

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MISSOURI—KANSAS CITY, KANSAS CITY, MISSOURI 64110Silyl- and Polysilanylhydrazines¹By JOHN W. CONNOLLY, BEN F. STOCKTON, CARL M. EMERICK,² AND EDWARD A. BERNHEIM²

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The reaction between α,ω -bis(chlorodimethylsilyl)- n -alkanes, $[\text{Cl}(\text{CH}_3)_2\text{Si}(\text{CH}_2)_n\text{Si}(\text{CH}_3)_2\text{Cl}]$, and hydrazine has been studied. The structure of the products depends on the length of the alkylene chain, varying from a bicyclic product where $n = 1$ to a cyclic dimer or tetramer where $n = 6$. Also several new bis(polysilanyl)hydrazines have been prepared and characterized. The uv spectra of these compounds have been recorded and are discussed in comparison with silazanes of similar structure.

Introduction

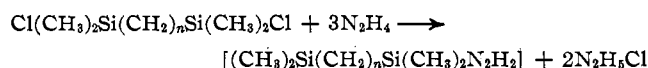
In recent years there have been several reports concerning the structure of bis(organosilyl)hydrazines.³⁻⁵ Several of these substances have been shown to exist as equilibrium mixtures of the 1,1- and 1,2-disubstituted isomers. The factors governing the equilibrium composition appear to be: (a) steric, which in the open-chain compounds favors the 1,2 isomer increasingly as the size of the silyl substituents increases, and (b) electronic, which favors the 1,1 isomer due to extended back-bonding over the Si-N-Si system.⁶ In the cyclic silylhydrazines, depending on the size of the ring, the steric factor can either oppose or reinforce the electronic factor.

In this study we have extended the earlier work on cyclic silyl hydrazines. We have also prepared bis(pentamethylsilyl)hydrazine and bis(n -heptamethyltrisilyl)hydrazine. The instability of these polysilyl compounds prevented us from obtaining equilibrium isomer composition data and so it has not been possible to evaluate the electronic factor in these compounds.

The uv spectra of several silylhydrazines are reported here also. They are in general found to be quite similar to silazanes of similar structure.

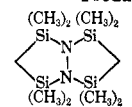
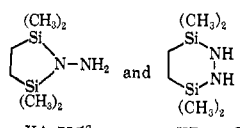
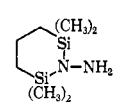
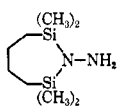
Results and Discussion

(A) **Synthetic Results.**—The reaction between α,ω -bis(chlorodimethylsilyl)- n -alkanes and hydrazine produces bicyclic, cyclic, or "linear" products depending on the length of the alkylene chain. Table I contains a summary of the results of this study plus pertinent information from the literature. These data were obtained in reactions where the quantities of reagents used were in accord with the equation



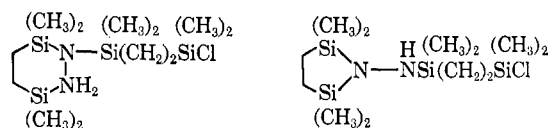
Pitt has shown that when a 1,2-bis(chlorodimethyl-

TABLE I
PRODUCTS OF THE REACTION BETWEEN
 $\text{Cl}(\text{CH}_3)_2\text{Si}(\text{CH}_2)_n\text{Si}(\text{CH}_3)_2\text{Cl}$ AND HYDRAZINE

Reactant	Product(s)	Yield, %	Ref
$n = 1$		79	This work
$n = 2$		75	5
$n = 3$		68	This work
$n = 4$		40	This work
$n = 6$	$[(\text{CH}_3)_2\text{Si}(\text{CH}_2)_6\text{Si}(\text{CH}_3)_2\text{N}_2\text{H}_2]$ ^b	...	This work

^a Equilibrium isomer composition. ^b See text concerning structure.

silyl)ethane to hydrazine ratio of 2:5 is used, the trisubstituted hydrazines



result and that further ring closure of these compounds does not occur.

