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ANIONIC REARRANGEMENT OF ORGANOSILYL GROUPS FROM CARBON TO CARBON IN β-TRIORGANOSILYLETHYLAMMONIUM YLIDES

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Summary

Reaction of β-triorganosilylethylammonium iodides with n-butyllithium in a HMPA/ether mixture at —15 to —20°C gave the corresponding α-triorganosilylalkylamines which were produced by 1,4-anionic rearrangement of organosilyl groups from carbon to carbon in β-triorganosilylethylammonium ylides. Small amounts of the Hofmann elimination products, triorganovinylsilane and *N*,*N*-dialkyl-2-trimethylsilylethylamines, were also detected.

Introduction

Various types of intramolecular migrations of organosilyl groups toward an anionic site * (1,2- [1], 1,3- [2], and 1,4-anionic rearrangements [3], in which X and/or Y are heteroatoms), (eq. 1), have been investigated by West, Brook, and others. The anionic rearrangement of an organosilicon moiety from carbon to carbon is not well-known. The only example has been shown by Schmidbaur [4] in the ring expansion of bis(phosphoranylidene)disilacyclobutane (eq. 2). In this paper, we describe a new 1,4-anionic rearrangement of triorganosilyl groups from carbon to carbon in β-silylethylammonium ylides.

$$\equiv\mathrm{Si}-\mathrm{X}-(\mathrm{C})_n-\mathrm{Y}^- \rightarrow {}^-\mathrm{X}-(\mathrm{C})_n-\mathrm{Y}-\mathrm{Si}\equiv$$

$$n = 0, 1, 2 \qquad (1)$$

$$\mathrm{X\ and/or\ Y} = \mathrm{O, S, N}$$

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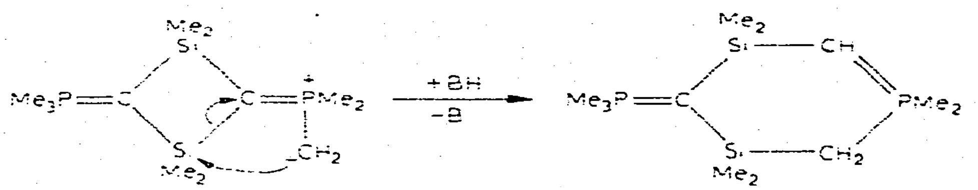
* For a review of silyl anionic rearrangement from carbon to oxygen see ref. 1a, for a review with original literature citations through 1969 see ref. 1b, and for original literature since 1970 see ref. 1c.



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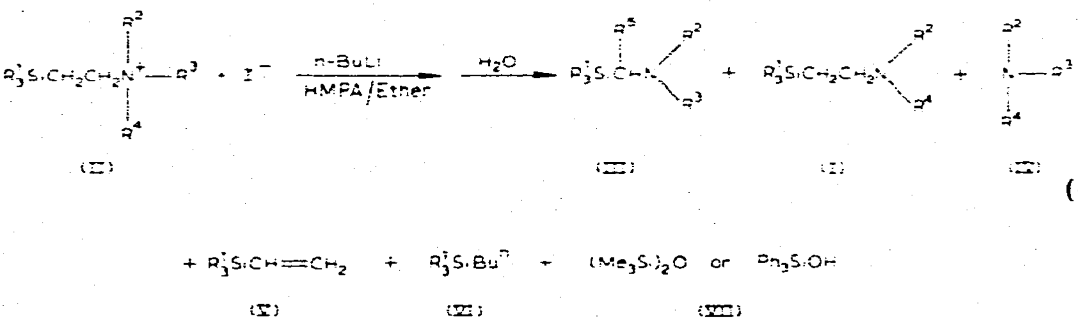
Results and discussion

Twelve β-triorganosilylethylamines (Ia—Im) were synthesized by four methods summarized in Table 1, and their quarternary ammonium iodides (IIa—IIm) were prepared in high yields (Table 2). These ammonium salts (II) were stable in protic solvents at room temperature, but in the presence of base (n-BuLi or KOH) [8], decomposed by nucleophilic attack of the anion at the silicon atom to give a butylsilane (or disiloxane), ethylene, and tertiary amine (eq. 3).

