New Anionic Rearrangements. VIII.[1] 1,4-Anionic Rearrangement of Silylethylenediamines[2,3]

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Abstract: Several organosilyl derivatives of ethylenediamine, N-phenylethylenediamine, and N-methylethylenediamine have been prepared and characterized. In the presence of *n*-butyllithium, N,N′-bis(organosilyl)-N-phenylethylenediamines undergo intramolecular 1,4-anionic rearrangement to the N,N-bis(organosilyl) isomers. For N,N-bis(trimethylsilyl)ethylenediamine (**1b**) and -N′-methylethylenediamine (**2b**), similar anionic rearrangement takes place in the opposite sense to provide N,N′-bis(trimethylsilyl) isomers **1a** and **2a**. When heated with *n*-butyllithium, **2a** and **2b** undergo condensation to silaimidazolidine ring compounds with elimination of methyllithium.[4]

The anionic rearrangement of organosilylhydrazines has been described in a series of recent papers.[5] In these rearrangements, the silyl substituent undergoes 1,2 migration from one nitrogen atom to the other in the hydrazide anion. These studies have now been extended to include silyl-substituted ethylenediamines, to examine the possibility of 1,4-anionic migration of silicon.

We find that 1,4 anionic rearrangement of organosilyl substituents takes place in each of four bis(organosilyl)-ethylenediamines studied. These rearrangements are the first examples of anionic rearrangement involving diamines, and can be considered as a new class of Smiles rearrangements.[6]

Only a few organosilyl derivatives of ethylenediamine were known at the time we began our investigation.[8-10] In order to obtain particular isomers of di- and trisubstituted ethylenediamines, it proved necessary to devise some new synthetic methods, which are described below.

Syntheses. N,N′-Bis(trimethylsilyl)ethylenediamine (**1a**) and N,N′-bis(trimethylsilyl)-N-methylethylenediamine (**2a**) were both prepared from the parent diamines and hexamethyldisilazane, in the presence of trimethylchlorosilane as a catalyst. This reaction gives the N,N′ compounds in high isomeric purity.

$$\mathrm{Me_3SiNHSiMe_3 + H_2NCH_2CH_2NHR \xrightarrow[\text{cat.}]{\mathrm{Me_3SiCl}} Me_3SiNHCH_2CH_2N(R)SiMe_3}$$

$$\mathbf{1a},\ \mathrm{R = H} \qquad \mathbf{2a},\ \mathrm{R = CH_3}$$

The isomers corresponding to **1a** and **2a** but with both silicon atoms on the same nitrogen were obtained by a two-step synthesis from **1a** and **2a**. First, the bis(trimethylsilyl) compounds were converted to tris(trimethylsilyl) derivatives **3** and **4** with *n*-butyllithium and trimethylchlorosilane. Selective cleavage with methanol removed the unique trimethylsilyl group without affecting the Si–N–Si structure, giving the N,N-bis(trimethylsilyl) compounds **1b** and **2b** in good yields.

$$\mathrm{Me_3SiNHCH_2CH_2N(R)SiMe_3 \xrightarrow[\mathrm{Me_3SiCl}]{n\text{-BuLi}} (Me_3Si)_2NCH_2CH_2N(R)SiMe_3}$$

$$\mathbf{3},\ \mathrm{R = H} \qquad \mathbf{4},\ \mathrm{R = CH_3}$$

$$\mathrm{(Me_3Si)_2NCH_2CH_2N(R)SiMe_3 + CH_3OH \longrightarrow (Me_3Si)_2NCH_2CH_2NHR + Me_3SiOCH_3}$$

$$\mathbf{1b},\ \mathrm{R = H} \qquad \mathbf{2b},\ \mathrm{R = CH_3}$$

The structural assignments for **1a** and **1b** follow from their proton nmr and infrared spectra (Table I). Compound **1a** showed a single methylsilyl resonance at τ 9.98, in the correct region for $\mathrm{(CH_3)_3Si{-}N{-}H}$ protons, whereas **2b** has its silylmethyl peak at 9.90, in the usual range for $\mathrm{[(CH_3)_3Si]_2N{-}}$ protons[11,12] (Table I). The $\mathrm{-CH_2CH_2-}$ resonance is much simpler for the symmetrical isomer **1a**, in which the protons are all equivalent, than for the isomer **1b** which has nonequivalent methylene groups. In addition, **1b** shows typical strong Si–N–Si stretching absorption bands at 1075 and 910 cm^{-1} in the infrared which **1a** lacks (Table I). It is easy to show from the nmr spectra alone that **2a** and **2b** have the structures indicated. The N,N compound **2b** has only a single methylsilyl resonance at τ 9.92, showing that all of the methylsilyl protons are equivalent. In

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[1] Previous paper in this series: R. West, H. F. Stewart, and G. R. Husk, *J. Amer. Chem. Soc.*, **89**, 5050 (1967).

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

[3] Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967. See Abstracts, L-132.

[4] The new condensation reaction has been reported in a preliminary communication: R. West and M. Ishikawa, *J. Amer. Chem. Soc.*, **89**, 5049 (1967).

