM THE RESEARCH TRIANGLE INSTITUTE, CHEMISTRY AND LIFE SCIENCES LABORATORY,
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27709

The Preparation, Isomerization, and Oxidation of Silylhydrazines[1]

BY COLIN G. PITT AND KENNETH R. SKILLERN

Received November 22, 1966

The reaction of 1,2-bis(dimethylchlorosilyl)ethane with hydrazine affords both 3,3,6,6-tetramethyl-1,2-diaza-3,6-disilacyclohexane (III) and 1-amino-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane (IV). It has been shown that III and IV are in equilibrium at room temperature in the absence of added catalysts. The thermal equilibration of 1,1- and 1,2-bis(trimethylsilyl)hydrazine has similarly been demonstrated. The oxidations of III and IV, and 1,1- and 1,2-bis(trimethylsilyl)hydrazine, with mercuric oxide and with ethyl azodicarboxylate have been investigated. The various oxidation products have been identified and their formation rationalized by invoking oxidation at both silicon and hydrogen.

Established methods for preparing small-ring compounds containing both carbon and silicon have utilized metal reduction of an appropriate α,ω-dihalide to effect ring closure.[2] Because of the limitations of this approach,[3] a study of alternative methods of ring closure appeared to be desirable. A particularly useful method for obtaining highly strained cyclic hydrocarbons[4,5] has involved the oxidation of cyclic hydrazines followed by mild pyrolytic elimination of the resulting azo group. We have been interested in whether this scheme might be adapted to the preparation of cyclic carbosilanes. The reported[6] oxidation of bis(trimethylsilyl)hydrazine to hexamethyldisilane would indicate that the oxidative elimination of the hydrazo group is applicable to the preparation of acyclic silicon derivatives. Unfortunately, despite the considerable interest in silicon–hydrazine chemistry,[7] there are no suitable examples of monocyclic silylhydrazines which contain the NH–NH function.[8] Thus it became necessary for us to investigate the synthesis of such compounds before proceeding to study their oxidation.

---

(1) (a) This work was supported in part by the Office of Naval Research; (b) a preliminary account of some of this work has been reported: C. G. Pitt and K. R. Skillern, *Inorg. Nucl. Chem. Letters*, **2**, 237 (1966).

(2) C. Eaborn, "Organosilicon Compounds," Butterworth and Co. Ltd., London, 1960, pp 367–376; W. H. Knoth and R. V. Lindsey, *J. Org. Chem.*, **23**, 1392 (1958).

(3) For example, see J. D. Roberts and S. Dev, *J. Am. Chem. Soc.*, **73**, 1879 (1951).

(4) R. Criegee and A. Rimmelin, *Ber.*, **90**, 414 (1957).

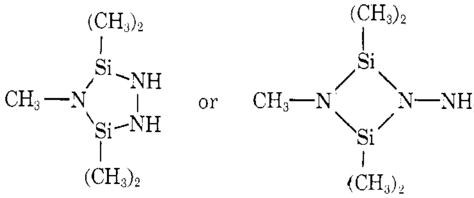
(5) C. G. Overberger, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **21**, 21 (1960).

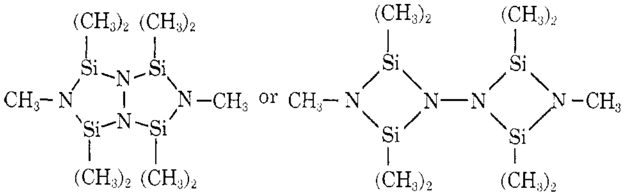
(6) H. Bock, *Z. Naturforsch.*, **17b**, 423 (1962).

(7) For recent reviews, see R. Fessenden and J. S. Fessenden, *Chem. Rev.*, **61**, 378 (1961); U. Wannagat, *Advan. Inorg. Chem. Radiochem.*, **6**, 243 (1964).

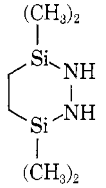
(8) For the single example of a monocyclic silylhydrazine containing (two) NH–NH groups, see H. Niederprüm and U. Wannagat, *Z. Anorg. Allgem. Chem.*, **311**, 270 (1961).

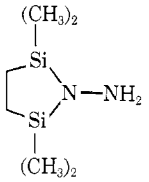
The Synthesis of Monocyclic Silylhydrazines.—Whereas iodosilane reacts with hydrazine to form tetrasilylhydrazine, trialkylhalosilanes afford bis(trialkylsilyl)hydrazines rather than the tetrasubstituted derivatives.[7] However, Wannagat has recently reported[9] that the bicyclic tetrasubstituted hydrazine (II), rather than the monocyclic disubstituted hydrazine (I), is formed from the interaction of 1,3-dichloropentamethyldisilazane and hydrazine. These and other observations[7] imply that the extent of reaction of a chlorosilane depends primarily on steric effects but that such steric limitations may be reduced when the hydrazino group becomes part of a ring system.

