

k_D for the total rate constant for all reactions between two phenylcyclohexadienyl radicals, k_T for the rate of eq 107 (presumed not reversible in the first of the approximations discussed), and $k_{\text{cross}} = k_{104} + k_{105}$. It is further assumed that reaction 103 is fast enough that all phenyl radicals are converted to phenylcyclohexadienyl radicals. Steady-state eq 108 and 109 then follow. Hence $T/D = (k_D/k_T)^{1/2}$ and the rates (not rate constants) for the two simple terminations 106 and 107

$$dD/dt = \text{rate 102} - k_{\text{cross}}TD - 2k_D D^2 = 0 \quad (108)$$

$$dT/dt = \text{rate 102} - k_{\text{cross}}TD - 2k_T T^2 = 0 \quad (109)$$

must be equal.⁴⁵ The ratio of cross products (CP) from reactions 104 and 105 to the phenylcyclohexadiene products (DP) (reaction 106) is given by eq 110. A limiting value of k_{cross} may be estimated as follows with $k_D = 1.5 \times 10^7$ (Table III) and $k_T = 3.6 \times 10^4$ ⁴⁶ and

$$CP/DP = k_{\text{cross}}TD / k_D D^2 = k_{\text{cross}} (k_D k_T)^{1/2} \quad (110)$$

setting $CP/DP = 100$ (on the assumption that if more than 1% of DP were formed they would be detectable), then $k_{\text{cross}} = 100(1.5 \times 3.6 \times 10^{11})^{1/2} = 7 \times 10^7$.

(45) The factor of 2 enters since two like radicals are removed, but the factor for product formation is 1 since only 1 mole of triphenylmethane, etc. is formed.

(46) Taken from the rates and activation energies in ref 4, p 530.

The same results were found by REMECH calculations using $k_{103} = 2000$ (Table I). If, however, reaction 107 is assumed rapidly reversible, then even with $k_{\text{cross}} = 1.5 \times 10^6$ there is less than 0.5% of DP formed. The reason for this pattern is that with (107) not reversible and with $k_{\text{cross}} = 0.5 \times 10^6$ there is a 25% yield of hexaphenylethane, but with (107) reversible, the yield of hexaphenylethane is small. A value of 10^6 – 10^7 for k_{cross} is certainly not exceptional, and the observed product distribution is thus readily predicted by reactions 102–107. Providing that the products of reaction 105 can be cracked quantitatively to biaryl and triphenylmethane, thermal decomposition of arylazotriphenylmethyls appears to be a most promising way for study of the arylation reactions.

Experimental Section

REMECH uses an iterative process.¹³ Time intervals of 400 sec were used and radical concentrations were adjusted to 0.2%. The process was checked using intervals of 100 sec and adjustment to 0.02%. The yields of several minor products (<0.1%) showed appreciable differences, but major products all agreed to better than 1% relative. Run time was about 5 min per 300 equations set for about 35% of reaction on the IBM 709, and about 20 sec on the CDC 6400.

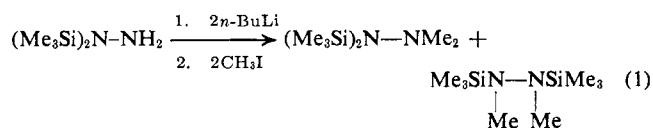
New Anionic Rearrangements. III. Catalytic Rearrangement of Organosilylhydrazines^{1,2}

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Contribution from the Department of Chemistry, The University of Wisconsin, Madison, Wisconsin. Received February 10, 1967

Abstract: When organosilylhydrazines are treated with *n*-butyllithium or other strong bases, a rapid rearrangement of organosilyl groups from one nitrogen to another takes place. The rearrangement was studied by proton nmr spectroscopy. It occurs either with equimolar or catalytic amounts of base, proceeds to equilibrium, and is intramolecular. Bis(organosilyl)hydrazines and bis(organosilyl)methylhydrazines give approximately equal amounts of 1,1- and 1,2-bis(organosilyl) compounds at equilibrium. With organosilylphenylhydrazines, the isomer bearing a hydrogen on the nitrogen atom attached to the aromatic ring is favored at equilibrium. Several new organosilyl hydrazines were prepared in connection with these studies; their physical properties are reported.

