Reaction of *N,N*-Dimethyl-2-triorganosilylethylamines with Benzyne

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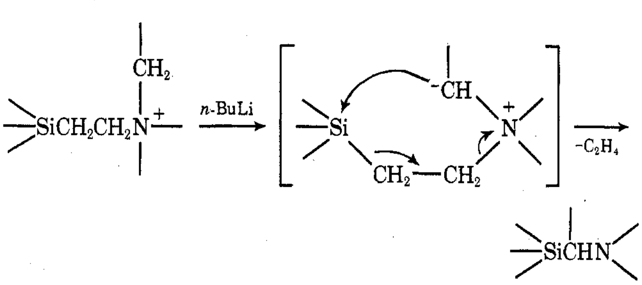
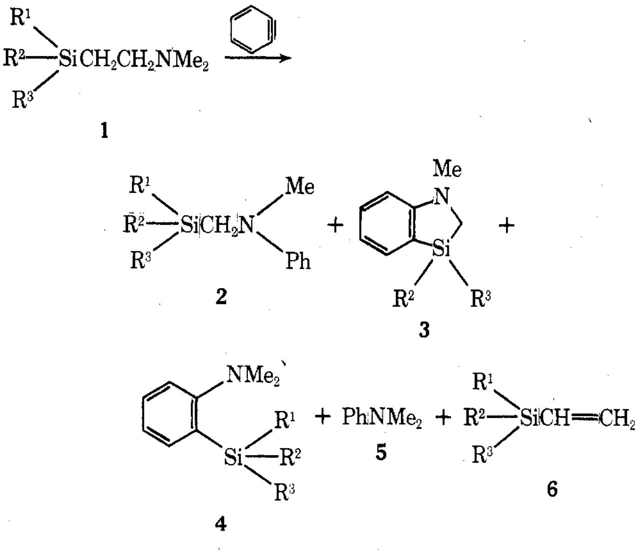
Reaction of *N,N*-dimethyl-2-triorganosilylethylamines (**1a–d**) with benzyne, produced from *o*-fluorobromobenzene and *n*-butyllithium, gave *N*-methyl-*N*-triorganosilylmethylanilines (**2a–d**), 1-methyl 3,3-disubstituted benzo[*d*]-1,3-azasilolines (**3b–d**), *N,N*-dimethylaniline (**5**), and triorganovinylsilanes (**6a–d**). It was revealed that the cyclization giving **3** was induced in the presence of excess *n*-butyllithium. The reaction mechanism also is discussed.

In our earlier paper[1] dealing with the reaction of β-triorganosilylethylammonium iodides with *n*-butyllithium, it was shown that 1,4-anionic rearrangement of the triorganosilyl groups from carbon to carbon occurred in the ylide intermediates to give *N*-triorganosilylmethylamines. Ammonium ylides can be formed by the reaction of tertiary amines with benzynes or carbenes, as well as by treatment of quaternary ammonium salts with strong bases.[2] The present paper describes the reaction of *N,N*-dimethyl-2-triorganosilylethylamines (1) with benzyne produced by the reaction of *o*-fluorobromobenzene with *n*-butyllithium.

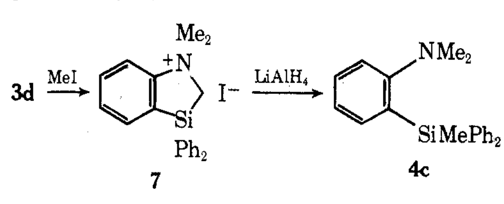


Scheme I

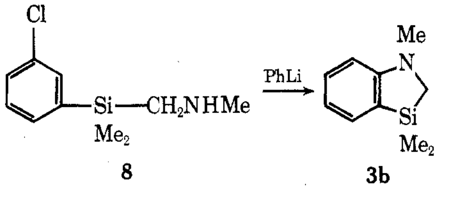


Addition of *o*-fluorobromobenzene to a mixture of *N,N*-dimethyl-2-trimethylsilylethylamine (**1a**) and 3 mol of *n*-butyllithium, upon workup, gave *N*-methyl-*N*-trimethylsilylmethylaniline (**2a**), *N,N*-dimethylaniline (**5**), and trimethylvinylsilane (**6a**). Their yields are shown in Table I. Formation of **2a** is regarded as a result of the 1,4-anionic rearrangement of the trimethylsilyl group in an ylide intermediate (**11**) produced by proton transfer from the first betaine intermediate (**9**) (path b in Scheme II), and **5** and **6** could be the Hofmann elimination products through another betaine intermediate (**10**) (path a).

