

once and individual ampoules were removed at recorded times and plunged into ice-cold water. The thermostat used regulated the temperature within 0.05°. The rate of the rearrangement was determined by measuring the change in absorbance at 460, 476, and 450 mμ, respectively, for the different compounds.

Acknowledgment. The financial support from the United Board for Christian Higher Education in Asia and the Graduate School of Yonsei University is gratefully acknowledged.

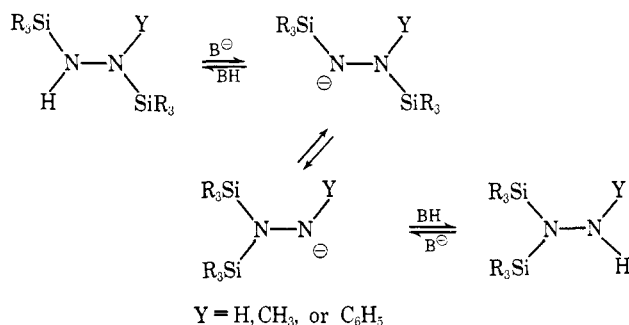
New Anionic Rearrangements. V. Anionic Rearrangement of *t*-Butyldimethylsilylhydrazines^{1,2}

Robert West and Mitsuo Ishikawa

Contribution from the Department of Chemistry, The University of Wisconsin, Madison, Wisconsin 53706. Received May 5, 1967

Abstract: The synthesis and properties of a series of *t*-butyldimethylsilylhydrazines are described. These compounds undergo catalyzed anionic rearrangement with migration of silicon as do other silylhydrazines, but the bulky *t*-butyldimethylsilyl group both retards the rate of rearrangement and alters the equilibrium isomer ratio. Nmr studies of competitive and sequential migration of trimethylsilyl and *t*-butyldimethylsilyl groups in hydrazines containing both substituents support the mechanism proposed for the rearrangement, in which protonation and deprotonation are the rate-determining steps.

Earlier papers in this series have shown that organosilylhydrazines undergo rapid equilibration in the presence of strong bases.²⁻⁴ As explained previously, the silyl groups are believed to migrate from one nitrogen to the other in the hydrazide anion.

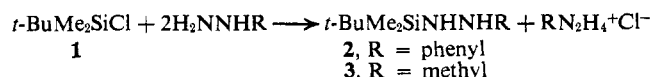


In the above reaction where $Y = H$ or CH_3 and $R_3Si =$ trimethylsilyl or ethyldimethylsilyl, the amounts of 1,1- and 1,2-bis(silyl) isomers present in the equilibrium mixture are nearly equal.⁵ Thus the steric preference for one isomeric form over the other appears to be negligible in these cases.

To investigate steric hindrance in the silylhydrazine rearrangement, we decided to employ a much bulkier migrating substituent, the *t*-butyldimethylsilyl group. This paper reports the synthesis and characterization of a number of *t*-butyldimethylsilylhydrazines, all of which are new compounds, and a study of their behavior in the anionic rearrangement reaction.

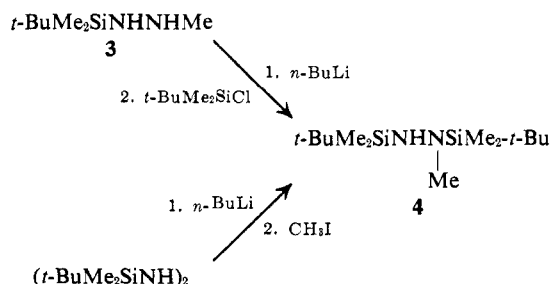
Synthesis. Most syntheses followed methods developed earlier, based originally on those of Wannagat and his co-workers.⁶ In an earlier paper we showed

that phenylhydrazine reacts with trimethylchlorosilane or ethyldimethylchlorosilane to form the 1,2-disubstituted product exclusively.⁵ Similarly, phenylhydrazine reacts with *t*-butyldimethylchlorosilane (1) to give only 1-*t*-butyldimethylsilyl-2-phenylhydrazine (2).