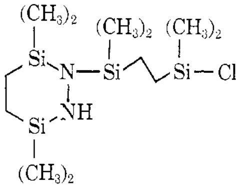

I

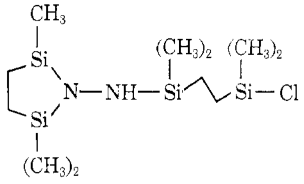

II

In preliminary experiments, the reaction of hydrazine with dimethyldichlorosilane[10] and with 1,3-dichlorotetramethyldisiloxane was found to afford polymeric fluids, to the exclusion of low molecular weight cyclic products. Heating either of these fluids in the presence of ammonium sulfate or sodium hydroxide[11] resulted in disproportionation, with the formation of a gel and hydrazine rather than monocyclic silylhydrazines. Dimethylcyclosiloxanes were also obtained from the polymer derived from hydrazine and 1,3-dichlorotetramethyldisiloxane. Transamination of 1,3-bis(N,N-diethylamino)tetramethyldisiloxane with hydrazine in the presence of ammonium sulfate gave only diethylamine and a nonvolatile fluid. In contrast to these results, when 1,2-bis(dimethylchlorosilyl)ethane was treated with 3 equiv of hydrazine in dry benzene, a mixture of the two monocyclic silylhydrazines (III and IV) was obtained in 75% yield. Furthermore, when the proportion of 1,2-bis(dimethylchlorosilyl)ethane to hydrazine was increased, the only reaction products were V and VI. The isolation of III and IV in good yield and the failure of V and VI to ring-close under the reaction conditions suggest that the ring conformations adopted by these compounds must impose considerable steric hindrance to further substitution.


III


IV


V


VI

The Equilibration of Silylhydrazines.—The complete separation of III and IV by fractional distillation could not be accomplished, for the two isomers were found to be in equilibrium at room temperature even in the absence of added catalysts. On the basis of the nuclear magnetic resonance (nmr) spectra and the infrared spectra (N–H absorption in the 3.2 and 6.3 μ regions)[12,13] of enriched samples, the equilibrium composition was determined to be approximately 27% of III and 73% of IV. The same equilibrium composition was attained regardless of which isomer initially predominated, and equilibration was complete in less than 24 hr at room temperature. The facility of the equilibrium III $\rightleftharpoons$ IV led us to reexamine the isomerization of 1,1- and 1,2-bis(trimethylsilyl)hydrazine.[13,14] The two isomers were prepared from the reaction of trimethylchlorosilane with hydrazine and separated by fractional distillation. As suggested by West,[13] equilibrium was rapidly attained in the presence of base and was complete in less than 2 hr at 100°, using 0.5% w/w potassium metal. It was also found that equilibration will occur more slowly in the absence of added catalysts but is complete in approximately 9 hr at 100°. Thermal isomerization during distillation may account for the disagreement between different laboratories[15] on the structures of products from chlorosilanes and hydrazines. By nmr spectral analysis, the equilibrium composition at 100° was determined to be approximately 60% of the 1,1 isomer and 40% of the 1,2 isomer. The fact that the two isomers are of comparable stability, despite the greater nonbonded interactions of the 1,1 isomer, is significant in that it indicates the 1,1 isomer is favored electronically. It is not clear whether this electronic stabilization is derived solely from the greater d_π–d_π interaction of the Si–N–Si grouping.[16] Interaction of the silicon d orbitals with the β-amino group, invoked by Wannagat[14] to explain the low nucleophilicity of this nitrogen atom, may also

---

[9] U. Wannagat and E. Bogusch, *Inorg. Nucl. Chem. Letters*, **1**, 13 (1965).

[10] This reaction has been reported previously: U. Wannagat and W. Liehr, *Angew. Chem.*, **69**, 783 (1957).

[11] Catalytic depolymerization has been used for the preparation of strained cyclic siloxanes: R. L. Merker, W. A. Piccoli, and G. G. Haberland, *J. Am. Chem. Soc.*, **82**, 1883 (1960).

[12] For the assignment of structures of isomeric silylhydrazines using nmr and infrared spectroscopy, see R. West, M. Ishikawa, and R. E. Bailey, *ibid.*, **88**, 4648 (1966).

[13] R. E. Bailey and R. West, *ibid.*, **86**, 5369 (1964); R. West and R. E. Bailey, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p 4M.

[14] U. Wannagat, F. Höfler, and H. Bürger, *Monatsh. Chem.*, **96**, 2038 (1965).

[15] K. A. Jensen, A. Holm, B. Kägi, and C. T. Pedersen, *Acta Chem. Scand.*, **19**, 772 (1965).

[16] C. G. Pitt and K. R. Skillern, *Inorg. Nucl. Chem. Letters*, **2**, 237 (1966).

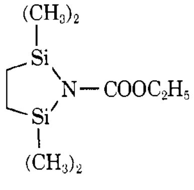
contribute to the stability of the 1,1 isomer. We are currently examining the equilibration of the bis(trimethylsilyl) derivatives of ethylenediamine to resolve this question.

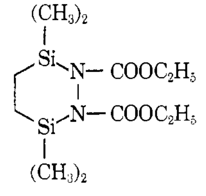
Wannagat[14] has recently described the isolation and characterization of 1,1-bis- and 1,2-bis(trimethylsilyl)hydrazine. Wannagat reports the two isomers, separated by glpc, do not undergo thermal isomerization, and, after 45 hr at 120°, in the presence of triethylamine hydrochloride, only partial isomerization was noted. Although samples used in this investigation had been repeatedly distilled, we cannot discount the presence of trace amounts of hydrazine hydrochloride. However, the difference in the observed rates of isomerization is not understood.