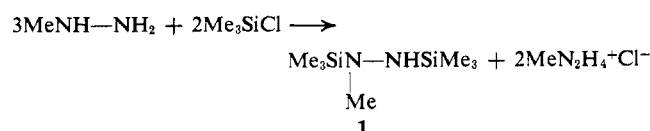
The anionic rearrangement of organosilyl hydrazines was first discovered for 1,1-bis(trimethylsilyl)hydrazine.^{2,3} This compound, upon treatment with 2 equiv of *n*-butyllithium followed by 2 equiv of methyl iodide, was transformed into a 1:1 mixture of the isomeric bis(trimethylsilyl)dimethylhydrazines.



In studying this reaction we were handicapped by the fact that the synthesis of bis(trimethylsilyl)hydrazine

gives a mixture of isomers which is difficult to separate. Moreover, at the time there was no unequivocal way to establish which of the isomers had the 1,1 structure and which the 1,2.⁴ We therefore turned to 1,2-bis(trimethylsilyl)methylhydrazine (1) as a more convenient substrate.

1 can easily be prepared by reaction of methylhydrazine with trimethylchlorosilane, according to the directions given by Wannagat and Liehr.⁵



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

(2) Previous paper in this series: R. West, M. Ishikawa, and R. E. Bailey, *J. Am. Chem. Soc.*, **88**, 4648 (1966).

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

(4) For a discussion of the controversy concerning the structures of these isomers and its resolution see ref 2.

(5) U. Wannagat and W. Liehr, *Z. Anorg. Allgem. Chem.*, **299**, 341 (1959).

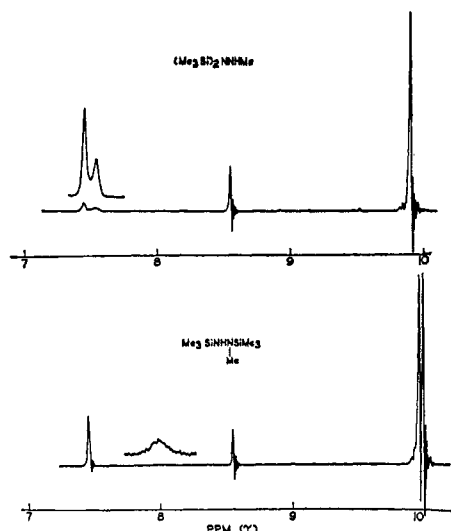
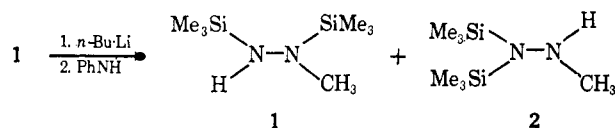


Figure 1. Proton nmr spectra of 1,1- and 1,2-bis(trimethylsilyl)methylhydrazine, with cyclohexane ($\tau = 8.56$) as internal reference.

The product, **1**, is obtained in 98% isomeric purity by simple distillation. Moreover, it can be shown unambiguously to have the 1,2 structure by proton nmr spectroscopy. Two different resonances of equal intensity from the protons on the two different Me_3Si groups are found at τ 10.00 and 9.97 (Figure 1). In the 1,1 isomer, all the methylsilyl protons are equivalent and so only a single resonance should be found in the methylsilyl region.

Treatment of **1** with 1 equiv of *n*-butyllithium followed by 1 equiv of methyl iodide led to the same mixture of nearly equal amounts of bis(trimethylsilyl)dimethylhydrazines found in reaction 1.³ To establish whether or not the methyl iodide was involved in the rearrangement, **1** was next treated with 1 equiv of *n*-butyllithium followed by 1 equiv of diphenylamine. Diphenylamine is a convenient protonating agent because its acid strength is great enough so that it transfers a proton to a silylhydrazide anion but not so great that it cleaves Si-N bonds rapidly. The bis(trimethylsilyl)methylhydrazine recovered from this treatment proved again to be a nearly equal mixture of 1,1 and 1,2 isomers. The mixture could be separated by prepara-



tive gas chromatography, and by this means the previously unknown 1,1 isomer (**2**) was obtained. As expected, the nmr spectrum shows a single methylsilyl proton resonance at τ 9.92 (Figure 1, Table I).