However, a similar treatment of *N,N*-dimethyl-2-triphenylsilylethylamine (**1d**) with benzyne gave an unexpected amine (**3d**) with a small amount of the expected rearrangement product, *N*-methyl-*N*-triphenylsilylmethylaniline (**2d**). Elemental, NMR, and mass spectral analyses of **3d** suggested its structure as 1-methyl-3,3-diphenylbenzo[*d*]-1,3-azasiloline. Lithium aluminum hydride reduction of the methiodide (**7**) of **3d** gave a high yield of *o*-methyldiphenylsilyl-*N,N*-dimethylaniline (**4c**), which was identical with an authentic sample prepared by reaction of *o*-bromo-*N,N*-dimethylaniline with methyldiphenylchlorosilane in the presence of *n*-butyllithium. In a previous paper[3] we showed that $SiCH_2–N^+$ bonds were cleaved more readily by lithium aluminum hydride reduction than $CH_3–N^+$ bonds in 1,2,3,4-tetrahydrobenzo[*d*]-1,3-azasiline methiodides.



The reaction of *N,N*-dimethyl-2-dimethylphenylsilylethylamine (**1b**) or *N,N*-dimethyl-2-methyldiphenylsilylethylamine (**1c**) with benzyne also gave *N*-methyl-*N*-dimethylphenyl- (or methyldiphenyl-) silylmethylaniline (**2b** or **2c**) and 1,3,3-trimethyl- (or 1,3-dimethyl-3-phenyl-) benzo[*d*]-1,3-azasiloline (**3b** or **3c**), respectively. Compound **3b** proved identical with one of the reaction products between (3-chlorophenyl)methylaminomethyldimethylsilane (**8**) and phenyllithium.



It is improbable that the cyclization product (**3**) is produced directly from the betaine (**9**) or ylide (**11**) intermediate. The presence of excess *n*-butyllithium used should cause the formation of **3**. In fact when the reaction was carried out using an equimolar amount of *n*-butyllithium, a small amount of **3d** was obtained instead of an increase in the yield of **2d**. Elevation of the reaction temperature from −50 to −10 °C induced again an increase in the yield of **3d** and a decrease in **2d**.

It is known that metalation of *N,N*-dimethylaniline by *n*-butyllithium takes place at the ortho position,[4] and that cyclization of 4-triphenylsilylbutyllithium to 1,1-diphenylsilolane occurs at −25 °C with elimination of phenyllithium.[5] On the basis of these experimental results, it seemed reasonable to assume that the cyclization reaction giving **3** proceeded via the rearrangement product (**2**). However, no reaction was observed between **2d** and *n*-butyllithium under the reaction condition.

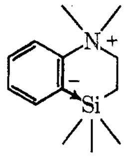
Table I. Reaction Products of *N,N*-Dimethyl-2-triorganosilylethylamines (1a–d) with Benzyne

				Reaction conditions			Yield,[a] %					
	R¹	R²	R³	*n*-BuLi, mol	Temp, °C	Time, h	2	3	4	5	6	1 (recovery)
a	Me	Me	Me	3	−50 to −55	6	33.6 (36.3)	0	0	15.1 (16.4)	9.1 (9.9)	7.5
b	Ph	Me	Me	3	−50 to −55	6	24.7 (34.1)	18.6 (25.8)	0	6.6 (9.1)	7.0 (9.7)	27.5
c	Ph	Ph	Me	3	−50 to −55	6	5.0 (6.6)	24.0 (31.8)	6.7 (8.8)	9.3 (12.2)	10.0 (13.1)	23.5
d	Ph	Ph	Ph	3	−50 to −55	6	5.1 (6.2)	24.6 (29.8)	0	20.0 (24.0)	25.9 (31.4)	17.8
				1	−50 to −55	6	29.7 (33.9)	Trace	0	37.5 (46.8)	49.6 (56.7)	12.7
				1	−10 to −15	3	Trace	21.2 (21.4)	0	40.9 (41.3)	55.5 (55.9)	9.1
				3[b]	−50 to −55	6	35.1 (45.3)	8.1 (10.5)	0	30.7 (39.6)	20.2 (26.0)	22.5

