

0.1 *M*, the racemization rate in acetone or acetonitrile is considerably greater than the ionization rate (estimated as above from the isomerization rate and the k_S/k_N ratio). Since in mechanism b the value of k_1 (eq 3) sets the upper limit of all processes occurring through the intermediacy of ion pairs (see, however, ref 23), exchange, and racemization through exchange, must occur largely by way of direct displacement on the substrate. Thus, also this piece of evidence favors mechanism a against b for the 4-chlorobenzhydryl substrate both in acetone and in acetonitrile and, *a fortiori*, for other more electron-attracting substrates.

Experimental Section

Solvents and Materials. Acetonitrile was first dried over Drierite, refluxed over phosphorous pentoxide, and distilled. From redistillation over potassium carbonate the fraction bp 81.5–81.6° was collected. Commercial reagent grade acetone was refluxed over potassium permanganate and distilled. From redistillation over potassium carbonate the fraction bp 56.4–56.5° was collected.

Labeled NaSCN (³⁵S) was obtained as previously described.³⁶

3-Chlorobenzhydryl Bromide. Friedel–Crafts reaction of 3-chlorobenzoic acid chloride with benzene gave 3-chlorobenzophenone. This was reduced with LiAlH₄ and the alcohol converted to the bromide with HBr in ether. The product was distilled under reduced pressure: bp 158–159° (0.4 mm). *Anal.* Calcd for C₁₃H₁₀ClBr: Br, 29.92. Found: Br, 28.84.

3-Chlorobenzhydryl Thiocyanate. Reaction of the bromide with KSCN in acetone⁵ afforded a thick oil which in our hands did not crystallize. After removal of volatiles, it was sublimed at 50° and 0.01 mm. No further purification was attempted. *Anal.* Calcd for C₁₄H₁₀NCIS: N, 5.37; Cl, 13.65; S, 12.32. Found: N, 5.31; Cl, 13.43; S, 12.50.

4,4'-Dinitrobenzhydryl Bromide. Diphenylmethane was nitrated to give 4,4'-dinitrodiphenylmethane, mp 183° (lit.³⁷ 183°). The bromide was obtained by reaction with bromine in CCl₄ in the presence of benzoyl peroxide, according to the method of Wragg,

*et al.*³⁸ To improve the bromination yield it was found useful to increase the reaction time from 0.5 hr at reflux, as suggested by Wragg, *et al.*,³⁸ to 1.5 hr.

After evaporation of the solvent, the residue was fractionally crystallized from acetone–petroleum ether. The first crop of crystals melted at 181°, contained no bromine, and appeared to be essentially pure 4,4'-dinitrodiphenylmethane. The second crop melted at 84–86° and had a high bromine content, 25.1%. It was fractionally crystallized from CCl₄, the first fraction, mp 92–93° (lit.³⁸ 90.5°), giving a satisfactory bromine analysis. *Anal.* Calcd for C₁₃H₉N₂O₄Br: Br, 23.7. Found: Br, 24.4.

4,4'-Dinitrobenzhydryl Thiocyanate. The bromide was treated with KSCN in acetone.⁵ After evaporation of the solvent, the residue was extracted with water–cyclohexane. The organic layer was washed, dried over Na₂SO₄, and evaporated. The residue was crystallized from acetone–light petroleum; mp 135–36°. *Anal.* Calcd for C₁₄H₉N₃O₄S: N, 13.33; S, 10.16. Found: N, 13.20; S, 10.23.

All other products used in this and in the previous work³ have been described.^{5,39}

Kinetics. Isotopic Exchange. In the “slow” runs, taking place at 70°, the solutions of organic thiocyanate, sodium thiocyanate, and sodium perchlorate were mixed at room temperature in the appropriate volumetric ratio to give the desired concentration of reactants. The two salts were so adjusted as to give a total 0.1 *M* concentration of electrolyte, while the ionic thiocyanate was varied between 0.001 and 0.01 *M*. Three-milliliter portions of the solution were sealed in ampoules and put in a thermostat from which they were withdrawn at appropriate time intervals. For the “fast” runs, taking place at, or below, room temperature, the solutions of the organic and of the ionic reactants were mixed at the temperature of the experiment by inverting the Y-shaped reaction vessel. Samples were pipetted out at appropriate time intervals. The work-up and counting procedures have been described.⁵ The rate constants reported in Table I are uncorrected for expansion.

Isomerization. The rates of isomerization in acetone, necessary to estimate the ionization rate (eq 5), have been measured by infrared spectrophotometry as previously described.⁵

(38) A. H. Wragg, T. S. Stevens, and D. H. Ostle, *J. Chem. Soc.*, 4057 (1958).

(39) A. Iliceto, A. Fava, U. Mazzucato, and P. Radici, *Gazz. Chim. Ital.*, 90, 919 (1960).