We have found that even when a fivefold excess of hydrazine is used in the reaction with bis(chlorodimethylsilyl)methane, only the bicyclic product (I) results. This indicates a large difference in steric requirement between the monocyclic products formed from bis(chlorodimethylsilyl)methane and 1,2-bis(chlorodimethylsilyl)ethane.

It has been reported that 1,3-dichloropentamethyl-disilazane reacts with hydrazine to give a tetrasubstituted bicyclic product also,⁷ whereas 1,3-dichlorotetra-

(1) Presented in part at the Fourth International Conference on Organometallic Chemistry, Bristol, England, July 1969.

(2) Work performed in partial fulfillment of the M.S. degree.

(3) U. Wannagat, F. Höfer, and H. Bürger, *Monatsh. Chem.*, **96**, 2038 (1965).

(4) R. West, M. Ishikawa, and R. E. Bailey, *J. Am. Chem. Soc.*, **88**, 4648 (1966).

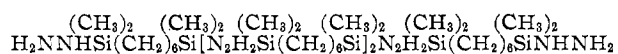
(5) C. G. Pitt and K. R. Skillern, *Inorg. Chem.*, **6**, 865 (1967).

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

methylidisiloxane⁵ and 1,3-dichlorohexamethyltrisilane react with hydrazine to give polymeric products. In these latter two cases apparently the Si-O-Si bond angle is too large and the Si₃ chain length is too great to allow cyclization.

In Table I the disubstituted cyclic products II-IV are capable of existing in more than one isomeric form. In III and IV the steric effect and the electronic effect both favor the smaller of the two possible rings (the 1,1 isomer) and only one isomer is thermodynamically stable in each case.

The structure of compound V is still uncertain. This material is the nonvolatile residue obtained when 1,6-bis(chlorodimethylsilyl)-*n*-hexane is treated with hydrazine. The apparent average molecular weight of this material is four times that of the repeating unit (CH₃)₂Si(CH₂)₆Si(CH₃)₂N₂H₂. There are several facts which argue against this material being a linear polymer of average structure



The first of these is that the nitrogen content of the linear material would be 14.70% whereas the value found is 12.00%. The second is that, barring severe line broadening, there are sufficient end groups that the hydrazyl end group nmr signals should be visible which would require four NH signals (assuming positional isomers in the internal hydrazyl groups) rather than the two observed. The third is that Wannagat has shown that monosilylhydrazines condense very readily.⁸ These facts taken together suggest that compound V is a cyclic product.

For monomeric silylhydrazines Pitt has shown that the vpo molecular weights obtained were too high by a factor of 2. If compound V is associated also, then the molecular formula which best fits the data is [(CH₃)₂Si(CH₂)₆Si(CH₃)₂N₂H₂]₂. There are still several isomers possible for this formula since the hydrazyl groups can be substituted either 1,1 or 1,2. An equilibrium measurement indicates that 36% of the hydrazyl groups are 1,1 disubstituted so the probable composition of this material is a mixture of 18-, 19-, and 20-membered rings.

The lack of a volatile product in this reaction definitely rules out the formation of a monomeric (9- or 10-member) cyclic product. Otherwise, the data do not rule out the presence of small amounts of rings containing more than two structural units. The structure(s) suggested is (are), however, the most consistent with the available data.

The reactions of chloropentamethylidisilane and 1-chloroheptamethyltrisilane with hydrazine produce primarily the 1,2 isomer as is shown in Table II. While the steric factor clearly prevails in the formation of these compounds, experimental difficulties prevented us from determining whether the isomer compositions reported are the equilibrium values.

The reaction of 1,2-dichlorotetramethylidisilane with hydrazine gives a modest yield of the cyclic compound VIII in Table II. This material was shown to be gas chromatographically pure. While it reacts with potassium extensively, it showed no change in composition after heating in solution for 66 hr at 100°. In view of the facile interconversion of IIA and IIB, it seems very likely that VIII is the thermodynamically stable isomer.

The reaction of 1,3-dichlorohexamethyltrisilane with hydrazine yields only a nonvolatile residue. The analytical and molecular weight data obtained for compound IX are consistent with an apparent molecular formula of [Si₃(CH₃)₆N₂H₂]₅. The ring *vs.* chain question is less definite than for compound V since the nmr spectrum of IX contains only complex signals, although again the nitrogen analysis is much closer to that required by the cyclic structure. If the material is cyclic, the odd number of repeating units would require either a mixture of ring sizes or a lack of association.