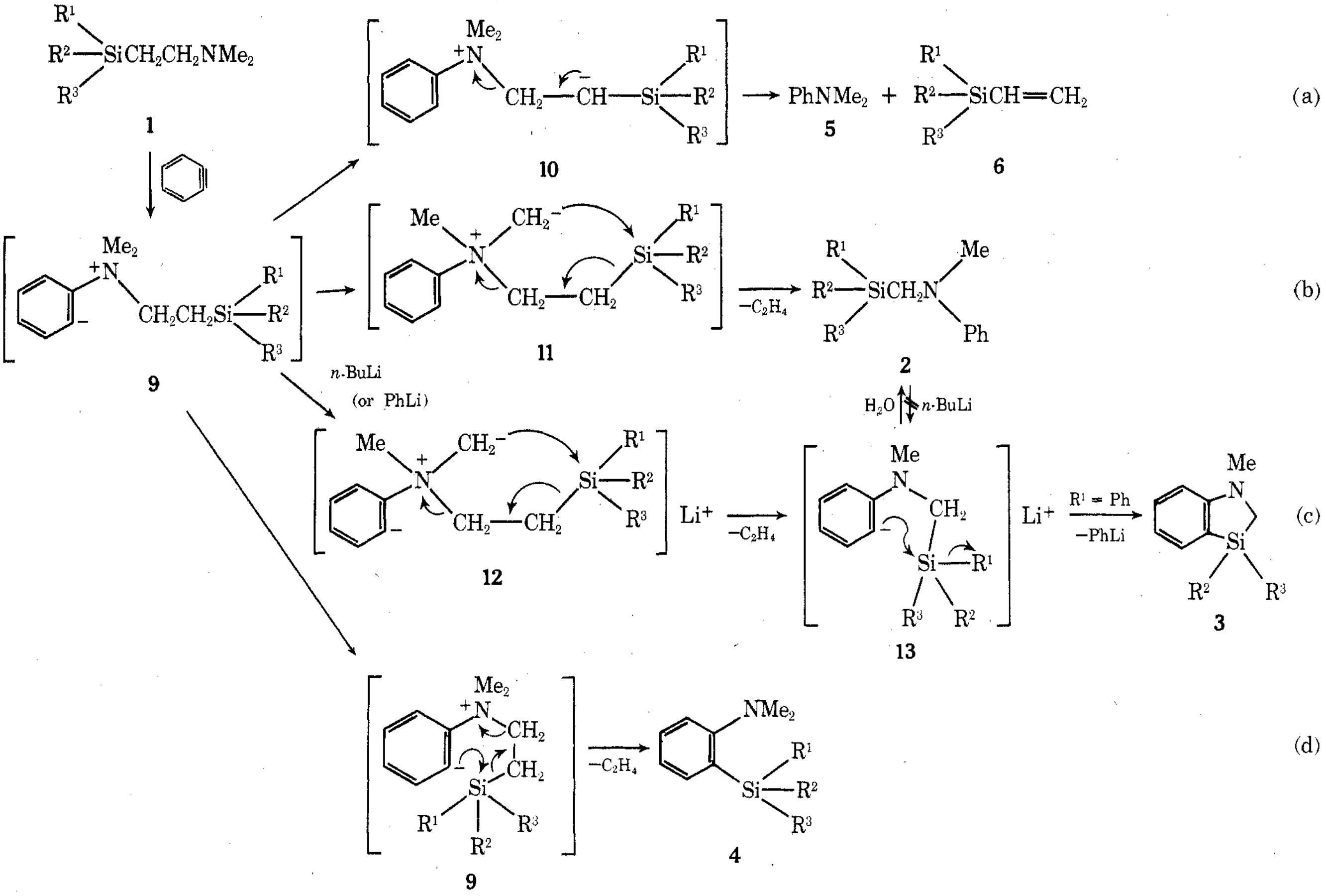
[a] Yields in parentheses are based on unrecovered **1**. [b] This reaction was carried out by addition of *n*-butyllithium, contrary to the other reactions, to a mixture of **1d** and *o*-fluorobromobenzene.