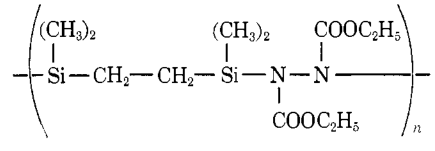
Molecular weight studies indicate that 1,1- and 1,2-bis(trimethylsilyl)hydrazine and III and IV are dimeric in benzene, a fact which we tentatively attribute to intermolecular hydrogen bonding (although intermolecular N→Si bonding[17] cannot be ruled out). While dimerization may influence the relative stabilities of the isomeric silylhydrazines, it is unlikely to account for their interesting chemical properties (*vide infra*).

Oxidation of Silylhydrazines.—Having successfully obtained the monocyclic silylhydrazine III, the oxidation of this compound, as a potential synthesis of the previously unreported[18] 1,2-disilacyclobutane ring system, was investigated. Since the complete separation of III from IV was not possible, an equilibrium mixture of the two isomers was employed. Based on Overberger's studies[5] of the oxidation of carbon analogs of III and IV, both isomers may in fact be considered potential precursors of 1,1,2,2-tetramethyl-1,2-disilacyclobutane. When a mixture of III and IV was added to a slurry of yellow mercuric oxide and anhydrous magnesium sulfate in cyclohexane, nitrogen evolution was noted, and glpc showed the presence of a single product identified, after isolation in 68% yield, as 2,2,-5,5-tetramethyl-1-oxa-2,5-disilacyclopentane. Addition of yellow mercuric oxide to an excess of the silylhydrazines gave only the cyclic siloxane and unchanged silylhydrazines. The use of manganese dioxide in place of mercuric oxide produced the same result.

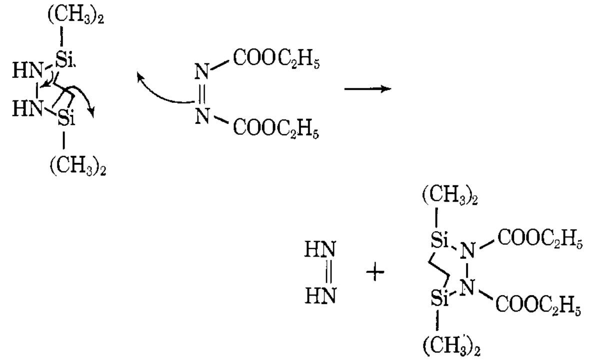
To avoid the use of an oxidant containing labile oxygen, the dehydrogenation of III and IV with ethyl azodicarboxylate was investigated. When the latter was added to the silylhydrazine mixture in xylene at 0°, nitrogen evolution was observed and 2 equiv of the ester was consumed. Glpc showed the presence of two volatile products, which were isolated by distillation and identified as VII and VIII by comparison with samples obtained by unambiguous syntheses. Hydrolysis of the nonvolatile reaction product afforded close to equimolar amounts of ethyl hydrazodicarboxylate and a polysiloxane possessing the 1,2-bis(oxydimethylsilyl)ethane skeleton. Structure IX is therefore assigned to the nonvolatile product.


VII


VIII


IX

The silylurethane (VII) must have arisen from the reaction of ethyl azodicarboxylate with IV without ring opening, for Diels[19] has observed that analogous products are formed from 1,1-diorgano hydrazines. If it is assumed that the reaction of ethyl azodicarboxylate with III (and IV[5]) does produce 1,1,2,2-tetramethyl-1,2-disilacyclobutane as anticipated, then the formation of the amide (VIII) and the copolymer (IX) is readily understood as ring expansion and copolymerization, respectively, involving the azo double bond and the labile silicon–silicon bond of the disilacyclobutane. There is ample precedent for the exceptional reactivity (diradical character) of the silicon–silicon bond in a four-membered ring.[20] However, an alternative mechanism for the formation of VIII, based on the similarity of silicon and hydrogen in many chemical transformations, is shown in reaction 1.


(1)

Similar considerations apply to the formation of 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane from the mercuric oxide oxidation of III and IV.

In order to determine which mechanism was operative, the oxidation of 1,1- and 1,2-bis(trimethylsilyl)hydrazine was studied under comparable conditions. When a mixture of the acyclic isomers was treated with yellow mercuric oxide, the only products obtained were identified as trimethylsilanol and hexamethyldisiloxane. No hexamethyldisilane could be detected by glpc. When ethyl azodicarboxylate was used as the oxidant, the only products formed were the mono- and bis(tri-

---

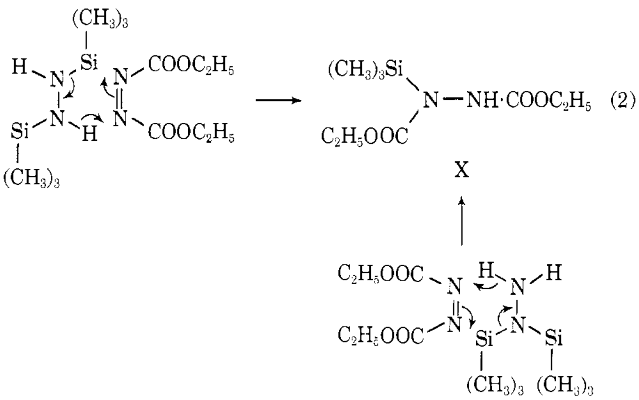
[17] S. Sujishi and S. Witz, *J. Am. Chem. Soc.*, **76**, 4631 (1954); we thank a referee for expressing this possibility.

[18] An unstable derivative of this ring system has been obtained recently: J. C. Thompson, J. L. Margrave, and P. L. Timms, *Chem. Commun.*, 566 (1966).