Next, **1** was treated with only 0.25 equiv of *n*-butyllithium, so as to convert just one-quarter of the hydrazine to its anion, and the mixture was examined by nmr. To our surprise, we observed that the neutral remaining **1** was completely rearranged to an equal mixture of the isomers **1** and **2**, within less than 1 min after addition of the organolithium compound! Further experiments showed that the rearrangement took place at a rapid but measurable rate at 25° in the presence of catalytic amounts (less than 0.05 equiv) of or-

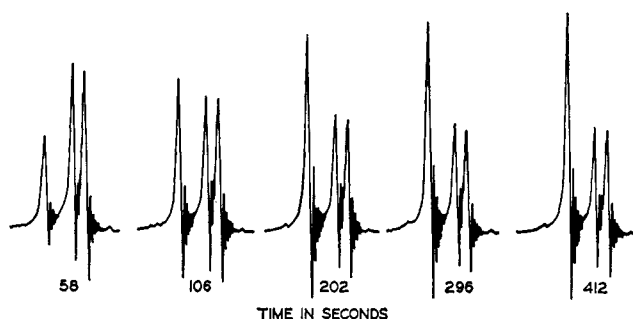


Figure 2. Proton nmr spectrum of 1,2-bis(trimethylsilyl)hydrazine, 0.4 M in cyclohexane, containing 0.08 M *n*-butyllithium. The spectrum is for the methylsilyl region only, as a function of time, showing rearrangement of the 1,2 to the 1,1 isomer. No further change is observable after 412 sec.

ganolithium base. The reaction can be carried out in an nmr sample tube and followed by successively tracing through the methylsilyl region. Some typical results are shown in Figure 2.

The equal proportions of **1** and **2** formed in the rearrangement are independent of the amount of base used. That the reaction reaches a true equilibrium is confirmed by the observation that equal amounts of **1** and **2** are also obtained by catalytic rearrangement of the pure 1,1 isomer **2**. Thus the equilibrium can be approached from either direction.

Table I. Equilibration of Organosilylhydrazines with *n*-BuLi

Compound	% at equilibrium ^a		<i>t</i> _{1/2} ^b min
	1,1 isomer	1,2 isomer	
(Me_3Si) ₂ NNH ₂ ^c	49	51	<1
(EtMe ₂ Si) ₂ NNH ₂ ^c	47	53	<1
Me ₃ Si(EtMe ₂ Si)NNH ₂	48	52	<1
Me ₃ SiNHN(CH ₃)SiMe ₃ ^c	50	50	3.5
EtMe ₂ SiNHN(CH ₃)SiEtMe ₂ ^c	47	53	4.5
Me ₃ SiNHNHPh	0 ^d	100 ^e	...
EtMe ₂ SiNHNHPh	0 ^d	100 ^e	...
Me ₃ SiNHN(SiMe ₃)Ph ^c	96	4	600
EtMe ₂ SiNHN(SiMe ₃ Et)Ph	91	9	900

^a $\pm 2\%$ for the first five compounds, $\pm 1\%$ for the last four.

^b Time required for one-half of the equilibrium amount of rearranged isomer to be formed. ^c Essentially identical amounts of 1,1 and 1,2 isomers at equilibrium also found starting with the other isomer of these compounds. ^d 1-Silyl-1-phenyl isomer. ^e 1-Silyl-2-phenyl isomer.

The initial reactions were carried out in saturated hydrocarbons, but other solvents are equally usable. The catalytic rearrangement of **1** takes place in hexane, cyclohexane, and benzene and (at an even more rapid rate) in diethyl ether, di-*n*-butyl ether, tetrahydrofuran, and 1,2-dimethoxyethane. Other strong bases besides *n*-butyllithium which catalyze the rearrangement include methyllithium, phenyllithium, methylmagnesium bromide, lithium dimethylamide, and the anion radicals of anthracene and biphenyl. Our observations suggest that any base strong enough to deprotonate the silylhydrazine will catalyze the rearrangement.⁶

Other examples of catalytic silylhydrazine rearrangement were then sought. It was easily shown that 1,1- and 1,2-bis(trimethylsilyl)hydrazine, known to re-

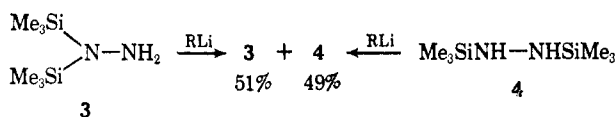
(6) The implications of these observations for the mechanism of the reaction are considered in paper IV in this series: R. West, M. Ishikawa, and R. E. Bailey, *J. Am. Chem. Soc.*, **89**, 4072 (1967).