However, the bulky *t*-BuMe₂Si group stabilizes certain hydrazines which cannot be prepared with nonhindering Si substituents. When methylhydrazine (R = CH₃) was used in the above reaction in place of phenylhydrazine, 1-*t*-butyldimethylsilyl-2-methylhydrazine (**3**) was produced. The analogous trimethylsilyl- and ethyldimethylsilylmethylhydrazines are unstable toward further condensation, and we were unable to isolate them.⁵ Both of the *t*-BuMe₂Si compounds were shown to have the 1,2 structure from their proton nmr spectra, which contained two peaks in the N-H region (Table I).

When **3** is treated with 1 equiv of *n*-butyllithium followed by 1 equiv of **1**, the product is 1,2-bis(*t*-butyldimethylsilyl)-1-methylhydrazine (**4**) formed in 99%



isomeric purity. The structure follows unambiguously from the nmr spectrum, which shows two peaks for Me_2Si protons and two for *t*-BuSi protons (Table I). The same compound was obtained by metalation and

133 (1958); **299**, 341 (1959); U. Wannagat, C. Krüger, and H. Niederprum, *ibid.*, **321**, 198 (1963); U. Wannagat, *Advan. Inorg. Chem. Radiochem.*, **6**, 225 (1964).

(1) Research sponsored by Air Force Office of Scientific Research (SRC)-O.A.R., USAF, Grant No. AF-AFOSR 1061-66.

(2) Previous paper in this series: R. West, M. Ishikawa, and R. E. Bailey, *J. Am. Chem. Soc.*, **89**, 4072 (1967).

(3) R. E. Bailey and R. West, *ibid.*, **86**, 5369 (1964).

(4) R. West, M. Ishikawa, and R. E. Bailey, *ibid.*, **88**, 4648 (1966).

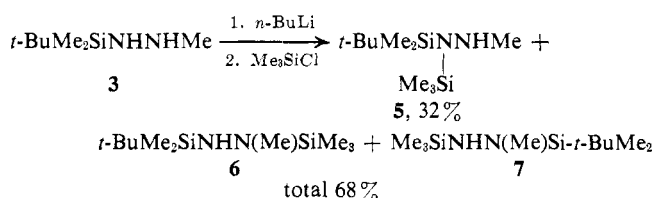
(5) R. West, M. Ishikawa, and R. E. Bailey, *ibid.*, **89**, 4068 (1967).

(6) U. Wannagat and W. Liehr, *Z. Anorg. Allgem. Chem.*, **274**, 129, (1951).

Table I. Proton Nmr Chemical Shift Values for *t*-Butyldimethylsilylhydrazines, τ

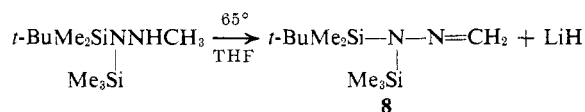
Compd	CH ₃ Si	(CH ₃) ₃ CSi	N-H	N-CH ₃	N-Ph
2	9.98	9.08	7.37, 5.27		3.50-2.80
3	9.97	9.05	7.56, 7.24	7.47	
4	9.98, 9.96	9.12, 9.08	7.75	7.11	
5	9.93, 9.86	9.11	7.54	7.45	
6	9.99, 9.96	9.12	7.99	7.46	
7	9.99, 9.96	9.09	7.76	7.32	
9	10.10, 9.80	9.09	6.87		3.45-2.75
10	10.00, 9.69	9.06	...		3.45-2.75
11	9.90	9.06	5.04		3.50-2.84

methylation of 1,2-bis(*t*-butyldimethylsilyl)hydrazine.⁴ However, when 3 was treated instead with *n*-BuLi followed by trimethylchlorosilane, a mixture of three isomers was produced.

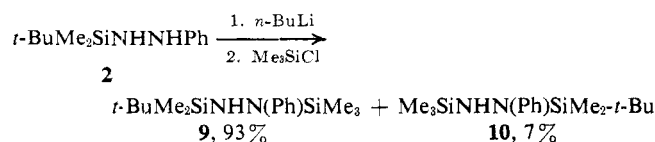


Preparative gas chromatography was used to separate 5 from the mixture, but 6 and 7 could not be separated under any of the conditions tried. The structures of isomers 6 and 7 are not absolutely certain, and the assignments given in Table I could conceivably be reversed. Our assignments are based on the following facts. (1) The Si-N-H resonance appears at higher field in 6 than in 7, and in every known pair of analogous compounds the Me₃Si-N-H group gives N-H resonance at higher field than *t*-BuMe₂Si-N-H.⁴ (2) 6 is present in much larger quantity than 7 at equilibrium, and the isomer with the *t*-BuMe₂Si- group remote from the methyl group should be much less hindered sterically.