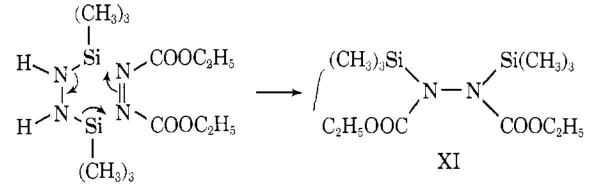
[19] O. Diels, *Ber.*, **56**, 1933 (1923).

[20] H. Gilman and G. L. Schwebke, *Advan. Organometal. Chem.*, **1**, 89 (1964).

methylsilyl) derivatives of ethyl hydrazodicarboxylate (X and XI, respectively). Again, no hexamethyldisilane was detected in the reaction mixture. In control experiments it was demonstrated that neither mercuric oxide nor ethyl azodicarboxylate will react with hexamethyldisilane. These results clearly indicate that, in the oxidation of the acyclic silylhydrazines, both silicon and hydrogen are directly involved in the oxidative process, for example, as illustrated for ethyl azodicarboxylate in reaction 2. A similar mechanism for the formation of both trimethylsilanol and hexamethyldisiloxane, using mercuric oxide, may be envisaged.


(2)

X


XI

In contrast to Bock's[6] findings, when 1,1- and 1,2-bis(trimethylsilyl)hydrazine were treated with chloranil in benzene, no hexamethyldisilane was formed, and the only product appeared to be 1,4-bis(trimethylsiloxy)-2,3,5,6-tetrachlorobenzene. The similarity in vapor pressures and molecular weights of hexamethyldisilane and hexamethyldisiloxane suggests that Bock may, in fact, have obtained the latter compound, formed by facile hydrolysis of 1,4-bis(trimethylsiloxy)-2,3,5,6-tetrachlorobenzene.

Experimental Section

Gas-liquid partition chromatographic analyses were performed with an F & M Model 300 instrument using a 6-ft column of 5% SE 30 or 5% 20M Carbowax on Anakrome, with a helium flow rate of 75 ml/min. Infrared spectra were obtained with a Perkin-Elmer Model 221 spectrophotometer. Nmr spectra were obtained with a Varian A-60 spectrometer and are reported downfield from tetramethylsilane (internal standard). Melting points and boiling points are not corrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Molecular weights were determined by vapor pressure osmometry. All reactions were carried out under an atmosphere of prepurified nitrogen.

1,2-Bis(dimethylchlorosilyl)ethane.[11]—This compound was prepared from the chloroplatinic acid catalyzed addition of dimethylchlorosilane to dimethylvinylchlorosilane, mp 37.5–39°; lit.[11] mp 37°.

1,3-Bis(N,N-diethylamino)tetramethyldisiloxane.—To a stirred solution of anhydrous diethylamine (13.54 g, 0.1851 mole) was cautiously added 91.5 ml of a 1.835 *M* solution of methyllithium in ether. When gas evolution was complete, 1,3-dichlorotetramethyldisiloxane[21] (17.07 g, 0.0843 mole) was added to the reaction mixture over a period of 50 min. The reaction mixture was refluxed for 25 min and then stirred overnight at room temperature. The precipitated lithium chloride was filtered, and the filtrate was fractionally distilled, to give 16.324 g of the desired product boiling at 110° (10 mm). The nmr spectrum (CCl_4) showed a singlet at 1.5 cps (12H, Si–CH_3), a triplet centered at 58 cps (12H, $J = 7$ cps, N–CH_2–CH_3), and a quartet centered at 169.5 cps (8H, $J = 7$ cps, N–CH_2–CH_3).

Anal. Calcd for $C_{12}H_{32}N_2OSi_2$: C, 52.11; H, 11.66; N, 10.15; Si, 20.23. Found: C, 52.21; H, 11.84; N, 10.34; Si, 20.38.

Reaction of 1,3-Dichlorotetramethyldisiloxane[21] with Hydrazine.—The chlorosilane (20.13 g, 0.09912 mole) in dry benzene (30 ml) was added dropwise to anhydrous hydrazine (9.272 g, 0.2893 mole) over a period of 40 min, stirring the mixture rapidly. The reaction mixture was diluted with benzene (20 ml), stirred overnight, and then refluxed for 3 hr. The precipitated hydrazine hydrochloride (13.48 g, 0.1967 mole) was filtered, and the solvent was distilled from the filtrate to leave a residual fluid which remained involatile at 100° (0.5 mm). Potassium hydroxide (0.1 g) was added to the fluid which was then heated (>300°, 760 mm) until distillation ceased. The bulk of the material remained in the distillation flask as an insoluble gel. The distillate (3.13 g) was a two-phase mixture of hydrazine and a neutral liquid. The latter was redistilled to afford octamethylcyclotetrasiloxane (1.34 g; mp 16–16.5°) and higher boiling dimethylcyclosiloxanes.

Reaction of 1,3-Bis(N,N-diethylamino)tetramethyldisiloxane with Hydrazine.—A mixture of the disiloxane (7.885 g, 0.02856 mole), anhydrous hydrazine (1.107 g, 0.03454 mole), and ammonium sulfate (71 mg, 0.00052 mole) was stirred and refluxed, separating liberated diethylamine (2.836 g, 0.03878 mole) by means of a 60-cm Teflon-coated spinning-band column. The residual fluid remained involatile at 150° (2 mm).