Table II. Proton Nmr of Silyl-Substituted Hydrazines^a

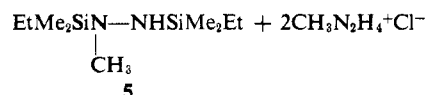
Compound	CH ₃ -Si	Et-Si	Si-N-H	Ph-N-H	N-CH ₃	N-C ₆ H ₅
Me ₃ SiNHN(Me)SiMe ₃	10.00, 9.97		8.05		7.45	
(Me ₃ Si) ₂ NNHMe	9.92		7.52		7.45	
EtMe ₂ SiNHN(Me)SiMe ₂ Et	10.03, 10.00	9.58-8.87	7.93		7.43	
(EtMe ₂ Si) ₂ NNHMe	9.95	9.69-9.06	7.56		7.48	
Me ₃ SiNHNHPh	9.92		7.24	5.08		3.51-2.74
EtMe ₂ SiNHNHPh	9.95	9.52-8.75	7.30	5.13		3.56-2.76
(Me ₃ Si) ₂ NNHPh	9.91			5.05		3.58-2.84
Me ₃ SiNHN(Ph)SiMe ₃	10.04, 9.81		6.99			3.49-2.77
(EtMe ₂ Si) ₂ NNHPh	9.92	9.60-8.86		5.04		3.54-2.81
EtMe ₂ SiNHN(Ph)SiMe ₂ Et	10.04, 9.80	9.63-8.93	6.93			3.45-2.80
Me ₃ SiNHN(Me)Ph	9.90		7.23		6.95	3.49-2.74

^a Chemical shift in τ units.

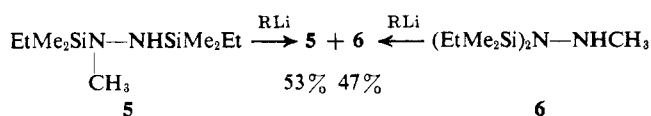
arrange in the presence of excess base,³ also underwent catalytic rearrangement to an equilibrium mixture of isomers (**3** and **4**). Two other bis(organosilyl)hy-



drazines whose syntheses and structure had been reported previously² were also found to undergo catalytic rearrangement to essentially equal amounts of isomers (Table I). Methylhydrazine was then treated with ethyldimethylchlorosilane, giving the isomerically pure new compound 1,2-bis(ethyldimethylsilyl)methylhydrazine (**5**). The isomeric structure of **5** was estab-



lished from its nmr spectrum (Table II). This compound is also rearranged by catalytic amounts of *n*-butyllithium to give a mixture of isomers. Gas chromatographic separation of the mixture gives the pure 1,1 isomer **6**, which likewise undergoes catalytic rearrangement to the same equilibrium mixture.

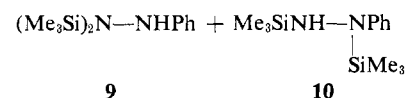
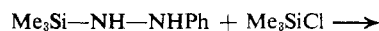


A mixture of **1** and **5** was then made up and treated with *n*-butyllithium and studied by nmr spectroscopy. Resonances due to **1**, **2**, **5**, and **6** were found, but there was no indication of the formation of any trimethylsilyl(ethyldimethylsilyl)methylhydrazines. Gas chromatography of the equilibrated mixture confirms that no "crossover products" are obtained; each rearrangement takes place independently of the other.

We then turned our attention to organosilylphenylhydrazines. 1-Trimethylsilyl-2-phenylhydrazine (**7**) initially was prepared from phenylhydrazine and trimethylchlorosilane according to the method of Wannagat and Liehr.^{5,7} It was found, however, that better yields were obtained by metalating the phenylhydrazine with 1 equiv of *n*-butyllithium and then adding 1 equiv of trimethylchlorosilane. When **7** was treated with *n*-butyllithium no change was observed in the nmr

spectrum. Even under forcing conditions, using large amounts of *n*-butyllithium at 60°, rearrangement was not found to take place. Identical results were obtained using the new compound 1-ethyldimethylsilyl-2-phenylhydrazine (**8**), synthesized similarly (Table I).

