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Reaction of *N*-(Triorganosilylmethyl)dialkylamines with Benzyne

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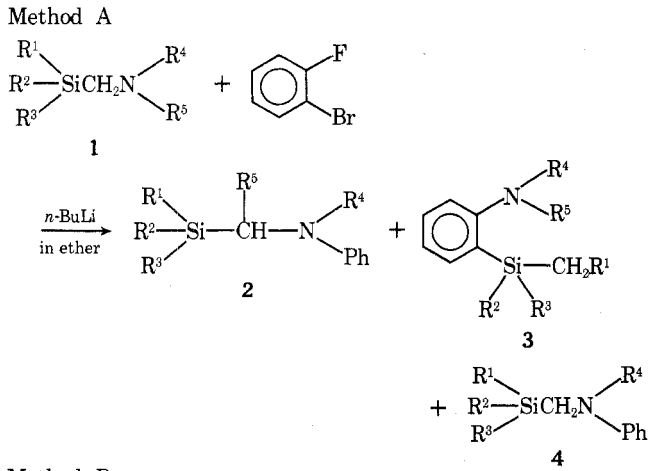
N-(Triorganosilylmethyl)dialkylamines (**1**) having at least one phenyl substituent on the silicon reacted with benzyne to give *N*-alkyl-*N*-(1-triorganosilylalkyl)anilines (**2**, Stevens rearrangement products) and *o*-diorganobenzylsilyl-*N*,*N*-dialkylanilines (**3**, anionic rearrangement products of the silyl group). The presence of two stable intermediates, betaine (**8**) giving **3** and ylide (**9**) giving **2**, was proved by carbonation or methylation.

Silicon has a high affinity for ylide carbanions and exerts a stabilizing effect on these carbanions.[1,2] Phosphorus, arsenic, and sulfur ylides having a silicon substituent directly attached to the carbanion have been synthesized as distillable oils.[3] The stabilizing effect of silicon upon a nitrogen ylide is not well investigated. In an earlier paper[4] we reported that the reaction of *N*-(trimethylsilylmethyl)dimethylamine (**1d**) with benzyne gave predominantly *N*-methyl-*N*-(1-trimethylsilylethyl)-aniline (**2d**) which was produced by the Stevens rearrangement of a silyl ylide intermediate (**9d**). However, the Stevens rearrangement competed with a new anionic rearrangement of the silyl group in the benzyne reaction of *N*-(triorganosilylmethyl)dialkylamines (**1a–c** and **1e–i**) having at least one phenyl substituent on the silicon atom. Aminomethyltriorganosilanes (**1a–j**) were synthesized by reaction of triorganosilyllithium with dialkylaminomethyl phenyl sulfides (method C in Table II) or by reaction of triorganochloromethylsilanes with dialkylamines (method D).

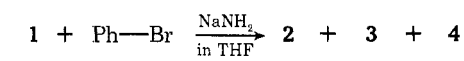
When to a mixture of *N*-(diorganophenylsilylmethyl)-dimethylamines (**1a–c**) and *o*-fluorobromobenzene in ether was added *n*-butyllithium at −25 to −40 °C, then the mixture was heated at reflux (method A in Scheme I and Table I), two

Scheme I

Method A

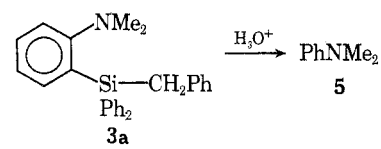


Method B



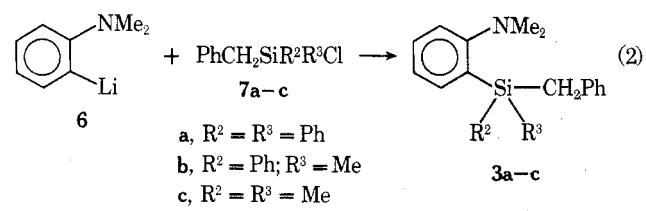
isomeric bases were obtained. Analytical data of these isomers revealed that they were grouped into two types of *N*-methylaniline derivatives (**2** and **3**). One group was assigned to the Stevens [1,2] rearrangement product, *N*-methyl-*N*-(1-diorganophenylsilylethyl)anilines (**2a–c**) (see Table III).

NMR spectra of the other group indicated the presence of benzyl and dimethylamino groups (Table IV). Acid hydrolysis of **3a** gave *N*,*N*-dimethylaniline (**5**, eq 1). Thus the structures



(1)

of **3a–c** were presumed to be *o*-diorganobenzylsilyl-*N*,*N*-dimethylaniline, and they were confirmed by spectroscopic comparisons with authentic samples prepared by the reaction of *o*-lithio-*N*,*N*-dimethylaniline (**6**) (prepared by reaction of *o*-bromo-*N*,*N*-dimethylaniline with *n*-butyllithium) with the corresponding diorganobenzylchlorosilane (**7a–c**) (eq 2).



(2)

When **1a–c** were allowed to react with benzyne generated by the reaction of bromobenzene with sodium amide in boiling THF (method B in Scheme I and Table I), the same reaction products were obtained in lower yields than those of method A. The benzyne reaction of *N*-(diorganophenylsilylmethyl)-dialkylamines (**1e–i**) having β hydrogens in *N*-alkyl substituents also gave predominantly the silyl rearrangement products (**3e–i**). Yields of the Stevens rearrangement product (**2h**) and the Hofmann elimination product (**4g**) were quite low.

