

New Anionic Rearrangements. X.¹ 1,4-Anionic and Thermal Rearrangement of Bis(organosilyl)-*o*-phenylenediamines²

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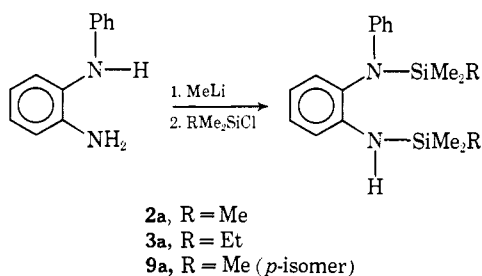
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Abstract: Fifteen new organosilyl derivatives of *o*-phenylenediamines were prepared and characterized. In the presence of methyllithium these compounds undergo rapid intramolecular 1,4-anionic rearrangement. When heated at 275° the N',N'-bis(organosilyl)-*o*-phenylenediamines undergo a new thermal, intramolecular 1,4-rearrangement to the N,N'-bis(organosilyl) isomers. Bis(organosilyl)-*o*-phenylenediamines condense to silyl-substituted 2-dimethylsilabenzimidazolines when heated with *n*-butyllithium.

Organosilicon moieties show unprecedented migratory aptitude in anionic rearrangements.^{1,3} Comparing the migration rate of trimethylsilyl with the homonuclear phenyl rearrangements in hydrazines⁴ and *o*-phenylenediamines,⁵ a conservative estimate places the migration rate of trimethylsilyl at least 10¹⁴ times faster than for phenyl. This enormous difference in mobility must reflect differences in the transition state for rearrangement, a bridged pentacoordinate transition state for a silicon atom being much more favorable than for a carbon atom.

The bis(organosilyl)-*o*-phenylenediamines are particularly good systems for the investigation of facile 1,4-anionic silyl rearrangements. We find that not only does 1,4-anionic rearrangement take place, but also a new *intramolecular, thermal* 1,4-rearrangement can occur at higher temperatures. In order to investigate these reactions several new silyl substituted *o*-phenylenediamines were prepared.

Syntheses. N-Phenyl-N,N'-bis(trimethylsilyl)-*o*-phenylenediamine (**2a**), N-phenyl-N,N'-bis(ethyltrimethylsilyl)-*o*-phenylenediamine (**3a**), and N-phenyl-N,N'-bis(trimethylsilyl)-*p*-phenylenediamine (**9a**) were conveniently prepared by treating the parent amine first with 2 equiv of methyllithium followed by excess organochlorosilane. That the N,N'-bis(organosilyl) isomers were obtained was shown by the presence of two methylsilyl resonances and an upfield Si-N-H peak in the nmr spectra. The N',N' isomers, **2b** and **3b**, were prepared by the anionic rearrangement of **2a** and **3a**, and showed only one kind of methylsilyl proton in



the nmr. These structure assignments were consistent with the relative chemical shifts and proton ratios.

(1) Previous paper in this series: R. West, P. R. Boudjouk, and T. A. Matuszko, *J. Amer. Chem. Soc.*, **91**, 5184 (1969).

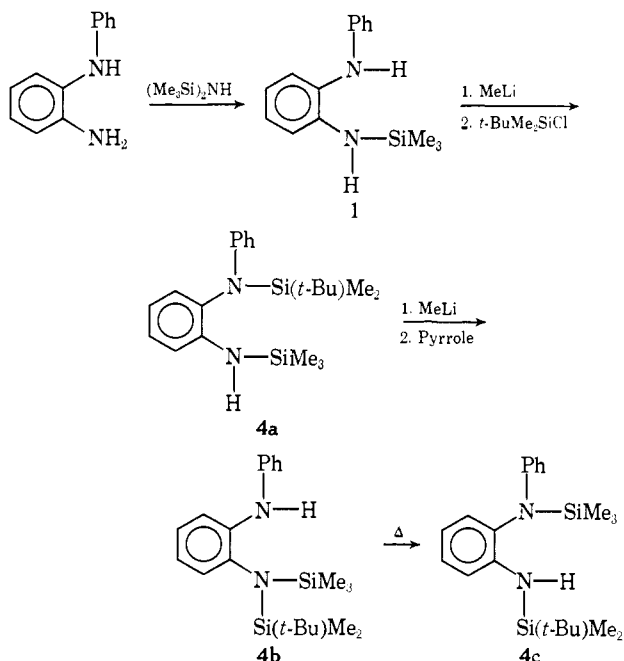
(2) Research sponsored by Air Force Office of Scientific Research (SRC), OAR, USAF Grant No. AF-AFOSR 1061-66.

(3) R. West, M. Ishikawa, and R. E. Bailey, *J. Amer. Chem. Soc.*, **89**, 4072 (1967).

(4) R. West, H. F. Stewart, and G. R. Husk, *ibid.*, **89**, 5050 (1967).

(5) R. West and H. F. Stewart, *ibid.*, **92**, 853 (1970).

The mixed organosilyl-substituted compound, N-phenyl-N-*t*-butyldimethylsilyl-N'-trimethylsilyl-*o*-phenylenediamine (**4a**), was obtained in high yield in a two-step synthesis by preparing N-phenyl-N'-trimethylsilyl-*o*-phenylenediamine (**1**), treating **1** with 1 equiv of methyllithium, and adding the lithium silylamide solution to excess *t*-butyldimethylchlorosilane. The N',N' isomer of **4a** (**4b**) was prepared by anionic rearrangement; the



back-rearranged isomer (**4c**) was obtained in good yield and high isomeric purity by heating **4b** at 275°. The proposed structures of these compounds were consistent with nmr (see Table I) and ir data. The nmr spectra of isomer **4b** was interesting in that the methyl groups on the *t*-BuMe₂Si moiety appeared to be nonequivalent at room temperature, two Me₂Si resonances being observed at 0.04 and 0.23 ppm. When the temperature of the nmr experiment was increased, the peaks merged together. An examination of molecular models suggests that **4b** is quite crowded about the disilylated nitrogen causing hindered rotation about the Si-N bond.

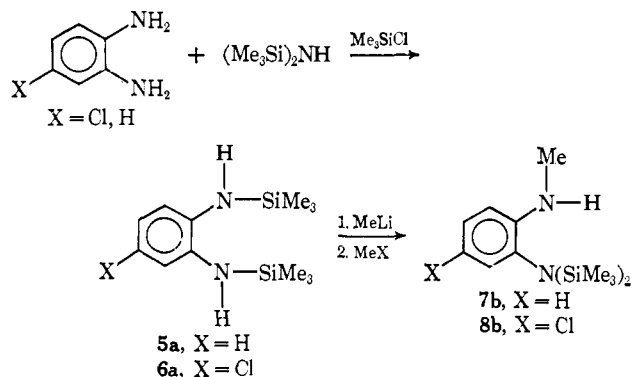
The compounds N,N'-bis(trimethylsilyl)-*o*-phenylenediamine (**5a**) and 4-chloro-N,N'-bis(trimethylsilyl)-*o*-phenylenediamine (**6a**) were both prepared from the parent diamines and hexamethyldisilazane, in the presence of trimethylchlorosilane as a catalyst. This reac-