Compound **7** was then treated with excess trimethylchlorosilane in refluxing cyclohexane to provide low yields of 1,1- and 1,2-bis(trimethylsilyl)phenylhydrazine.⁷



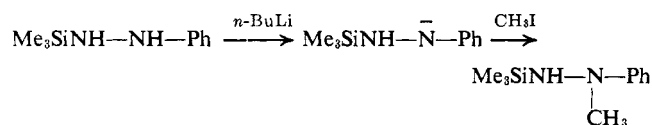
Preparative gas chromatography was used to separate **9** and **10**, whose structures were assigned from their nmr spectra (Table II). Catalytic rearrangement of either **9** or **10** took place much more slowly than for the other hydrazines studied. The equilibrium mixture contained about 96% **9** and only 4% **10**. Similar equilibration of 1,1- and 1,2-bis(ethyldimethylsilyl)phenylhydrazines, prepared from **8**, also gave a preponderance of the 1,1 isomer at equilibrium (Table I). The amounts of silylhydrazine isomers present at equilibrium after base-catalyzed rearrangement are summarized in Table I. The equilibrations were ordinarily carried out with about 0.2 equiv of base, but results with several systems indicate that the proportion of isomers present at equilibrium is essentially independent of the amount of base used.

All of the bis(organosilyl)hydrazines and bis(organosilyl)methylhydrazines give, at equilibrium, *essentially equal amounts* of their two isomers. This finding is in itself surprising, for it might be expected that the silyl or methyl substituents would stabilize one form of the hydrazine more than another. The simplest rationalization of the results is that the organosilyl and methyl substituents have little influence on the stability of the hydrazines. However, examination of models shows that there is moderate steric interference between trimethyl- or ethyldimethylsilyl groups attached to the same nitrogen atom in the 1,1 isomers, which is relieved in the 1,2 compounds. This steric hindrance might be compensated by increased N→Si π bonding in the 1,1 isomers, which would stabilize the 1,1 bisilyl compounds electronically relative to the 1,2. This explanation requires that special stabilization is conferred by the silazane bond (Si-N-Si) over and above that of two separate N-Si linkages.

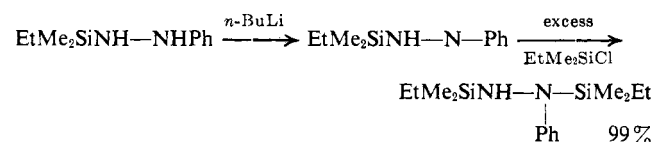
(7) U. Wannagat, C. Krüger, and H. Niederprum, *Z. Anorg. Allgem. Chem.*, **321**, 198 (1963).

The (organosilyl)phenylhydrazines show a decided preference for the form with hydrogen on the same nitrogen atom as phenyl.⁸ This can be explained as due to increased steric interaction between phenyl and organosilyl substituents, or to an electronic effect, or both. Electronic effects consistent with the results include (1) decreased N→Si π bonding in Ph-N-Si compounds, leading to destabilization of the Ph-N-Si isomers, and (2) specific stabilization due to the presence of the Ph-N-H system.

Only indirect information is available about the equilibrium between the hydrazide anions. However, as explained above, protonation or methylation of the anion from either isomer of bis(trimethylsilyl)hydrazine yields about equal amounts of the 1,1 and 1,2 derivatization products.³ Indirect evidence suggests that the equilibrium for phenylhydrazide anions lies far toward the side of the anion with negative charge on the same nitrogen as the aromatic ring. Thus, metalation of **7** and alkylation with methyl iodide yields exclusively the new compound 1-methyl-1-phenyl-2-trimethylsilylhydrazine.



N-Phenyl alkylation of **7** was also observed by Wannagat, Krüger, and Niederprum,⁷ using ethyl iodide as the alkylating agent. Likewise, metalation followed by silylation of **8**, under conditions where chlorosilane is always in excess, led exclusively to the 1,2-bis(silyl) isomer.



Further information about the nature of the hydrazide anion and the mechanism of the rearrangement will be presented in succeeding papers.

Experimental Section

Separations by preparative gas chromatography were carried out using a $\frac{3}{8}$ in. \times 25 ft column packed with 30% SE-30 silicone fluid on 20–40 mesh Chromosorb W, and a helium flow rate of 200 cc/min. Proton nmr spectra were determined with a Varian A-60 spectrometer; chemical shifts were obtained by internal referencing with cyclohexane.