[5] (a) R. E. Bailey and R. West, *ibid.*, **86**, 5369 (1964); (b) R. West, M. Ishikawa, and R. E. Bailey, *ibid.*, **89**, 4068 (1967); (c) R. West, M. Ishikawa, and R. E. Bailey, *ibid.*, **89**, 4072 (1967); (d) R. West and M. Ishikawa, *ibid.*, **89**, 4981 (1967).

[6] For a general review of Smiles rearrangements, see J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 362 (1951). The example most closely similar to the one reported here is the O–O rearrangement of aryl groups in catechols.[7]

[7] J. D. Louden and J. A. Scott, *J. Chem. Soc.*, 265 (1953).

[8] Of the compounds reported in this paper, **1a**,[9,10] **3**,[10] and **13**[9] have been reported previously; to the best of our knowledge the others are all new. While this work was in progress we learned of the independent preparation of **2b** by Dr. Colin Pitt, who has also studied the equilibration of **1a** and **2b** at high temperatures (C. Pitt, private communication).

[9] D. Kummer and E. G. Rochow, *Z. Anorg. Allgem. Chem.*, **321**, 21 (1963).

[10] High-temperature condensation reactions leading to silaimidazolidines, possibly related mechanistically to our reaction, have been reported previously. See W. Fink, *Ber.*, **99**, 2267 (1966).

[11] The assignment agrees with that previously given for **1a** by Kummer and Rochow.[9]

[12] R. West, M. Ishikawa, and R. E. Bailey, *J. Amer. Chem. Soc.*, **88**, 4648 (1966).

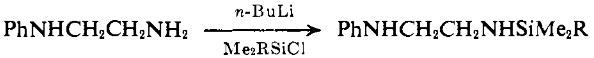
Table I. Proton Nmr Resonances for Organosilylethylenediamines, τ,[a] and Significant Infrared Bands, cm^{-1}

Compd	C*H*$_3$Si	*Et*Si	C*H*$_2$C*H*$_2$	C*H*$_3$N	PhN*H*	*Ph*N	N–H	Si–N–Si
1a	9.98		7.43–7.33				3440	None
1b	9.89		7.65–7.06				3290, 3400	1075, 910
2a	10.00, 9.97		7.39–7.28	7.60			3400	None
2b	9.90		7.73–7.02	7.54			3320	1073, 910
3	10.00, 9.92		7.44–7.35				3430	1073, 910
4	9.97, 9.90		7.45–7.18	7.54			None	1070, 900
5	9.95		7.09–6.89		6.25	3.60–2.81	3400	None
6	9.99	9.74–8.85	7.55–6.80		6.24	3.62–2.83	3400	None
7a	10.01, 9.81		7.09–6.89		6.75	3.60–2.81	3405	None
7b	9.84		7.04–6.99		6.61	3.69–2.91	3420	1075, 905
8a	10.04, 9.84	9.64–8.82	7.58–6.71			3.44–2.81	3410	None
8b	9.87	9.61–8.82	7.05–7.00		6.66	3.71–2.92	3450	1075, 900
11	9.84		7.17–6.68	7.11		3.55–2.78	None	1068, 900

[a] Si–N–H resonances were not generally observed, as they are quite broad and normally lie under the –CH$_2$CH– resonance. Ph–N–H resonances are generally sharp and were observed in every compound containing this structural feature. The relative intensities of peaks agreed with those predicted from the assigned structure in every case.

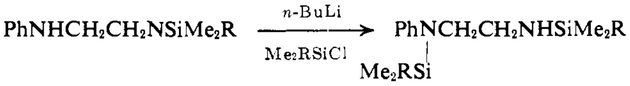
the N,N′ compound the two trimethylsilyl groups are nonequivalent, and in the spectrum of **2a** two trimethylsilyl peaks of equal intensity are found at τ 9.97 and 10.00 (Table I).

Rather different methods were used to synthesize the isomeric bis(trialkylsilyl)phenylethylenediamines. First, N-phenylethylenediamines were treated with *n*-butyllithium and either trimethyl- or ethyldimethylchlorosilane to produce the monosilylphenylethylenediamines **5** and **6**. Compounds **5** and **6** have Ph–N–H proton resonances at τ 6.24 and 6.25, respectively, indicating that they have the N,N′ structure shown (Table I). When these compounds were treated with a second equivalent of *n*-butyllithium and trialkylchlorosilane, the products were the N,N′-bis(silyl) compounds **7a** and **8a**. Compounds **7a** and **8a** were obtained in high isomeric purity so long as no excess *n*-butyllithium was present. The N,N′ structures are substantiated by the nmr spectra, which show two equal CH$_3$Si resonances for each compound and no Ph–N–H peak, and by the lack of infrared absorption in the Si–N–Si region (Table I). The corresponding N,N-bis(silyl) isomers were obtained by rearrangement of **7a** and **8a**, as described below.