When 3 mol of *n*-butyllithium was added, contrary to the above-mentioned procedures, to a mixture of **1d** and *o*-fluorobromobenzene, the yield of **2d** was increased but **3d** was decreased (see Table I). This result suggests that the presence of excess *n*-butyllithium is required at the initial stage of the reaction but not the final stage for the formation of **3**.

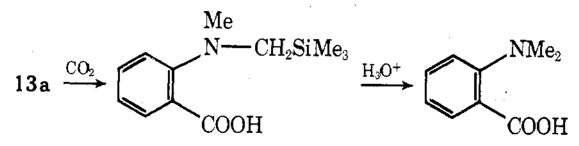
The formation of **3** may proceed by the following steps. Deprotonation by excess *n*-butyllithium takes place in part of the first intermediate (**9**), in which the betaine carbanion is presumably stabilized by coordination with the silicon atom, to give the second intermediate (**12**). Subsequently **12** is converted into the third intermediate (**13**) by silyl rearrangement with loss of ethylene. Then the cyclization reaction of **13** gives **3** with elimination of phenyllithium. When an equimolar amount of *n*-butyllithium was employed at −10 °C, this phenyllithium could be available as the deprotonating agent from **9** to **12**.



Scheme II

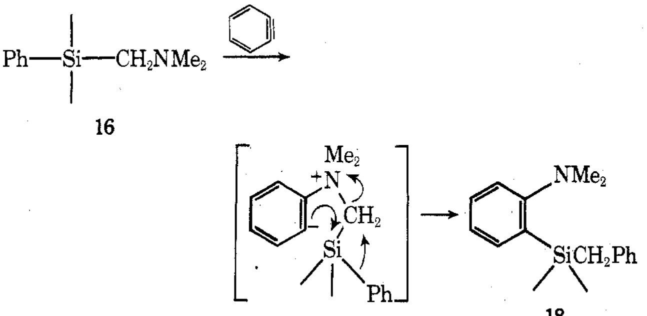


If the postulated reaction path is reasonable, the third intermediate (**13a**) having no phenyl substituent on the silicon atom, which is converted into **2a** by addition of water, should have remained in the reaction mixture, because an alkyl substituent is not easily cleaved from silicon by nucleophilic reagents.[6] Addition of carbon dioxide to the reaction mixture from **1a** with benzyne gave *o*-(*N*-methyl-*N*-trimethylsilylmethylamino)benzoic acid (**14**), which produced *o*-(dimethylamino)benzoic acid (**15**) upon acid hydrolysis.



14 **15**

In the reaction of dimethylaminomethylphenylsilanes (**16**) with benzyne, a new rearrangement of the silyl group toward the anion in betaine (**17**) was observed in our laboratory.[7] In spite of the fact that a similar rearrangement might be possible in the first intermediate (**9**), none or at best small amounts of the rearrangement products, *o*-triorganosilyl-*N*,*N*-dimethylanilines (**4**), were isolated. The low contribution of this reaction path (path d) could be explained by the rate of 1,5 rearrangement of the silyl group being slower than 1,4 rearrangement (path b and c), as suggested by West[8] on the basis of the studies of N,N′-anionic silyl rearrangement in N-silylated ethylenediamine and propylenediamine.