(36) A. Fava and A. Iliceto, *Ric. Sci.*, 25, 54 (1955).

(37) N. Staedel, *Ann.*, 283, 151 (1895).

Anionic Rearrangement of Hydrazines. II.¹ Isomers of Bis(organosilyl)hydrazines²

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Contribution from the Department of Chemistry, The University of Wisconsin, Madison, Wisconsin 53706. Received July 11, 1966

Abstract: Eight new bis(organosilyl)hydrazines have been prepared, comprising four sets of 1,1 and 1,2 isomers. Isomeric structural assignments are made based mainly on a new method involving the splitting between the infrared N–H stretching modes, which is greater for 1,1- than for 1,2-hydrazines. Structures are also assigned for the known bis(trimethylsilyl)hydrazines, reversing the assignment made previously.^{1,3,4}

Rearrangement of silylhydrazines in the presence of *n*-butyllithium was first observed in our laboratories in 1964.¹ Work following this original discovery

(1) For part I see R. E. Bailey and R. West, *J. Am. Chem. Soc.*, 86, 5369 (1964).

(2) Research sponsored by Air Force Office of Scientific Research (SRC), O.A.R., U.S.A.F., Grant No. AF-AFOSR 1061–66.

(3) (a) U. Wannagat and H. Liehr, *Angew. Chem.*, 69, 783 (1957); (b) *Z. Anorg. Allgem. Chem.*, 297, 129, 133 (1958); (c) U. Wannagat and C. Krüger, *Monatsh. Chem.*, 93, 613 (1964).

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

shows that the anionic rearrangement of organosilylhydrazines is a remarkably general and surprisingly rapid reaction.⁵ The experimental evidence and conclusions drawn from it will be explained in succeeding papers in this series.

The rearrangement reaction was first noted for bis(trimethylsilyl)hydrazine,¹ and many of the later rear-

(5) R. West and R. E. Bailey, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p 4M.

Table I. N-H Infrared Stretching Frequencies, Proton Nmr Chemical Shifts, and Relative Gas Chromatographic Retention Times of Bis(organosilyl)hydrazines

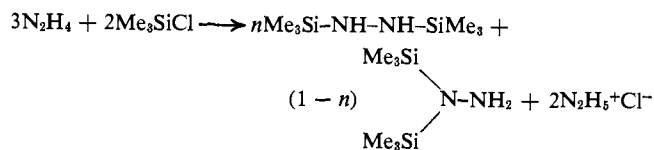
Compound	ν_{N-H} , cm ⁻¹	$\Delta\nu$	δ_{N-H} , τ	δ_{SiCH_3} , τ	δ_{SiCCH_3} , τ	RT, gc
Me ₃ SiNHNHSiMe ₃	3370, 3347	23	7.71	9.99		1
(Me ₃ Si) ₂ NNH ₂	3347, 3267	80	7.31	9.92		1.6
EtMe ₂ SiNHNHSiMe ₂ Et	3346	0	7.74	10.03	<i>a</i>	1
(EtMe ₂ Si) ₂ NNH ₂	3349, 3261	88	7.35	9.97	<i>a</i>	1.3
<i>t</i> -BuMe ₂ SiNHNHSiMe ₂ - <i>t</i> -Bu	3343	0	7.67	10.02	9.11	1
(<i>t</i> -BuMe ₂ Si) ₂ NNH ₂	3350, 3274	76	7.25	9.92	9.08	1.4
EtMe ₂ SiNHNHSiMe ₃	3340	0	7.73	10.02, 10.00	<i>a</i>	1
EtMe ₂ SiN(SiMe ₃)NH ₂	3347, 3265	82	7.34	9.97, 9.94	<i>a</i>	1.2
<i>t</i> -BuMe ₂ SiNHNHSiMe ₃	3351, 3343	7	7.74, 7.67	10.03, 9.99	9.11	1
<i>t</i> -BuMe ₂ SiN(SiMe ₃)NH ₂	3355, 3270	85	7.27	9.92, 9.90	9.09	1.3

^a Complex Si-CH₂-CH₃ pattern in the region τ 8.94-9.59.

rangement experiments also involve 1,1- and 1,2-bis-(trialkylsilyl)hydrazines. Knowledge of the correct isomeric structure for such compounds is obviously important in this research. However, identification of the isomers of a bis(trialkylsilyl)hydrazine presents a difficult problem because, as will be shown below, chemical methods generally fail to distinguish between the 1,1 and 1,2 isomers. As a result, all previous workers, ourselves included, have made what now appear to be erroneous structural assignments for 1,1- and 1,2-bis(trimethylsilyl)hydrazine.^{1,3,4}

In this paper, isomeric structures are given for five pairs of bis(organosilyl)hydrazines. All of the compounds except the two bis(trimethylsilyl)hydrazines are previously unreported. The structural assignments are based on a new method using the differences in N-H stretching absorption patterns for 1,1- and 1,2-disubstituted hydrazines.