Table I. Proton Nmr Resonances for Organosilyl-*o*-phenylenediamines, Ppm^a

Compd	(CH ₃) ₃ Si	(CH ₃) ₂ Si	<i>t</i> -BuSi	EtSi	Ph-N-H	MeN-(H)	SiNH	C ₆ H ₄
1	0.13				4.66		3.86	6.33-7.18
2a	0.22, 0.13						4.00	6.34-7.16
b	0.11				6.25			6.46-7.28
3a		0.19, 0.12		1.08-0.51			4.05	6.39-7.17
b		0.06		1.06-0.26	6.30			6.44-7.30
4a	0.007	0.145	0.79				3.98	6.44-7.21
b	0.09	0.04, 0.23 ^b	0.88		6.38			6.87-7.30
c	0.21	0.12	0.76				4.08	6.45-7.25
5a	0.15						3.04	6.44-6.85
6a	0.19, 0.14						2.70, 3.34	6.54-6.82
b	0.06					(3.68)		6.50-6.78
7a	0.01, 0.18					2.67	4.43	6.42-6.98
b	0.04					2.68, 2.78 ^c (4.07)		6.30-7.03
8a	0.01, 0.18					2.66	4.35	6.37-6.92
b	0.03					2.68, 2.71 (4.28)		6.34-6.84
9a	0.21, 0.17						4.77	6.30-7.09

^a Chemical shifts were shown to be solvent dependent. All data presented above were measured in cyclohexane. The relative intensities of peaks agreed with those predicted from assigned structure in every case. ^b The two resonances for Me₂Si are due to steric crowding causing hindered rotation about the Si-N bond. At higher temperatures these peaks merge. ^c The MeN is split into a doublet by the N-H bond. This was proven by irradiating with a secondary field at 4.07 ppm and observing the collapse of the doublet to a singlet.

tion affords the N,N' compound with >98% isomeric purity. These compounds were treated with 1 equiv of methyllithium followed by methyl bromide or iodide to obtain, surprisingly, N-methyl-N',N'-bis(trimethylsilyl)-*o*-phenylenediamine (**7b**) and 4-chloro-N-methyl-N',N'-bis(trimethylsilyl)-*o*-phenylenediamine (**8b**) in >75% yields. These isomers must have been formed



during the slow derivatization step in the preparation, because rapid reaction with pyrrole gives different isomer distributions (see Table II). The corresponding bis(organosilyl) isomers **6b**, **7a**, and **8a** were obtained as side products from these reactions. The N',N' structure of **7b** and **8b** was confirmed by spin decoupling the N-H (4.07 and 4.28 ppm, respectively) from the methyl protons which were doublets centered at 2.73 and 2.70 ppm, respectively. These doublets did not change when the compounds were heated to 190° or dissolved in pyrrole. This indicates very slow proton exchange, probably due to crowding about the N-H moiety. N',N'-Bis(trimethylsilyl)-*o*-phenylenediamine (**5b**) could not be isolated because its gas chromatographic retention time was identical with that for **5a**. Its presence was monitored by observing a singlet in the nmr spectra, upfield from **5a**, at 0.075 ppm.

Generally the N',N'-bis(organosilyl) isomers (**b** isomers) were characterized by having only one methylsilyl resonance in the nmr, showing that all of the methylsilyl protons were equivalent. In the N,N'-bis(organosilyl) isomers (**a** isomers), the two methylsilyl groups were nonequivalent and two methylsilyl peaks of

Table II. Anionic Rearrangements

Compd	% N',N' isomer (b)
2a,b, R = Ph; R' = R'' = Me; X = H	85
3a,b, R = Ph; R' = R'' = Et; X = H	86
4a,b,c, R = Ph; R' = Me; R'' = <i>t</i> -Bu; X = H	12 ^a
5a,b, R = H; R' = R'' = Me; X = H	17
6a,b, R = H; R' = R'' = Me; X = Cl	31
7a,b, R = Me; R' = R'' = Me; X = H	8
8a,b, R = Me; R' = R'' = Me; X = Cl	28 ^b

^a Composition at equilibrium is 12% **4b**, 35% **4a**, and 53% **4c** formed by the back rearrangement of **4b**. ^b Reaction was complicated by the formation of condensation product **15**.

equal intensity were generally found, **5a** being the only exception. See Table I for a summary of the nmr data for the *o*-phenylenediamine derivatives.

Anionic Rearrangements. Table II summarizes the anionic-rearrangement equilibrium data collected on all the compounds investigated. The systems most extensively studied were **2a,b**, **3a,b**, **4a,b**, and **7a,b**. Compounds **2** through **8** were treated with 2.0 equiv of methyllithium in ether and allowed to stand at 25° until no change could be observed in the nmr spectra of the anionic solution, and then treated with 2.2 equiv of pyrrole to protonate the nitrogen anion. Generally the isomeric distribution of the anions was the same as for the amines obtained on protonation. In every example, except **4a** which had a half-life of several minutes, the rearrangement was complete before an nmr of the anion could be obtained.

The rearranged anion **2b** was also trapped with methyl iodide, leading to N-methyl-N-phenyl-N',N'-bis(trimethylsilyl)-*o*-phenylenediamine (**2c**).

The results shown in Table II were in general agreement with the equilibrium data collected previously with bis(organosilyl)ethylenediamines.⁶ The position of

(6) R. West, M. Ishikawa, and S. Murai *J. Amer. Chem. Soc.*, **90**, 727 (1968).

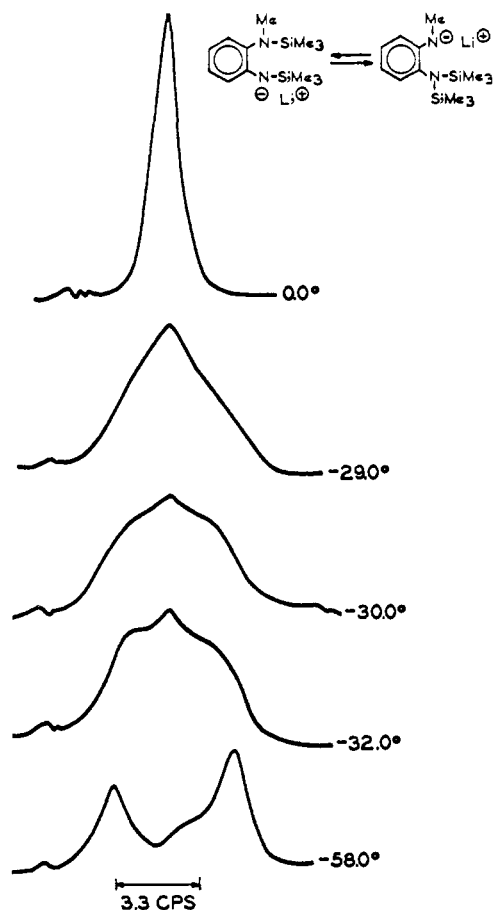
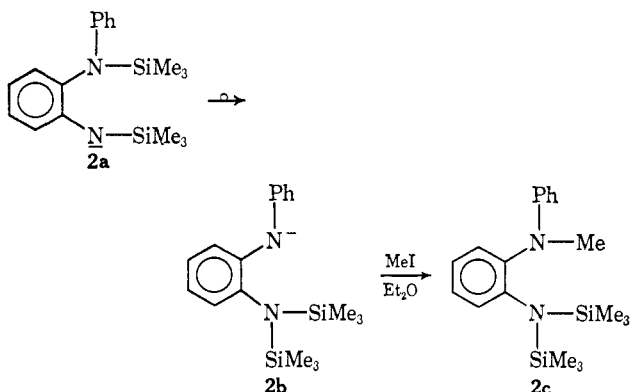


Figure 1. Silylmethyl region of nmr spectrum of anion from **7a** or **7b** in ether solution at various temperatures.

the equilibrium appears to be due largely to electronic effects, except in **4a**, in which the *t*-butyldimethylsilyl moiety exerts steric requirements which dramatically change the isomer distribution at equilibrium. When R



is phenyl the N',N' -bis(organosilyl) anion is favored by the negative charge being delocalized into two aromatic systems. When R is hydrogen or methyl the relative stability of the N',N' anion is decreased, resulting in a shift in equilibrium to the N,N' structure. These changes in equilibrium concentrations are substantial, but the free-energy differences involved are small, being 5 kcal for system **2** vs. **7**. The 4-chloro group in systems **6** and **8** changed the isomer distribution somewhat for systems **5** and **7**, showing that even small electronic effects can change the position of equilibrium.