The formation of **3** could be explicable as a result of the anionic rearrangement of a silyl group to a carbanion in a betaine intermediate (**8**) accompanied by the shift of a phenyl group from the silicon to the neighboring carbon (eq 3 in Scheme II). The related rearrangements have been observed

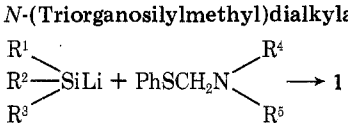
Table I. Reaction Products of *N*-(Triorganosilylmethyl)dialkylamines (1) with Benzyne

	R¹	R²	R³	R⁴	R⁵	Reaction conditions: Method	Temp, °C	Time, h	Yield, %: 2	3	1 (recovery)
a	Ph	Ph	Ph	Me	Me	A	−25 to −30	7	27.2	46.0	0
							Reflux	7[a]			
						B	Reflux	3	4.5	8.7	37.2
b	Ph	Ph	Me	Me	Me	A	−35 to −40	3	25.0	63.0	0
							Reflux	2			
						B	Reflux	4	7.8	12.7	45.7
c	Ph	Me	Me	Me	Me	A	−35 to −40	3	43.8	37.1	0
							Reflux	2			
						B	Reflux	4	11.1	10.8	35.4
d	Me	Me	Me	Me	Me	A	−35 to −40	3	78.6	0	0
							Reflux	2			
						B	Reflux	2	60.0[b]	0	0
e	Ph	Ph	Ph	Et	Et	B	Reflux	3	0	6.4	55.5
f	Ph	Ph	Me	Et	Et	B	Reflux	3	0	29.9	52.5
g[c]	Ph	Me	Me	Et	Et	B	Reflux	3	0	30.3	28.4
h	Ph	Ph	Ph	$-(CH_2)_4-$		B	Reflux	3	1.4	21.8	35.0
i	Ph	Ph	Ph	$-(CH_2)_2O(CH_2)_2-$		B	Reflux	3	0	7.4	58.2
j	Me_3Si	Me	Me	Me	Me	A	−35 to −40	3	0	94.0	0
						B	Reflux	2	0	33.2	29.9

[a] Refluxed in THF. [b] Reference 4. [c] *N*-Ethyl-*N*-(dimethylphenylsilylmethyl)aniline (4g) was obtained in 3.7% yield.

Table II. *N*-(Triorganosilylmethyl)dialkylamines (1)

Method C



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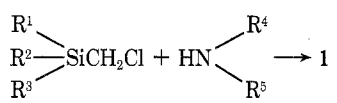
Method D



Registry no.	Compd[a]	Method	Yield, %	Bp [mp], °C (mmHg)	NMR ($CDCl_3$), δ $SiCH_2N$
53174-43-9	1a[b]	C	48.0	172–174 (0.6) [111–113][c]	2.70
54926-32-8	1b	C	70.9	106–110 (0.4) [163–164][d]	2.39
54926-29-3	1c	D	42.3	88–90 (6)	2.08
18182-40-6	1d[e]	D	55.0	115–118	1.91
53174-46-2	1e[b]	C	48.2	150–152 (0.1)	2.82
54926-35-1	1f	C	74.0	118–120 (0.3)	2.46
54926-36-2	1g	D	49.2	121–126 (18)	2.15
60030-75-3	1h	C	44.7	165–168 (0.15) [114–116][c]	2.88
60030-76-4	1i	C	38.0	173–175 (0.2) [97–99][c]	2.74
60030-77-5	1j	D	68.1	85–89 (53) [121–122][f]	2.08

[a] Satisfactory analytical data (±0.4% for C, H, and N) were reported for all new compounds listed in the table. [b] Reference 1. [c] Recrystallized from *n*-hexane. [d] Oxalate, recrystallized from ethanol. [e] Reference 4. [f] Oxalate, recrystallized from ethanol–ether.

Table III. *N*-Alkyl-*N*-(1-triorganosilylalkyl)anilines (2)

Registry no.	Compd[a]	Mp, °C	NMR ($CDCl_3$), δ: R^2 and R^3	Si-CH-N	R^4	R^5	Aromatic H
57341-06-7	2a	88–89[b]		4.50 (1, q, 7.5)	2.68 (3, s)	1.34 (3, d, 7.5)	6.54–7.74 (20, m)
57341-07-8	2b	64–66[b]	0.64 (3, s)	4.07 (1, q, 7.5)	2.68 (3, s)	1.28 (3, d, 7.5)	6.52–7.72 (15, m)
57341-08-9	2c	150–151[c] (HCl salt)	0.32 (3, s) 0.39 (3, s)	3.64 (1, q, 7.5)	2.72 (3, s)	1.19 (3, d, 7.5)	6.48–7.60 (10, m)
60030-78-6	2h	122–124[b]		4.44–4.72 (1, m)	2.92–3.60 (2, m, NCH_2)	1.72–2.00 (2, m, $CHCH_2$)	6.52–7.88 (20, m)