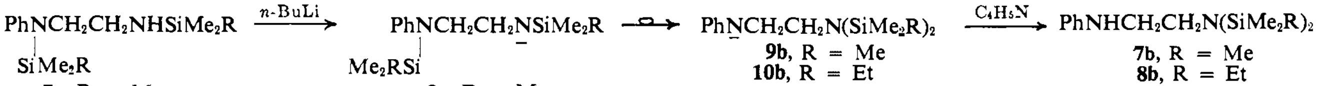
$$\text{PhNHCH}_2\text{CH}_2\text{NH}_2 \xrightarrow[\text{Me}_2\text{RSiCl}]{n\text{-BuLi}} \text{PhNHCH}_2\text{CH}_2\text{NHSiMe}_2\text{R}$$

5, R = Me
6, R = Et



$$\text{PhNHCH}_2\text{CH}_2\text{NSiMe}_2\text{R} \xrightarrow[\text{Me}_2\text{RSiCl}]{n\text{-BuLi}} \text{Ph}\underset{\text{Me}_2\text{RSi}}{\text{N}}\text{CH}_2\text{CH}_2\text{NHSiMe}_2\text{R}$$

7a, R = Me
8a, R = Et



$$\text{Ph}\underset{\text{SiMe}_2\text{R}}{\text{N}}\text{CH}_2\text{CH}_2\text{NHSiMe}_2\text{R} \xrightarrow{n\text{-BuLi}} \text{Ph}\underset{\text{Me}_2\text{RSi}}{\text{N}}\text{CH}_2\text{CH}_2\underset{-}{\text{N}}\text{SiMe}_2\text{R} \longrightarrow \text{Ph}\underset{-}{\text{N}}\text{CH}_2\text{CH}_2\text{N(SiMe}_2\text{R)}_2 \xrightarrow{\text{C}_4\text{H}_5\text{N}} \text{PhNHCH}_2\text{CH}_2\text{N(SiMe}_2\text{R)}_2$$

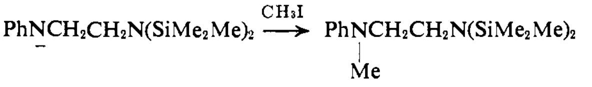
7a, R = Me
8a, R = Et

9a, R = Me
10a, R = Et

9b, R = Me
10b, R = Et

7b, R = Me
8b, R = Et

Anionic Rearrangements. Rearrangement was studied most thoroughly for the phenylethylenediamine derivatives **7a** and **8a**. When these compounds were treated with 1 equiv of *n*-butyllithium in ether, allowed to stand at 25°, and then treated with 1 equiv of pyrrole to protonate the nitrogen anion, they were transformed into their N,N isomers **7b** and **8b**. The N,N structure for **7b** and **8b** follows from the fact that each compound shows a single silylmethyl resonance, and also a Ph–N–H resonance, in the nmr spectrum. The rearranged anion **9b** can also be trapped with methyl iodide, leading to N,N-bis(trimethylsilyl)-N′-methyl-N′-phenylethylenediamine (**11**). Reaction of **7a** with *n*-butyllithium is rapid; the formation of **9a** is complete within a few seconds at room temperature. But the actual rearrangement of **9a** to **9b**, unlike the extremely rapid 1,2 rearrangement of silylhydrazide anions, is not a particularly fast reaction. The ethylenediamine rearrangement can be followed at room temperature by nmr spectroscopy (Figure 1). The anion **9a** gradually disappears in the nmr spectrum and is replaced by **9b**. At 0.40 *M* in benzene the half-time for rearrangement is about 20 min. Rearrangement takes place to virtual completion, the amount of **9a** declining to less than 1% of the total. **9b** is expected to be more stable than **9a**, because of more effective delocalization of the negative charge by the aromatic ring than by the trimethylsilyl group. In the trapping experiments, **7b**, **8b**, and **11** were also produced in isomerically pure form, containing less than 1% of the unrearranged N,N′-bis(silyl) isomers.



$$\text{Ph}\underset{-}{\text{N}}\text{CH}_2\text{CH}_2\text{N(SiMe}_2\text{Me)}_2 \xrightarrow{\text{CH}_3\text{I}} \text{Ph}\underset{\text{Me}}{\text{N}}\text{CH}_2\text{CH}_2\text{N(SiMe}_2\text{Me)}_2$$

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The anionic rearrangement of **7a** to **7b**, like the rearrangement of silylhydrazines studied earlier,[5b] will take place catalytically in the presence of less than 1 equiv of base. Even under catalytic conditions, rearrangement of **7a** is complete, showing that **7b** is the more stable isomer.[13] With 0.40 *M* **7a** and 0.040 *M* *n*-butyllithium in tetrahydrofuran at 30° the half-time for rearrangement is about 4 hr. In benzene, with 0.40 *M* **7a** and 0.20 *M* *n*-BuLi, rearrangement only takes place to the extent of 50% after 24 hr at 30°. Apparently, proton exchange between **7a** and the rearranged anion is slow.