In order to establish the inter- or intramolecular nature of the 1,4-rearrangement, two "mixing" experiments were done. Equivalent amounts of compounds **2a** and **3a** (which rearrange at similar rates) were mixed and treated with excess methyllithium and then with pyrrole. The products were **2b** and **3b** only; no "cross-over product" containing both ethyldimethylsilyl and trimethylsilyl was formed. In the other experiment, when **4a** was treated in a similar manner as above, **4b** and **4c** were the only products obtained. These results indicate that the rearrangement is intramolecular, as are anionic rearrangements in silylethylenediamines⁶ and hydrazines described earlier.⁷

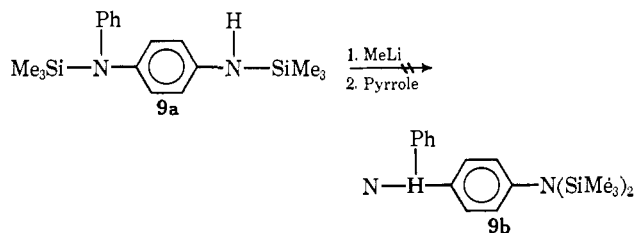
Unlike the anionic rearrangement of silylhydrazines and silylethylenediamines, the anionic rearrangements of silyl-*o*-phenylenediamines were not catalytic. For example when **2a** was treated with 0.5 equiv of methyllithium only about 25% rearrangement to **2b** was observed. This can be explained if proton exchange between lithium amide and free amine is slow.

The half-time for the rearrangement of anion **7a** to the anion **7b** in ether solution was shown to be approximately 5×10^{-2} sec at -29.0° . These data were obtained by variable temperature nmr analysis of the rearranging anionic solution of **7a** and **b** (Figure 1). As the temperature of the experiment was decreased, the peak observed in the methylsilyl region (0.087 ppm) continually broadened until at -29.0° the single methylsilyl peak began to separate into three peaks, which were resolved at -58° . The two large peaks, separated by 5 cps, were assigned to anion **7a**. The small peak in the middle of the **7a** resonances was assigned to anion **7b**. Only approximate rate data could be obtained because the peaks overlapped somewhat so that peak widths and shifts had to be estimated.

The rate of rearrangement of **7a** to **7b** appears to be distinctly faster than silyl migration in anions of open-chain ethylenediamines.⁸ This difference can be rationalized in terms of the bridging transition state which is probable for both rearrangements. Attainment of the transition state is made easier in the *o*-phenylenediamine rearrangement because the nitrogen atoms are restricted to the same plane by the aromatic ring.



If a bridging transition state is involved in the intermediate, then no rearrangement would be expected when **9a** was treated with excess base, and in fact no re-



(7) (a) R. West, M. Ishikawa, and R. E. Bailey, *J. Amer. Chem. Soc.*, **89**, 4068 (1967); (b) R. West and M. Ishikawa, *ibid.*, **89**, 4981 (1967).

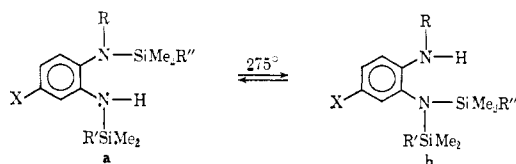
(8) (a) Rearrangement of N,N' -bis(trimethylsilyl)-*N*-phenylethylenediamine anion has a half-time of about 20 min at 30° in benzene.⁸ Other cases have not been studied in detail, but the rearrangements are slow enough so that individual anions can be observed at room temperature by nmr. The rate of rearrangements of **7a** approaches that of trimethylsilylhydrazide anions.^{8b} (b) R. West and M. Ishikawa, *J. Amer. Chem. Soc.*, **89**, 5049 (1967).

arrangement to **9b** was observed. This suggests that in order for the intramolecular rearrangement to occur the two sites involved must be close enough at some time during the reaction to allow bridging by the migrating group.

Thermal Rearrangement. A new *intermolecular, thermal rearrangement* was discovered when attempts were made to isolate **2b**, obtained by anionic rearrangement from **2a**, by distillation or preparative gas chromatography. Both purification procedures resulted in the rearrangement back to **2a**. Isolation of **2b** by gas chromatography was possible only when the injector port and detector of the instrument were kept below 265°.

The thermal rearrangement was studied by sealing the silylamine in an nmr tube with decalin as the solvent and heating. At 275° the rearrangement occurred at a convenient rate for study. Table III summarizes the

Table III. Thermal Rearrangements



Compd	Time, hr ^a	% N',N' isomer ^b (b)	% Inter-molecular rearrangement ^c
2a,b	60	30	<1
3a,b	26	20	2
4b,c	60	7	<1
5a,b	29	8	2
6a,b	16	5	2
7a,b	10	58	<1
8a,b	13	58	<1

^a The time beyond which further heating caused no change in composition. ^b Percentages were determined by integration of the methylsilyl region of the nmr, and the results were checked by glpc area percentages. Agreement with generally within $\pm 2\%$. ^c Products formed by intermolecular rearrangement were not isolated but were other than those expected from intramolecular rearrangement. Higher temperatures (290–300°) increased the amounts of these products.

data collected for 1,4-silyl rearrangement in various silyl-substituted *o*-phenylenediamines.

Although there are probably many factors which dictate the position of equilibrium obtained in the thermal rearrangement, a comparison of the data in Table III suggests that steric factors outweigh electronic influences. For example, there was very little difference in the position of equilibrium in systems **5** and **6** and no difference in systems **7** and **8**. These systems varied from each other in the anionic rearrangements. A particularly interesting example was the exclusive migration of the trimethylsilyl group in compound **4b** to form **4c**. This must be due to steric control (see Figure 2 for nmr spectra of the rearranging system). Comparing systems **2** and **3** indicates that more crowding occurs with the ethyldimethylsilyl moiety in **3**, thus leading to less N',N' isomer formation in **3**.

At higher temperatures, intermolecular processes⁹

(9) The intermolecular thermal rearrangements in bis(silyl)ethylenediamines have been reported by C. G. Pitt and M. S. Habercorn, *J. Organometal. Chem.*, **12**, 397 (1968).

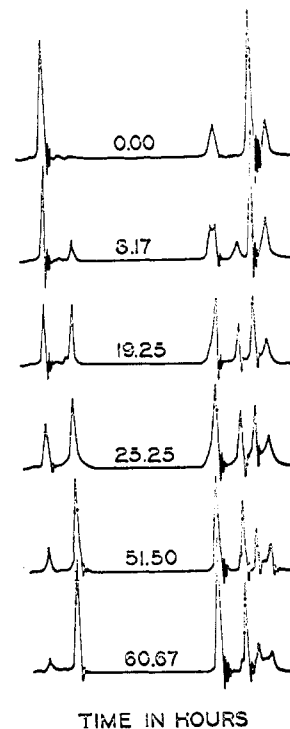


Figure 2. *t*-Butyl and methylsilyl region of the nmr spectrum of **4b** rearranging to **4c** at 275°. The proportion of **4c** at the various times is 0, 13, 50, 62, 78, and 93%.

leading to disproportionation begin to compete with intramolecular rearrangement. For example when **2a** was heated at 290° for 15 hr, 6% disproportionation was detected by glpc analysis.