Preparation of Bis(trialkylsilyl)hydrazines. Most of our present knowledge of organosilylhydrazines is due to the synthetic studies of Wannagat and his co-workers.⁵ In 1957 Wannagat and Liehr reported the synthesis of bis(trimethylsilyl)hydrazine from the reaction of trimethylchlorosilane with 1.5 molar equiv of hydrazine.^{3a} Basing their conclusions on chemical evidence only, these workers assigned the 1,2 structure to the product.³ This substance was also prepared in 1962 by Bock, who used similar reasoning from chemical reactions to make the same deduction about its structure.⁴ When the reaction was repeated in our laboratories following the directions of Wannagat and Liehr we obtained a liquid product having the properties described by the previous workers and analyzing for bis(trimethylsilyl)hydrazine. The proton nmr spectrum of the material indicated, however, that both 1,1 and 1,2 isomers were present in nearly equal amount (Figure 1).¹



Separation of the pure isomers was effected by gas chromatography. The isomer with longer retention time had two proton nmr peaks at τ 9.92 and 7.31 in the ratio 9:1, assignable to CH₃-Si and N-H resonances respectively, and the other isomer had

(6) For a review see U. Wannagat, *Advan. Inorg. Chem. Radiochem.*, **6**, 225 (1964).

similar resonances at τ 9.99 and 7.71 with the same intensity ratio (Table I, Figure 1).

When a similar synthesis was carried out using ethyldimethylchlorosilane and hydrazine, a mixture of the two isomers of bis(ethyldimethylsilyl)hydrazine was obtained, this time in a 64:36 mole ratio. However, when the reaction was carried out with *t*-butyldimethylchlorosilane, the product consisted exclusively of one isomer. Inspection of models suggests, and the results of further experiments confirm, that attachment of two *t*-butyldimethylsilyl groups to a single nitrogen atom is greatly hindered sterically. It therefore seems probable *a priori* that the isomer of bis(*t*-butyldimethylsilyl)hydrazine produced in large amount is the 1,2 isomer.

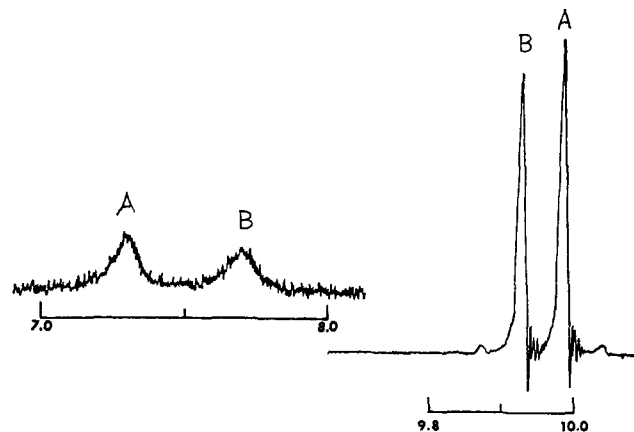
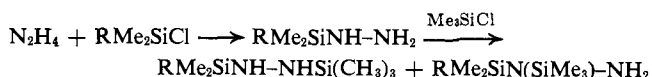


Figure 1. Proton nmr spectrum of mixture of bis(trimethylsilyl)hydrazine isomers obtained in the synthesis from hydrazine and trimethylchlorosilane. Peaks marked A and B are due to the 1,2 isomer and 1,1 isomer, respectively. Units are τ values.

Preparation of bis(trialkylsilyl)hydrazines with different R₃Si groups was accomplished by sequential reaction of hydrazine with two different chlorosilanes, *i.e.*



For R = ethyl a mixture of isomers was produced as expected, but for R = *t*-butyl a single substance, later identified as the 1,2 isomer, was again obtained almost exclusively.

The anionic rearrangement reaction described in our earlier communication^{1,5} was used to obtain the 1,1

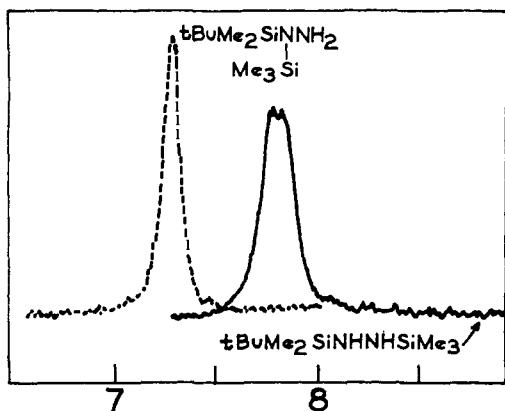
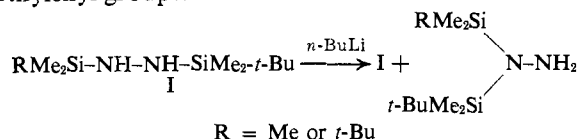


Figure 2. Nmr spectra of N-H protons for *t*-butyldimethylsilyl-(trimethylsilyl)hydrazine isomers, 20% in carbon tetrachloride.

isomers of the two compounds containing *t*-butyldimethylsilyl groups.