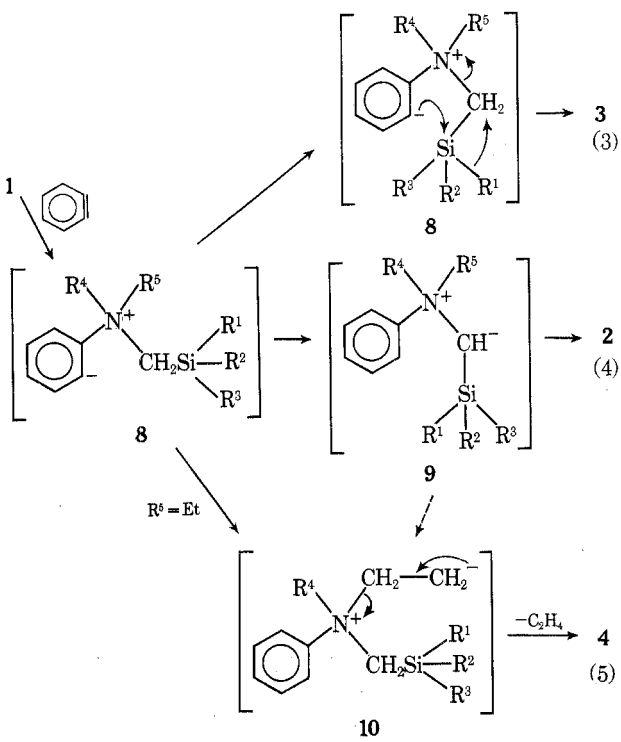
[a] Satisfactory analytical data (±0.4% for C, H, and N) were reported for all new compounds listed in the table. [b] Recrystallized from ethanol. [c] Recrystallized from ethanol–ether.

Table IV. *o*-Diorganobenzylsilyl-*N,N*-dialkylanilines (3a–i) and *o*-Dimethyl(trimethylsilylmethyl)silyl-*N,N*-dimethylaniline (3j)

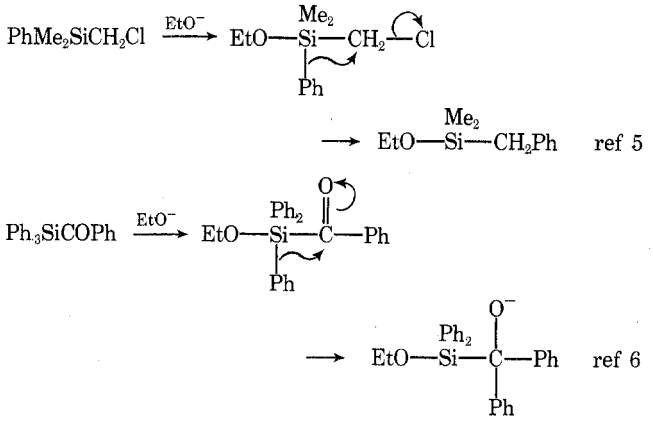
Registry no.	Compd[a]	Mp [bp], °C (mmHg)	NMR ($CDCl_3$), δ			
			R^1, R^2, and R^3	$SiCH_2$	R^4 and R^5	Aromatic H
57341-03-4	3a	110–111[b]		3.04 (2, s)	2.26 (6, s)	6.64–7.52 (19, m)
57341-04-5	3b	70–72[b]	0.43 (3, s)	2.73 (2, s)	2.36 (6, s)	6.77–7.56 (14, m)
57341-05-6	3c	51–53[b]	0.20 (6, s)	2.40 (2, s)	2.63 (6, s)	6.85–7.48 (9, m)
60030-79-7	3e	76–78[b]		3.16 (2, s)	0.74 (6, t) 2.79 (4, q)	6.72–7.60 (19, m)
60030-80-0	3f	[165–171 (0.2)]	0.47 (3, s)	2.72 (2, s)	0.80 (6, t) 2.75 (4, q)	6.72–7.60 (14, m)
60030-81-1	3g	[122–126 (0.1)]	0.22 (6, s)	2.41 (2, s)	1.02 (6, t) 2.96 (4, q)	6.88–7.52 (9, m)
60030-82-2	3h	123–125[b]		3.04 (2, s)	1.39–1.83 (4, m) 2.55–2.91 (4, m)	6.71–7.63 (19, m)
60030-83-3	3i	132–133[c]		3.07 (2, s)	2.37–2.69 (4, m) 3.25–3.45 (4, m)	6.65–7.65 (19, m)
60030-84-4	3j	[141–145 (19)]	0.04 (9, s) 0.40 (6, s)	0.16 (2, s)	2.69 (6, s)	7.08–7.60 (4, m)

[a] Satisfactory analytical data (±0.4% for C, H, and N) were reported for all new compounds listed in the table. [b] Recrystallized from ethanol. [c] Recrystallized from *n*-hexane.

Scheme II



when, for example, dimethylphenylsilylmethyl chloride or benzoyltriphenylsilane was treated with nucleophilic reagents.



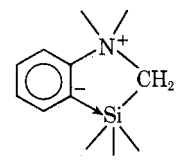
When the benzyne reaction by method A was quenched by the addition of water before elevation of the reaction temperature, neither **2** nor **3** was obtained but the corresponding triorganosilanol (and hexaorganosiloxane) only was formed. It thus appeared that two rearrangements giving **2** and **3** do not occur below −25 or −35 °C but they are induced by the elevation of temperature. The betaine intermediate (**8**) predominates in the cold reaction mixture.

Addition of hydriodic acid to the cold reaction mixture of **1c** with benzyne (method A) gave *N,N*-dimethyl-*N*-(dimethylphenylsilylmethyl)anilinium iodide (**11**) which was identified with an authentic sample prepared from *N*-methyl-*N*-(dimethylphenylsilylmethyl)aniline (**12**, eq 6 in Scheme III). Addition of carbon dioxide produced *o*-[*N,N*-dimethyl-*N*-(dimethylphenylsilylmethyl)ammonio]benzoate (**13**), which was reduced by lithium aluminum hydride to *o*-(*N*-methyl-*N*-dimethylphenylsilylmethylamino)benzyl alcohol (**14**, eq 7). The structure of **14** was confirmed by comparison with an authentic sample prepared from *o*-(formylamino)benzoic acid (**16**) via a dimethylphenylsilylmethylation product (**17**, eq 9).