Condensation Reaction. 2-Dimethylsilabenzimidazoline was recently prepared by the reaction of dimethyldichlorosilane and *o*-phenylenediamine in the presence of an acid acceptor.¹⁰ Treatment of our silyl *o*-phenylenediamines with *n*-butyllithium in tetrahydrofuran led to a cyclization to 2-silabenzimidazolines with elimination of methyllithium. This reaction provides a new method for synthesis of substituted 2-dimethylsilylbenzimidazolines in good yields and in high purity. Identification of products was based on nmr (see Table IV) and ir analyses.

The condensation reaction proceeded slowly at room temperature for all the silylamines studied, except for **2a**, which did not form any condensation product after 6 days. Compounds **7b** and **8b**, when treated with 0.5 equiv of *n*-butyllithium for 6 days were quantitatively converted into **13** and **15**, respectively, indicating that the condensation reaction proceeded catalytically with base at room temperature.

In refluxing tetrahydrofuran only **5a** and **6a** could be quantitatively cyclized using less than 1 equiv of base. For example if 0.5 equiv of *n*-butyllithium was heated with amine **2a**, only a 50% yield of **12** was obtained. Similar results were found in the preparations of **13** and **15**. Higher reaction temperature must cause the methyllithium, formed from the cyclization, to be destroyed by reaction with solvent before deprotonation of the silylamine can occur.

When **5a** and **6a** were heated with *n*-butyllithium, two new, unexpected products, **11** and **16**, were formed in

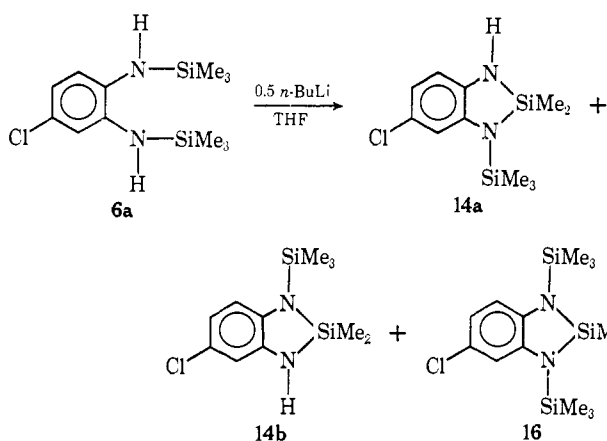
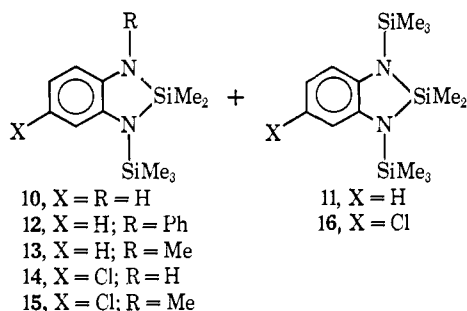
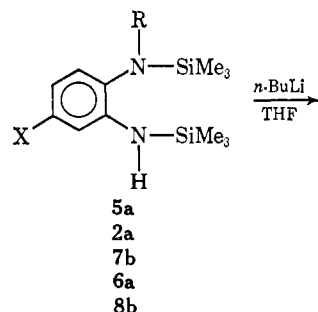
(10) M. Wieber and M. Schmidt, *Angew. Chem.*, **75**, 1116 (1963).

Table IV. Proton Nmr Resonances for 2-Silabenzimidazolines, Ppm^a

Compd	(CH ₃) ₃ Si	(CH ₃) ₂ Si	N-H	N-Me	N-Ph	C ₆ H ₄	C ₆ H ₃
10	0.27	0.28	3.26			6.30-6.75	
11	0.27	0.36				6.33-6.83	
12	0.34	0.34			7.14	6.49	
13	0.30	0.29		2.71		6.73-6.12	
14a	0.27	0.26	3.08				6.25-6.82
b	0.25	0.25	3.42				6.25-6.82
15	0.28	0.29		2.71			6.32, 6.42-6.53
16	0.27, 0.29	0.36					6.54, 6.69

^a Internal reference and solvent was cyclohexane. The relative intensities of peaks agreed with those predicted from the assigned structure in every case.

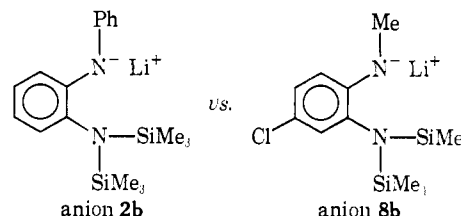
yields of 18 and 45%, respectively, in addition to the expected compounds 10 and 14a, b. Presumably 11 and 16 were formed by intramolecular exchange. Com-



pounds 14a and 14b comprised 55% of the reaction mixture and were present in a ratio of 54:46, respectively.

A qualitative trend in reactivity toward condensation was established for the various amines. Arranging them in order of increasing reactivity they are: 2a < 5a, 6a < 7b < 8b. The more reactive compounds, 7b and 8b, undergo the condensation reaction at room temperature in ether-cyclohexane solution, while 2a condenses only very slowly in refluxing tetrahydrofuran. If the condensation reaction is considered to be an intramolecular nucleophilic attack of the lithium amide on silicon,

the observed reactivity order seems to follow increasing base strength of the anion. Further investigations of new condensation reactions are being carried out.



Experimental Section

Analytical and preparative gas chromatography were carried out using a Barber-Coleman 5340 TC chromatograph equipped with a Model 5000 temperature programming unit. The analytical column used was a 1/4 in. × 10 ft aluminum column packed with a 25% 50-50 mixture of SE-30 silicone fluid and FS-1265 fluid on 60-80 mesh Chromosorb P, with a helium flow rate of 100 cc/min. The temperature was routinely programmed from 75 to 300° at 10°/min. The preparative separations were carried out using a 3/8 in. × 20 ft aluminum column packed with 20% SE-30 silicone fluid on 20-40 mesh Chromosorb W and a helium flow rate of 200 cc/min. The preparative separations were done isothermally, usually 50-100° below the boiling point of the desired compound. Proton nmr spectra were determined with a Varian A-60A and/or HA-100 spectrometer equipped with variable temperature probes and proton decoupling equipment; chemical shifts were obtained by internal referencing with cyclohexane. Ir spectra were obtained on a Perkin-Elmer 457 grating spectrophotometer. All boiling points and melting points were uncorrected.

Materials. All chemicals were reagent grade materials. Solvents such as cyclohexane, benzene, decalin, THF, and ether were further purified by refluxing over sodium or lithium aluminum hydride followed by fractional distillation from these drying agents just before use. Trimethylchlorosilane and hexamethyldisilazane were obtained from the Dow Corning Corporation. N-Phenyl-*o*-phenylenediamine, N-phenyl-*p*-phenylenediamine, 4-chlorophenylenediamine, pyrrole, and *o*-phenylenediamine, were used as obtained from Aldrich Chemical Co. *n*-Butyllithium (cyclohexane solution) and methyllithium (ether solution) were obtained from Foote Mineral Co. Ethyldimethylchlorosilane¹¹ was prepared in the standard manner by the reaction of dimethyldichlorosilane (Dow Corning Corp.) with ethylmagnesium bromide (Arapahoe Chemicals, Inc.). *t*-Butyldimethylchlorosilane was prepared analogously by treating *t*-butyllithium (pentane solution) with excess dimethyldichlorosilane. Its physical properties were identical with those reported earlier.¹²

All preparations and reactions were carried out in apparatus which was carefully dried while being swept with dry nitrogen. A dry nitrogen atmosphere was used in all experiments. All compound nmr data are summarized in Tables I and IV. Analyses were performed by Galbraith Laboratories, Inc.