16 **17** **18**

Experimental Section

NMR spectra were recorded using a JNM-MH-100 (JEOL) spectrometer employing tetramethylsilane as internal standard. Ir spectra were taken on an IRA-2 (Jasco) spectrometer. Mass spectra were recorded using a M-52 (Hitachi) spectrometer. GLC analyses were performed on JGC-750FID and JGC-1100FID (JEOL) chromatographs using stainless steel columns with a nitrogen flow rate of 50 ml/min. Quantitative analysis of the reaction mixtures was carried out by the internal standard method. Fractional distillation was accomplished by a GKR-50 (Büchi) Kugelrohr distillation apparatus. All boiling points and melting points are uncorrected. *n*-Butyllithium, 15% in hexane, was obtained from Nakarai Chemicals Ltd., Kyoto. Ether and THF were dried by distillation from lithium aluminum hydride just prior to use.

***N*,*N*-Dimethyl-2-dimethylphenylsilylethylamine (1b).** A solution of dimethylphenylsilyllithium[9] prepared from dimethylphenylchlorosilane (25.6 g, 0.15 mol) and lithium clippings (3.1 g, 0.45 g-atom) in THF (150 ml) was added to an ice-cold solution of 2-dimethylaminoethyl chloride (6.46 g, 0.06 mol) in THF (50 ml). After 15 h of stirring at room temperature, the reaction mixture was hydrolyzed with saturated aqueous NH_4Cl. The THF layer was separated and the aqueous layer was extracted with ether. The combined organic layer was concentrated, and the residue was extracted with 5% HCl. The acid extract was neutralized with potassium carbonate and extracted with ether. Distillation of the ethereal extract gave 5.30 g (42.6%) of **1b**: bp 129–131 °C (30 mm); NMR ($CDCl_3$) δ 0.28 (s, 6, $SiCH_3$), 0.90–1.12 (m, 2, $SiCH_2$), 2.20 (s, 6, NCH_3), 2.20–2.42 (m, 2, NCH_2), 7.18–7.60 (m, 5, aromatic H); picrate, mp 135–137 °C (recrystallized from ethanol).

Anal. Calcd for $C_{18}H_{24}N_4O_7Si$: C, 49.53; H, 5.54; N, 12.84. Found: C, 49.71; H, 5.58; N, 12.10.

***N*,*N*-Dimethyl-2-methyldiphenylsilylethylamine (1c).** In a manner similar to that described for **1b**, methyldiphenylsilyllithium [prepared from methyldiphenylchlorosilane (27.9 g, 0.12 mol) and lithium clippings (2.5 g, 0.36 g-atom)][10] and 2-dimethylaminoethyl chloride (7.44 g, 0.07 mol) were treated in THF (200 ml) giving 13.00 g (67.0%) of **1c**: bp 110–114 °C (0.06 mm); NMR ($CDCl_3$) δ 0.56 (s, 3, $SiCH_3$), 1.20–1.44 (m, 2, $SiCH_2$), 2.16 (s, 6, NCH_3), 2.24–2.50 (m, 2, NCH_2), 7.24–7.66 (m, 10, aromatic H); oxalate, mp 164–166 °C (recrystallized from ethanol).

Anal. Calcd for $C_{19}H_{25}NO_4Si$: C, 63.48; H, 7.01; N, 3.90. Found: C, 63.42; H, 6.93; N, 3.93.

Reaction of *N*,*N*-Dimethyl-2-trimethylsilylethylamine[1] (1a) with Benzyne. A. A solution of *o*-fluorobromobenzene (2.31 g, 13 mmol) in ether (10 ml) was added within 5 min to a mixture of **1a** (1.74 g, 12 mmol) and *n*-butyllithium (25 ml, 39 mmol) in ether (60 ml) at −50 to −55 °C. After 6 h of stirring at the same temperature, the mixture was hydrolyzed with saturated aqueous NH_4Cl below −40 °C and extracted with ether. The ether layer was extracted with 5% HCl.

The HCl extract was neutralized with potassium carbonate and extracted with ether. The ethereal extract (basic part) was analyzed by GLC using a 3 mm × 1 m column filled with 30% Tergitol NP-35, programed from 60 to 200 °C at 6 °C/min. The chromatogram showed the presence of *N*-methyl-*N*-trimethylsilylmethylaniline (**2a**, 33.6%), *N*,*N*-dimethylaniline (**5**, 15.1%), and unchanged **1a** (7.5%). Samples of the products were isolated by fractional distillation and identified with authentic samples, respectively. Compound **2a**, bp 115–118 °C (15 mm) [lit.[1] bp 112–118 °C (13 mm)].