Identification of Isomers by Physical Methods. An unambiguous structural assignment from the proton nmr spectrum is possible, in principle, for disubstituted hydrazines in which the two substituents are different. In such compounds, the two nitrogens and their attached protons are equivalent in the 1,1 isomer, RR'N-NH₂, but different in the 1,2 isomer, RNH-NHR'. Only one N-H resonance is possible for the 1,1 isomer but two are predicted for the 1,2 compound. Examples are provided by the *t*-butyldimethylsilyl-(trimethylsilyl)hydrazines, whose proton nmr spectra in the N-H region are shown in Figure 2. The spectrum of one isomer has only a single, relatively sharp N-H resonance. However, the isomer which is produced in overwhelming amount in the synthesis from hydrazine and chlorosilanes shows a broad band in which two different N-H resonances are nearly resolved. The latter compound must therefore be the 1,2 isomer, as predicted above.

The nmr method of course cannot be used for disubstituted hydrazines when the substituents are the same, for then the N-H protons are chemically equivalent in both isomers. It also fails if the two N-H resonances for the 1,2-disubstituted compound happen to overlap, as is likely if the two substituents are not very different. Thus only one N-H peak is found in the N-H region for both isomers of ethyldimethylsilyl-(trimethylsilyl)hydrazine (Table I), although the peak for the 1,2 isomer is unusually broad.

The infrared spectra of the two isomers of disubstituted hydrazines should differ in the N-H stretching region, whether or not the substituent groups are different. In RRN-NH₂, the two N-H modes should interact strongly to give in-phase and out-of-phase stretching bands of markedly different frequency. In RNH-NHR, coupling between the two N-H stretching modes should be weak, and the splitting should be small or nonexistent.

N-H stretching frequencies of substituted hydrazines have not been studied previously and are not easy to observe. The bands are quite weak, but the compounds

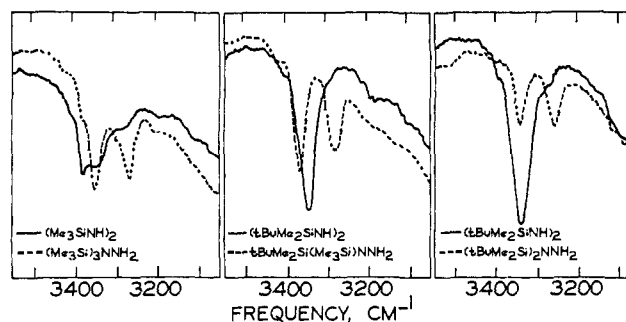


Figure 3. Infrared N-H stretching bands for bis(organosilyl)hydrazine isomers, 2.5% in dry carbon tetrachloride; —, 1,2 isomers; ---, 1,1 isomers.

must nevertheless be studied at high dilution to avoid complications due to hydrogen bonding. An unusually long path length therefore is necessary. Proton-containing solvents interfere, so a halogenated solvent must be used, but hydrazines react fairly rapidly with chlorinated solvents including ordinary reagent grade carbon tetrachloride. However, solutions prepared in *carefully dried* carbon tetrachloride were found to be stable for many hours and so were suitable for spectral study.

Infrared spectra in the N-H stretching region for typical isomer pairs are shown in Figure 3. Data in Table I show that this infrared method distinguishes between the 1,1 and 1,2 isomers of diorganosilylhydrazines in each of the five cases studied. The frequency shift between the symmetric and antisymmetric N-H bands in the 1,1 isomers is remarkably constant, falling between 76 and 88 cm⁻¹. The frequency shift for the 1,2 isomers is sometimes so small as to be unobserved, but rises to a maximum of 23 cm⁻¹ for Me₃SiNH-NHSiMe₃.

This infrared method for determining the structures of disubstituted hydrazine isomers appears to be generally applicable. In dimethyl-, diphenyl-, and methylphenylhydrazine cases, where isomeric structures are certain from chemical evidence, a greater NH splitting is always found for the 1,1 isomer. However, the method will be useful principally for organometallic and other reactive hydrazines for which chemical methods of structural assignment are unsuitable.