N-Phenyl-N'-trimethylsilyl-*o*-phenylenediamine (1). To a solution of 22.8 g (0.21 mol) of *o*-phenylenediamine in 150 ml of THF were added 55.0 g (0.34 mol) of hexamethyldisilazane and 0.5 ml of trimethylchlorosilane as a catalyst. The mixture was refluxed for

(11) R. N. Lewis, *J. Amer. Chem. Soc.*, **69**, 717 (1947).

(12) L. H. Sommer and L. J. Tyler, *ibid.*, **76**, 1030 (1954).

22 hr, concentrated and distilled to yield 47 g (88%) of crude **1**. Redistillation using a spinning band column gave pure **1**, bp 128–130° (0.3 Torr). The proposed structure was consistent with the nmr and ir spectra.

Anal. Calcd for $C_{15}H_{20}N_2Si$: C, 70.26; H, 7.86; N, 10.92. Found: C, 71.15; H, 7.94; N, 11.13.

The compound was also synthesized by metalation of N-phenyl-*o*-phenylenediamine with *n*-butyllithium, followed by treatment with trimethylchlorosilane. The N,N isomer is first formed in the reaction, but (as shown by nmr) rearranges thermally to the N,N' isomer upon distillation.

N-Phenyl-N,N'-bis(trimethylsilyl)-*o*-phenylenediamine (2a). A 1.67 M diethyl ether solution of methylolithium (126 ml, 0.21 mol) was added, with stirring, to a solution of 18.43 g of N-phenyl-*o*-phenylenediamine (0.10 mol) in 70 ml of dry diethyl ether. After 16 hr at room temperature, 23.8 g (0.22 mol) of trimethylchlorosilane was added over a 35-min period. Twenty-four hours later the reaction was filtered under nitrogen and the filtrate distilled through a short-path column, bp 135–139° (1.0 Torr). The distillate was a colorless thick oil which did not darken on standing; 25 g (76%) was collected. Gas chromatographic analysis showed two peaks having an area ratio of 80:20 corresponding to **2a** and **2b**, respectively. The two isomers were separated by preparative glpc in order to obtain pure **2a**.

Anal. Calcd for $C_{18}H_{28}N_2Si_2$: C, 65.81; H, 8.58; N, 8.53; Si, 17.70. Found: C, 65.79; H, 8.67; N, 8.60; Si, 17.41.

N-Phenyl-N,N'-bis(trimethylsilyl)-*o*-phenylenediamine (2b). To a solution of 30 ml of diethyl ether and 6.0 g (0.018 mol) of **2a** was added 40 ml of 1.5 M methylolithium (0.06 mol). After 4 hr 6.7 g (0.1 mol) of pyrrole was added. The reaction mixture was filtered and the ether removed by rotary evaporator. Nmr analysis of the crude reaction mixture indicated 83% of **2b** was present *via* area integration of the trimethylsilyl region. The residue was distilled at 157–159° (10 Torr). The distillate was a light yellow oil weighing 4.6 g (76%). Glpc of the distillate showed two components with area ratios of 60:40. Internal glpc standards showed the 60% component to be **2a** (formed by thermal rearrangement of **2b** to **2a**, *vide infra*). The other component was separated by preparative glpc using a column temperature of 245° with the injector and detector set at 265°. Nmr analysis showed this component to be **2b**.

Anal. Calcd for $C_{18}H_{28}N_2Si_2$: C, 65.81; H, 8.58; N, 8.53; Si, 17.70. Found: C, 65.32; H, 9.12; N, 8.64; Si, 17.07.

N-Methyl-N-phenyl-N,N'-bis(trimethylsilyl)-*o*-phenylenediamine (2c). The same procedure as used in the preparation of **2b** was repeated except that 2.84 g (0.020 mol) of methyl iodide was used to derivatize the anion. The product was distilled at 137–139° (0.35 Torr), 5.0 g (80%) being collected. Two components were shown to be present in the distillate by glpc analysis in a ratio of 85:15. The largest component was purified by preparative glpc and was shown to be **2c** by nmr analysis, mp 40–42.5°: nmr analysis (ppm) Me₃Si, 0.10; N-Me, 3.12; Ph, 6.45–7.25; relative intensities 18.2:3.0:9.2, respectively.

Anal. Calcd for $C_{19}H_{30}N_2Si_2$: C, 66.62; H, 8.83; N, 8.18; Si, 16.37. Found: C, 66.42; H, 8.78; N, 8.36; Si, 16.18.

N-Phenyl-N,N'- (3a) and N-Phenyl-N,N'-bis(ethylidimethylsilyl)-*o*-phenylenediamine (3b). These isomers were prepared in the manner of **2a** by adding 180 ml of 0.80 M methylolithium (0.14 mol) to a solution of 10.0 g of N-phenyl-*o*-phenylenediamine (0.054 mol) of 70 ml of dry diethyl ether over a 30-min period at room temperature. After 16 hr 17.6 g (0.14 mol) of ethyldimethylchlorosilane was added, and the reaction was stirred for 24 hr. The mixture was then filtered; the filtrate was fractionally distilled under reduced pressure to give 15.3 g (80%) of a 90:10 mixture of **3a** and **3b**, respectively, bp 157–162° (10 Torr). The two isomers were separated by preparative glpc in order to obtain pure samples, and their nmr and ir analysis were consistent with proposed structure. Elemental analysis was obtained on the isomeric mixture.

Anal. Calcd for $C_{20}H_{32}N_2Si_2$: C, 67.35; H, 9.04; N, 7.85; Si, 15.75. Found: C, 67.71; H, 9.10; N, 7.62; Si, 15.73.

N-Phenyl-N-*t*-butyldimethylsilyl-N'-trimethylsilyl-*o*-phenylenediamine (4a). Using an inverse Grignard apparatus, a reaction solution, formed by mixing 6.96 g (0.027 mol) of **1**, 20.6 ml of 1.5 M methylolithium (0.031 mol), and 25 ml of dry diethyl ether at 0° for 24 hr, was added to 8.17 g (0.054 mol) of *t*-butyldimethylchlorosilane in 100 ml of tetrahydrofuran at 0°. The mixture was stirred 10 hr after being warmed to room temperature, and filtered. The filtrate after concentration was fractionally distilled yielding 8.5 g (85%) of **4a**, bp 157–164° (10 Torr). Glpc analysis showed the isomeric purity to be 91%. The sample was further purified by preparative glpc.

Anal. Calcd for $C_{21}H_{34}N_2Si_2$: C, 68.04; H, 9.25; N, 7.56; Si, 15.15. Found: C, 67.97; H, 9.02; N, 7.36; Si, 15.04.

N,N'-Bis(trimethylsilyl)-*o*-phenylenediamine (5a). The following reagents were combined and heated with stirring at tetrahydrofuran reflux for 22 hr: *o*-phenylenediamine (22.8 g, 0.21 mol); hexamethyldisilazane (55.0 g, 0.34 mol); dry tetrahydrofuran (150 ml); and a trace of trimethylchlorosilane as catalyst. After this reaction period no ammonia odor was detected at the nitrogen exit. The mixture was purified by fractional distillation through a 24-in. Teflon spinning band column to yield 45 g (83%) of **5a**, bp 106–108° (1.8–2.0 Torr), mp 32–34.5°. Nmr and ir were consistent with the proposed structure.