The rearrangements of **9a** and **10a** take place at similar

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[13] Also among the organosilyl phenylhydrazines, isomers with hydrogen on the same nitrogen as the phenyl ring are more stable than isomers not having the Ph–N–H structure.[5b]

rates. To check on the possibility that rearrangement might take place through an intermolecular (elimination–addition) pathway a mixture of **9a** and **10a** was treated with *n*-butyllithium and then with pyrrole. The products were **9b** and **10b** only; no "crossover product" containing both trimethylsilyl and ethyldimethylsilyl groups was formed. These results suggest that the ethylenediamine rearrangement is intramolecular, like the anionic rearrangement of hydrazines described earlier.[5c,d]

It is interesting to consider why the products of the initial silylation of phenylhydrazine anions are the N-phenyl-N′-silyl isomers, **5** and **6**. The anion should be most stable in the form with the negative charge adjacent to the aromatic ring.

$$\underset{-}{\mathrm{PhN}}\mathrm{CH_2CH_2NH_2} \rightleftarrows \mathrm{PhNHCH_2CH_2}\underset{-}{\mathrm{NH}}$$

One possibility to account for the results is that the anion $\mathrm{PhNHCH_2CH_2NH^-}$ reacts very much more rapidly than its tautomer with trimethylchlorosilane. Alternatively, silylation at the nitrogen atom bearing the phenyl ring may takes place initially, followed by anionic rearrangement of the resulting N-phenyl-N-silyl isomer to the N,N′ isomer. Such rearrangement would have to be quite rapid, for even "inverse addition" of lithiophenylhydrazine to excess trimethylchlorosilane fails to produce any of the N,N isomers.

$$\begin{array}{ll} \mathrm{(Me_3Si)_2NCH_2CH_2NHR} \xrightarrow{n\text{-BuLi}} & \\ \mathbf{1b},\ \mathrm{R = H} & \\ \mathbf{2b},\ \mathrm{R = CH_3} & \mathrm{Me_3SiNHCH_2CH_2N(R)SiMe_3},\ >97\% \\ & \mathbf{1a},\ \mathrm{R = H} \\ & \mathbf{2a},\ \mathrm{R = CH_3} \end{array}$$

Rearrangements of **1a**–**1b** and **2a**–**2b** were also studied by nmr spectroscopy. Using either catalytic (0.1 equiv) or equimolar amounts of *n*-butyllithium essentially complete rearrangement of **1b** to **1a** and **2b** to **2a** takes place. These reactions proceed so as to produce the isomers with the silyl substituents on *different* nitrogen atoms, just the opposite of the results found for the N-phenyl compounds **7a**, **7b** and **8a**, **8b**.

The results also differ from those found for the analogous bis(trimethylsilyl)hydrazines, where about equal amounts of N,N- and N,N′-bis(silyl) isomers are present at equilibrium.[5b] Many different effects probably influence the position of these equilibria, but it is possible to account for the differences between the hydrazine and ethylenediamine series on steric grounds alone. Examination of models shows that steric interactions in **1b** and **2b** are relieved in rearrangement to **1a** and **2a**. These steric interactions in **1b** and **2b** result in part from the long chain of atoms attached to the nitrogen bearing the trimethylsilyl groups. The steric interactions are less severe in N,N-bis(trimethylsilyl)hydrazines, so these are about as stable as their N,N′ isomers.

In the phenyl-substituted compounds, both in the hydrazine and ethylenediamine series, electronic effects apparently dominate over steric, and the more stable isomers containing the Ph–N–H structure are formed at equilibrium.

Condensation Reaction. Rearrangement reactions, with either 1 equiv or 0.1 equiv of base, were normally carried out at room temperature. When either **2a** or **2b** were *heated* to 65° with *n*-butyllithium in tetrahydrofuran, a totally unexpected reaction took place forming the substituted silaimidazolidine **12**.[10] The

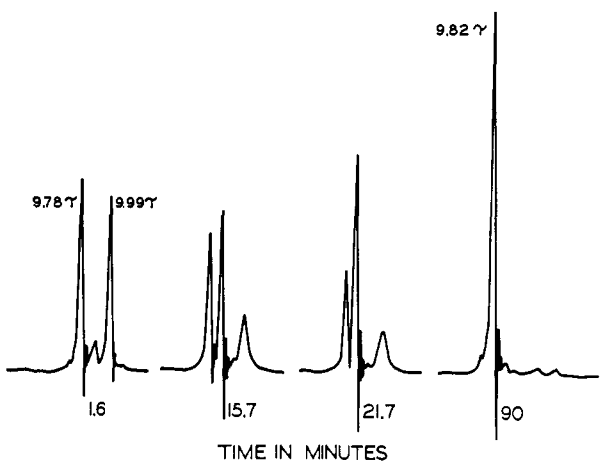
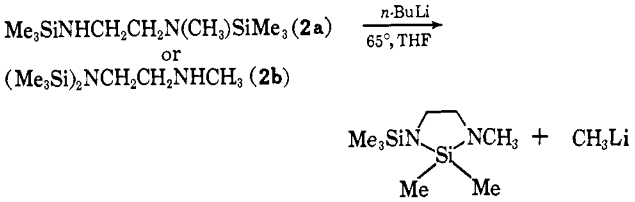


Figure 1. Proton nmr spectrum in the methylsilyl region of the anion **9a**, 0.40 *M* in benzene–cyclohexane, showing rearrangement to anion **9b** with time.



$$\begin{array}{l} \mathrm{Me_3SiNHCH_2CH_2N(CH_3)SiMe_3}\,(\mathbf{2a}) \xrightarrow[65^\circ,\,\mathrm{THF}]{n\text{-BuLi}} \\ \text{or} \\ \mathrm{(Me_3Si)_2NCH_2CH_2NHCH_3}\,(\mathbf{2b}) \end{array}$$

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structure of **12** was deduced from its nmr spectrum which shows two $\mathrm{CH_3Si}$ resonances with relative area 3:2. The by-product methyllithium was identified both by its nmr spectrum and by protonation with pyrrole to give methane.