The 1,1 and 1,2 isomers of diorganosilylhydrazines can be distinguished by other properties which compounds of each type have in common. Knowing the structures of the hydrazine isomers in Table I, it is possible to assign the strong band at 1000 cm⁻¹ in the infrared spectrum of each of the 1,1 isomers (Table II) to an Si-N-Si stretching mode. A band at similar frequency appears in the infrared spectrum of hexamethylsilazane and other silazanes. It is also apparent that in the disilylhydrazines studied, the 1,1 compounds all have longer gas chromatographic retention times than their 1,2 isomers (Table I). Moreover, in every case the silylmethyl protons appear at lower field in the nmr spectrum for the 1,1 isomers. These patterns of similarity provide corroborative evidence for the correctness of the structural assignments made on the basis of the infrared and nmr data.^{7,8}

(7) The mass spectra of the two isomers of bis(trimethylsilyl)hydrazine also confirm our structural assignment.⁸

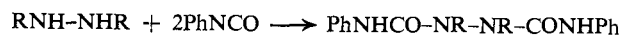
(8) Unpublished studies by J. V. Urenovitch and H. Hobrecht, privately communicated by J. V. U.

Table II. Infrared Spectral Absorption Frequencies (cm⁻¹) for Bis(organosilyl)hydrazines

(Me ₃ Si) ₂ - NNH ₂	(Me ₃ - SiNH) ₂	(EtMe ₂ Si) ₂ - NNH ₂	(EtMe ₂ - SiNH) ₂	EtMe ₂ Si- (Me ₃ Si)- NNH ₂	EtMe ₂ - SiNHNH- SiMe ₃	(<i>t</i> -BuMe ₂ - Si) ₂ NNH ₂	(<i>t</i> -BuMe ₂ - SiNH) ₂	<i>t</i> -BuMe ₂ N- (Me ₃ Si)- NH ₂	<i>t</i> -BuMe ₂ - SiNHNH- SiMe ₃	Assignment
3350 w 2970 s	3350 w 2970 s	3360 w 2970 vs	3360 w 2970 vs	3350 w 2960 vs	3340 w 2960 vs	3360 w 2960 vs	3360 w 2960 vs	3350 w 2970 vs	3350 w 2970vs	N-H stretch
						2940 vs	2940 vs	2940 s	2940 s	
2910 m	2910 m	2920 m 2890 m	2930 m 2890 m	2900 m 2880 m	2900 m 2880 m	2890 m 2870 s	2895 m 2870 s	2890 m 2870 s	2900 m 2870 s	C-H stretch
1450 w	1460 w	1465 w	1465 w	1460 w	1455 w	1480 m 1475 m	1475 m 1465 m	1475 m 1465 m	1475 m 1465 m	
1405 w	1415 m	1410 w	1410 w	1400 w	1390 w	1390 w 1365 w	1390 w 1365 w	1390 w 1360 w	1390 m 1365 w	C-H def
1255 s	1270 s	1255 vs	1250 vs	1250 vs	1250 vs	1260 vs	1255 vs	1250 vs	1250 vs	
1070 m	1110 w 1020 w	1070 w	1070 w 1020 m	1065 m	1050 m	1070 w	1000 w	1075 m	1075 w	CH ₃ -Si def
1010 vs		1000 vs		1000 vs		1015 s 1000 vs		1000 vs	1010 w	
		960 m	960 w	960 w	950 w	940 w	930 w	885 s	990 w	C-C stretch
900 s	880 s	875 s	858 vs	880 s	870 s	880 s	850 vs	885 s	880 s	
830 vs	835 s	840 vs	835 vs	835 vs	835 vs	840 vs	830 vs	835 vs	840 vs	Si-C stretch and CH ₃ rocking
		780 vs		800 s		795 s	810 m	800 s	815 s	
755 m	745 m			775 s	775 s	780 s	775 s	770 s	785 s	
685 m		710 m	710 m	740 m	735 m			750 w	750 m	
				680 m		685 w		680 m	685 m	
					650 m	670 m	650 m		650 m	

Chemical Evidence for Isomer Structure. Our structural assignment conflicts with that previously made for the bis(trimethylsilyl)hydrazines.^{1,3,4} We shall now reexamine the evidence previously put forward for the structure of these two isomers, which led earlier workers to incorrect assignments. Most of the previous workers who identified their product as the 1,2 isomer were probably dealing with mixtures of the two isomers; but we find that the 1,2 isomer is preferentially decomposed upon heating with metals such as platinum,⁹ and so some of the earlier samples may have been mostly the 1,1 isomer.

All of the previous assignments were based on chemical reactions. Of these the most carefully studied are the reaction of the hydrazine with phenyl isocyanate (or isothiocyanate) to give N,N'-hydrazine dicarboxanilide (or its dithio analog). This is a well-known reaction which ordinarily takes place only with the 1,2 isomer of disubstituted hydrazines.