(B) **Ultraviolet Spectra.**—Table III contains uv spectra obtained for some silylhydrazines and amines.

These spectra are quite similar to those reported for silazanes of similar structure. In their report on the uv spectra of silazanes Pitt and Fowler assigned the long-wavelength absorption to an *n* → *σ** transition and they attributed the blue shift accompanying the replacement of an *N*-alkyl group with an *N*-silyl group to the stabilization of the ground state by back-donation of electron density from nitrogen to silicon.⁹ Similar arguments have been presented by Bell and Walsh¹⁰ and it seems reasonable to propose the same explanation here.

It has been possible to measure the spectra of the 1,1 and 1,2 isomers of the same compound only in the case of X. The long-wavelength maxima of these two compounds (200 and 220 mμ, respectively) closely parallel the long-wavelength maxima of *unsym*- and *sym*-dimethylhydrazine, respectively (215, 245 mμ).¹¹ It is tempting to consider that the absence of the 220-mμ absorption band in VI and VII is due to increased back-bonding with the polysilanyl groups. However, this band is very weak and the presence of the polysilanyl chromophores in VI and VII may simply make it unobservable.

Normally the interaction of the lone pairs in substituted hydrazines is quite small¹¹ but the spectra of I, VIII, and XI show evidence for it. The structure of I requires that the lone pairs be quite close to one another and this apparently causes a destabilization of the ground state. The spectra of both VIII and XI indicate that there is a 1,4 interaction which causes destabilization of the ground state. A similar effect has been observed in *p*-dithianes.¹² In compounds VIII and XI intraannular interaction of the silicon 3d orbitals is ruled out since no such effect shows up in the

(9) C. G. Pitt and M. S. Fowler, *J. Am. Chem. Soc.*, **89**, 6792 (1967).

(10) S. Bell and A. D. Walsh, *Trans. Faraday Soc.*, **62**, 3005 (1966).

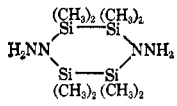
(11) H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules," Academic Press, New York, N. Y., 1967.

(12) D. S. Breslow and H. Skolnik, "Multisulfur and Sulfur and Oxygen Five- and Six-Membered Heterocycles," Vol. 2, Interscience Publishers, New York, N. Y., p 1057.

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

(8) U. Wannagat, *Advan. Inorg. Chem. Radiochem.*, **6**, 225 (1964).

TABLE II
REACTION BETWEEN SOME MONO- AND DICHLOROPERMETHYLPOLYSILANES AND HYDRAZINE

Reactant	Product(s)	Yield, %
$\text{Si}_2(\text{CH}_3)_6\text{Cl}$	$(\text{Si}_2(\text{CH}_3)_6)_2\text{NNH}_2$ and $\text{Si}_2(\text{CH}_3)_6\text{NHNHSi}_2(\text{CH}_3)_6$ VIA, 20% VIB, 80%	54
1- $\text{Si}_3(\text{CH}_3)_7\text{Cl}$	$\text{Si}_3(\text{CH}_3)_7\text{NHNHSi}_3(\text{CH}_3)_7$ VII	80
$\text{Cl}(\text{CH}_3)_2\text{SiSi}(\text{CH}_3)_2\text{Cl}$	 VIII	37
$\text{Cl}(\text{CH}_3)_2\text{SiSi}(\text{CH}_3)_2\text{Si}(\text{CH}_3)_2\text{Cl}$	$[\text{Si}_3(\text{CH}_3)_6\text{N}_2\text{H}_2]_x^a$ IX	...