Reaction of Trimethylchlorosilane with Hydrazine.—Trimethylchlorosilane (68.00 g, 0.6261 mole) was added over a period of 3 hr to a stirred suspension of anhydrous hydrazine (30.15 g, 0.9407 mole) in dry ether (125 ml) cooling the reaction mixture with iced water. After stirring at room temperature overnight, the hydrazine hydrochloride was filtered and the filtrate was fractionally distilled to afford 32.22 g (58%) of a mixture of 1,1- and 1,2-bis(trimethylsilyl)hydrazine, boiling at 109–111° (157 mm). A second fraction (8.51 g, 14%), boiling at 111–114° (157 mm) was also obtained. Nmr analyses showed the ratios of the 1,1 and 1,2 isomers in the two fractions were 50:50 and 66:34, respectively.

In a second experiment, the above procedure was repeated, with the exception that the reaction products were isolated by distillation under reduced pressure (10 mm) with the pot temperature not exceeding 44°. The product (26.94 g, 49%) boiling at 38–39° (10 mm) was shown by nmr analysis to be a mixture of 1,1- and 1,2-bis(trimethylsilyl)hydrazine in the approximate ratio of 1:3.

In the third experiment, when inverse addition of the reagents was employed and the products were distilled at a maximum pot temperature of 45°, the ratio of 1,1- to 1,2-bis(trimethylsilyl)hydrazine was again found to be 1:3.

The two isomers were separated by repeated fractional distillation, using a 60-cm Teflon-coated spinning-band column. Data for these two compounds follow.

1,2-Bis(trimethylsilyl)hydrazine: bp 145–146°; nmr (CCl_4): 2 cps (Si–CH_3), 139 cps (N–H); $\nu_{\max}^{CCl_4}$: 3340 (w), 2960 (s), 2900 (m), 1430 (sh), 1405 (m), 1300 (w), 1250 (s), 1110 (w), 1065 (m), 865 (vs), and 835 (vs) cm^{-1}.

Anal. Calcd for $C_6H_{20}N_2Si_2$: C, 40.85; H, 11.43; N, 15.88; mol wt, 176.4. Found: C, 40.60; H, 11.28; N, 15.96; mol wt (benzene), 357.

1,1-Bis(trimethylsilyl)hydrazine: bp 154–155°; nmr (CCl_4): 5.5 cps (Si–CH_3), 164 cps (N–H); $\nu_{\max}^{CCl_4}$: 3350 (w), 3265 (w),

---

[21] R. L. Elliott and L. W. Breed, *Inorg. Chem.*, **4**, 1455 (1965).

2960 (s), 2900 (m), 1565 (w), 1430 (sh), 1405 (m), 1300 (w), 1250 (s), 1065 (m), 1000 (s), 885 (vs), and 835 (vs) cm^{-1}.

Anal. Calcd for $C_6H_{20}N_2Si_2$: C, 40.85; H, 11.43; N, 15.88; mol wt, 176.4. Found: C, 40.65; H, 11.36; N, 16.01; mol wt (benzene), 361.

Reaction of Hydrazine with 1,2-Bis(dimethylchlorosilyl)ethane. A. Molar Ratio 3:1.—The chlorosilane (27.46 g, 0.1275 mole) in dry benzene (30 ml) was added dropwise to anhydrous hydrazine (12.24 g, 0.3819 mole) in dry benzene (70 ml), stirring the homogeneous mixture rapidly. After 2 hr at room temperature, hydrazine hydrochloride was filtered and the filtrate was distilled to afford 16.65 g (75%) of a mixture of III and IV as a clear liquid, bp 75–76° (25 mm). *Anal.* Calcd for $C_6H_{18}N_2Si_2$: C, 41.32; H, 10.40; N, 16.06; Si, 32.21; mol wt, 174.4. Found: C, 43.31; H, 10.56; N, 16.10; Si, 32.13; mol wt, 350 (benzene), 174 (mass spectrum). The isomers were partially separated by fractional distillation using a 60-cm Teflon-coated spinning-band column. A fraction, bp 90.5° (57 mm), containing IV (90%) and III (10%) showed absorption at 3335, 3260 (NH_2 stretching), and 1580 (NH_2 deformation) cm^{-1}, as well as at 2960 (s), 2920 (s), 2895 (s), 2800 (w), 1420 (m), 1365 (w), 1250 (s), 1140 (s), 1095 (m), 1080 (m), 1040 (m), 980 (s), 920 (s), 900 (vs), and 840 (s) cm^{-1}. A fraction, bp 93° (59 mm), containing III (66%) and IV (34%) showed diminished bands due to IV and additional absorption at 3380 and 855 cm^{-1}. Both fractions reverted to an equilibrium mixture of III and IV in less than 24 hr. Nmr spectra (CCl_4): III: 2 cps, 12.2H ($Si-CH_3$), 43 cps, 4H ($Si-CH_2$), 165 cps, 1.8H (NH); IV: 4 cps, 11.0H ($Si-CH_3$), 41 cps, 4.0H ($Si-CH_2$), 165 cps, 2.0H (NH).