An unexpected additional product was obtained when this reaction was carried out in tetrahydrofuran at 65° instead of under the usual conditions (ether solution, 35°). Besides 5, 6, and 7, formaldehyde N-trimethylsilyl-N-*t*-butyldimethylsilylhydrazone (8) was produced in 16% yield. This product must arise by elimination of lithium hydride from a lithium hydrazide.



When 2 was treated with 1 equiv of *n*-butyllithium followed by 1 mole of trimethylchlorosilane, no 1,1-bis(silyl) isomer was produced. The reaction product was a 93:7 mixture of the two 1,2 isomers.



Once again, isomers 9 and 10 could not be separated by gas chromatography. However, it proved possible to obtain 9 in >99% isomeric purity by inverse addition of the lithiohydrazide from 2 to trimethylchlorosilane. The isomeric structural assignments for 9 and 10, like those for 6 and 7, are not completely unambiguous. However, models show that there is very great steric

hindrance to attachment of a *t*-butyldimethylsilyl substituent on the same nitrogen atom as a phenyl group, strongly indicating that our assignments are correct. Moreover, other 1-silyl-2-phenylhydrazines upon metalation and derivatization are always found to undergo substitution at the nitrogen bearing the aromatic ring.^{5,7}

Rearrangement Reactions. The results of equilibration experiments on *t*-butyldimethylsilylhydrazines are summarized in Table II. All five bis(organosilyl)-

Table II. Equilibration of *t*-Butyldimethylsilylhydrazines with *n*-Butyllithium in Benzene

Compound	Original isomer, %	Rearranged isomer(s), %	<i>t</i> _{1/2} , min
<i>t</i> -BuMe ₂ SiNHNHMe ^a	~100	~0	
<i>t</i> -BuMe ₂ SiN(SiMe ₃)NH ₂ ^b	27	73	<2
(<i>t</i> -BuMe ₂ Si) ₂ NNH ₂ ^b	14	86	4
<i>t</i> -BuMe ₂ SiNHN(Me)SiMe ₂ - <i>t</i> -Bu ^a	99	1	...
<i>t</i> -BuMe ₂ SiN(SiMe ₃)NHMe ^c	32	50 (6) 18 (7)	80
<i>t</i> -BuMe ₂ SiNHNHPh	~100	~0	
<i>t</i> -BuMe ₂ SiNHN(Ph)SiMe ₃ ^e	20	4 (10) 76 (11)	2800 ^d

^a Identical results obtained at 65° in cyclohexane. ^b Preparation and physical properties of isomers are given in ref 5. ^c The ratio of 5 to the mixture of 6 and 7 was determined gas chromatographically; the ratio of 6 to 7 by nmr using the areas of the N-CH₃ peaks. ^d Reaction carried out at 65° ^e Ratio of 10 to 11 determined by nmr.

hydrazines undergo rearrangement as expected, but the *t*-butyldimethylsilyl group affects the product ratios. The 1,2-bis(silyl) isomers are present in excess in each of the four systems at equilibrium. However, steric preference for the 1,2 structures is not great except in the bis(*t*-butyldimethylsilyl)methylhydrazine system, where the 1,2 isomer is favored by about 100:1.

The *t*-butyldimethylsilyl substituent also affects the rates of anionic rearrangements. The rate of equilibration of 5 is slower by a factor of 23 than that of the analogous compound with two Me₃Si groups, and the rearrangement of 9 appears to be even more markedly retarded compared to that of the analogous bis(trimethylsilyl)phenylhydrazine. The equilibration of silylhydrazines containing two N-H bonds is generally too rapid to follow, so that for such compounds the retarding effect of the bulky *t*-butyldimethylsilyl substituent, though present, cannot be measured accurately (Table II).

(7) R. West and M. Ishikawa, unpublished work.