Materials. Trimethylchlorosilane was obtained from the Dow Corning Corp. and was redistilled before use. Phenylhydrazine and methylhydrazine were reagent grade; methylhydrazine was dried over BaO and distilled before use. Ethyldimethylchlorosilane was synthesized from ethylmagnesium bromide and dimethyldichlorosilane (Dow Corning); its properties agreed with the literature.⁹

All preparations and reactions were carried out in an atmosphere of dry nitrogen.

Catalytic Rearrangement Reactions. In a thoroughly clean and dry nmr sample tube was placed 0.7 ml of dry cyclohexane, 0.1 ml of the test compound, and 0.2 ml of 0.4 M *n*-butyllithium in cyclohexane. The concentrations of *n*-BuLi and substrate after mixing were 0.08 and \sim 0.4 M, respectively. The sample tube was placed

in the spectrometer (probe temperature 35°) and the methylsilyl proton region was scanned repeatedly until the ratio of peaks due to the two isomers became constant.

The final ratio of isomers was determined from peak areas by cutting and weighing the chart paper. The results were checked in most instances by gas chromatographic analysis. Results are summarized in Table I.

1,2-Bis(trimethylsilyl)methylhydrazine (1). A solution of 45 g (0.42 mole) of trimethylchlorosilane in 100 ml of dry diethyl ether was added slowly with cooling to 29 g (0.64 mole) of methylhydrazine in 100 ml of ether. The mixture was refluxed for 20 hr and then filtered, and the precipitate was washed with ether. Ether was evaporated from the combined filtrate and washings, and the residue was fractionally distilled using a spinning-band column, yielding 23 g (57%) of pure **1**, bp 159–160°, n_D^{20} 1.4209; lit.⁸ bp 73–75° (40 torr), n_D^{20} 1.3820 (!). The isomeric purity, determined by nmr, was about 98%.

Anal. Calcd for $\text{C}_7\text{H}_{22}\text{N}_2\text{Si}_2$: C, 44.14; H, 11.65; N, 14.71. Found: C, 44.04; H, 11.55; N, 14.90.

1,2-Bis(ethyldimethylsilyl)methylhydrazine (5). Ethyldimethylchlorosilane (42 g, 0.34 mole) and methylhydrazine (23 g, 0.50 mole) were allowed to react as in the synthesis of **1**. The crude product first rapidly distilled under reduced pressure and then fractionally distilled to give 21.5 g (59%) of pure **5**, bp 90–91° (16 torr), n_D^{20} 1.4372.

Anal. Calcd for $\text{C}_9\text{H}_{28}\text{N}_2\text{Si}_2$: C, 49.46; H, 12.00; N, 12.82; Si, 25.71. Found: C, 49.69; H, 12.01; N, 12.78; Si, 25.64.

1,1-Bis(ethyldimethylsilyl)methylhydrazine (6). In a 50-ml flask were placed 7 g (32 mmoles) of **5**, 7 ml of cyclohexane, and 1 ml of 1.8 M *n*-butyllithium in cyclohexane. The solution was stirred for 1.5 hr at 25°, after which 0.3 g of diphenylamine was added. Distillation under reduced pressure gave 6.4 g (91%) of a colorless liquid product, bp 102–110° (29 torr). Gas chromatographic analysis showed two peaks having an area ratio 52:48, corresponding to **5** and **6**, respectively. The two isomers were separated by preparative gas chromatography in order to obtain pure **6**.

Anal. Found: C, 49.73; H, 12.06; N, 12.65; Si, 25.85.

1,1-Bis(trimethylsilyl)methylhydrazine (2). This isomer was obtained by the *n*-butyllithium-catalyzed rearrangement of **1**; the reaction was similar to that employed for **6**. The distilled reaction product, containing about equal amounts of **1** and **2**, was separated by preparative gas chromatography.

Anal. Calcd for $\text{C}_7\text{H}_{22}\text{N}_2\text{Si}_2$: C, 44.14; H, 11.65; N, 14.71. Found: C, 43.82; H, 11.87; N, 14.56.