$$\equiv\mathrm{SiCH_2CH_2}\overset{|}{\underset{|}{\mathrm{N}}}{}^{+}\!- \xrightarrow{X^-} \equiv\mathrm{Si{-}X}\ (\text{or} \equiv\mathrm{SiOSi}\equiv) + \mathrm{CH_2{=}CH_2} + \overset{|}{\underset{|}{\mathrm{N}}}\!- \qquad (3)$$

$$X^- = \mathrm{Bu}^-, \mathrm{OH}^-$$

When the addition of n-butyllithium was carried out at −15 to −20°C to a solution of II in hexamethylphosphoramide (HMPA)/ether mixture, a red or yellow color appeared immediately and faded away after a few seconds. An α-triorganosilylalkylamine (IIIa—IIIm) was isolated from every reaction mixture as a main product. The structures of these products were confirmed by elemental and NMR spectral analyses, or by spectral comparison with authentic samples prepared by the reaction of chloromethyltrimethylsilane with a secondary amine [9] or from dialkylaminomethyl phenyl sulfides with triphenylsilyllithium. From the reaction mixtures of IIb—IId and IIf, small amounts of *N,N*-dialkyl-2-trimethylsilylethylamines (Ib—Id and If) were also isolated. In the neutral part of every reaction mixture, triorganovinylsilane (V), n-butyltriorganosilane (VI), and hexamethyldisiloxane (or triphenylsilanol) (VII) were detected and determined by GLC analyses (eq. 4).



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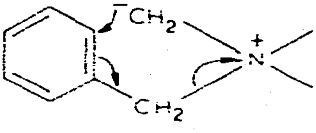
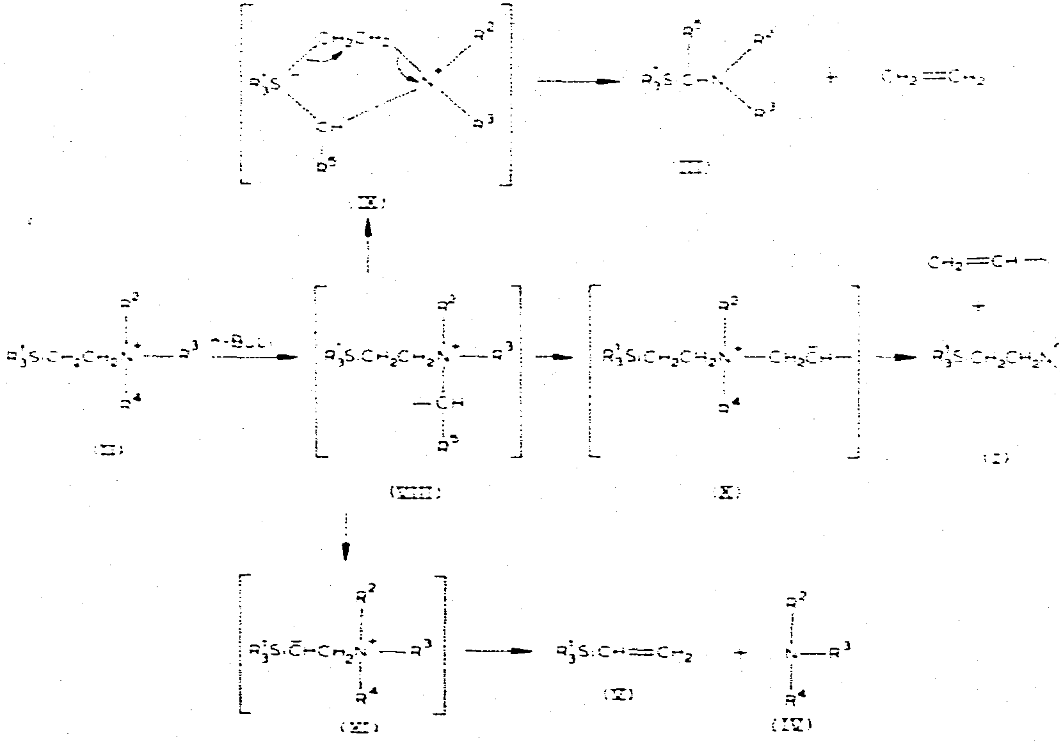
In order to test the intramolecular nature of the reaction path giving III, equimolar amounts of IIa and IIl were mixed and treated in a similar manner as above. The silylmethylamines in the reaction mixture were IIIa and IIIl only; no "crossover products" (IIIb and IIIj) were detected.