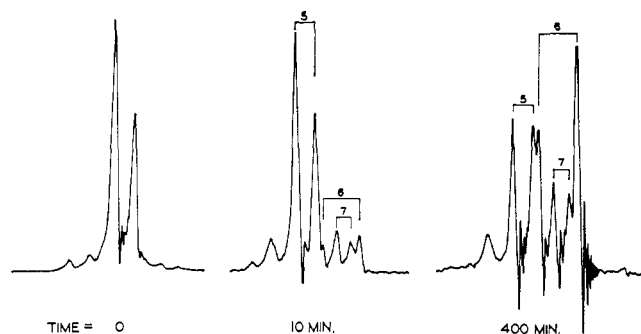
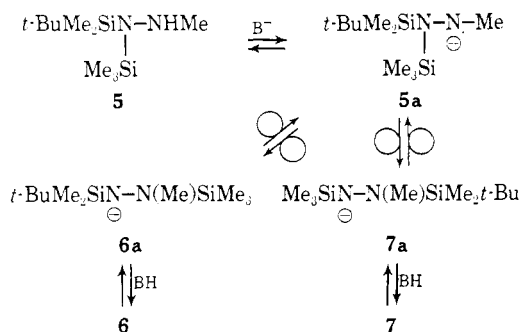


Figure 1. Nmr spectra of methylsilyl region as a function of time, showing catalytic rearrangement of **5** to **6** and **7**.

The relatively slow rates of rearrangement of the unsymmetrically substituted compounds **5** and **8a** provided an opportunity to study competitive and sequential migration of different R_3Si^- groups. Consider first the rearrangement of **5**. Deprotonation produces the anion **5a**, which can rearrange with migration either of a trimethylsilyl group or of a *t*-butyldimethylsilyl group, to give anions **6a** and **7a**, respectively. These anions can undergo protonation to the hydrazines **6** and **7**.



By studying the nmr spectrum in the methylsilyl region as a function of time, the decay of **5** and the growth of **6** and **7** can be followed.⁷ Typical spectra are shown in Figure 1. The results indicate that **7** is initially formed slightly faster than **6**. The amount of **7** in the system levels off after about 30 min, whereas the amount of **6** continues to increase, as shown in Figure 2.

Assuming our structural assignments are correct, the results indicate that the *more* hindered isomer **7** is initially formed more rapidly than the less hindered **6**. At a later stage, kinetic control of the product distribution gives way to thermodynamic control, and the less hindered isomer **6** is favored. These results are consistent with the view presented earlier that the protonation step is rate determining. Rearrangement of the anion **5a** to **6a** is expected to be faster, if anything, than to **7a**, so that if the rearrangement itself were rate determining **6** should be formed at least as fast as **7**. But protonation of **7a** to **7** should be more rapid than protonation of **6a** to **6**, because in **6a** the proton must be added to the sterically blocked nitrogen bearing the *t*-butyldimethylsilyl group.

Equally interesting results are obtained by similar study of the equilibration of **9** as a function of time. This rearrangement must take place sequentially. Formation of **10** must take place through, first, migration of the Me_3Si substituent to give the 1,1-bis(silyl) anion **11a**. Only afterward can migration of the *t*-

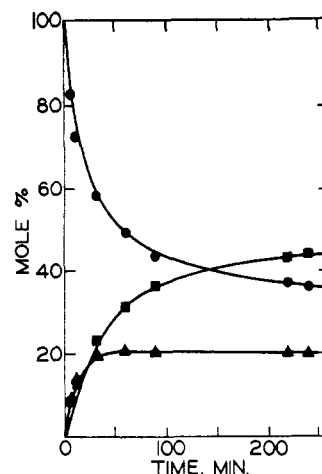


Figure 2. Catalytic rearrangement of 1-*t*-butyldimethylsilyl-1-trimethylsilyl-2-methylhydrazine (**5**) as a function of time: ●, **5**; ▲, **7**; ■, **6**.