Elevation of the reaction temperature to room temperature after the addition of methyl iodide produced **3c** and *N,N*-dimethyl-*N*-(1-dimethylphenylsilylethyl)anilinium iodide (**15**, eq 8). Methylation of **2c** to **15** was achieved by heating with methyl iodide for many hours, but no reaction occurred at room temperature.

Cope and co-workers[7] have reported that lithium aluminum hydride reduction of amine methiodides gave predominantly demethylation products. The reduction of three quaternary ammonium salts, **11**, **13**, and **15** also gave the corresponding demethylation products, **12**, **14**, and **2c**.

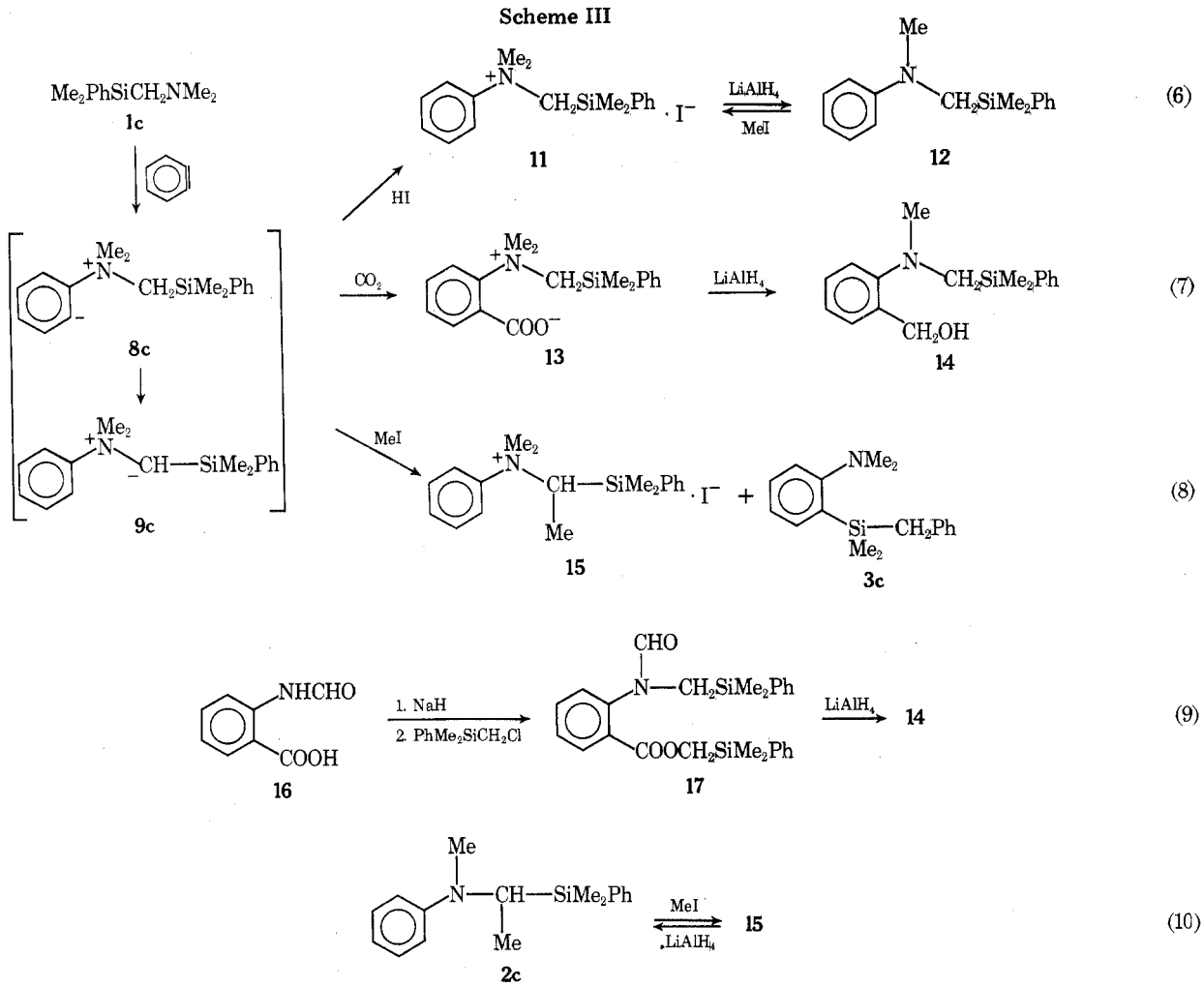
The formation of **13** indicates that the betaine intermediate (**8**), in which the carbanion could be stabilized by coordination



with the silicon atom, exists in the cold reaction mixture. A similar stabilizing effect of silicon for the betaine carbanion has been observed in the reaction of *N,N*-dimethyl-2-triorganosilylethylamine with benzyne.[8]

Methiodide **15** should be produced from the ylide intermediate (**9c**) which is stabilized by the adjacent silicon. The

Scheme III



presence of **3c** and **15** in the same reaction mixture suggests that, as the temperature is raised, proton transfer in **8c** giving **9c** (eq 4) competes with the rearrangement of the silyl group to the betaine carbanion accompanied by the migration of a phenyl from the silicon to the neighboring carbon (eq 3). Contribution of the Hofmann elimination path (eq 5) is very low even in the diethylamine derivatives (**1e–g**).