Using this approach, Wannagat and Krüger^{3c} reported that bis(trimethylsilyl)hydrazine reacted with phenyl isocyanate to give, after hydrolysis, a nearly quantitative yield of PhNHCO-NHNH-CONHPh. The intermediate bisilyl compound could not be isolated. In the reaction with phenyl isothiocyanate a product was obtained which after purification analyzed for PhNHCS-NSiMe₃-NSiMe₃-CSNHPh, and hydrolyzed to give PhNHCS-NH-NH-CSNHPh. However, from the experimental description it seems likely that the original product may have contained other materials.

We find, however, that *both* the 1,1 and 1,2 isomers of bis(trimethylsilyl)hydrazine, when treated with PhNCO and then hydrolyzed, give PhNHCO-NHNH-CONHPh in high yield. Phenyl isocyanate must cleave Si-N bonds to give a 1,2-disubstituted product in its reaction with the 1,1 isomer. This conclusion is substantiated

(9) Some isomerization of 1,2- to 1,1-bis(trimethylsilyl)hydrazine appears to accompany the preferential decomposition of the 1,2 isomer in this reaction, which is not yet well understood.

by the work of Fink, who shows that Si-N bond cleavage takes place readily in other Si-N compounds when they are treated with phenyl isocyanate.¹⁰ Indeed, the Si-N bonds are labile toward all of the usual reagents which react with N-H linkages in hydrazines. It is apparent that reactions of this kind cannot be used for assignment of structures to organosilylhydrazines.

Experimental Section

Spectra. Infrared spectra of thin liquid films were determined using a Perkin-Elmer Model 237 Infracord grating spectrometer. Observed absorption bands are listed in Table II. The N-H stretching region was studied with a Perkin-Elmer Model 421 spectrometer, using 5 and 2.5% solutions in P₂O₅-dried carbon tetrachloride in a 1.0-mm cell with sodium chloride windows. Proton nmr spectra were determined with a Varian Model A-60 spectrometer using 20% carbon tetrachloride solutions containing cyclohexane as an internal standard. Chemical shifts were converted to τ values taking 1.44 ppm as the shift between cyclohexane and tetramethylsilane; data are given in Table I.

Gas Chromatography. An Aerograph Model A-700 gas chromatograph with a thermal conductivity detector was used for separations reported here. Silylhydrazine isomers were easily separated by using a column containing 30% methyl silicone polymer (3/8 in. \times 25 ft) on 20-40 mesh Chromosorb W. The best results were obtained with column temperatures 30 to 50° below the boiling point of the silylhydrazine and a helium flow rate of 200 ml/min.

Materials. Anhydrous hydrazine (Eastman Organic Chemicals) was purified by two distillations from barium oxide under an aspirator vacuum. *n*-Butyllithium (hexane solution) was obtained from the Foote Mineral Co. 2-Bromopropene (Columbia Organic Chemicals Co., Inc.), required as starting material for the preparation of *t*-butyldimethylchlorosilane, was purified by distillation using a spinning band column. Trimethylchlorosilane (Dow Corning) was used as received. Ethyldimethylchlorosilane¹¹ was prepared in the standard manner by the reaction of dimethyldichlorosilane (Dow Corning) with ethylmagnesium bromide. All syntheses were carried out under an atmosphere of dry nitrogen.

***t*-Butyldimethylchlorosilane.** Isopropenyltrimethylsilane¹² was prepared by the reaction of isopropenylmagnesium bromide with trimethylchlorosilane. This compound was converted to *t*-butyl-

(10) W. Fink, *Chem. Ber.*, **97**, 1424, 1433 (1964).

(11) (a) R. N. Lewis, *J. Am. Chem. Soc.*, **69**, 717 (1947); (b) C. Eaborn, *J. Chem. Soc.*, 494 (1953).

(12) L. H. Sommer and F. J. Evans, *J. Am. Chem. Soc.*, **76**, 1186 (1954).

dimethylfluorosilane by treatment with concentrated sulfuric acid and ammonium hydrogen fluoride, according to the method of Kumada, *et al.*¹³

The preparation of *t*-butyldimethylchlorosilane from the chloro compound also followed a method developed by Kumada and his co-workers.¹⁴ A mixture of 59 g (0.44 mole) of *t*-butyldimethylfluorosilane, 82 g (0.76 mole) of trimethylchlorosilane, and 0.6 g of anhydrous aluminum chloride was heated in a distillation apparatus fitted with a packed column, from the top of which trimethylfluorosilane was collected as it formed. After 18 hr, 33 g (94%) of trimethylfluorosilane was obtained. The residue was fractionally distilled to give 63 g (95%) of *t*-butyldimethylchlorosilane, bp 124–125°, mp 81–82° (lit.¹⁵ bp 125°, mp 91.5°).