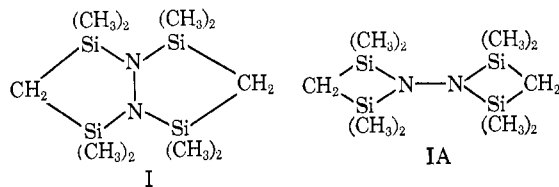
^a See text for comments about the structure.

spectrum of dodecamethycyclohexasilane.¹³

The only other 1,1-bis(silyl)hydrazines in which the two lone pairs give rise to two absorption bands above 190 $m\mu$ are XIII and XIV. In these two compounds one lone pair is stabilized due to back-bonding to silicon and the other is destabilized due to the inductive effect of the alkyl groups. In the remaining 1,1-bis(silyl)hydrazines reported here the lone-pair energy differences are too small to give rise to two bands in the spectrum.

Similar to the findings reported by Pitt and Fowler, there is no evidence in these uv data to indicate interaction between silyl or polysilyl groups across a nitrogen, nor is there conclusive evidence that back-bonding to a polysilanyl group offers any more stabilization than back-bonding to a silyl group.

(C) **Structural Assignments.**—Both the structures I and IA are consistent with the analytical data reported



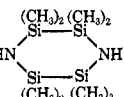
for compound I. We have chosen structure I on the basis of the mass spectrum and uv spectrum of this material. The mass spectra of VI, VIII, IX, and XB, in addition to that of I, were determined. All of them were quite complicated and have resisted detailed analysis, but only that of compound I showed a strong parent peak at 70 eV. It is unlikely that the N-N bond in IA would survive such a high-energy bombardment. The 250- $m\mu$ absorption exhibited by I gives indication of strong lone-pair electron interaction which is consistent only with structure I.

The structural assignment for compound III is based on the facts that the gas chromatograph and the nmr spectrum of this material showed it to be isomerically pure and the ir spectrum showed a doublet in the NH stretch region, indicating the presence of the NH_2 group.⁴ The structural assignments for compounds IV and VIII are based on analogous evidence.

The structural assignment for compound V is based

on the ir and nmr spectra of the material. The presence of the NH and Si-N-Si asymmetric stretching frequencies requires that the hydrazine be both 1,2 and 1,1 substituted. Also there are two NH nmr signals separated by 0.32 ppm. The separation of the NH and NH_2 signals for compounds XA and XB in the same solvent is 0.38 ppm. Compound V also exhibits two silicon methyl nmr signals and the relative area of these signals was used for estimation of the amount of 1,1- and 1,2-disubstituted hydrazyl groups.

TABLE III^a
UV DATA FOR SOME SELECTED
SILYLHYDRAZINES AND AMINES

Compound	λ_{max} , $m\mu$	ϵ ($\times 10^3$)
XA, $(\text{CH}_3)_3\text{Si}_2\text{NNH}_2$	200	2.3
XB, $(\text{CH}_3)_3\text{SiNHNHSi}(\text{CH}_3)_3$	220, 200	0.5, 3.5
I	250, 210	0.50, 2.5
IIC	200	2.1
III	200	2.3
IV	200	2.1
VIC	195	15
VIII	215	16
XI, 	210, 195 ^b	17, 20
VII	217, 194	15, 60
XII, $(\text{CH}_3)_2\text{NNH}_2$	215	0.13
XIII, $(\text{CH}_3)_2\text{NNHSi}(\text{CH}_3)_3$	215, 200 ^b	2.2, 4.0
XIV, $(\text{CH}_3)_2\text{NN}(\text{Si}(\text{CH}_3)_3)_2$	225, ^b 202	1.4, 5.6

^a The C refers to an unresolved mixture. ^b Inflection point.

The isomer composition estimation of the mixture of compounds VIA and VIB was done on the basis of the relative area of the NH nmr signals. The lower field signal was assigned to the NH_2 group and the higher field signal was assigned to the NH signal. The ir spectrum shows both the NH and NH_2 asymmetric stretching bands and the Si-N-Si asymmetric stretching band, all of which are consistent with a mixture of isomers.

The structure assigned to VII is also based on the ir and nmr spectra of this material. The ir spectrum shows an NH asymmetric stretching band, and the NH_2 and Si-N-Si asymmetric stretches are absent. These data do not preclude the presence of a small amount of the 1,1 isomer; however, the nmr spectrum

shows only a single α SiCH₃ signal which indicates isomeric purity.