It has been well recognized that, under influence of base, a trimethylsilyl group migrates from silicon to carbon much more easily than does a phenyl group.[9] The reaction of (dimethylaminomethyl)pentamethyldisilane (**1j**) with benzyne proceeded very fast and, without heating (method A), gave exclusively *o*-dimethyl(trimethylsilylmethyl)silyl-*N*,*N*-dimethylaniline (**3j**) (Table I).

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*-(Triphenylsilylmethyl)dialkylamines (1a, 1e, 1h, and 1i) (Method C in Table II).** To an ice-cold solution of dialkylaminomethyl phenyl sulfide[10] (**18a, 18e, 18h,** and **18i**, 56 mmol) in THF (30 ml) was added dropwise a solution of triphenylsilyllithium[11] prepared from triphenylchlorosilane (23.6 g, 80 mmol) and lithium clippings (1.7 g, 0.25 g-atom) in THF (100 ml). After 3 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 dried and concentrated. The residue was dissolved in ether and extracted with 10% HCl. The acid extract was neutralized with sodium carbonate and extracted with ether. The ethereal extract was dried, concentrated, and distilled giving **1a, 1e, 1h,** or **1i.**

Characterizing data are summarized in Table II.

***N*-(Methyldiphenylsilylmethyl)dialkylamines (1b and 1f).** In a similar manner as above, dialkylaminomethyl phenyl sulfide (**18b** or **18f**, 50 mmol) was treated with methyldiphenylsilyllithium[11] prepared from methyldiphenylchlorosilane (23.3 g, 0.1 mol) and lithium clippings (2.1 g, 0.3 g-atom) in THF (130 ml). The results are summarized in Table II.

***N*-(Dimethylphenylsilylmethyl)dialkylamines (1c and 1g) (Method D in Table II).** A mixture of dimethylphenylsilylmethyl chloride[5] (18.5 g, 0.1 mol) and 0.25 mol of dimethylamine or diethylamine was heated in a sealed tube at 130–140 °C for 8 h. After the addition of 10% NaOH (100 ml), the reaction mixture was extracted with ether. The ethereal extract was dried, concentrated, and distilled giving **1c** or **1g.**

(Dimethylaminomethyl)pentamethyldisilane (1j). A mixture of (chloromethyl)pentamethyldisilane[12] (10.0 g, 55 mmol) and dimethylamine (12.6 g, 0.28 mol) was heated in a sealed tube at 130–140 °C for 8 h. The reaction mixture was neutralized with 10% NaOH and extracted with ether. The ethereal extract was dried, concentrated, and distilled giving 7.13 g (68.1%) of **1j.**

Reaction of *N*-(Triphenylsilylmethyl)dimethylamine (1a) with Benzyne (Method A). *n*-Butyllithium (7.7 ml, 12 mmol) was dropped into a solution of **1a** (3.17 g, 10 mmol) and *o*-fluorobromobenzene (2.28 g, 13 mmol) in ether (85 ml) at −25 to −30 °C. Stirring was continued for 7 h at the same temperature, then for 3 h at room temperature. After the addition of THF (100 ml), the ether was evaporated and the mixture was heated at 63 °C for 7 h. Then the mixture was hydrolyzed with water and extracted with ether. The ethereal extract was dried, concentrated, and distilled. The distillate of bp 180–190 °C (0.2 mm) was chromatographed on a silica gel col-

umn (n-hexane–benzene, 2:1). The first fraction gave o-benzyldiphenylsilyl-N,N-dimethylaniline (**3a**), and the second fraction afforded N-methyl-N-(1-triphenylsilylethyl)aniline (**2a**). Their yields were determined by quantitative GLC analysis (10% AN-600, 3 mm × 1 m) of the distillate.

Characterizing data are shown in Tables I, III, and IV.

Reaction of N-(Methyldiphenylsilylmethyl)dimethylamine (1b) with Benzyne (Method A). n-Butyllithium (7.7 ml, 12 mmol) was added dropwise to a solution of **1b** (2.55 g, 10 mmol) and o-fluorobromobenzene (2.28 g, 13 mmol) in ether (65 ml) at −35 to −40 °C. The mixture was stirred at the same temperature for 3 h, then at reflux for 2 h. After the addition of water, the mixture was extracted with ether. The distillate of bp 140–165 °C (0.3 mm) of the ethereal extract was chromatographed on an alumina column (n-hexane) to give o-benzylmethylphenylsilyl-N,N-dimethylaniline (**3b**) from the first fraction and N-methyl-N-(1-methyldiphenylsilylethyl)aniline (**2b**) from the second fraction. Their yields were determined by GLC (10% AN-600, 3 mm × 1 m) of the distillate.

Reaction of N-(Dimethylphenylsilylmethyl)dimethylamine (1c) with Benzyne (Method A). A. In a similar manner as described for above **1b**, a solution of **1c** (1.93 g, 10 mmol) and o-fluorobromobenzene (2.28 g, 13 mmol) in ether (45 ml) was treated with n-butyllithium (7.7 ml, 12 mmol). The distillate of bp 114–130 °C (0.3 mm) was chromatographed to give o-benzyldimethylsilyl-N,N-dimethylaniline (**3c**) and N-methyl-N-(1-dimethylphenylsilylethyl)aniline (**2c**) which was purified as hydrochloride. The yields were determined by GLC of the distillate.