The condensation of **2a** or **2b** will also take place with only catalytic quantities of *n*-butyllithium. Methyllithium eliminated in one ring-closure reaction presumably metallates another molecule of the amine until all of the latter has been consumed. Methane is evolved continuously in the catalytic reaction, and can be trapped in good yield. The net reaction is

$$\mathbf{2a}\text{ or }\mathbf{2b} \xrightarrow[\mathrm{THF},\ 65^\circ]{\mathrm{RLi,\ cat.}} \mathbf{12} + \mathrm{CH_4}$$

Condensation of **3** also takes place to give the known compound, N,N′-bis(trimethylsilyl)-Si,Si-dimethylsilaimidazolidine, **13**.[9] The properties of **13** agreed with those reported in the literature. Further studies of the new condensation reaction are under way.

Experimental Section

All reactions were carried out in an atmosphere of dry nitrogen. Diamines were purchases from Aldrich Chemical Co. and were redistilled before use. Trimethylchlorosilane (Dow Corning Corp.) was also redistilled before use; ethyldimethylchlorosilane was prepared as described in an earlier paper.[12] *n*-Butyllithium in hexane was obtained from Foote Mineral Co. Solvents were of reagent grade, further dried, and distilled.

Infrared spectra were determined on thin liquid films using a Perkin-Elmer Model 237 Infracord spectrometer. Gas chromatographic separations were carried out using columns packed with 25% SE-30 silicone on Chromosorb W. Nmr spectra were determined using a Varian A-60 spectrometer. Solutions in carbon tetrachloride, 20% v/v, were used in determination of chemical shifts. Analyses were performed by Galbraith Laboratories, Inc.

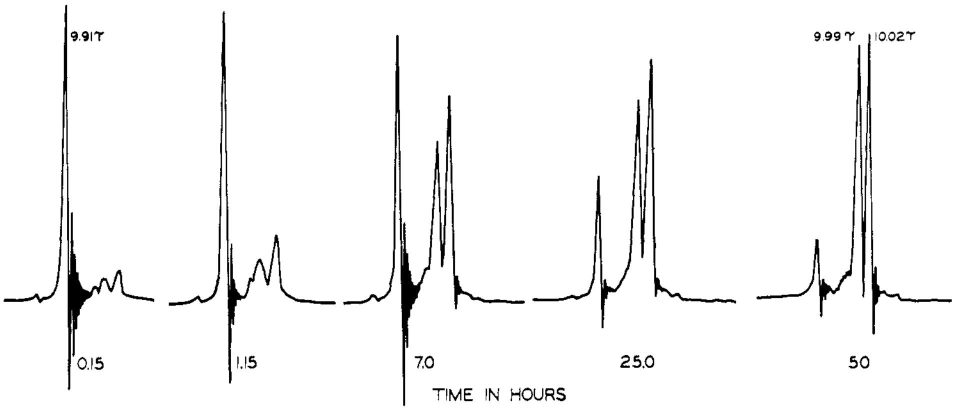

Figure 2. Proton nmr spectrum in the methylsilyl region of **2b**, 0.40 *M* in cyclohexane containing 0.0405 *M* *n*-butyllithium, showing catalyzed rearrangement to **2a** with time. The peak at τ 9.91 after 50 hr is due to the anion of **2a** overlapping with a small residual amount of **2b**.

N,N'-Bis(trimethylsilyl)ethylenediamine (1a). Ethylenediamine (30.5 g, 0.50 mol) was mixed with 80.5 g (0.50 mol) of hexamethyldisilazane and three drops of trimethylchlorosilane was added. The mixture was heated to 110–150° for 20 hr, then fractionally distilled under reduced pressure to give 71 g (70%) of colorless liquid **1a**, bp 70° (8 torr), n^{25}D 1.4256 (lit.[9] bp 192–193°, n^{20}D 1.4276).

N,N'-Bis(trimethylsilyl)-N-methylethylenediamine (2a). This compound was obtained in 60% yield following the method described for **1a**, bp 76° (9 torr); n^{22}D 1.4289.

Anal. Calcd for $C_9H_{26}N_2Si_2$: C, 49.47; H, 11.99; N, 12.82; Si, 25.71. Found: C, 49.57; H, 12.05; N, 12.59; Si, 25.33.