Three types of the base-promoted reactions of quarternary ammonium salts are well-known [11]; the Stevens rearrangement, the Sommelet—Hauser rearrangement, and the Hofmann elimination. The main reaction path giving III is comparable with the Sommelet—Hauser [3,2] sigmatropic rearrangement (structure A). However, the rearrangement of a silyl group could occur without the above symmetry restrictions through a pentacoordinate transition state (IX) [12], which is converted into III with elimination of ethylene (eq. 5). This silyl migration competes with two Hofmann elimination paths (eq. 6 and 7) in which I, IV, and V are produced via two betaine intermediates (X and XI) *. The contribution of X is less than that of XI which is stabilized by $(p-d)\pi$ conjugation [13] with the adjacent silicon atom.



(A)



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Peterson [14] suggested that the transmetalation of *N*-pyrrolidylmethyltri-

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* Silyl methyl hydrogens are somewhat acidic, thus the metalation of n-butyltrimethylsilane was achieved by contact at room temperature with a n-butyllithium—TMEDA complex [15]. However the direct formation of XI from II would be difficult under the above-mentioned reaction conditions.

TABLE 1

β-TRIORGANOSILYLETHYLAMINES (I)

Method A: $R^1_3SiCH{=}CH_2 + HN{<}^{R^2}_{R^3} \xrightarrow{Li} R^1_3SiCH_2CH_2N{<}^{R^2}_{R^3}$

(I)

Method B: $R^1_3SiCH_2MgCl + PhSCH_2N{<}^{R^2}_{R^3} \rightarrow I$

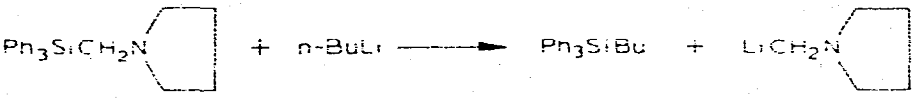
Method C: $R^1_3SiLi + ClCH_2CH_2N{<}^{R^2}_{R^3} \rightarrow I$

Method D: $R^1_3SiCl + BrCH_2CON{<}^{R^2}_{R^3} \xrightarrow{Zn} R^1_3SiCH_2CON{<}^{R^2}_{R^3} \xrightarrow{LiAlH_4} I$

	R^1	R^2	R^3	Method	B.p. (°C/mmHg) [m.p.]	Yield (%)	M.p. (°C) of oxalate[a]	Formula	Analysis found (calcd.) (%)		
									C	H	N
Ia	Me	Me	Me	B	135–136[b]	53,8					
Ib	Me	Me	Et	A	70–71/45	27,2	117–117,5	$C_8H_{21}NSi \cdot C_2H_2O_4$	48,01 (48,16)	9,21 (9,30)	5,45 (5,62)
Ic	Me	Et	Et	A	59–60/14[c]	65,0					
Id	Me	n-Pr	n-Pr	A	87–88/18	52,8	125–126	$C_{11}H_{27}NSi \cdot C_2H_2O_4$	53,52 (53,57)	9,99 (10,03)	4,64 (4,81)
Ie	Me	n-Bu	n-Bu	A	113–115/18	51,9		$C_{13}H_{31}NSi$	67,73 (68,04)	13,30 (13,62)	5,99 (6,10)
If	Me	Me	n-Bu	A	103–105/49	42,1	122–125	$C_{10}H_{25}NSi \cdot C_2H_2O_4$	51,84 (51,95)	9,65 (9,81)	5,00 (5,05)
Ig	Me	$-(CH_2)_4-$		A	77,5–78/21	59,1	159–160	$C_9H_{21}NSi \cdot C_2H_2O_4$	50,30 (50,55)	8,78 (8,87)	5,22 (5,36)
Ih	Me	$-(CH_2)_5-$		A	85,5–86/18[d]	63,8					
Ii	Me	Me	Ph	D	137–138/19	14,2		$C_{12}H_{21}NSi$	69,69 (69,50)	10,00 (10,21)	7,06 (6,75)
Ij	Ph	Me	Me	C	[66–72]	56,2		$C_{22}H_{25}NSi$	79,36 (79,70)	7,57 (7,60)	,08 (4,23)
Il	Ph	Et	Et	C	164–166/0,04	54,5		$C_{24}H_{29}NSi$	80,51 (80,16)	7,75 (8,13)	3,72 (3,90)
Im	Ph	Me	Ph	C	[102–103]	62,7		$C_{27}H_{27}NSi$	82,13 (82,39)	6,90 (6,66)	3,59 (3,56)