B. The above benzyne reaction was repeated. After 3 h of stirring at −35 to −40 °C, 3% aqueous HI (50 ml) was added to the reaction mixture. The ether layer was separated and the aqueous layer was extracted with chloroform. After evaporation of the chloroform, the residue was recrystallized from a mixture of ethanol and ethyl acetate to give 2.00 g (50.3%) of N,N-dimethyl-N-(dimethylphenylsilylmethyl)anilinium iodide (**11**): mp 132.5–133.5 °C; NMR ($CDCl_3$) δ 0.16 (s, 6, $SiCH_3$), 3.83 (s, 6, NCH_3), 4.53 (s, 2, NCH_2), and 7.16–7.96 (m, 10, aromatic H).

Anal. Calcd for $C_{17}H_{24}INSi$: C, 51.38; H, 6.09; N, 3.52. Found: C, 51.11; H, 5.95; N, 3.02.

When the above reaction mixture was hydrolyzed with water instead of aqueous HI, the ether layer afforded a mixture of dimethylphenylsilanol and bis(dimethylphenyl)disiloxane.

C. The above benzyne reaction (A) was repeated. After 3 h of stirring at −35 to −40 °C, carbon dioxide was bubbled into the reaction mixture at −45 to −50 °C for 4 h. Then the mixture was hydrolyzed with water. The ether layer was separated and the aqueous layer was extracted with chloroform. After removal of the chloroform, the residue was recrystallized from ethanol–ether to give 0.32 g (9.7%) of o-[N,N-dimethyl-N-(dimethylphenylsilylmethyl)ammonio]benzoate monohydrate (**13**): mp 113–115 °C dec; NMR ($CDCl_3$) δ 0.16 (s, 6, $SiCH_3$), 3.73 (s, 6, NCH_3), 4.43 (s, 2, NCH_2), and 7.04–7.78 (m, 9, aromatic H); ir (KBr) 1635 (CO), 3480 cm^{-1} (OH).

Anal. Calcd for $C_{18}H_{23}NO_2Si \cdot H_2O$: C, 65.22; H, 7.60; N, 4.23. Found: C, 64.92; H, 7.61; N, 4.17.

D. The above benzyne reaction (A) was repeated. After 3 h of stirring at −35 to −40 °C, a solution of methyl iodide (2.84 g, 20 mmol) in ether (5 ml) was added to the reaction mixture. The mixture was stirred for 4 h at the same temperature, then for 1 h at room temperature. After the addition of water, the ether layer was separated and the aqueous layer was extracted with ether. The combined ether layer was dried and concentrated. Recrystallization of the residue from ethanol gave 0.68 g (25.2%) of **3c**.

The aqueous layer was extracted with chloroform. Evaporation of the solvent gave 0.88 g (21.4%) of N,N-dimethyl-N-(1-dimethylphenylsilylethyl)anilinium iodide (**15**) as a viscous oil: NMR ($CDCl_3$) δ 0.44 (s, 3, $SiCH_3$), 0.47 (s, 3, $SiCH_3$), 1.40 (d, 3, J = 7.0 Hz, $CHCH_3$), 3.57 (s, 3, NCH_3), 3.66 (s, 3, NCH_3), 4.81 (q, 1, J = 7.0 Hz, $CHCH_3$), and 7.27–8.20 (m, 10, aromatic H).

Reaction of N-(Trimethylsilylmethyl)dimethylamine (1d) with Benzyne (Method A). In a similar manner as described for above **1b**, a solution of **1d** (1.31 g, 10 mmol) and o-fluorobromobenzene (2.28 g, 13 mmol) in ether (45 ml) was treated with n-butyllithium (7.7 ml, 12 mmol). Distillation of the ethereal extract gave 1.63 g (78.6%) of N-methyl-N-(1-trimethylsilylethyl)aniline (**2d**), bp 136–140 °C (21 mm), which was identical with an authentic sample.[4]

Reaction of (Dimethylaminomethyl)pentamethyldisilane (1j) with Benzyne (Method A). n-Butyllithium (7.7 ml, 12 mmol) was added dropwise to a solution of **1j** (1.89 g, 10 mmol) and o-fluorobromobenzene (2.28 g, 13 mmol) in ether (45 ml) at −35 to −40 °C. After 3 h of stirring at the same temperature, the reaction mixture was hydrolyzed with water. Distillation of the ethereal extract gave 2.50 g (94.0%) of o-dimethyl(trimthylsilylmethyl)silyl-N,N-dimethylaniline (**3j**), bp 141 –145 °C (19 mm). Data are shown in Table IV.

Reaction of N-(Triorganosilylmethyl)dialkylamines (1a–j) with Benzyne (Method B). Bromobenzene (2.35 g, 15 mmol) was added dropwise to a boiling mixture of **1a–j** (10 mmol) and sodium amide (0.62 g, 16 mmol) in THF (30 ml). After 3–4 h of heating at reflux, 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 dried, concentrated, and distilled to recover unchanged **1**. Column chromatography or fractional distillation of the residue gave **2** and **3**. Results are shown in Tables I, III, and IV.

In the case of **1g**, N-ethyl-N-(dimethylphenylsilylmethyl)aniline (**4g**) was isolated with **3g** by column chromatography (alumina, n-hexane–benzene, 2:1) as a viscous oil, which was purified as hydrochloride: mp 146–147 °C (recrystallized from ethanol–ether); NMR ($CDCl_3$, free base) δ 0.32 (s, 6, $SiCH_3$), 0.97 (t, 3, ethyl CH_3), 2.98 (s, 2, $SiCH_2$), 3.21 (q, 2, ethyl CH_2), and 6.48–7.60 (m, 10, aromatic H).