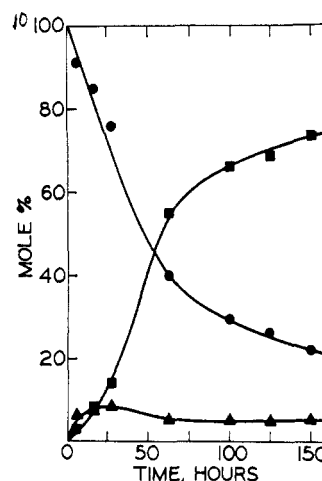
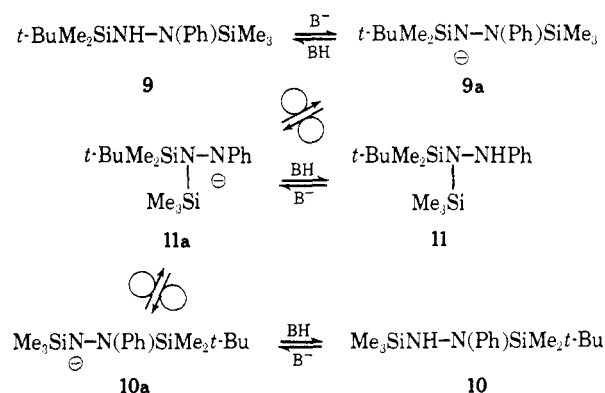


Figure 3. Catalytic rearrangement of **9** as a function of time: ●, **9**; ▲, **10**; ■, **11**.

butyldimethylsilyl group take place to give **10a**, which can be protonated to yield **10**.



The results of nmr experiments to follow the formation of **10** and **11** are summarized in Figure 3. The double-rearrangement product **10** is formed more rapidly than **11** in the early stages of the reaction. The amount of **10** in the mixture passes through a maximum after about 30 hr, and then declines to the equilibrium value of 5%, as kinetic control is supplanted by thermodynamic control of the product distribution. These

results appear consistent *only* with protonation as the rate-limiting step, and further require that protonation of **10a** is more rapid than that of **11a**. We believe that **11a** is stabilized electronically against rapid protonation, because of charge delocalization by the phenyl ring attached to the anionic nitrogen.

Thus all of the rate studies are fully consistent with the reaction mechanism discussed in detail elsewhere,² in which the equilibration of hydrazide anions by 1,2 migration of silicon is rapid compared to protonation and deprotonation.

Experimental Section

All preparations were carried out under an atmosphere of dry nitrogen. *t*-Butyldimethylchlorosilane was prepared as described elsewhere;⁴ trimethylchlorosilane was used as received from Dow Corning Corp. *n*-Butyllithium in hexane solution was obtained from Foote Mineral Co. Other materials were all of reagent grade.

Gas chromatographic separations were carried out on a $\frac{3}{8}$ in. \times 25 ft column packed with 30% methyl silicone polymer on Chromosorb W, 20–40 mesh. An Aerograph A700 gas chromatograph was used, with a helium flow rate of about 200 cc/min.

Proton nmr spectra were determined with a Varian A-60 spectrometer, on 20% solutions in dry carbon tetrachloride, using cyclohexane as an internal standard.

Catalytic Rearrangement Reactions. In a thoroughly clean and dry nmr sample tube was placed 0.7 ml of dry benzene, 0.1 ml of the test compound, and a measured amount, usually 0.20 ml, of 0.40 *M* *n*-butyllithium in cyclohexane. Use of larger or smaller amounts of *n*-BuLi catalyst had no measurable effect on the proportion of isomers present at equilibrium. The sample tube was sealed and placed in the spectrometer, and the methylsilyl proton region was scanned until the ratio of peaks due to the two isomers became constant. Results are summarized in Table II.

1-*t*-Butyldimethylsilyl-2-phenylhydrazine (1). To a solution of 7.6 g (0.070 mole) of phenylhydrazine in 20 ml of anhydrous diethyl ether, cooled to -40° , was added 40 ml of *n*-butyllithium, 1.8 *M* in cyclohexane (0.072 mole of *n*-BuLi). After addition was complete the mixture was allowed to warm to room temperature and stirred for 1 hr. Over a 15-min period, 10.5 g (0.070 mole) of *t*-butyldimethylchlorosilane in 30 ml of dry ether was then added with stirring. The reaction mixture was heated to reflux for 10 hr, then the solvent ether was distilled off and replaced by tetrahydrofuran and refluxing was continued for an additional 30 hr. After filtration to remove LiCl, the filtrate was concentrated and distilled under reduced pressure to give 11.7 g (74%) of **1**, bp $114\text{--}116^\circ$ (3 torr). The product crystallized when cooled; the solid was recrystallized once from petroleum ether (bp $35\text{--}38^\circ$) to give colorless crystals, mp $44\text{--}45^\circ$.