1,1- and 1,2-Bis(trimethylsilyl)hydrazine. The procedure of Wannagat and Liehr was followed.^{3a} Trimethylchlorosilane (324 g, 3.0 moles) in 250 ml of dry ether was slowly added to 133 g (4.15 moles) of anhydrous hydrazine mixed with 1 l. of dry ether, with stirring and cooling. The mixture was then refluxed for 18 hr. with stirring. The solution was decanted from the granular precipitate of hydrazine hydrochloride and the ether distilled off. The product, a mixture of isomers, was distilled through a short column under reduced pressure, bp 74–75.5° (47 torr), yield 130 g (55%), n_D^{25} 1.4252, lit.³ n_D^{25} 1.4268. The proportions of the two isomers varied from 40:60 to 50:50 (1,1:1,2) in different preparations. The two isomers were separated by preparative gas chromatography.

Pure 1,1-Bis(trimethylsilyl)hydrazine from a Mixture of Isomers. A 1:1 mixture of 1,1- and 1,2-bis(trimethylsilyl)hydrazines was refluxed for about 24 hr after a small amount of finely divided platinum (in the form of PtO₂) had been added. The mixture was then distilled at atmospheric pressure. Approximately 25% of the original quantity was recovered as hexamethyldisilazane, and 5% as tris(trimethylsilyl)hydrazine. The rest of the mixture was found to be bis(trimethylsilyl)hydrazine, about 95% in the form of the 1,1 isomer, n_D^{25} 1.4320.

1,1- and 1,2-Bis(ethyl dimethylsilyl)hydrazine. To 4.8 g (0.15 mole) of anhydrous hydrazine mixed with 70 ml of dry ethyl ether, 12.3 g (0.10 mole) of ethyldimethylchlorosilane in 50 ml of dry ether was added with stirring. The reaction flask was cooled during the addition, which required about 20 min, and then heated to reflux for 15 hr. The reaction mixture was filtered and washed with ether, and the filtrate and washings were concentrated by evaporation of ether. The residue was distilled under reduced pressure yielding 6.0 g (58%) of colorless liquid product, bp 88–92° (22 torr). Gas chromatographic analysis showed two peaks having an area ratio of 1:1.8 (36:64%) corresponding to the 1,1 and 1,2 isomers of bis(ethyl dimethylsilyl)hydrazine, respectively. The two isomers were separated by preparative gas chromatography.

Anal. Calcd for C₈H₂₂N₂Si₂: C, 46.99; H, 11.83; N, 13.70; Si, 27.48. Found, 1,1 isomer: C, 47.09; H, 11.80; N, 13.50; Si, 27.35. Found, 1,2 isomer: C, 47.18; H, 12.00; N, 13.52; Si, 27.32.

1,1 and 1,2 Isomers of Ethyldimethylsilyl(trimethylsilyl)hydrazine. A solution of 31.9 g (0.26 mole) of ethyldimethylchlorosilane in 30 ml of dry ethyl ether was added to 25 g (0.78 mole) of anhydrous hydrazine in 150 ml of ether, over a period of 15 min with cooling and stirring. Then 28.1 g (0.26 mole) of trimethylchlorosilane was similarly added to the reaction mixture. The flask was stirred for an additional 30 min with cooling and then heated to reflux for 20 hr. The organic layer was decanted from the precipitated hydrazine salts, and the ether was distilled off. Distillation of the residue under reduced pressure gave 38 g of colorless liquid, boiling from 25 to 94° at 14 torr.

Gas chromatographic analysis showed five main peaks having an area ratio of 3.0:1.4:6.2:1.0:3.3, in order of elution. These were ultimately identified as due to 1,2- and 1,1-bis(trimethylsilyl)hydrazine, 1-ethyldimethylsilyl-2-trimethylsilyl- and 1-ethyldi-

methyl-1-trimethylsilylhydrazine, and 1,2-bis(ethyl dimethylsilyl)hydrazine, respectively. The 1,1 and 1,2 isomers of ethyldimethylsilyl(trimethylsilyl)hydrazine were separated by preparative gas chromatography.

Anal. Calcd for C₇H₂₂N₂Si₂: C, 44.75; H, 11.64; N, 14.71; Si, 29.50. Found, 1,1 isomer: C, 44.02; H, 11.49; N, 14.55; Si, 29.29. Found, 1,2 isomer: C, 44.30; H, 11.46; N, 14.62; Si, 29.69.