Anal. Calcd for $C_{17}H_{23}NSi \cdot HCl$: C, 66.75; H, 7.91; N, 4.58. Found: C, 66.69; H, 8.15; N, 4.47.

Acid Hydrolysis of Benzyldiphenylsilyl-N,N-dimethylaniline (3a). A mixture of **3a** (0.30 g, 0.76 mmol), 47% HBr (2.4 g), and acetic acid (5 ml) was heated at reflux for 19 h, and then it was neutralized with sodium carbonate solution. The ethereal extract of the reaction mixture was dried, concentrated, and distilled giving 32 mg (35.0%) of N,N-dimethylaniline (**5**).

o-Diorganobenzylsilyl-N,N-dimethylanilines (3a–c). n-Butyllithium (11.5 ml, 18 mmol) was added to a solution of o-bromo-N,N-dimethylaniline (3.0 g, 15 mmol) in ether (80 ml) at 0–10 °C, and stirring was continued for 2 h. Then to the mixture was added a solution of benzyldiphenyl- (**7a**), benzylmethylphenyl- (**7b**), or benzyldimethylchlorosilane (**7c**, 18 mmol) in ether (60 ml). After 4 h of heating at 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 ethanol gave 2.00 g (33.9%) of **3a**, 3.01 g (60.6%) of **3b**, or 2.43 g (60.1%) of **3c**.

N,N-Dimethyl-N-dimethylphenylsilylmethylanilinium Iodide (11). A solution of N-methyl-N-dimethylphenylsilylmethylaniline[8] (**12**, 1.28 g, 5 mmol) and methyl iodide (3.55 g, 25 mmol) in acetone (15 ml) was heated at reflux for 48 h. After removal of the solvent, the residue was recrystallized from a mixture of ethanol and ethyl acetate to give 1.61 g (80.9%) of **11**, which was identified with the sample obtained by the benzyne reaction of **1c** followed by the addition of hydriodic acid.

N,N-Dimethyl-N-(1-dimehylphenylsilylethyl)anilinium Iodide (15). A solution of **2c** (0.25 g, 0.9 mmol) and methyl iodide (0.64 g, 4.5 mmol) in acetone (10 ml) was heated at reflux for 60 h. Evaporation of the solvent gave 0.36 g (94.3%) of **15** which was identical with the sample obtained by the benzyne reaction of **1c** followed by the treatment with methyl iodide.

Lithium Aluminum Hydride Reduction of 11. A mixture of **11** (0.40 g, 1 mmol) and lithium aluminum hydride (0.38 g, 10 mmol) in THF (40 ml) was heated at reflux for 9 h. After the addition of 5% HCl, the acid layer was washed with ether and neutralyzed with sodium carbonate. The ethereal extract of the aqueous layer was dried, concentrated, and distilled giving 0.19 g (73.9%) of **12**, bp 151–153 °C (6 mm).

Lithium Aluminum Hydride Reduction of 13. A mixture of **13** (0.52 g, 1.5 mmol) and lithium aluminum hydride (0.57 g, 15 mmol) in THF (50 ml) was heated for 8 h and then it was treated in the same manner as described for **11** to give 0.12 g (26.8%) of o-(N-methyl-N-dimethylphenylsilylmethylamino)benzyl alcohol (**14**): bp 125–130 °C (0.09 mm); NMR ($CDCl_3$) δ 0.30 (s, 6, $SiCH_3$), 2.58 (s, 3, NCH_3), 2.72 (s, 2, NCH_2), 4.58 (s, 2, OCH_2), and 6.76–7.61 (m, 9, aromatic H); ir (neat) 3420 cm^{-1} (OH); mass spectrum m/e 285 (M^+).

Anal. Calcd for $C_{17}H_{23}NOSi$: C, 71.53; H, 8.12; N, 4.91. Found: C, 71.27; H, 7.98; N, 4.37.

Lithium Aluminum Hydride Reduction of 15. A mixture of **15** (0.26 g, 0.63 mmol) and lithium aluminum hydride (0.24 g, 6.3 mmol) in THF (30 ml) was heated at reflux for 9 h and then it was treated in the same manner as described for **11** to give 60 mg (35.2%) of **2c**.

Dimethylphenylsilylmethyl o-(N-Formyl-N-dimethylphenylsilylmethylamino)benzoate (17). A mixture of o-formylaminobenzoic acid (**16**, 1.65 g, 10 mmol) and sodium hydride (0.58 g, 24 mmol) in DMF (60 ml) was heated at 100 °C for 6 h. Then to the mixture was added a solution of dimethylphenylsilylmethyl chloride (4.07 g, 24 mmol) in DMF (10 ml) at room temperature. After 4 h of stirring at 100 °C, the reaction mixture was poured into water and

extracted with ether. The ethereal extract was dried, concentrated, and distilled giving 2.03 g (44.0%) of **17**: bp 205–210 °C (0.1 mm); NMR ($CDCl_3$) δ 0.23 (s, 6, $SiCH_3$), 0.39 (s, 6, $SiCH_3$), 3.39 (s, 2, NCH_2), 4.17 (s, 2, OCH_2), 6.80–7.88 (m, 14, aromatic H), and 8.07 (s, 1, CHO); ir (neat) 1675, 1720 cm^{-1} (CO).

Anal. Calcd for $C_{26}H_{31}NO_3Si_2$: C, 67.64; H, 6.77; N, 3.03. Found: C, 67.72; H, 6.49; N, 3.30.