Anal. Calcd for $C_{12}H_{24}N_2Si_2$: C, 57.08; H, 9.58; N, 11.09; Si, 22.25. Found: C, 57.42; H, 9.66; N, 11.04; Si, 21.99.

N,N'-Bis(trimethylsilyl)-4-chloro-*o*-phenylenediamine (6a). Compound **6a** was prepared in a manner analogous to **5a**, by heating at tetrahydrofuran reflux for 58 hr a solution of 29.8 g (0.21 mol) of 4-chloro-*o*-phenylenediamine, 55.0 g (0.34 mol) of hexamethyldisilazane, 150 ml of tetrahydrofuran, and a trace of trimethylchlorosilane. Fractional distillation yielded 35 g (85%) of **6a**, bp 110–115° (0.8 Torr), n_D^{20} 1.5189. The N,N'-bis(trimethylsilyl) structure was supported by the observation of two methylsilyl resonances of equal intensity in the nmr at 0.19 and 0.14 ppm, which were assigned to N'- and N-trimethylsilyl groups, respectively.

Anal. Calcd for $C_{12}H_{23}ClN_2Si_2$: C, 50.23; H, 8.08; Cl, 12.35; N, 9.76; Si, 19.58. Found: C, 50.13; H, 8.28; Cl, 12.30; N, 10.05; Si, 19.24.

N-Methyl-N,N'- (7a) and N-Methyl-N,N'-bis(trimethylsilyl)-*o*-phenylenediamine (7b). A solution of (66.5 ml, 1.5 M, 0.10 mol) *n*-butyllithium was added at 0° to a mixture containing (25.3 g, 0.10 mol) **5a** in 100 ml of dry diethyl ether. The addition required 53 min and caused the reaction to turn a deep royal blue. After stirring at 0° for 19 hr, the reaction was cooled to –78°, a Dry Ice condenser was attached to the apparatus, and 11.4 g (0.12 mol) of methyl bromide was rapidly added. No reaction was noted as the temperature was slowly increased, until at 10° the reaction mixture turned a dark green. Stirring was continued at room temperature for 21 hr. The product was distilled from the salts and 20.0 g (75%) of distillate was collected, bp 96–98° (2.3 Torr). Glpc of the distillate showed two components in a ratio of 35:65. Analyses were done on glpc prepared samples.

The largest component had the longest retention time and was found to be **7b** by nmr analysis. The trimethylsilyl region consisted of a singlet at 0.04 ppm and the N-CH₃ was a doublet centered at 2.73 ppm. This doublet was collapsed to a singlet by irradiating with a secondary field at the N-H resonance at 4.07 ppm. Molecular weight determined by benzene freezing point lowering was 261 (266.5 theory).

Anal. Calcd for $C_{13}H_{26}N_2Si_2$: C, 58.58; H, 9.83; N, 10.51; Si, 21.07. Found: C, 58.82; H, 9.75; N, 10.70; Si, 20.90.

The smaller component was identified by nmr analysis to be **7a**. It was also consistent with this proposed structure.

Anal. Calcd for $C_{13}H_{26}N_2Si_2$: C, 58.58; H, 9.83; N, 10.51; Si, 21.07. Found: C, 58.71; H, 9.75; N, 10.45; Si, 21.24.

N-Methyl-N,N'- (8a) and N-Methyl-N,N'-bis(trimethylsilyl)-4-chloro-*o*-phenylenediamine (8b). Compounds **8a** and **8b** were prepared by the same procedure used in obtaining **7a** and **7b**. A solution of 20.0 g (0.07 mol) of **6a** in (100 ml) dry diethyl ether was treated with 37 ml of 2.08 M methylolithium–lithium bromide complex (0.077 mol of methylolithium). After stirring at the reaction temperature of –78° for 4 hr, 11.2 g (0.08 mol) of methyl iodide was added. This solution was stirred for 20 hr at 0°. During this period the solution changed from royal blue to bright green. The green solution, when exposed to the air, turned brown and a precipitate formed.

The solvent was removed by vacuum stripping and the product was distilled directly from the salts; 18.0 g (84%) of colorless distillate was collected, bp 103–105° (0.4 Torr). Glpc analysis showed two peaks in a ratio of 17:83, the largest component being the last to elute. These two components were separated by preparative glpc and shown by their nmr spectra to be **8a** and **8b**, the latter being identified as the largest component. For **8b** n_D^{20} 1.5215.

Anal. Calcd for $C_{13}H_{25}ClN_2Si_2$: C, 51.88; H, 8.37; Cl, 11.78; N, 9.31; Si, 18.66. Found (**8a**): C, 52.01; H, 8.33; Cl, 12.01; N, 9.50; Si, 18.08. Found (**8b**): C, 52.03; H, 8.25.

N-Phenyl-N,N'-bis(trimethylsilyl)-*p*-phenylenediamine (9a). To an ice-cooled solution of 18.43 g (0.10 mol) of N-phenyl-*p*-phenylenediamine in 70 ml of dry diethyl ether was added 272 ml of 0.8 M methylolithium (0.22 mol) over 1 hr. The addition of methylolithium appeared to cause some polymer formation. After stirring this

solution for 24 hr at 0°, 37.0 g (0.34 mol) of trimethylchlorosilane was added over 30 min. This mixture was stirred at room temperature for 10 hr, filtered, and concentrated by vacuum stripping. The residue was vacuum distilled at 134–136° (0.5 Torr), 6.6 g (25%) being collected. Glpc analysis showed two components in a ratio of 80:20. The larger component was shown to be isomer **9a** by nmr analysis. Attempts to obtain pure **9a** by preparative glpc were not successful, as it appeared that intermolecular rearrangement occurred at the high temperature (> 250°) necessary for glpc work. The 20% component was shown to be *N*-phenyl-*N*-trimethylsilyl-*p*-phenylenediamine. This mixture was used for our anionic rearrangement studies.

Anionic Rearrangement Reactions. a. General Procedure. The same general procedure was used for all the anionic rearrangement reactions. A thin-walled Varian nmr tube was fitted with a small rubber serum stopper wired securely in place with thin copper wire. Two hypodermic needles, one the inlet for high purity, dry nitrogen, the other the exit, were inserted through the stopper. With a rapid nitrogen flow, the tube was heated to 200–250° with a heat gun.