B. Molar Ratio 5:2.—Anhydrous hydrazine (4.891 g, 0.1526 mole) was added dropwise to a stirred solution of the chlorosilane (11.07 g, 0.05142 mole) in dry benzene (40 ml) over a 2-hr period. At this time glpc showed a mixture of III and IV (73%) and V and VI (17%). A further 10.68 g (0.04960 mole) of chlorosilane and 0.533 g (0.0166 mole) of hydrazine were separately added to the mixture, which was stirred at room temperature over the weekend. Glpc then showed the absence of I and II. Hydrazine hydrochloride was filtered, and the filtrate was distilled to afford unchanged chlorosilane (5.785 g) and a viscous liquid (9.251 g), bp 77–100° (0.18 mm); yield 71% (based on unchanged chlorosilane). The crude product was redistilled to give 4.747 g (36%) of an analytically pure sample; bp 83° (0.12 mm); $\nu_{\max}^{CCl_4}$: 2960 (s), 2905 (s), 2800 (w), 1420 (m), 1255 (s), 1140 (m) 1055 (m), 995 (m), 940 (m), 850 (sh), and 835 (vs) cm^{-1}. The nmr spectrum was complex, showing signals at 2, 3, 4.5, 23.5, 37, and 47 cps, demonstrating the presence of both V and VI, even though glpc showed only one peak.

Anal. Calcd for $C_{12}H_{33}ClN_2Si_4$: C, 40.81; H, 9.42; Cl, 10.04; N, 7.93; Si, 31.81. Found: C, 41.07; H, 9.43; Cl, 9.83; N, 8.02; Si, 31.55.

The Equilibration of Silylhydrazines.—The compositions of equilibrating mixtures were determined from the relative nmr peak areas of the isomers, using a sweep width of 50 cps. The uncertainty in the determined isomer ratios results from incomplete resolution of the peaks and is expressed as the percentage area overlap of the isomer peaks relative to the total peak area. After equilibration was complete, the compositions of the isomer mixtures were qualitatively confirmed by infrared spectroscopy and by glpc.

Equilibration of III and IV.—Undiluted samples were sealed in nmr tubes, and the equilibration was followed at room temperature: 0 hr, 11.7 ± 1.2% III, 88.3 ± 1.2% IV; 2.17 hr, 10.6 ± 2.7% III, 89.4 ± 2.7% IV; 24 hr, 20.4 ± 6.3% III, 79.6 ± 6.3% IV; 18 days, 27.3 ± 2.4% III, 72.7 ± 2.4% IV. 0 hr, 65.7 ± 4.0% III, 34.3 ± 4.0% IV; 2.08 hr, 40.7 ± 3.4% III, 59.3 ± 3.4% IV; 24 hr, 21.7 ± 5.4% III, 78.3 ± 5.4% IV; 18 days, 29.5 ± 2.4% III, 70.5 ± 2.4% IV.

Equilibration of 1,1- and 1,2-Bis(trimethylsilyl)hydrazine. Base Catalysis.—After 1.928 g of a mixture of 38.8 ± 3.1% of the 1,1 isomer and 61.2 ± 3.1% of the 1,2 isomer was heated for 17.5 hr at 100° in the presence of 3.5 mg of potassium metal, the composition of the mixture was determined to be 57.0 ± 0.0% of the 1,1 isomer and 43.0 ± 0.0% of the 1,2 isomer. After 42 hr at 100°, the composition of the mixture was 61.3 ± 0.7% of the 1,1 isomer and 38.7 ± 0.7% of the 1,2 isomer.

When 0.7986 g of a mixture of 90.7 ± 1.0% of the 1,1 isomer and 9.3 ± 1.0% of the 1,2 isomer was heated for 1.5 hr at 100° in the presence of 3.65 mg of potassium metal, the composition of the mixture was determined to be 63.7 ± 4.4% of the 1,1 isomer and 36.3 ± 4.4% of the 1,2 isomer. After 17.5 hr, the composition of the mixture was 60.9 ± 1.1% of the 1,1 isomer and 39.1 ± 1.1% of the 1,2 isomer.

Thermal Equilibration.—Undiluted samples were sealed in nmr tubes and then heated at 100°: 0 hr, 43.9 ± 2.2% 1,1 isomer, 56.1 ± 2.2% 1,2 isomer; 3 hr, 52.0% 1,1 isomer, 48.0% 1,2 isomer; 9 hr, 55.3% 1,1 isomer, 44.7% 1,2 isomer. 0 hr, 88.5 ± 0.9% 1,1 isomer, 11.5 ± 0.9% 1,2 isomer; 3 hr, 62.0 ± 2.8% 1,1 isomer, 38.0 ± 2.8% 1,2 isomer; 9 hr, 58.4 ± 0.0% 1,1 isomer, 41.6 ± 0.0% 1,2 isomer.

Oxidation of III and IV with Yellow Mercuric Oxide.—An equilibrium mixture of III and IV (2.243 g, 0.01286 mole) was added dropwise to a stirred suspension of yellow mercuric oxide (5.00 g, 0.0231 mole) and anhydrous magnesium sulfate (5.00 g) in anhydrous cyclohexene (15 ml). Vigorous gas evolution and the formation of mercury were noted. The mixture was stirred for 2 hr after addition was complete and then allowed to stand at room temperature for 2 days. The solids were filtered and washed with dry xylene, and the filtrate was distilled. A fraction (1.175 g) boiling at 74–75° (120 mm) was shown by glpc and infrared analysis to be 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane contaminated with cyclohexene (7%). A second fraction (0.535 g), boiling at 75–76° (120 mm), contained 60% cyclic siloxane and 40% xylene; total yield, 68%. The distillation residue contained xylene and polysiloxane ($\nu_{\max}^{liq}$ 1050 cm^{-1}).