[a] Recrystallized from an ethanol/ether mixture. [b] Lit. b.p. 131°C, prepared at 80°C by method A [5]. [c] Lit. b.p. 66°C/18 mmHg [6]. [d] Lit. b.p. 80–81°C/12 mmHg [7].

phenylsilane occurred with n-butyllithium at room temperature (eq. 8). But the



(8)

rate of this transmetalation was negligible at —10 to —15°C. Therefore, the yield of VI corresponds to the contribution of the attack of n-butyllithium at the silicon atom of II. A portion of the IV and VII obtained would be produced during the work-up of the reaction mixture, because of lability of II in an alkaline aqueous solution.

Experimental

NMR spectra were recorded using a JNM-MH-100 (JEOL) spectrometer employing tetramethylsilane or dichloromethane as internal standard. IR spectra were obtained using an IRA-2 (JASCO) spectrometer. GLC analyses were performed on JGC-750 and JGC-1100 (JEOL) chromatographs. All boiling points and melting points are uncorrected.

N,N-Dimethyl-2-trimethylsilylethylamine (Ia)

A solution of trimethylsilylmethylmagnesium chloride (0.3 mol) in ether (200 ml) was added dropwise to an ice-cold solution of dimethylaminomethyl phenyl sulfide (45.16 g, 0.27 mol) in ether (70 ml). After the addition, the mixture was stirred at room temperature for 15 h, then was hydrolyzed with a saturated ammonium chloride solution. The ether layer was extracted with 10% hydrochloric acid solution. The acid extract was neutralized and extracted with ether. The ethereal extract was dried, concentrated, and distilled to give 21.11 g (53.8%) of Ia, b.p. 135—136°C (lit. [5] b.p. 131°C).

N,N-Dialkyl-2-trimethylsilylethylamine (Ib—Ih)

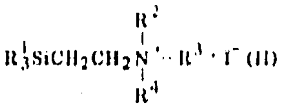
A solution of trimethylvinylsilane (2.00 g, 20 mmol) in n-hexane (5 ml) was added dropwise to a mixture of 80 mmol of dialkylamine (*N*-methylethylamine, diethylamine, n-dipropylamine, n-dibutylamine, *N*-methylbutylamine, pyrrolidine, or piperidine) and lithium clippings (60 mg, 8 mg-atom) in n-hexane (10 ml). After the addition, the mixture was heated at 40—45°C for 15 h, and was then hydrolyzed with water. The ethereal extract of the reaction mixture was dried, concentrated, and distilled to give the corresponding β-silylethylamine (Ib—Ih). Characterizing data are summarized in Table 1.

N-Methyl-N-(2-trimethylsilylethyl)aniline (Ii)

A mixture of *N*-methyl-α-bromoacetanilide (9.12 g, 40 mmol) and trimethylchlorosilane (8 g, 80 mmol) in benzene (60 ml) was added slowly to a suspension of zinc powder (4 g, 60 mg-atom) in benzene (20 ml) at 40—50°C. After 2 h of stirring, the mixture was poured into an ice-cold potassium bicarbonate solution, and the mixture was extracted with benzene. The benzene extract was dried and concentrated. The residue was added to a suspension of lithium aluminum hydride (2 g, 50 mmol) in ether (50 ml). The resulting mixture was heated at reflux for

TABLE 2

β-TRIORGANOSILYLETHYLAMMONIUM IODIDES,



$R^1_3SiCH_2CH_2\overset{R^2}{\underset{R^4}{N^+}}-R^3 \cdot I^-$ (II)