The reason for the complexity of the NH (three lines) and β -SiCH₃ (two lines) portion of the nmr spectrum of this material remains unknown. Spin decoupling experiments rule out hydrazylmethyl proton coupling. Variable-temperature nmr experiments indicate the occurrence of hydrazyl proton exchange (this was observed with compounds XA and XB also) but at the same time indicate that the observed complexity is not of an intermolecular origin. Variable-concentration nmr experiments also indicate that the complexity is not of an intermolecular origin. One possibility which has not yet been excluded is ¹⁴N-H coupling, although the observed signal patterns are hard to explain on this basis and the observed separations are much smaller than reported ¹⁴N-H coupling constants would dictate.¹⁴

The ir spectrum of IX indicates the presence of NH, NH₂, and Si-N-Si groups, but the nmr spectrum of this material affords little information about its structure.

Experimental Section

Infrared spectra were obtained with the use of a Perkin-Elmer Model 621 spectrophotometer. The measurements made in the 3350-3200-cm⁻¹ region were made on 5% solutions in dried carbon tetrachloride in a 1.0-mm sodium chloride cell. The rest of the measurements were made on films or mulls between CsI plates. The uv measurements were made using a Cary Model 14 spectrophotometer. Both cyclohexane and *n*-pentane were used as solvents. The λ_{max} and ϵ for the 220-m μ band in XB were obtained by difference assuming that the shape of the 200-m μ band in XB is the same as that of XA.

The nmr spectra were obtained using a JEOL Co. Model 4H-100 spectrometer. Solutions were approximately 40% in benzene, using benzene as the lock signal. Concentration dependences of the chemical shifts reported were not determined. The τ values reported are based on the assignment of τ 2.63 for the chemical shift of benzene. The integral values for all protons were satisfactory.

Gas chromatographs were obtained with a Varian Aerograph Model A 90-P chromatograph containing SF-96 or XE-30 columns. Molecular weights were obtained with a Mechrolab Model 301A vapor-phase osmometer. Mass spectra were obtained with an Atlas CH 4B spectrometer. Chemical analyses, other than the chloride analyses, were done by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Preparation of Starting Materials.—All of the starting materials used in this work have been previously prepared with the exception of 1,3-bis(chlorodimethylsilyl)-*n*-propane and 1,6-bis(chlorodimethylsilyl)-*n* hexane. The former was prepared in 70% yield by the (Speier's) catalyzed addition of dimethylchlorosilane to allyldimethylchlorosilane; bp 211-212°. *Anal.* Calcd for C₇H₁₈Cl₂Si₂: Cl, 31.00. Found: Cl, 30.12.

The latter was prepared in 50% yield by the (Speier's) catalyzed addition of dimethylchlorosilane to 1,5-hexadiene; bp 99° (1 mm). *Anal.* Calcd for C₁₀H₂₄Cl₂Si₂: Cl, 26.19. Found: Cl, 27.30.

Preparation of the Silylhydrazines.—The preparation of III is described in detail below; the other silylhydrazines were prepared in an analogous manner.

A three-necked 250-ml round-bottom flask was equipped with a magnetic stirrer, an addition funnel, a condenser, and a gas inlet tube. Into this flask were put 5 g (0.16 mol) of hydrazine (distilled from barium oxide) and 50 ml of petroleum ether (bp

30-60°). The vessel was then flushed with argon for 20 min with stirring. At this point 12 g (0.052 mol) of 1,3-bis(chlorodimethylsilyl)-*n*-propane dissolved in 50 ml of petroleum ether was introduced into the addition funnel and the solution was added dropwise. Immediately, a white precipitate formed. After the addition was complete the mixture was refluxed for several hours. Subsequently the mixture was suction filtered in an inert-atmosphere box under argon, and the solution was transferred to a distillation flask which was attached to a 6-in. Vigreux column. The solvent was removed at about 100 mm pressure with stirring. The distillation was then done at 23 mm pressure. A fraction weighing 7.3 g (68% yield) was collected at 87-88° (23 mm).

Immediately after collection the material was examined gas chromatographically. Anomalous peaks showed up unless the flow rate was kept above 100 ml/min. Under this condition the material appeared to be pure.