After the tube cooled to room temperature the exit needle was removed and the reagents added. Usually 0.4–0.6 mmol (0.1–0.3 g) of glpc prepared silylamine substrate was added to the tube which was then cooled with Dry Ice before 0.8–1.2 mmol (0.6–1.0 ml) of methylolithium was added. The reaction was carefully mixed while warming to room temperature. These solutions were homogeneous, varying in color from light yellow to light green and permitting the convenient observation of the nmr spectrum of the amine anions. When no further change was noted in the nmr spectrum of the anionic species, usually within the time of mixing to several minutes, excess pyrrole was added. In order to hasten the separation of salts and to serve as an internal nmr standard, 0.2–0.4 ml cyclohexane was added. The salts were centrifuged to the top of the tube and a nmr analysis made by integration of appropriate resonances from the various isomers. In every reaction a glpc analysis was made of the reaction mixture and the glpc area percentages always agreed with the nmr mole percentages within $\pm 3\%$. Internal glpc standards were used to confirm the identity of the reaction components. When two isomers were involved, as in systems **2**, **3**, and **7**, the equilibrium was approached starting from both isomers with similar results being obtained. In "mixing" experiments, the lack of crossover products was established by gas chromatographic separation of the mixture determination of the nmr spectra of the components, which were identical with the known "unmixed" isomers. The data collected from this study are summarized in Table II.

b. The Effect of Base Stoichiometry. These experiments were carried out as described above for anionic rearrangements except that the quantity of methylolithium was varied in a series of experiments, in steps of 0.25, 0.50, 0.75, 1.00, 1.25, and 2.0 equiv to 1 equiv of silylamine **2a**. The progress of the anionic reaction was followed by scanning the methylsilyl region of the nmr, but the peaks observed were those of the protonated *o*-phenylenediamines at low-concentration base. As the amount of base increased the peaks assigned to the protonated species decreased until at 2.0 equiv of base only one peak was observed. When 0.25 equiv of base was added to **2a** in ether no reaction was observed. (Probably the methylolithium reacted with a trace of moisture or oxygen.) At 0.50 equiv of base, approximately 25% rearrangement was detected, 0.75 equiv, 50%, and with 1.0 equiv, 75% rearrangement with other species present. It therefore appears that the rearrangement is not catalytic in this example. Rearrangement also proceeded more rapidly when excess base was used.

c. Nmr Investigation of 7a and 7b Anion. Using the general procedure above, isomers **7a** and **7b** were treated with 2 equiv of methylolithium and a small amount of cyclohexane added as an internal reference. Both anionic isomers afford the same nmr spectra, with the trimethylsilyl region being a singlet at 0.087 ppm Me-N, a singlet at 2.64 ppm; phenyl protons a multiplet at 7.04–6.13 ppm, and the excess methylolithium at -1.90 ppm. The integration of the protons agreed with theory, and the mole ratio of methylolithium vs. Me-N indicated the former is present in 100% excess. The $1/2$ -height line width of the Me₃Si peak at 36.5° was 0.5 cps.

As the temperature of the nmr experiment was decreased the width of the trimethylsilyl region increased as can be seen in Figure 1. At -29.0° the $1/2$ -height line width was 4.1 cps, and the peak was fairly symmetric. A decrease in temperature of one degree, to -30.0° , caused shoulders to appear. Separation of peaks continued as the temperature dropped, until at -58.0° three peaks were observed. It was assumed the two large peaks were due to anion

7a and the small peak between them, anion **7b**. A crude measure of the area under the curves via a planimeter indicated 89% of **7a** anion. (Protonation of the reaction with pyrrole afforded 92% **7a**.) Using estimates for the $1/2$ -height line width of **7a** and **7b**, assuming a peak separation between **7a** and **7b** of 3.3 cps at -58° , and substituting this data into the appropriate equations,¹³ afforded a very crude value for $\tau_{1/2}$ of 0.05 ± 0.03 sec at -29° .

Thermal Rearrangement Reactions. The glpc pure silyl-*o*-phenylenediamine substrates (0.4–0.6 mmol) were put into carefully dried nmr tubes with 0.6–0.8 ml of dry decalin. The tube was sealed under a dry nitrogen atmosphere. The sealed tube was put into a steel pipe for protection against explosion and then heated in an oven at $275 \pm 5^\circ$. The tube was removed periodically, cooled rapidly, and analyzed by nmr analysis. When equilibrium was reached the tube was opened and also examined by glpc analysis. See Table III for a summary of data. As noted in other experiments, (preparation of **2a,b**), thermal rearrangement must have occurred in impure samples at lower temperatures. Compound purity may also account for the different reaction times noted in Table III.

After equilibrium was achieved heating was continued at higher temperatures. Generally it was found that at 290–305° products which must arise from intermolecular rearrangement started to form at an appreciable rate.

The equilibrium was approached from both isomers in systems **2**, **7**, and **8**.

General Procedure for the Preparation of Silyl-Substituted 2-Dimethylsilylabenzimidazolines. *n*-Butyllithium (1.6 M in hexane) was slowly added to a solution of silyl-substituted *o*-phenylenediamine in anhydrous tetrahydrofuran at -78° . These highly colored solutions, usually blue-green, were slowly warmed to room temperature over 4 to 5 hr with stirring, and then heated at tetrahydrofuran reflux for 40 to 48 hr. (Reactions at room temperature omitted this heating step.) After being cooled to room temperature, 10% excess (over *n*-butyllithium) pyrrole was added which caused a slight exotherm. The solvents were removed by vacuum stripping and the residue was fractionally distilled under vacuum. Pure isomers were obtained by preparative glpc. The nmr data for all products were summarized in Table IV. Characteristic strong ir absorptions were generally observed close to 2970, 1580, 1470, 1250, 1220, 1190, 1110, 1020, 950, 890, and 830 cm⁻¹.

1-Trimethylsilyl-2-dimethylsilylabenzimidazoline (10) and 1,3-Bis-(trimethylsilyl)-2-dimethylsilylabenzimidazoline (11). A solution of **5a** (12.6 g, 0.05 mol) in 50 ml of tetrahydrofuran was allowed to react with 15.6 ml (0.025 mol) of *n*-butyllithium. After treatment with pyrrole (1.84 g, 0.0275 mol), the product was distilled at 130–134° (4.2 Torr), 10.2 g (86%) being collected. Glpc showed two components in a ratio of 82:18, which were shown to be **10** and **11**, respectively, by nmr analysis. Pure products were obtained by preparative glpc.

Compound **10** was a white solid, mp 119–120°.

Anal. Calcd for C₁₁H₂₀N₂Si₂: C, 55.87; H, 8.53; N, 11.85; Si, 23.75. Found: C, 55.70; H, 8.48; N, 11.70; Si, 23.52.

Compound **11** was a white solid, mp 72–76°.

Anal. Calcd for C₁₄H₂₈N₂Si₃: C, 54.58; H, 9.14; N, 9.08; Si, 27.30. Found: C, 54.71; H, 9.16; N, 8.92; Si, 27.02.

1-Phenyl-3-trimethylsilyl-2-dimethylsilylabenzimidazoline (12). A 78% **2a**, 22% **2b** mixture (5.11 g, 0.0156 mol) in solution with 55 ml of tetrahydrofuran was treated with 4.9 ml (0.0078 mol) of *n*-butyllithium. After derivatization with pyrrole the product was distilled at 159–161° (0.8 Torr), 4.0 g (79%) being collected. Glpc analysis showed 52% starting material and 48% condensation product **12**. The glpc prepared product was a thick yellow oil which very slowly crystallized.

Anal. Calcd for C₁₈H₂₄N₂Si₂: C, 66.61; H, 7.45; N, 8.63; Si, 17.31. Found: C, 65.95; H, 7.59; N, 8.95; Si, 17.59.

1-Methyl-3-trimethylsilyl-2-dimethylsilylabenzimidazoline (13). An 80% **7b**, 20% **7a** mixture (5.9 g, 0.022 mol) in solution with 50 ml of tetrahydrofuran was treated with 10.3 ml (0.0165 mol) of *n*-butyllithium. After treating with 1.5 g (0.022 mol) of pyrrole the product was distilled at 107–111° (0.4 Torr), yielding 5.0 g (85%) of distillate. Glpc analysis indicated the distillate to be 70% **13** and 30% starting material. The glpc prepared product was a white solid, mp 52.0–53.5°.

Anal. Calcd for C₁₂H₂₂N₂Si₂: C, 57.53; H, 8.85; N, 11.19; Si, 22.42. Found: C, 57.46; H, 8.86; N, 10.96; Si, 22.19.