***o*-(*N*-Methyl-*N*-dimethylphenylsilylmethylamino)benzyl Alcohol (14).** A mixture of **17** (1.17 g, 2.5 mmol) and lithium aluminum hydride (0.95 g, 25 mmol) in THF (50 ml) was heated at reflux for 3 h, and then it was hydrolyzed with 5% HCl. After the addition of ether (400 ml), the acid layer was separatd. The acid layer was made alkaline with aqueous sodium hydroxide and extracted with ether. Distillation of the extract gave 0.58 g (80.2%) of **14** which was identical with the product of lithium aluminum hydride reduction of **13**.

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Registry No.—**4g,** 60030-85-5; **4g** HCl, 60030-86-6; **7a,** 18670-77-4; **7b,** 27977-47-5; **7c,** 1833-31-4; **11,** 60030-87-7; **12,** 58617-52-0; **13,** 60030-88-8; **14,** 60030-89-9; **15,** 60030-90-2; **16,** 3342-77-6; **17,** 60030-91-3; **18a,** 43180-39-8; **18e,** 13865-52-6; **18h,** 60030-92-4; **18i,** 10316-03-7; triphenylsilyllithium, 791-30-0; methyldiphenylsilyllithium, 3839-30-3; dimethylphenylsilylmethyl chloride, 1833-51-8; chloromethylpentamethyldisilane, 5181-46-4; benzyne, 462-80-6; *o*-bromo-*N*,*N*-dimethylaniline, 698-00-0.

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Derivatives of 4-Chloro-3,5-dinitrobenzotrifluoride. 1. Synthesis of *S,S'*-[2,2'-Dithiobis(6-nitro-α,α,α-trifluoro-*p*-tolyl)] Bis(*N,N*-dimethylcarbamothioate) and Related Compounds[1,2]

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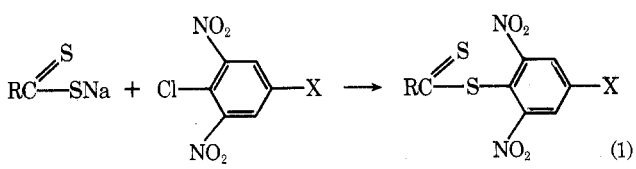
The reaction of sodium or triethylamine salts of disubstituted dithiocarbamic acids with 4-chloro-3,5-dinitrobenzotrifluoride afforded the unexpected novel title compounds (**4–9**). The reaction of the triethylamine salt of ethyldithiocarbamic acid with 4-chloro-3-nitrobenzotrifluoride or 4-chloro-3,5-dinitrobenzotrifluoride furnished a novel synthesis of substituted phenyl sulfides (**10–11**). Possible mechanisms and supporting NMR, ir, Raman, mass spectra, and single-crystal x-ray structure analysis for **4** are discussed.

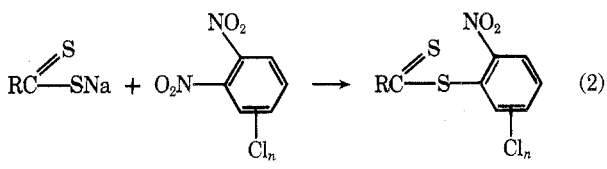
Prakasch and Mohan Lal Garg[3] reported that the reaction of activated aromatic compounds, such as 1-chloro-2,6-dinitrobenzene and 1,4-dichloro-2,6-dinitrobenzene, with sodium salts of disubstituted dithiocarbamic acids furnished the 2,6-dinitrophenyl and 4-chloro-2,6-dinitrophenyl esters of the dithiocarbamic acids, respectively.



(1)

R = morpholino or piperidino; X = H or Cl

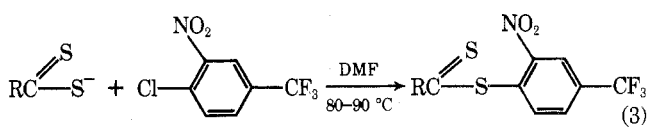
However, in more activated halogenated aromatic nitro compounds,[4] nitro groups are displaced nucleophilically and aromatic esters of dithiocarbamic acids are obtained in 72–92% yields.



(2)

R = dialkylamino, morpholino, or piperidino; *n* = 0–4

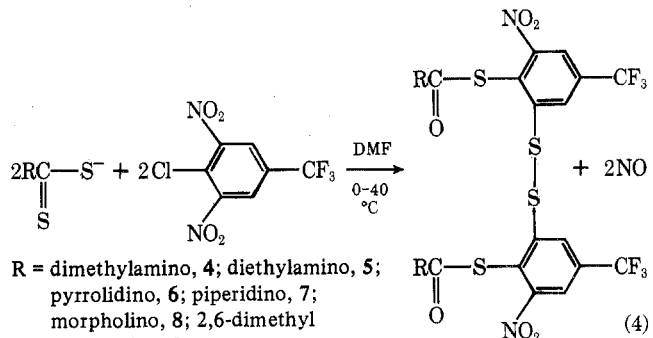
We wish to report that the reaction of sodium or triethylamine salts of disubstituted dithiocarbamic acids with 4-chloro-3-nitrobenzotrifluoride in dimethylformamide at 80–90 °C furnished the expected products (**1–3**) in 82–97% yields.



(3)

R = dimethylamino, **1**; morpholino, **2**; diethylamino, **3**

However, when 4-chloro-3-nitrobenzotrifluoride was replaced with 4-chloro-3,5-dinitrobenzotrifluoride, the expected



(4)

R = dimethylamino, **4**; diethylamino, **5**; pyrrolidino, **6**; piperidino, **7**; morpholino, **8**; 2,6-dimethyl morpholino, **9**