In small-scale experiments, the addition of mercuric oxide to an excess of the silylhydrazines III and IV in dry xylene containing magnesium sulfate was shown by glpc to produce only the cyclic siloxane and unchanged silhydrazines. The use of manganese dioxide in place of mercuric oxide gave identical results. When hexamethyldisilane (1.009 g) was refluxed over yellow mercuric oxide for 3.5 hr, no reaction was observed. Glpc showed the complete absence of hexamethyldisiloxane, and only unchanged hexamethyldisilane was detected.

Oxidation of III and IV with Ethyl Azodicarboxylate.—Ethyl azodicarboxylate (9.170 g, 0.05264 mole) was added over a 4-hr period to a stirred, ice-cooled solution of an equilibrium mixture of III and IV (4.537 g, 0.02601 mole) in anhydrous xylene (25 ml). At this time the yellow color of the azo ester persisted. Nitrogen evolution was noted throughout the course of the addition. The reaction mixture was filtered, affording 3.027 g (0.01718 mole) of ethyl hydrazodicarboxylate. The filtrate was distilled to give the following compounds: 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane, bp 86° (145 mm), 0.248 g (6%); VII, bp 73° (3.4 mm), 1.060 g (18%); VIII, bp 110° (0.5 mm), 2.563 g (31%). A fraction (0.488 g) containing both VII and VIII was also obtained. The distillation residue was hydrolyzed with water to give ethyl hydrazodicarboxylate (1.252 g, 7.110 mmole) and a polysiloxane (1.376 g, 8.580 mmole), the infrared spectrum of which was identical with that of the product derived from base-catalyzed polymerization of 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane.

The structures of all of the compounds isolated in this experiment were confirmed by comparison with authentic samples.

N-Carbethoxy-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane (VII).—A solution of 1,2-bis(dimethylchlorosilyl)ethane (9.732 g, 0.04520 mole) and ethyl carbamate (4.030 g, 0.04524 mole) in dry benzene (60 ml) was added dropwise to a stirred suspension of sodium hydride (0.09949 mole) in dry benzene (70 ml) and dry dimethylformamide (40 ml). The reaction was exothermic, and gas evolution was noted. After stirring at room temperature overnight, the mixture was filtered, and the filtrate was fractionally distilled to afford 4.496 g (43%) of the desired product, bp 65.5–67° (2.75 mm); $\nu_{\max}^{liq}$: 1695, 1290, 1260, 1110, 1030, 960, 860, and 805 cm^{-1}. The nmr spectrum (CCl_4) showed singlets at 10 cps (12H, Si–CH_3) and 40 cps (4H, Si–CH_2), a triplet centered at 70 cps (J = 7 cps, 3H, O–CH_2–CH_3), and a quartet centered at 240.5 cps (J = 7 cps, 2H, O–CH_2–CH_3).

Anal. Calcd for $C_9H_{21}NO_2Si_2$: C, 46.70; H, 9.15; N, 6.05; Si, 24.27. Found: C, 46.93; H, 9.25; N, 5.85; Si, 24.06.

N,N′-Dicarbethoxy-3,3,6,6-tetramethyl-1,2-diaza-3,6-disilacyclohexane (VIII).—1,2-Bis(dimethylchlorosilyl)ethane (3.077 g, 0.01429 mole) in dry benzene (28 ml) was added to a stirred suspension of sodium hydride (0.0322 mole) and ethyl hydrazodicarboxylate (2.538 g, 0.01440 mole) in dry benzene (9 ml). No reaction was evident, even after refluxing the mixture for 6.5 hr. Dry dimethylformamide (15 ml) was added to the mixture which was refluxed for 5 hr, at which time glpc indicated the reaction was complete. Filtration of the precipitated solids and fractional distillation of the filtrate afforded 1.646 g (36%) of the desired product as a viscous liquid, bp 97° (0.4 mm); $\nu_{max}^{CCl_4}$: 1725, 1695, 1255, 845 cm^{-1}. The nmr spectrum showed singlets at 15.5 and 25 cps (nonequivalent Si–CH_3), a poorly resolved multiplet centered at 43 cps (Si–CH_2–CH_2–Si, nonequivalent), a triplet centered at 76 cps (J = 7 cps, $COOCH_2$–CH_3), and a quartet centered at 249 cps (J = 7 cps, $COOCH_2$–CH_3).

Anal. Calcd for $C_{12}H_{26}N_2O_4Si_2$: C, 45.25; H, 8.23; N, 8.79; Si, 17.63; mol wt, 318.5. Found: C, 45.15; H, 8.09; N, 9.07; Si, 17.39; mol wt ($CHCl_3$), 328.

Oxidation of 1,1- and 1,2-Bis(trimethylsilyl)hydrazine. A. With Mercuric Oxide.—An equilibrium mixture of 1,1- and 1,2-bis(trimethylsilyl)hydrazine (4.428 g, 0.02408 mole) was added dropwise to a stirred slurry of yellow mercuric oxide (10.10 g, 0.04663 mole) and anhydrous magnesium sulfate (10.10 g) in dry xylene (30 ml), regulating the temperature of the mixture at 25–30°. After stirring overnight, the mixture was filtered, washing the solids with dry xylene. Glpc of the filtrate showed trimethylsilanol (84%) and hexamethyldisiloxane (16%) to be the only products. The products were isolated by distillation and their structures confirmed by comparison with the infrared spectra of authentic samples; yield, 3.168 g.