Anal. Calcd for $\text{C}_{12}\text{H}_{20}\text{N}_2\text{Si}$: C, 64.80; H, 9.97; N, 12.39. Found: C, 65.20; H, 9.89; N, 12.39.

1-*t*-Butyldimethylsilyl-2-methylhydrazine (3). To a solution of 17.6 g (0.38 mole) of freshly distilled methylhydrazine in 50 ml of anhydrous diethyl ether was added 29 g (0.19 mole) of *t*-butyldimethylchlorosilane in 100 ml of ether, over 30 min with cooling. The reaction mixture was stirred for 1 hr at room temperature, refluxed for 12 hr, then cooled, and filtered to remove methylhydrazine hydrochloride. The filtrate was washed with ether, and then ether was distilled off of combined filtrate and washings. The residue was distilled rapidly under vacuum and the portion boiling at $48\text{--}69^\circ$ (16 torr) was finally fractionally distilled using a spinning-band column to give 23 g (74%) of pure **3**, bp $46\text{--}46.5^\circ$ (8 torr), n_D^{25} 1.4362.

Anal. Calcd for $\text{C}_7\text{H}_{20}\text{N}_2\text{Si}$: C, 52.43; H, 12.57; N, 17.48; Si, 17.52. Found: C, 52.39; H, 12.43; N, 17.25; Si, 17.36.

1,2-Bis(*t*-butyldimethylsilyl)-1-methylhydrazine (4). **Method 1.** A solution of 5.0 g (0.031 mole) of **3** in 30 ml of dry tetrahydrofuran was cooled to -70° and 17 ml of *n*-butyllithium, 1.8 *M* in cyclohexane, was added with stirring over 10 min (0.031 mole of *n*-BuLi). The reaction mixture was allowed to warm to room temperature and stirred for 4 hr. Then 4.5 g (0.031 mole) of **1** in 20 ml of tetrahydrofuran was added, and the reaction mixture was refluxed for 15 hr. The mixture was then filtered, and the filtrate was concentrated and fractionally distilled to give 6.8 g (81%) of colorless liquid **4**, bp $70\text{--}71^\circ$ (0.2 torr), n_D^{25} 1.4530. Gas chromatographic

analysis and nmr indicated that the product was at least 99% the 1,2 isomer (Table I).

Method 2. To 5.2 g (0.020 mole) of 1,2-bis(*t*-butyldimethylsilyl)hydrazine was slowly added 0.020 mole of *n*-butyllithium, as a 1.6 *M* solution in cyclohexane. The reaction mixture was heated to $60\text{--}65^\circ$ for 48 hr, then 3.5 g (0.025 mole) of methyl iodide was added, and the mixture was heated to the same temperature for 15 hr. The mixture was filtered and distilled to give 4.0 g of reaction product, bp $55\text{--}64^\circ$ (0.1 torr). Gas chromatographic analysis showed that the liquid was a 60:40 mixture of **4** with unchanged starting materials. Preparative gas chromatography was employed to separate pure **4**, identical with that obtained by method 1.

Anal. Calcd for $\text{C}_{13}\text{H}_{24}\text{N}_2\text{Si}_2$: C, 56.86; H, 12.48; N, 10.20; Si, 20.46. Found: C, 57.00; H, 12.59; N, 10.41; Si, 20.29.

Reaction of 3 with *n*-Butyllithium and Trimethylchlorosilane. A solution of 6.0 g (0.038 mole) of **3** in 25 ml of ether was treated with 24 ml of 1.6 *M* *n*-butyllithium in hexane, with cooling to -60° . The reaction mixture was stirred for 2 hr at room temperature, then 4.3 g (0.040 mole) of trimethylchlorosilane was added and stirring was continued for an additional 20 hr. The lithium salts were then removed by filtration, and the residue was distilled under reduced pressure to give 8.5 g (95%) of a colorless liquid, bp $104\text{--}122^\circ$ (32 torr). Gas chromatographic analysis showed two peaks having area ratios 68:32. The mixture was separated by gas chromatography, and the two fractions were identified by nmr. The larger peak consisted of a mixture of the two 1,2-bis(silyl) isomers **6** and **7**, in 66:34 ratio, respectively. The smaller constituent was identified as 1-trimethylsilyl-1-*t*-butyldimethylsilyl-2-methylhydrazine (**5**).