From the ether layer (neutral part), trimethylvinylsilane (**6a**, 9.1%) was detected and determined by GLC analysis (30% dioctyl sebacate, 3 mm × 3 m).

B. The above benzyne reaction was repeated. After 6 h of stirring, carbon dioxide was bubbled into the reaction mixture at −60 to −70 °C for 1 h, and then it was extracted with 5% NaOH. Dimethyl sulfate (3.8 g, 30 mmol) was added to the NaOH extract at room temperature. After 3 h of stirring, the mixture was extracted with ether. The ethereal extract was dried, concentrated, and distilled to give 90 mg (3.0%) of methyl *o*-(*N*-methyl-*N*-trimethylsilylmethylamino)benzoate: bp 150–155 °C (12 mm); NMR ($CDCl_3$) δ 0.10 (s, 9, $SiCH_3$), 2.80 (s, 2, NCH_2), 2.92 (s, 3, NCH_3), 3.96 (s, 3, OCH_3), 6.68–7.80 (m, 4, aromatic H); ir (neat) 1720 cm^{-1}.

Anal. Calcd for $C_{13}H_{21}NO_2Si$: C, 62.11; H, 8.42; N, 5.57. Found: C, 61.89; H, 8.20; N, 5.31.

Methyl *o*-(*N*-methyl-*N*-trimethylsilylmethylamino)benzoate (50 mg, 0.2 mmol) was dissolved in 30% HCl–EtOH (20 ml), and the mixture was heated under reflux for 12 h. After the addition of water (70 ml), the reaction mixture was made alkaline with 20% NaOH and washed with ether. The aqueous solution was neutralized with 10% HCl and extracted with chloroform to give 10 mg (30%) of *o*-(dimethylamino)benzoic acid (**15**).

Reaction of 1b with Benzyne. In a similar manner as described for **1a**, *o*-fluorobromobenzene (1.93 g, 11 mmol), **1b** (2.07 g, 10 mmol), and *n*-butyllithium (21 ml, 33 mmol) were allowed to react in ether (60 ml), and the reaction mixture was treated. GLC analysis (10% PEG-20M, 3 mm × 1 m, programmed from 80 to 250 °C at 6 °C/min) of the basic part showed the presence of **2b** (24.7%), **3b** (18.6%), **5** (6.6%), and unchanged **1b** (27.5%). Samples of the products were isolated by fractional distillation and characterized as follows.

1,3,3-Trimethylbenzo[*d*]-1,3-azasiloline (**3b**): bp 120–125 °C (28 mm); NMR ($CDCl_3$) δ 0.32 (s, 6, $SiCH_3$), 2.64 (s, 2, NCH_2), 2.88 (s, 3, NCH_3), 6.44–6.88 and 7.12–7.48 (m, 4, aromatic H).

Anal. Calcd for $C_{10}H_{15}NSi$: C, 67.73; H, 8.53; N, 7.90. Found: C, 67.45; H, 8.40; N, 7.85.

N-Methyl-*N*-dimethylphenylsilylmethylaniline (**2b**): bp 151–153 °C (6 mm); NMR ($CDCl_3$) δ 0.34 (s, 6, $SiCH_3$), 2.82 (s, 3, NCH_3), 3.06 (s, 2, NCH_2), 6.50–6.76 and 7.04–7.64 (m, 10, aromatic H).

Anal. Calcd for $C_{16}H_{21}NSi$: C, 75.23; H, 8.29; N, 5.48. Found: C, 75.10; H, 8.11; N, 5.30.

From the neutral part, dimethylphenylvinylsilane (**6b**, 7.0%) was detected and determined by GLC analysis (10% PEG-20M, 3 mm × 1 m).