Of the other compounds prepared I and VIII showed no tendency to decompose during gas chromatography, IV behaved similarly to III, no trace of volatile product was found with V and IX, and VI and VII gave a complex pattern of gas chromatographic peaks indicating complete decomposition.

Compound I is a greasy solid and during distillation the condenser had to be heated periodically to keep it clear. In an early preparation compound VIII was isolated by distillation. During this process an explosion occurred while the last trace of distillate was being driven over with a heat gun. Subsequently, work-up was done in a sublimator as described below.

Compounds II, X, XI, XIII, and XIV were prepared by previously reported methods.^{3,5,15,16} The following are analytical and physical data for the new compounds prepared in this study.

For compound I the yield was 79%; bp 122-125° (25 mm). *Anal.* Calcd for C₁₀H₂₈N₂Si₄: C, 41.66; H, 9.72; N, 9.72; Si, 38.90. Found: C, 41.82; H, 9.75; N, 10.36; Si, 40.55.

The nmr spectrum shows signals at τ 9.88 (methyl) and 10.05 (methylene).

The ir spectrum shows the following absorptions (in cm⁻¹): 2907 (s), 2895 (m) (CH str); 1390 (w), 1300 (w) (CH def); 1240 (s) (CH₃Si def); 1040 (m) (NN str);³ 1000 (s), 970 (s) (SiNSi asym str, SiCH₃Si str); 810 (s), 790 (s), 740 (m), 700 (s), 680 (w), 650 (w), 630 (w) (SiC str, CH₃ rock); 550 (w) (SiNSi sym str).

For compound III the yield was 68%; bp 87-88° (23 mm). *Anal.* Calcd for C₇H₂₀Si₂N₂: C, 44.68; H, 10.64; N, 14.89; Si, 29.75. Found: C, 44.32; H, 10.36; N, 15.40; Si, 29.99.

The nmr spectrum of this material shows signals at τ 7.33 (NH₂), 8.11 (β -methylene), 9.16 (α -methylene), and 9.78 (methyl).

The ir spectrum shows the following absorptions (in cm⁻¹): 3310 (w), 3240 (w) (NH₂ str); 2940 (s), 2890 (s), 2840 (m) (CH str); 1550 (m) (NH₂ def); 1450 (w), 1400 (m), 1330 (w) (CH def); 1240 (s) (CH₃Si def); 1090 (m), 1075 (m) (NN str); 1020 (w), 985 (s) (SiNSi asym str); 930 (m), 900 (s), 870 (s), 820 (s), 780 (s), 670 (m), 615 (w), 600 (w) (SiC str, CH₃ rock); 490 (w) (SiNSi sym str).

A solution of this material in benzene with a few milligrams of potassium dissolved in it was sealed off in an nmr tube and heated at 90° for 48 hr. Periodic examination of the nmr spectrum showed no change.

For compound IV the yield was 40%; bp 84-85° (10 mm). During work-up the hydrazine hydrochloride codistilled with this material. For final purification it was centrifuged at 7000 rpm for 5 min. *Anal.* Calcd for C₈H₂₂N₂Si₂: C, 47.52; H, 10.89; N, 13.86; Si, 27.72. Found: C, 47.34; H, 10.95; N, 14.22; Si, 27.49.

The nmr spectrum of this material shows signals at τ 7.31 (NH₂), 8.13 (β -methylene), 9.18 (α -methylene), and 9.75 (methyl). This material was sealed in an nmr tube with a few milligrams of

(14) J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 4495 (1956).

(15) U. Wannagat and E. O. Brandstatter, *Angew. Chem.*, **75**, 345 (1963).
(16) F. Hofer and E. U. Wannagat, *Monatsh. Chem.*, **97**, 2038 (1966).

potassium and heated to 90° for 96 hr. The nmr spectrum was recorded periodically with no change being observed. The viscosity of the nmr solution remained (qualitatively) the same throughout this period.