Anal. Calcd for $\text{C}_{10}\text{H}_{28}\text{N}_2\text{Si}_2$: C, 51.65; H, 12.14; N, 12.05; Si, 24.16. Found (compound **5**): C, 51.43; H, 12.20; N, 12.25; Si, 24.24. Found (mixture of **6** and **7**): C, 51.87; H, 12.04; N, 12.15; Si, 24.09.

When the above reaction was carried out in tetrahydrofuran with heating of the lithiohydrazide solution to $60\text{--}65^\circ$ for 48 hr, and refluxing of the solution after addition of trimethylchlorosilane for 40 hr, the products were found to be 42% **6**, 21% **7**, 21% **5**, and 16% formaldehyde N-trimethylsilyl-N-*t*-butyldimethylsilylhydrazide (**8**). **8** was separated by gas chromatography and identified by nmr spectroscopy and analysis. Singlet proton resonances were found at τ 9.89, 9.81, and 9.11 with relative intensities 2:3:3, assigned to dimethyl-, trimethyl-, and *t*-butylsilyl groups, respectively. The nonequivalent $\text{N}=\text{CH}_2$ protons give an AB pattern with peaks at τ 3.54, 3.34, 3.10, and 2.90.

Anal. Calcd for $\text{C}_{10}\text{H}_{26}\text{N}_2\text{Si}_2$: C, 52.10; H, 11.37; N, 12.16; Si, 24.37. Found: C, 51.85; H, 11.95; N, 12.24; Si, 24.21.

1-Phenyl-1-trimethylsilyl-2-*t*-butyldimethylsilylhydrazine (9). Ten grams (0.045 mole) of **2** was dissolved in 30 ml of ether and treated with 30 ml of 1.6 *M* *n*-butyllithium-hexane solution at -60° . The reaction mixture was stirred for 20 hr at 25° and then transferred to a dropping funnel and added to a solution of 7.0 g (0.065 mole) of trimethylchlorosilane in 25 ml of THF, at -60° . The reaction mixture was warmed to room temperature, stirred for 20 hr, and worked up in the usual way to yield 10.5 g (85%) of pure **9**, bp $81\text{--}82^\circ$ (0.1 torr), n_D^{25} 1.5024.

Anal. Calcd for $\text{C}_{15}\text{H}_{30}\text{N}_2\text{Si}_2$: C, 61.15; H, 10.27; N, 9.55; Si, 19.07. Found: C, 61.40; H, 10.28; N, 9.77; Si, 18.89.

When the same reaction was carried out with addition of trimethylchlorosilane to the lithiohydrazide (rather than "inverse" addition of lithiohydrazide to chlorosilane) the product was shown by nmr to be 93% **9** and 7% of the isomeric compound **10**. These isomers could not be separated by gas chromatography. None of the 1,1 isomer **11** was observed in either preparation.

1-*t*-Butyldimethylsilyl-1-trimethylsilyl-2-phenylhydrazine (11). A solution of 10.0 g (0.034 mole) of **9** in 15 ml of cyclohexane was treated with 2 ml of 1.6 *M* *n*-butyllithium in cyclohexane and heated to $60\text{--}65^\circ$ for 62 hr. Diphenylamine (0.6 g) was then added to protonate the lithiohydrazide, and the mixture was distilled under reduced pressure to give 8.7 g (87%) of a pale blue liquid. Gas chromatographic analysis showed that the product contained 32% of a mixture of **9** and **10** and 68% of **11**; the latter was separated by preparative gas chromatography as a colorless liquid, n_D^{25} 1.5116.

Anal. Calcd for $\text{C}_{15}\text{H}_{30}\text{N}_2\text{Si}_2$: C, 61.15; H, 10.27; N, 9.55; Si, 19.07. Found: C, 61.01; H, 10.02; N, 10.11; Si, 19.75.

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