N,N,N'-Tris(trimethylsilyl)ethylenediamine (3). To a solution of 16.4 g, (0.080 mol) of **1a** in 60 ml of ether was added 50 ml of 1.6 *M* *n*-butyllithium in hexane, with cooling. The reaction mixture was stirred for 18 hr at 25°, then 8.4 g (0.080 mol) of trimethylchlorosilane in 20 ml of ether was added, again with cooling. The mixture was again stirred for 10 hr at room temperature, and then filtered. The filtrate was concentrated and fractionally distilled using a spinning-band column to give 18 g (81%) of **3**. The product is a colorless liquid, bp 103–104° (18 torr), n^{25}D 1.4420 (lit.[10] bp 237–239°, n^{20}D 1.4437).

N,N,N'-Tris(trimethylsilyl)-N'-methylethylenediamine (4). An 85% yield was obtained from **2a** and trimethylchlorosilane, following the method given for **3**, bp 114–115° (8 torr), n^{25}D 1.4466.

Anal. Calcd for $C_{12}H_{34}N_2Si_3$: C, 49.62; H, 11.72; N, 9.65; Si, 29.01. Found: C, 49.95; H, 11.59; N, 9.63; Si, 29.12.

N,N-Bis(trimethylsilyl)ethylenediamine (1b). To 10.0 g (0.036 mol) of **3** in 50 ml of ether was added 1.5 g (0.047 mol) of methanol. The mixture was stirred for 16 hr at room temperature, concentrated, and fractionally distilled to give 7.0 g (94%) of **1b** as a colorless liquid, bp 107–108° (24 torr), n^{25}D 1.4488.

Anal. Calcd for $C_8H_{24}N_2Si_2$: C, 49.99; H, 11.83; N, 13.70; Si, 27.48. Found: C, 49.83; H, 11.80; N, 13.65; Si, 27.46.

N,N-Bis(trimethylsilyl)-N'-methylethylenediamine (2b). The method given above for **1b** produced **2b** in 95% yield, from **4**, bp 111–113° (24 torr), n^{25}D 1.4450.

Anal Calcd for $C_{12}H_{34}N_2Si_3$: C, 49.62; H, 11.72; N, 9.65; Si, 29.01. Found: C, 49.95; H, 11.59; N, 9.63; Si, 29.12.

N-Trimethylsilyl-N'-phenylethylenediamine (5). N-Phenylethylenediamine (10.0 g, 0.074 mol) was dissolved in 50 ml of ether and, with good cooling, 46 ml of 1.6 *M* *n*-butyllithium solution in hexane was slowly added. The reaction mixture was stirred for 3 hr at room temperature, then cooled to −70°. A solution of 8.0 g (0.074 mol) of trimethylchlorosilane in 10 ml of ether was added and the reaction mixture was stirred for 2 hr at −70°, then warmed to room temperature, stirred for an additional 20 hr, and filtered. The filtrate was concentrated by solvent evaporation and then fractionally distilled under reduced pressure yielding 14.0 g (91%) of colorless liquid **5**, bp 74–75° (1 torr), n^{22}D 1.5178.

Anal. Calcd for $C_{11}H_{20}N_2Si$: C, 63.40; H, 9.67; N, 13.44; Si, 13.48. Found: C, 63.11; H, 9.55; N, 13.67; Si, 13.74.

N-Ethyldimethylsilyl-N'-phenylethylenediamine (6). The method of synthesis was identical with that for **5** except that ethyldimethylchlorosilane was used. The product was twice distilled, yielding 68% of **6**, bp 89–90° (0.1 torr), n^{22}D 1.5166.

Anal. Calcd for $C_{12}H_{22}N_2Si$: C, 64.80; H, 9.97; N, 12.60; Si, 12.63. Found: C, 65.05; H, 10.12; N, 12.50, Si, 12.22.

N,N'-Bis(trimethylsilyl)-N-phenylethylenediamine (7a). A solution of 8.2 g (0.040 mol) of **5** in 50 ml of ether was cooled to −70° and 25 ml of 1.6 *M* *n*-butyllithium in hexane was added. The mixture was warmed to room temperature and stirred for 16 hr, becoming violet in color. The reaction mixture was transferred to a separatory funnel and added to a solution of 4.6 g (0.042 mol) of trimethylchlorosilane in 20 ml of ether, at −30° over 45 min. The mixture was then stirred for 25 hr at room temperature and filtered. Concentration and fractional distillation gave 9.5 g (85%) of colorless **7a**, bp 104–107° (1 torr), 79–80° (0.1 torr), n^{22}D 1.4950.

Anal. Calcd for $C_{14}H_{28}N_2Si_2$: C, 59.93; H, 10.06; N, 9.99. Found: C, 59.79; H, 10.05; N, 9.97.

N,N'-Bis(ethyldimethylsilyl)-N-phenylethylenediamine (8a). The method of synthesis was similar to that for **7a**, but starting from **6** and ethyldimethylchlorosilane. The product (85% yield) had bp 91–92° (0.1 torr), n^{22}D 1.4977.

Anal. Calcd for $C_{16}H_{32}N_2Si_2$: C, 62.27; H, 10.45; N, 9.08; Si, 18.20. Found: C, 62.16; H, 10.36; N, 9.14; Si, 18.17.