The ir spectrum of this material shows the following absorptions (in cm^{-1}): 3315 (w), 3250 (w) (NH_2 str); 2940 (s), 2890 (s), 2840 (m) (CH str); 1550 (m) (NH_2 def); 1440 (m), 1400 (m), 1330 (w) (CH def); 1230 (s) (CH_3Si def); 1110 (m), 1060 (m) (NN str); 1000 (s) (SiNSi asym str); 880 (s), 845 (s), 810 (s), 780 (s), 690 (m), 610 (w) (SiC str, CH_3 rock); 490 (w) (SiNSi sym str).

For compound V, which was nonvolatile, the final step of the work-up involved simply pumping off the pentane. Care was taken not to heat the material before the equilibrium studies. The resulting viscous liquid was cloudy, indicating the presence of hydrazine hydrochloride. The material was then centrifuged for 60 min at 10,000 rpm. A clear upper layer was thus formed and further studies were carried out on this upper layer. *Anal.* Calcd for $\text{C}_{10}\text{H}_{28}\text{N}_2\text{Si}_2$: C, 51.28; H, 12.82; N, 12.00; Si, 23.93. Found: C, 52.09; H, 11.25; N, 12.00; Si, 23.68. The molecular weight is 938.

The nmr spectrum shows signals at τ 7.30 (NH_2), 7.62 (NH), 8.41 (β , γ -methylene), 9.21 (α -methylene), 9.69 (methyl), and 9.73 (methyl). The sample prepared in the method indicated above appeared to be, on the basis of the τ 9.69 and 9.73 signal ratio, 16% in the form of the 1,1 isomer. It was heated for 96 hr at 100° and the spectrum was run (at room temperature) after 12, 36, 48, 72, and 96 hr. The sample was 36% 1,1 isomer after 12 hr and did not change in composition thereafter.

The ir spectrum of the freshly prepared material shows the following absorptions (in cm^{-1}): 3340 (w) (NH str); 2940 (m), 2910 (s), 2850 (m) (CH str); 1450 (w), 1390 (w) (CH def); 1240 (s) (CH_3Si def); 1180 (w), 1140 (w) (CH_2 wag); 1000 (w) (SiNSi asym str); 830 (s), 780 (s), 680 (w) (SiC str and CH_3 rock).

For compound VI the yield was 54%; bp 80° (1 mm). *Anal.* Calcd for $\text{C}_{10}\text{H}_{22}\text{N}_2\text{Si}_4$: C, 41.09; H, 10.95; N, 9.59; Si, 37.67. Found: C, 41.44; H, 10.90; N, 9.34; Si, 38.21.

The nmr spectrum of this material shows signals at τ 7.30 (NH_2), 7.53 (NH), 9.63 (α -methyl), and 9.68 (β -methyl). The ratios of the NH_2 to NH signals of two separately prepared samples indicate that the material is 20% 1,1 isomer. A sample of this material, heated for several days at 100° in a sealed nmr tube in the absence of a catalyst, showed a gradual increase of a signal at τ 7.23 while the NH_2 :NH signal ratio remained constant. By the end of this period of heating several new signals in the τ 9.50–9.70 region had appeared. A sample heated in the presence of a trace of sodium in an nmr tube for 24 hr showed an nmr signal at τ 7.10 which was approximately equal in size to the τ 7.53 signal. The NH_2 :NH signal ratio again stayed approximately constant. When this latter experiment was concluded, the nmr tube was broken and the ir spectrum of the solution was recorded. The 3315:3250 cm^{-1} band ratio had not been altered.

The spectrum of VI shows absorptions (in cm^{-1}) at: 3315 (w), 3250 (vw) (NH, NH_2 str); 2910 (s), 2880 (s), (CH str); 1550 (vw) (NH_2 def); 1480 (w), 1380 (m) (CH def); 1230 (s) (CH_3Si def); 1040 (m) (SiOSi asym str); 980 (m) (SiNSi asym str); 830 (s), 780 (s), 680 (m) 600 (m) (SiC str, CH_3 rock); 500 (w) (SiNSi sym str); 480 (vw); 420 (vw) (SiSi str).