Reaction of 1c with Benzyne. In a similar manner as described for **1a**, *o*-fluorobromobenzene (1.93 g, 11 mmol), **1c** (2.69 g, 10 mmol), and *n*-butyllithium (21 ml, 33 mmol) were allowed to react in ether (60 ml), and the reaction mixture was treated. Distillation of the basic part gave **5** (9.3%) and unchanged **1c** (23.5%). GLC analysis (10% Silicone AN-600, 3 mm × 1 m, programed from 110 to 250 °C at 6 °/min) of the neutral part showed the presence of **2c** (5.0%), **3c** (24.0%), **4c** (6.7%), and methyldiphenylvinylsilane (**6c**, 10.0%) (Compounds **2c**, **3c**, and **4c** were not extracted with 5% HCl.) Samples of the products were isolated by fractional distillation and characterized as follows.

1,3-Dimethyl-3-phenylbenzo[*d*]-1,3-azasiloline (**3c**); bp 80–82 °C (0.03 mm); NMR ($CDCl_3$) δ 0.64 (s, 3, $SiCH_3$), 2.80 (s, 2, NCH_2), 2.90 (s, 3, NCH_3), 6.44–6.80 and 7.12–7.68 (m, 9, aromatic H).

Anal. Calcd for $C_{15}H_{17}NSi$: C, 75.26; H, 7.16; N, 5.85. Found: C, 75.11; H, 6.89; N, 5.79.

o-Methyldiphenylsilyl-*N,N*-dimethylaniline (**4c**): bp 140–145 °C (0.07 mm); mp 67–70 °C (recrystallized from hexane); NMR ($CDCl_3$) δ 0.84 (s, 3, $SiCH_3$), 2.28 (s, 6, NCH_3), 6.96–7.72 (m, 14, aromatic H)

Anal. Calcd for $C_{21}H_{23}NSi$: C, 79.44; H, 7.30; N, 4.41. Found: C, 79.30; H, 6.99; N, 4.16.

N-Methyl-*N*-methyldiphenylsilylmethylaniline (**2c**): bp 147–149 °C (0.07 mm); NMR ($CDCl_3$) δ 0.60 (s, 3, $SiCH_3$), 2.72 (s, 3, NCH_3), 3.38 (s, 2, NCH_2), 6.52–6.80 and 7.04–7.72 (m, 15, aromatic H).

Anal. Calcd for $C_{21}H_{23}NSi$: C, 79.44; H, 7.30; N, 4.41. Found: C, 79.26; H, 7.58; N, 4.43.

Reaction of *N,N*-Dimethyl-2-triphenylsilylethylamine[1] (1d) with Benzyne. A. In a similar manner as described for **1a**, *o*-fluorobromobenzene (1.93 g, 11 mmol), **1d** (3.32 g, 10 mmol), and *n*-butyllithium (21 ml, 33 mmol) were allowed to react in ether (60 ml), and the reaction mixture was treated. Distillation of the basic part gave **5** (20.0%) and unchanged **1d** (17.8%). GLC analysis (10% Silicone AN-600, 3 mm × 1 m, programmed from 150 to 300 °C at 6 °C/min) of the neutral part showed the presence of **2d** (5.1%), **3d** (24.6%), and triphenylvinylsilane (**6d**, 25.9%) (compounds **2d** and **3d** were not extracted with 5% HCl). Samples of the products were isolated by fractional distillation and characterized as follows.

1-Methyl-3,3-diphenylbenzo[*d*]-1,3-azasiloline (**3d**): bp 120–125 °C (0.01 mm); mp 92–93 °C (recrystallized from hexane); NMR ($CDCl_3$) δ 2.96 (s, 3, NCH_3), 3.10 (s, 2, NCH_2), 6.50–6.76 and 7.12–7.80 (m, 14, aromatic H); mass spectrum *m/e* 301 (M^+).

Anal. Calcd for $C_{20}H_{19}NSi$: C, 79.68; H, 6.35; N, 4.65. Found: C, 79.10; H, 6.13; N, 4.53.

N-Methyl-*N*-triphenylsilylmethylaniline (**2d**): bp 160–165 °C (0.01 mm); mp 73–74 °C (lit.[1] mp 73–74 °C).

B. The above reaction was repeated using an equimolar amount of *n*-butyllithium to give **2d** (29.7%), **3d** (trace), **5** (37.5%), **6d** (49.6%), and unchanged **1d** (12.7%).