1-*t*-Butyldimethylsilyl-2-trimethylsilylhydrazine. Anhydrous hydrazine (15.4 g, 0.48 mole) was mixed with 100 ml of dry ethyl ether. With stirring and cooling, over a period of 2 hr, 24 g (0.16 mole) of *t*-butyldimethylchlorosilane in 100 ml of ether followed by 17 g (0.16 mole) of trimethylchlorosilane in 50 ml of ether were added. The reaction mixture was heated to reflux for 20 hr. The organic layer was decanted, and the ether solvent was stripped off. The residue was flash-distilled under vacuum and then fractionally distilled, yielding 19 g (54%) of pure 1-*t*-butyldimethylsilyl-2-trimethylsilylhydrazine, bp 69–70° (7 torr), n_D^{25} 1.4355. By-products included 4.0 g (9%) of 1,2-bis(*t*-butyldimethylsilyl)hydrazine as well as some mixed bis(trimethylsilyl)hydrazines.

Anal. Calcd for C₉H₂₆N₂Si₂: C, 49.47; H, 12.00; N, 12.82; Si, 25.71. Found: C, 49.66; H, 12.15; N, 12.83; Si, 25.50.

1,2-Bis(*t*-butyldimethylsilyl)hydrazine. A mixture of 10.2 g (0.32 mole) of anhydrous hydrazine with 50 ml of dry ethyl ether was treated with 32 g (0.21 mole) of *t*-butyldimethylchlorosilane in 150 ml of ether. The reaction and work-up were similar to those described above. Fractional distillation gave 19 g (70%) of colorless liquid product, bp 118–119° (9 torr), n_D^{25} 1.4456.

Anal. Calcd for C₁₂H₃₂N₂Si₂: C, 55.31; H, 12.38; N, 10.75; Si, 21.56. Found: C, 55.49; H, 12.54; N, 10.97; Si, 21.75.

1-*t*-Butyldimethylsilyl-1-trimethylsilylhydrazine. The 1,2 isomer was rearranged as follows: 10 g of 1-*t*-butyldimethylsilyl-2-trimethylsilylhydrazine was dissolved in 10 ml of cyclohexane and 2.0 ml of 1.6 *M* *n*-butyllithium in hexane was added. The reaction mixture was heated to reflux (100–105°) for 48 hr. To convert the lithium hydrazide to free hydrazine, 0.60 g (0.0036 mole) of diphenylamine was then added. The mixture was then distilled under reduced pressure yielding 8.9 g (89%) of liquid product, bp 88–95° (15 torr). Gas chromatographic analysis showed two peaks with relative areas 28:72 corresponding to the 1,1 and 1,2 isomers, respectively; these were separated by preparative gas chromatography.

Anal. Calcd for C₉H₂₆N₂Si₂: C, 49.47; H, 12.00; N, 12.82; Si, 25.71. Found: C, 49.55; H, 12.10; N, 12.74; Si, 25.47.

1,1-Bis(*t*-butyldimethylsilyl)hydrazine. To 7 ml of cyclohexane was added 7.0 g (0.027 mole) of 1,2-bis(*t*-butyldimethylsilyl)hydrazine and 2 ml of 1.6 *M* *n*-butyllithium in hexane. The mixture was heated to reflux for 62 hr, then cooled and treated with 0.60 g (0.0036 mole) of diphenylamine. Distillation under reduced pressure afforded 6.0 g (86%) of a colorless liquid, bp 67–75° at 2 to 3 torr. Gas chromatographic analysis showed two peaks with an area ratio of 7:93 corresponding to the 1,1 and 1,2 isomers, respectively. The two isomers were separated by gas chromatography.

Anal. Calcd for C₁₂H₃₂N₂Si₂: C, 55.31; H, 12.38; N, 10.75; Si, 21.56. Found: C, 55.49; H, 12.50; N, 10.84; Si, 21.77.

Reaction of Mixed Bis(trimethylsilyl)hydrazines with Phenyl Isocyanate. A sample known from nmr analysis to be a 1:1 mixture of the 1,1 and 1,2 isomers of bis(trimethylsilyl)hydrazine (3.2 g, 0.018 mole) was dissolved in 30 ml of dry *n*-heptane and 4.8 g (0.040 mole) of phenyl isocyanate was added to the solution. The mixture was heated to reflux for 30 min, and then the solvent and excess phenyl isocyanate were removed by distillation under vacuum. The residue was recrystallized from ethanol yielding, after purification, 3.9 g (80%) of N,N'-hydrazinedicarboxyanilide, mp 244–246°, lit.^{3a} 245°.

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(13) M. Kumada, M. Ishikawa, S. Maeda, and K. Ikura, *J. Organometal. Chem.*, **2**, 146 (1964).

(14) M. Kumada, M. Ishikawa, S. Maeda, and K. Naka, unpublished.

(15) L. H. Sommer and L. J. Tyler, *J. Am. Chem. Soc.*, **76**, 1030 (1954).