For compound VII the yield was 80%; bp 106° (1 mm). *Anal.* Calcd for $\text{C}_{14}\text{H}_{44}\text{N}_2\text{Si}_8$: C, 41.17; H, 10.78; N, 6.86; Si, 41.17. Found: C, 39.95; H, 10.50; N, 6.32; Si, 39.61.

The nmr spectrum of VII shows signals at τ 7.31, 7.43, and 7.48, with the τ 7.43 signal containing about 70% of the area (NH), and at τ 9.55 (α -methyl), 9.60, 9.61 (β -methyl), and 9.63

(γ -methyl).¹⁷ This spectrum was run at room temperature and several temperatures up to 120°. Increasing the temperature brought about a broadening of the NH signals and a narrowing of the methyl signals. The splitting of the β -methyl signal remained at 1 cps throughout.

The spin decoupling experiment was done by irradiating the NH signal and observing the methyl signals. The splitting of the β -methyl signal did not collapse.

In a subsequent experiment the sample was diluted stepwise from 40 to 2% and the nmr spectrum of each solution was recorded. The splitting of the β -methyl signal remained at 1 cps throughout.

The ir spectrum of XI shows absorptions (in cm^{-1}) at: 3310 (w) (NH str); 2935 (s), 2880 (s) (CH str); 1420 (m), 1380 (s) (CH def); 1250 (s) (CH_3Si def); 1030 (w) (SiOSi asym str); 830 (s), 770 (s), 720 (m), 680 (m), 625 (m), 610 (m) (SiC str, CH_3 rock); 460 (w) (SiSi asym str).

For compound VIII, work-up was completed by vacuum sublimation at 100° (0.2 mm). The yield was 37%; mp 83–87°. *Anal.* Calcd for $\text{C}_8\text{H}_{28}\text{N}_4\text{Si}_4$: C, 32.86; H, 9.64; N, 19.18; Si, 38.21. Found: C, 32.58; H, 9.66; N, 19.37; Si, 38.04.

The nmr spectrum of this material shows signals at τ 7.30 (NH_2) and 9.58 (methyl). The nmr spectrum of a solution of this material which was heated at 90° in a sealed tube for 66 hr showed no change. When a similar solution containing a few milligrams of potassium was heated for 66 hr the τ 7.30 signal completely disappeared and a broad signal at τ 7.09 appeared.

The ir spectrum of VIII shows the following absorptions (in cm^{-1}): 3310 (w), 3240 (w) (NH_2 str); 2940 (s), 2880 (m) (CH str); 1550 (m) (NH_2 def); 1420 (m); 1380 (m) (CH def); 1235 (s) (CH_3Si def); 1070 (m) (NH str); 980 (s) (SiNSi asym str); 880 (s), 800 (s), 650 (m) (SiC str, CH_3 rock); 500 (m) (SiNSi sym str).

For compound IX, which is not volatile, the final step of the work-up entails only pumping off the pentane. The resulting viscous opaque liquid was centrifuged at 10,000 rpm for 30 min and the upper, clear layer was used for further observations. *Anal.* Calcd for $\text{C}_6\text{H}_{20}\text{N}_2\text{Si}_3$: C, 35.30; H, 9.80; N, 13.72; Si, 41.17. Found: C, 35.11; H, 9.58; N, 13.31; Si, 41.51. The molecular weight is 1030.

The nmr spectrum of XII consists of a broad complex signal centered at τ 7.28 (NH_2 , NH) and a broad signal centered at τ 9.63 with sharp signals at τ 9.60 and 9.66 superimposed (methyl).

The ir spectrum of IX shows the following absorptions (in cm^{-1}) at: 3310 (w), 3240 (sh) (NH_2 , NH str); 2940 (s), 2880 (s) (CH str); 1400 (m) (CH def); 1230 (s) (CH_3Si def); 1040 (m) (SiOSi asym str); 990 (m) (SiNSi asym str); 820 (s), 780 (s), 640 (w), 620 (w) (SiC str, CH_3 rock); 400 (vw) (SiSi str).

For compound X, the nmr spectrum of X was run at room temperature and at 120°. The isomer ratio remained 1:1 at 120° for over 60 min. The only effect of the increased temperature was a broadening of the hydrazyl proton signals and a sharpening of the methyl signals.

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