	R^1	R^2	R^3	R^4	Reaction time (h)	M.p. (°C) (recrystallization solvent)	Yield (%)	Formula	Analysis found(calcd.) (%)		
									C	H	N
IIa	Me	Me	Me	Me	3	263—265 (decomp.) (acetone/ether)	95	$C_8H_{22}INSi$	33.17 (33.45)	7.85 (7.72)	4.91 (4.88)
IIb	Me	Et	Et	Me	5	165—166 [a] (acetone/ether)	90				
IIc	Me	Et	Et	Et	24	162—164 (acetone/ether)	85	$C_{11}H_{28}INSi$	40.25 (40.12)	8.31 (8.57)	4.22 (4.25)
IId	Me	n-Pr	n-Pr	n-Pr	72	111—112 (acetone/ether)	32	$C_{14}H_{34}INSi$	44.98 (45.27)	9.01 (9.23)	3.43 (3.77)
IIf	Me	n-Bu	n-Bu	Me	7	55 68	88	$C_{14}H_{34}INSi$	45.07 (45.27)	9.03 (9.23)	3.63 (3.77)
IIg	Me	—(CH$_2$)$_4$—		Me	5	183.5—184 (acetone/ether)	89	$C_{10}H_{24}INSi$	38.09 (38.34)	7.71 (7.72)	4.75 (4.47)
IIh	Me	—(CH$_2$)$_5$—		Me	6	220—221 [b] (acetone/ether)	93				
IIi	Me	Me	Ph	Me	4	155—157 (decomp.) (ethanol/ether)	90	$C_{13}H_{24}INSi$	44.23 (44.70)	6.86 (6.92)	4.03 (4.01)
IIj	Ph	Me	Me	Me	1	254—256 (methanol)	91	$C_{23}H_{28}INSi$	58.43 (58.35)	5.99 (5.96)	2.96 (2.96)
IIk	Ph	Me	i-Pr	Me	19	228—229 (methanol)	85	$C_{25}H_{32}INSi$	59.53 (59.87)	6.47 (6.43)	2.77 (2.79)
IIl	Ph	Et	Et	Me	4	223—224 (ethanol)	90	$C_{25}H_{32}INSi$	59.65 (59.87)	6.58 (6.43)	2.81 (2.79)
IIm	Ph	Me	Ph	Me	7	190—191 (decomp.) (ethanol)	81	$C_{28}H_{30}INSi$	62.58 (62.80)	5.51 (5.65)	2.58 (2.62)

[a] Lit. m.p. 164°C [8]. [b] Lit. m.p. 220°C [8].

4 h, and was then hydrolyzed with a saturated ammonium chloride solution. The ethereal extract of the reaction mixture was dried, concentrated, and distilled to give 2.34 g (14.2%) of Ii, b.p. 137—138°C/19 mmHg.

N,N-Dimethyl-2-triphenylsilylethylamine (Ij)

A solution of triphenylsilyllithium (50 mmol) in THF (80 ml) was added to an ice-cold solution of 2-dimethylaminoethyl chloride (3.67 g, 34 mmol) in THF (20 ml). After the addition, the mixture was stirred at room temperature for 7 h, and was then hydrolyzed with a saturated ammonium chloride solution. 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% hydrochloric acid solution. The acid extract was neutralized and extracted with ether. Alumina column chromatography of the ethereal extract gave 6.34 g (56.2%) of Ij, m.p. 66—72°C.

N,N-Diethyl-2-triphenylsilylethylamine (Il)

In a similar manner as for Ij, triphenylsilyllithium (40 mmol) and 2-diethylaminoethyl chloride (3.80 g, 28 mmol) were treated in THF (90 ml). The combined organic layer was dried, concentrated and distilled to give 5.54 g (54.5%) of Il, b.p. 163—164°C/0.04 mmHg.

N-Methyl-N-(2-triphenylsilylethyl)aniline (Im)

In a similar manner as for Ij, triphenylsilyllithium (40 mmol) and N-methyl-N-(2-chloroethyl)aniline (4.82 g, 28 mmol) were allowed to react in THF (90 ml). The combined organic layer was dried and concentrated. Recrystallization of the residue from ethanol gave 6.90 g (62.7%) of Im, m.p. 102—103°C.