N,N-Bis(trimethylsilyl)-N'-phenylethylenediamine (7b). A solution of 5.0 g (0.018 mol) of **7a** in 20 ml of ether was cooled to −70° and 11 ml of 1.6 *M* *n*-butyllithium in hexane was added. The mixture was warmed to room temperature and stirred for 20 hr. Then 1.2 g (0.018 mol) of pyrrole dissolved in 10 ml of ether was added. The mixture was stirred for 30 min at room temperature and then filtered. The filtrate was concentrated and twice distilled to give 4.6 g (92%) of colorless liquid **7b**, bp 113–114° (0.3 torr), n^{22}D 1.5120.

Anal. Calcd for $C_{14}H_{28}N_2Si_2$: C, 59.93; H, 10.06, N, 9.99; Si, 20.02. Found: C, 59.90; H, 10.03; N, 10.02; Si, 19.83.

N,N-Bis(ethyldimethylsilyl)-N'-phenylethylenediamine (8b). Rearrangement of **8a** according to the directions given above for the conversion of **7a** to **7b** gave the desired product in 86% yield, bp 130–133° (0.3 torr), n^{22}D 1.5151.

Anal. Calcd for $C_{16}H_{32}N_2Si$: C, 62.27; H, 10.47, N, 9.08; Si, 18.20. Found: C, 62.50; H, 10.47; N, 8.89; Si, 18.46.

In another experiment an equimolar mixture of **7a** and **8a** was treated with 1 equiv of *n*-butyllithium followed by 1 equiv of pyrrole, following the procedure outlined above. The liquid product was analyzed by gas chromatography and shown to be a mixture of **7b** and **8b**, with no other products in detectable amount.

Anionic Rearrangement Reactions. In a carefully dried nmr sample tube was placed 0.40 mmol of silylethylenediamine substrate (about 0.1 ml) and 0.90 ml of a solution of *n*-butyllithium, its concentration adjusted so as to contain 0.40 mmole of *n*-BuLi. The solvent was cyclohexane for **1b** and **2b**, and 1:3 cyclohexane–benzene for **7a** and **8a**. The methylsilyl region of the proton nmr spectrum was scanned repeatedly to follow the disappearance of the starting anion and the formation of the rearranged anion (Figure 1). Rearrangements took place with half-times of a few minutes for **1b** and **2b**, and 20–30 min for **7a** and **8a**.

When no further change was observed in the nmr spectrum, 0.40 mmol of pyrrole was added. A white precipitate formed, but this did not interfere with determination of the nmr spectrum. The nmr spectra after pyrrole quenching corresponded to those of the rearranged isomers, **1a**, **2a**, **7b**, and **8b**.

Catalytic Rearrangement Reactions. These experiments were carried out as described above for anionic rearrangements, except that the quantity of *n*-butyllithium was adjusted to be 0.040 mmol. Cyclohexane was used as a solvent for **1a**; 1:9 cyclohexane–THF was used for **7a** and **8a**. The progress of the reaction was again followed by scanning the methylsilyl region of the nmr, but the peaks observed were those of the protonated ethylenediamines rather than their anions. Rearrangements were generally much slower than with 1 equiv of base (Figure 2).

N,N-Bis(trimethylsilyl)-N′-methyl-N′-phenylethylenediamine (11). To a solution of 5.0 g (0.018 mol) of **7b** in 20 ml of ether was added 11 ml of 1.6 *M* *n*-butyllithium–hexane solution, at −30°. The reaction mixture was allowed to warm to room temperature and stirred for 24 hr, turning to a red color. Methyl iodide (5.2 g, 0.036 mol) was added and the mixture was stirred for an additional 4 hr. Work-up in the usual way gave 4.7 g (72%) of colorless **11**, bp 134–137° (1 torr), $n^{22}\text{D}$ 1.5127.

Anal. Calcd for $C_{15}H_{30}N_2Si_2$: C, 61.15; H, 10.27; N, 9.51; Si, 19.07. Found: C, 61.40; H, 10.11; N, 9.72; Si, 18.79.

1,1,2-Trimethyl-5-trimethylsilyl-1-sila-2,5-diazacyclopentane (12). To a solution of 8.0 g (0.037 mol) of **2b** in 30 ml of tetrahydrofuran, cooled in a −70° bath, was added 21 ml of 1.6 *M* *n*-butyllithium–hexane solution (0.037 mol of *n*-BuLi). The reaction mixture was warmed to room temperature and then heated to reflux for 48 hr. Pyrrole (2.5 g, 0.037 mol) was added, and half of the solvent was removed by distillation. The residue was distilled twice under reduced pressure, yielding 6.5 g (81%) of colorless liquid **12**, bp 80–84° (22 torr), $n^{22}\text{D}$ 1.4413. The nmr spectrum showed sharp resonances at τ 9.98, 9.94, and 7.55, with relative intensities 2:3:1 respectively, assigned to the dimethylsilyl, trimethylsilyl, and N-methyl protons, and a complex pattern at τ 6.84–7.35 due to the methylene protons.