1-Trimethylsilyl-2-phenylhydrazine (7). To a solution of 5.4 g (50 mmoles) of phenylhydrazine in 30 ml of dry ether was added slowly 28 ml of 1.8 M *n*-butyllithium in cyclohexane, at -70° . The reaction mixture was then allowed to warm to room temperature and stirred for 1 hr. A solution of 5.4 g (50 mmoles) of trimethylchlorosilane in 20 ml of ether was then added, and the reaction was stirred for 2 more hr. The mixture was then filtered; the filtrate was fractionally distilled under reduced pressure to give 7.2 g (80%) of 1-trimethylsilyl-2-phenylhydrazine, bp 83–86° (2.0 torr), n_D^{20} 1.5201; lit.⁷ bp 86° (1 mm), n_D^{20} 1.5245.

1-Ethyldimethylsilyl-2-phenylhydrazine (8). Ethyldimethylchlorosilane (20.8 g, 0.17 mole) was added with stirring to a solution of phenylhydrazine (27.6 g, 0.23 mole) in 150 ml of diethyl ether. The mixture was heated to reflux for 20 hr, then cooled, and filtered. The filtrate after concentration was fractionally distilled yielding 20 g (59%) of product, bp 84–86° (2 torr), n_D^{20} 1.5223.

Anal. Calcd for $\text{C}_{10}\text{H}_{18}\text{N}_2\text{Si}$: C, 61.78; H, 9.35; N, 14.41; Si, 14.45. Found: C, 61.75; H, 9.37; N, 14.35; Si, 14.26.

1,1- and 1,2-Bis(trimethylsilyl)phenylhydrazine. In 15 ml of dry cyclohexane were dissolved 16 g (0.09 mole) of **7** and 21.6 g (0.20 mole) of trimethylchlorosilane. The reaction mixture was refluxed for 40 hr, cooled, and filtered. Distillation under reduced pressure of the filtrate gave 15.3 g of colorless liquid, bp 95–101° (4 torr). Gas chromatographic analysis of this product showed three peaks having area ratio 11:10:1.6, relative retention times 1:1.30:1.58 with the first and largest peak corresponding to unchanged starting material. The other two components were separated by preparative gas chromatography and shown by their nmr spectra to be the 1,2 and 1,1 isomers of bis(trimethylsilyl)phenylhydrazine, **10** and **9**, respectively.

Anal. Calcd for $\text{C}_{12}\text{H}_{24}\text{N}_2\text{Si}_2$: C, 57.07; H, 9.58; N, 11.10; Si, 22.25. Found (1,1 isomer): C, 57.22; H, 9.65; N, 10.98; Si, 22.39. Found (1,2 isomer): C, 57.21; H, 9.62; N, 11.27; Si, 21.98.

1,2- and 1,1-Bis(ethyldimethylsilyl)phenylhydrazines. To a solution of 6.0 g (0.031 mole) of **8** in 30 ml of tetrahydrofuran,

(8) For the monosilyl phenylhydrazines **7** and **8**, the equilibrium presumably lies so far toward the 1,2 isomers that no rearrangement can be detected. This conclusion could be checked by observing rearrangement of the corresponding 1,1 isomers, but to date we have been unable to prepare these compounds.

(9) R. N. Lewis, *J. Am. Chem. Soc.*, **69**, 717 (1947).

cooled to -60° , was added 14.5 ml of *n*-butyllithium, 1.8 *M* in cyclohexane (0.026 mole). The mixture was warmed to room temperature and stirred for 2 hr to complete formation of the lithiohydrazide. Then, at 0° , the reaction mixture was slowly added to a solution of 7.6 g (0.062 mole) of ethyldimethylchlorosilane in 20 ml of ether, over 30 min. The reaction was stirred for 1 hr, refluxed with stirring for 2 hr, and then filtered. The filtrate on fractional distillation gave 6.2 g (81%) of colorless product, bp $98-100^{\circ}$ (0.3 torr), n_D^{25} 1.5061. Gas chromatographic analysis showed the product to have an isomeric purity exceeding 99%; by nmr the product was found to be the 1,2 isomer.

Rearrangement of the 1,2 isomer with 1 equiv of *n*-butyllithium in hexane (15 hr at 25°) followed by treatment with diphenylamine gave a 10:1 mixture of 1,1 isomer:1,2 isomer, which was separated (after distillation) by preparative gas chromatography to give the pure 1,1 compound, n_D^{25} 1.5167. Relative retention times were 1:1.25 for the 1,2:1,1 isomers, respectively.