(13) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, Inc., New York, N. Y., 1959, pp 222–223.

6-Chloro-3-trimethylsilyl-2-dimethylsilabenzimidazoline (14a), 6-Chloro-1-trimethylsilyl-2-dimethylsilabenzimidazoline (14b), and 6-Chloro-1,3-bis(trimethylsilyl)-2-dimethylsilabenzimidazoline (16). A solution of (8.6 g, 0.03 mol) **6a** in 50 ml of tetrahydrofuran was allowed to react with 9.4 ml (0.015 mol) of *n*-butyllithium. After protonation with pyrrole, the product was distilled at 133–134° (0.5 Torr), 7.7 g (85%) being collected. Glpc analysis showed three peaks, two eluting very close to each other. Preparative glpc was used to separate the components into two portions; the two peaks (55% of the total) eluting next to each other were found to be a 54:46 mixture of isomers **14a** and **14b** respectively, mp 28–34°.

Anal. Calcd for $C_{11}H_{19}ClN_2Si_2$: C, 48.77; H, 7.07; N, 10.35; Si, 20.73. Found: C, 49.04; H, 7.11; N, 10.43; Si, 20.47.

The component with the longest retention time was identified as **16** by nmr and ir analysis, mp 85.0–86.5°.

Anal. Calcd for $C_{14}H_{27}ClN_2Si_3$: C, 49.01; H, 7.93; N, 8.17; Si, 24.56. Found: C, 47.95; H, 7.67; N, 8.19; Si, 25.11.

6-Chloro-1-methyl-3-trimethylsilyl-2-dimethylsilylbenzimidazoline (15). *n*-Butyllithium (9.4 ml, 0.015 mol) was added to a solution of 6.0 g (0.02 mol) of **8b** in 50 ml of tetrahydrofuran. After treating with 1.34 g (0.02 mol) of pyrrole the product was distilled at 138–140° (1.4 Torr), 5.1 g (85%) being collected; glpc analysis indicated 77% **15**, a waxy solid, and 23% starting material.

Anal. Calcd for $C_{12}H_{21}ClN_2Si_2$: C, 50.58; H, 7.42; Cl, 12.46; N, 9.83; Si, 19.71. Found: C, 50.96; H, 7.67; Cl, 11.98; N, 9.83; Si, 19.46.

New Anionic Rearrangements. XI.¹ Anionic Rearrangement of Arylhydrazines^{2,3}

Robert West and H. Franklin Stewart

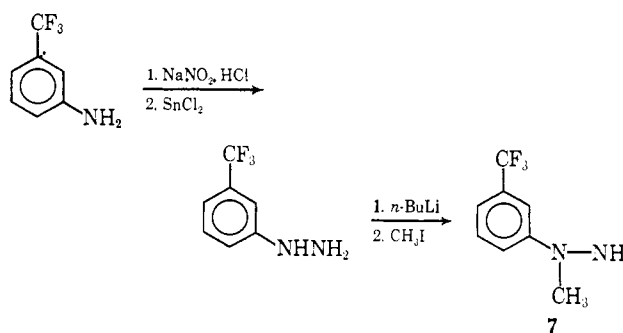
Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received July 17, 1969

Abstract: 1,2-Anionic rearrangement of aryl groups from one nitrogen atom to another takes place in 1,1-diaryl and 1-aryl-1-methylhydrazines when the latter are converted to dianions. No migration of aryl groups takes place in arylhydrazine monoanions. The kinetics of rearrangement of 1,1-diphenylhydrazine and 1,1-di-*p*-tolylhydrazine dianions was studied by nmr spectroscopy. The reaction is intramolecular and first order in dianion; the rearrangement step is rate limiting, although deprotonation to the dianion is also slow. A 1,4-N → N anionic rearrangement of phenyl in *N*-methyl-*N*-phenyl-*o*-phenylenediamine dianion is also described.

Aryl groups have frequently been studied as migrating substituents in anionic rearrangements. For instance, aryl groups migrate from one carbon atom to another in the 1,2-anionic rearrangement of substituted ethanes.^{4,5} After discovery of the very rapid 1,2-anionic rearrangement of organosilyl hydrazines,⁶ it was of interest to find out whether aromatic groups would also undergo migration in arylhydrazine anions.

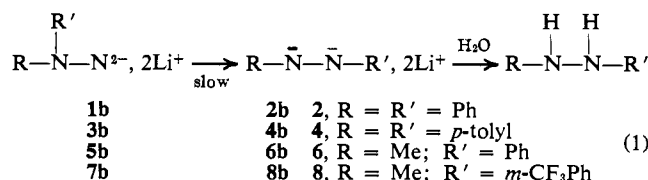
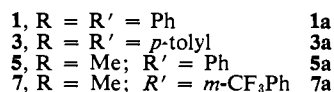
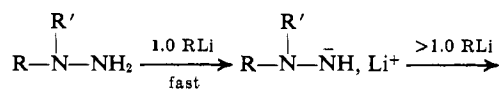
The compounds chosen for study were 1,1-diphenylhydrazine (**1**), 1,1-di-*p*-tolylhydrazine (**3**), 1-methyl-1-phenylhydrazine (**5**), and 1-methyl-1-*m*-trifluoromethylphenylhydrazine (**7**). Compounds **1** and **5** were obtained commercially, and **3** was prepared by a standard method.⁷ To synthesize the new compound **7**, *m*-aminobenzotrifluoride was diazotized and reduced to form *m*-trifluoromethylphenylhydrazine, which was methylated using *n*-butyllithium and methyl iodide.

Treatment of the four hydrazines with 1 equiv of an alkyl lithium compound converted them to their monoanions, **1a**, **3a**, **5a**, and **7a**, by rapid proton transfer. In



striking contrast to the organosilyl hydrazine monoanions, which rearrange rapidly even at -80° , no rearrangement whatsoever was observed for the arylhydrazine monoanions. Even long heating at 110° did not lead to migration of the aryl groups (at still higher temperatures decomposition resulted).

Anionic rearrangement of arylhydrazines did take place, however, when they were converted to their dian-



(1) Previous paper in this series: H. F. Stewart, D. G. Koepsell, and R. West, *J. Amer. Chem. Soc.*, **92**, 846 (1970).

(2) For a preliminary communication on this topic see R. West, H. F. Stewart, and G. R. Husk, *ibid.*, **89**, 5050 (1967).

(3) Research sponsored by Air Force Office of Scientific Research, (SRC), OAR, USAF Grant No. AF-AFOSR 1061-66.

(4) (a) E. Grovenstein, *J. Amer. Chem. Soc.*, **79**, 4985 (1957); (b) E. Grovenstein and G. Wentworth, *ibid.*, **89**, 1852 (1967).

(5) (a) H. E. Zimmerman and F. J. Smentowski, *ibid.*, **79**, 5455 (1957); (b) H. E. Zimmerman and A. Zweig, *ibid.*, **83**, 1196 (1961).

(6) (a) R. E. Bailey and R. West, *ibid.*, **86**, 5369 (1964); (b) R. West, M. Ishikawa, and R. E. Bailey, *ibid.*, **88**, 4648 (1966); (c) R. West, M. Ishikawa, and R. E. Bailey, *ibid.*, **89**, 4068 (1967); (d) R. West, M. Ishikawa, and R. E. Bailey, *ibid.*, **89**, 4072 (1967); (e) R. West and M. Ishikawa, *ibid.*, **89**, 4981 (1967).

(7) O. F. Bennett, J. Bornstein, S. A. Leone, and W. F. Sullivan, *ibid.*, **79**, 1745 (1957).