When the oxidation was carried out using cyclohexene as the solvent, the same results were obtained. However, because of the similarity in boiling points, the separation of the products from the solvent was impractical.

B. With Ethyl Azodicarboxylate.—Ethyl azodicarboxylate (12.81 g, 0.7354 mole) was added dropwise to a stirred solution of 1,1- and 1,2-bis(trimethylsilyl)hydrazine (7.859 g, 0.04455 mole; 43% of 1,1 isomer, 57% of 1,2 isomer) in dry xylene (50 ml) at room temperature until the color of the oxidant persisted. The reaction mixture was filtered, to give ethyl hydrazodicarboxylate (5.035 g, 0.02857 mole). Glpc of the filtrate showed the presence of two products—diethyl N-trimethylsilylhydrazodicarboxylate (X, 20%) and diethyl N,N′-bis(trimethylsilyl)hydrazodicarboxylate (XI, 80%). No hexamethyldisilane was detected. The filtrate was distilled to afford 11.283 g of a mixture of X and XI, boiling at 82–90° (0.44 mm). Repeated fractional distillation of the mixture afforded analytical samples of the two products.

The nmr spectrum (CCl_4) of X showed a singlet at 15 cps (9H, Si–CH_3), a triplet centered at 75.5 cps (6H, J = 7 cps, O–CH_2–CH_3), two overlapping quartets centered at 243.5 and 245 cps (4H, J = 7 cps, O–CH_2–CH_3), and broad absorption from 410 to 420 cps (1H, NH); ν_{max}^{liq}: 3305 (broad, NH), 1730 (broad, N–$COOC_2H_5$), 1260 (Si–CH_3), and 855 (Si–N) cm^{-1}; bp 73.5° (0.09 mm).

Anal. Calcd for $C_9H_{20}N_2O_4Si$: C, 43.53; H, 8.12; N, 11.28; Si, 11.31. Found: C, 43.46; H, 7.98; N, 11.39; Si, 11.11.

The nmr spectrum (CCl_4) of XI showed a singlet at 12 cps (18H, Si–CH_3), a triplet centered at 75.5 cps (6H, J = 7.5 cps, O–CH_2–CH_3), and a quartet centered at 238.5 cps (4H, J = 7.5 cps, O–CH_2–CH_3); ν_{max}^{liq}: 1730, 1700 (N–$COOC_2H_5$), 1260 (Si–CH_3), 855 (Si–N) cm^{-1}; bp 60° (0.1 mm).

Anal. Calcd for $C_{12}H_{28}N_2O_4Si_2$: C, 44.97; H, 8.80; N, 8.74; Si, 17.52. Found: C, 45.09; H, 8.65; N, 8.92; Si, 17.31.

C. With Chloranil.—A solution of chloranil (250 mg, 0.834 mmole) in dry xylene (6 ml) was added in portions to a solution of 1,1- and 1,2-bis(trimethylsilyl)hydrazine (202 mg, 1.15 mmoles; 24% of 1,1- isomer, 76% of 1,2 isomer) in dry xylene (1 ml). No hexamethyldisilane could be detected by glpc and, after half of the chloranil solution had been added, the only product formed in the reaction was shown to have the same retention time as 1,4-bis(trimethylsiloxy)-2,3,5,6-tetrachlorobenzene.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORK

Intermediates in the Formation of N-Methylaminoborane Trimer and N,N-Dimethylaminoborane Dimer

BY O. T. BEACHLEY, JR.[1]

Received December 19, 1966

Experimental evidence for the intermediates in the formation of N-methylaminoborane trimer, $(H_2BNHCH_3)_3$, and N,N-dimethylaminoborane dimer, $(H_2BN(CH_3)_2)_2$, has been obtained by synthetic methods and trapping procedures. The pyrolysis of methylamine borane, $H_3BNH_2CH_3$, yields the six-membered ring of $(H_2BNHCH_3)_3$ by initially forming $H_2B(NH_2CH_3)_2{}^+BH_4{}^-$, then $[H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3]^+BH_4{}^-$ through a series of successive dehydrogenation condensation reactions. The final step of the proposed mechanism is ring closure by dehydrogenation. The new compound, $[H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3]^+Cl^-$, was prepared by heating a mixture of $H_2B(NH_2CH_3)_2{}^+Cl^-$ and $H_3BNH_2CH_3$ and was characterized by elemental analysis, its reactions with $FeCl_3$ and $NaBH_4$, and its pmr spectrum. The experimental evidence for the intermediates during the pyrolysis of dimethylamine borane to form $(H_2BN(CH_3)_2)_2$ is consistent with monomeric $H_2BN(CH_3)_2$ species which then associate to give the dimer.

Introduction

Amine boranes, which have at least one hydrogen bound to the nitrogen, readily undergo elimination reactions,[2] such as dehydrogenation or dehydrohalogenation, to form aminoboranes. The aminoboranes have been observed as monomers or associated species,

---

[1] Correspondence and requests for reprints should be sent to the State University of New York at Buffalo, Buffalo, N. Y. 14214.

[2] K. Niedenzu and J. W. Dawson, "Boron–Nitrogen Compounds," Academic Press Inc., New York, N. Y., 1965, p 8.