Anal. Calcd for $C_{14}H_{28}N_2Si_2$: C, 59.93; H, 10.06; N, 9.99; Si, 20.02. Found (1,1 isomer): C, 60.31; H, 9.55; N, 9.69. Found (1,2 isomer): C, 60.42; H, 10.14; N, 10.22.

1-Trimethylsilyl-2-methyl-2-phenylhydrazine. To a solution of 5.0 g (28 mmoles) of **7** in 25 ml of ether was added 17 ml of 1.67 *M*

methylithium in ether, at -10 to -20° . After addition was complete the reaction mixture was warmed to room temperature and then refluxed for 30 hr. Next, 5.7 g (40 mmoles) of methyl iodide in 10 ml of ether was added and the mixture was refluxed for an additional 20 hr. Work-up in the usual way gave 4.3 g (79%) of pale yellow liquid, bp $94-97^{\circ}$ (4 torr), n_D^{25} 1.5145.

The product gave a single peak upon gas chromatographic analysis. The structure was assigned as that of the 1-silyl-2-methyl-2-phenyl isomer from the proton nmr, which showed a peak at τ 7.23 (Si-N-H) but none near τ 5.1 (Ph-N-H).

Anal. Calcd for $C_9H_{18}N_2Si$: C, 61.80; H, 9.33; N, 14.22; Si, 14.45. Found C, 61.81; H, 9.45; N, 14.39; Si, 14.18.

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New Anionic Rearrangements. IV. Kinetics of Catalyzed Anionic Rearrangement of Bis(organosilyl)methylhydrazines¹

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Abstract: The kinetics of the *n*-butyllithium-catalyzed equilibration between 1, 1- and 1,2-bis(organosilyl)methylhydrazines have been investigated, where the organosilyl groups are Me_3Si and $EtMe_2Si$. The approach to equilibrium follows first-order kinetics. The results are explained in terms of a deprotonation-rearrangement-protonation mechanism (eq 1) in which the deprotonation and protonation steps are rate limiting.

Earlier papers in this series²⁻⁴ have described a new rearrangement reaction of hydrazines containing an organosilicon substituent, in which a silicon atom moves from one nitrogen to another. The previous paper discussed experiments which show that the reaction is relatively rapid, intramolecular, base catalyzed, and proceeds to equilibrium.⁴ In this paper, we present some studies of the kinetics of the catalyzed rearrangement, which is of a complex and unusual kind, and a tentative description of the reaction mechanism.

Rearrangement of bis(trialkylsilyl)hydrazines was first investigated, but proved so rapid that it could not be followed kinetically, the half-time for equilibration being less than 1 min at 30° .⁴ We therefore used bis(trialkylsilyl)methylhydrazines in the kinetic study. For these compounds equilibration half-times are typically of the order of a few minutes, so that the reaction kinetics could be studied by nmr spectroscopy. The kinetic runs were carried out in an nmr sample tube. By tracing repeatedly through the methylsilyl region, the disappearance of one isomer and formation of the other was followed quantitatively, as explained in the previous paper.⁴

In the kinetic studies, *n*-butyllithium was used as the catalyst. This base reacts rapidly and irreversibly to abstract protons from hydrazines. In our experiments, *n*-butyllithium could be shown to be consumed essentially within the time of mixing; proton transfer from the hydrazine to *n*-butyllithium is clearly much faster than the net hydrazine rearrangement. The bis-(trialkylsilyl)methylhydrazide anion is known from earlier experiments to undergo rearrangement.^{2,4} Because the rearrangement of organosilylhydrazines is catalyzed only by bases sufficiently strong to deprotonate the hydrazine,⁴ we will assume that rearrangement takes place only through the anion, as in other intramolecular anionic rearrangements.⁵

Now consider a catalytic rearrangement reaction after the initial *n*-butyllithium has been used up. At that point the system contains only free hydrazine, hydrazide anion (*i.e.*, lithium hydrazide), and solvent. The sequence of events in rearrangement would be as outlined in eq 1.

A molecule of AH can be deprotonated by a B⁻ anion, as shown in eq 1, or by an A⁻ anion, but the latter reaction can be ignored since it leads to no net change in the system. Only deprotonation of AH by

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(2) R. E. Bailey and R. West, *J. Am. Chem. Soc.*, **86**, 5369 (1964).

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

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

(5) For a summary of previously known anionic rearrangements and their mechanisms, see H. E. Zimmerman in "Molecular Rearrangement," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1963, p 345.