The infrared spectrum showed bands at 680 (w), 712 (w), 750 (w), 775 (m), 798 (m), 833 (s), 939 (s), 1010 (s), 1055 (s), 1090 (w), 1183 (m), 1218 (w), 1253 (s), 1345 (m), 1450 (w), 1470 (w), 2800 (w), 2880 (w), and 2960 (m) cm^{-1}.

Anal. Calcd for $C_8H_{22}N_2Si_2$: C, 47.49; H, 10.88; N, 13.85; Si, 27.77. Found: C, 47.35; H, 10.86; N, 13.76; Si, 27.76.

When an identical reaction was carried out, but stirred 48 hr at room temperature instead of refluxed, only the starting material (**2b**) was found after work-up.

A reaction on the same scale, but with only 2.1 ml of the 1.6 *M* *n*-butyllithium–hexane (0.0036 mol of *n*-BuLi), produced 5.6 g (76%) of **12**, as well as 75% of the theoretical volume of methane.

1,1-Dimethyl-2,5-bis(trimethylsilyl)-1-sila-2,5-diazacyclopentane (13). The method of synthesis was similar to that for **12**, except that **3** was used as the starting material. The product (94%) was a colorless liquid, bp 119–120° (23 torr), $n^{25}\text{D}$ 1.4452 (lit.[9] bp 63–64° (4 torr), $n^{21.5}\text{D}$ 1.4438). The nmr spectrum showed sharp resonances at τ 9.94 (Me_3Si), 9.89 (Me_2Si), and 7.03, with relative intensities of 9:3:2, respectively. The infrared spectrum contained bands at 675 (w), 748 (w), 773 (m), 787 (m), 827 (s), 855 (w), 943 (s), 1020 (s), 1074 (s), 1110 (m), 1250 (s), 1332 (w), 1400 (w), 1430 (w), 1465 (w), 2830 (w), 2900 (w), and 2960 (m) cm^{-1}.

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Unsaturated Macrocyclic Compounds. LV.[1] The Synthesis of 1-Bromocyclotrideca-1,2-diene-4,8,10-triyne, a Highly Unsaturated 13-Membered Ring Cyclic Allene

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Abstract: The synthesis of trideca-1,5,8,12-tetrayn-7-ol (**2**) from hexa-1,5-diyne (**1**) is described. Oxidative coupling of **2** with oxygen, cuprous chloride, and ammonium chloride gave the cyclic "monomer" **3** in 80% yield, as well as the cyclic "dimer" **5**. Treatment of **3** with phosphorus tribromide led to 1-bromocyclotrideca-1,2-diene-4,8,10-triyne (**8**), a highly unsaturated 13-membered ring cyclic allene.

Fully conjugated carbocyclic systems incorporating an allene grouping, containing an odd number of carbon atoms in the ring, are an interesting class of compound.[3] No such conjugated cyclic allene has been prepared yet, although a number of simple cyclic allenes are known.[4] We now report the synthesis of 1-bromocyclotrideca-1,2-diene-4,8,10-triyne (**8**), a highly unsaturated 13-membered ring cyclic allene. Although it has not been possible to rearrange this substance to a fully conjugated system, the method employed should serve as a model for the synthesis of the related fully conjugated cyclic bromo allenes **12a** and **12b**.

Treatment of hexa-1,5-diyne (**1**)[5] with 1 molar equiv of ethylmagnesium bromide, followed by 0.5 molar equiv of ethyl formate,[6] gave trideca-1,5,8,12-tetrayn-7-ol (**2**) in 23% yield. Oxidative coupling of the alcohol **2** with oxygen, cuprous chloride, and ammonium chloride in aqueous ethanol and benzene[7] then led to the 13-membered ring cyclic monomer **3** in 80% yield. The remarkably high yield is unusual for this type of coupling reaction, not involving high-dilution conditions. The structure of **3** was based on the analytical and spectral data, and confirmation was provided by

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(1) Part LIV: R. H. Mitchell and F. Sondheimer, *J. Amer. Chem. Soc.*, **90**, 530 (1968).

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(3) Molecular orbital calculations of "odd" annulenes have been reported: E. Heilbronner, *Tetrahedron Letters*, 1923 (1964); see also H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564 (1966); M. J. S. Dewar, *Tetrahedron Suppl.*, **8**, 75 (1966).

(4) A. T. Blomquist, R. E. Burge, and A. C. Sucsy, *J. Amer. Chem. Soc.*, **74**, 3636 (1952); A. T. Blomquist, L. H. Liu, and J. C. Bohrer, *ibid.*, **74**, 3643 (1952); W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); L. Skatteböl, *Tetrahedron Letters*, 167 (1961); *Acta Chem. Scand.*, **17**, 1683 (1963); W. J. Ball and S. R. Landor, *Proc. Chem. Soc.*, 143 (1961); *J. Chem. Soc.*, 2298 (1962).

(5) R. A. Raphael and F. Sondheimer, *ibid.*, 120 (1950).

(6) See E. R. H. Jones, L. Skatteböl, and M. C. Whiting, *ibid.*, 4765 (1956).

(7) The benzene serves to keep the products in solution (see R. Wolovsky and F. Sondheimer, *J. Amer. Chem. Soc.*, **87**, 5720 (1965)).