C. The benzyne reaction described above for **B** was repeated at −10 to −15 °C. After 3 h of stirring, the reaction mixture was treated giving **2d** (trace), **3d** (21.2%), **5** (40.9%), **6d** (55.5%), and unchanged **1d** (9.1%).

D. *n*-Butyllithium (18 ml, 28 mmol) was added slowly over a 3-h period to a mixture of **1d** (2.98 g, 9 mmol) and *o*-fluorobromobenzene (1.75 g, 10 mmol) in ether (45 ml) at −50 to 55 °C, and stirring was continued for 3 h. The reaction mixture was treated giving **2d** (35.1%), **3d** (8.1%), **5** (30.7%), **6d** (20.2%), and unchanged **1d** (22.5%).

1,1-Dimethyl-3,3-diphenylbenzo[*d*]-1,3-azoniasiloline Iodide (7). A mixture of **3d** (0.13 g, 0.44 mmol) and methyl iodide (3 ml) in acetone (20 ml) was heated at 40–50 °C for 15 h. After removal of the acetone, the residue was recrystallized from ethanol to give 0.18 g (90.9%) of **7**, mp 187–188 °C.

Anal. Calcd for $C_{21}H_{22}INSi$: C, 56.89; H, 5.00; N, 3.16. Found: C, 56.78; H, 5.03; N, 3.06.

Lithium Aluminum Hydride Reduction of 7. A mixture of **7** (0.18 g, 0.4 mmol) and lithium aluminum hydride (0.1 g, 2.6 mmol) in THF (20 ml) was heated under reflux for 2 h. After the addition of saturated aqueous NH_4Cl, the THF layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried and concentrated. Recrystallization of the residue from hexane gave 0.12 g (94.5%) of **4c**, mp 68–70 °C.

***o*-Methyldiphenylsilyl-*N,N*-dimethylaniline (4c).** *n*-Butyllithium (5 ml, 7.8 mmol) was added to a solution of *o*-bromo-*N,N*-dimethylaniline (1.56 g, 7.8 mmol) in ether (40 ml) at 0–10 °C, and stirring was continued for 2.5 h at the same temperature. Then to the mixture was added a solution of methyldiphenylchlorosilane (1.63 g, 7 mmol) in ether (10 ml) at room temperature. After 3 h of heating under reflux, the reaction mixture was hydrolyzed with saturated aqueous NH_4Cl and extracted with ether. The ethereal extract was dried and concentrated. Recrystallization of the residue from hexane gave 1.03 g (41.5%) of **4c**, mp 68–70 °C.

1,3,3-Trimethylbenzo[*d*]-1,3-azasiloline (3b). A solution of phenyllithium (33 mmol) in ether (20 ml) was added to a boiling solution of (3-chlorophenyl)methylaminomethyldimethylsilane (**8**, 6.40 g, 30 mmol) in ether (130 ml). After 2 h of heating, the reaction mixture was hydrolyzed with saturated aqueous NH_4Cl and extracted with ether. Distillation of the extract gave 2.10 g (40%) of **3b**, which was identified by spectroscopic comparison with the sample obtained by the reaction of **1b** with benzyne.

Acknowledgment. The authors are grateful to the Shin-Etu Chemical Industry Co., Ltd., for a generous gift of chlorosilanes.

Registry No.—**1a**, 23138-94-5; **1b**, 58617-49-5; **1b** picrate, 58617-61-1; **1c**, 58617-50-8; **1c** oxalate, 58617-62-2; **1d**, 58617-51-9; **2b**, 58617-52-0; **2c**, 58617-53-1; **3b**, 58617-54-2; **3c**, 58617-55-3; **3d**, 58617-56-4; **4c**, 58617-57-5; **7**, 58617-58-6; **8**, 58617-59-7; 14 methyl ester, 58617-60-0; dimethylphenylsilyllithium, 3839-31-4; methyldiphenylsilyllithium, 3839-30-3; benzyne, 462-80-6; *o*-bromo-*N,N*-dimethylaniline, 698-00-0; methyldiphenylchlorosilane, 144-79-6.

References and Notes

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