2-Triorganosilylethylammonium iodide (IIa—IIm)

A mixture of Ia—Im (10 mmol) and alkyl iodide (50 mmol) in acetone (40 ml) was heated at 40—50°C for 1—72 h. After removal of the acetone, the residue was recrystallized from the appropriate solvent shown in Table 2 to give the corresponding IIa—IIm. Their data are summarized in Table 2.

The reaction of II with n-butyllithium

General procedure. To 4.3 mmol of II dissolved in a mixture of HMPA (20 ml) and ether (10 ml) was added dropwise a solution of n-butyllithium (5.4 mmol) in ether * (15 ml) at —15 to —20°C. After the addition, stirring was continued at —15 to —20°C for 0.5 h, then at —10 to —15°C for 2—4 h. The mixture was poured into a cold saturated potassium bicarbonate (or ammonium chloride) solution (150 ml) and was extracted with ether. The ether layer was extracted with 10% hydrochloric acid solution.

The acid extract was made alkaline with potassium carbonate, and extracted with ether. Fractional distillation or preparative GLC (30% Tergitol NP-35 column) of the ethereal extract gave α-triorganosilylalkylamine (IIIa—IIIl) and β-trimethylsilylethylamine (Ib—Id or If) (or *N,N*-dimethylaniline). *N*-Methyl-*N*-triphenylsilylmethylaniline (IIIm) was isolated by alumina column chromatography

(Continued on p. 124)

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* The n-butyllithium content was determined by the double titration method [16].

TABLE 3

REACTION PRODUCTS OF β-TRIORGANOSILYLETHYLAMMONIUM IODIDES (IIa–IIm) WITH n-BUTYLLITHIUM

	R^1	R^2	R^3	R^4	R^5	Yield (%) [a]						II (recovery)
						III	I	IV	V	VI	VII	
IIa	Me	Me	Me	Me	H	40.1(61.0)	0	— [b]	11.2(27.1)	2.8(4.3)	2.1(3.2)	34.2
IIb	Me	Et	Et	Me	H	20.2(29.6)	4.3(6.3)	—	8.5(12.4)	4.5(6.6)	4.1(6.1)	31.7
IIc	Me	Et	Et	Et	Me	49.0(61.4)	14.0(17.6)	—	5.5(6.9)	1.7(2.2)	2.7(3.3)	20.2
IId	Me	n-Pr	n-Pr	n-Pr	Et	9.8(13.6)	2.8(3.9)	—	12.1(16.7)	13.9 (19.3)	11.5(15.9)	27.6
IIf	Me	n-Bu	n-Bu	Me	H	31.5	4.8	—	11.8	10.0	7.2	0
IIg	Me	—$(CH_2)_4$—		Me	H	14.7(36.8)	0	—	9.0(22.4)	8.4(21.2)	3.3(8.2)	60.0
IIh	Me	—$(CH_2)_5$—		Me	H	35.0(39.0)	0	—	6.8(7.6)	12.5(14.0)	2.1(2.4)	10.7
IIi	Me	Ph	Me	Me	H	26.7	0	59.6	9.7	10.2	1.4	0
IIj	Ph	Me	Me	Me	H	50.1(55.7)	0	—	2.5(2.8)	6.1(6.8)	13.0(14.5)	9.9
IIk	Ph	Me	i-Pr	Me	H	19.0(32.9)	0	—	11.4(19.6)	7.9(13.6)	13.2(22.7)	41.9
IIl	Ph	Et	Et	Me	H	16.9(46.8)	0	—	11.0(31.0)	trace	3.1(8.6)	63.9
IIm	Ph	Ph	Me	Me	H	4.5(9.0) [c]	0	35.1(70.0)	7.0(14.0)	2.4(4.9)	10.1(20.2)	43.4

[a] Based on GLC analysis using internal standards. Yields in parentheses are based on unrecovered II. [b] The corresponding tertiary amines were detected in every reaction mixture by GLC analysis, but their yields were not determined because of their volatility. [c] In a previous communication [10], we misunderstood that no *N*-methyl-*N*-triphenylsilylmethylaniline (IIIm) was formed in the reaction, because IIIm was not extracted with 10% hydrochloric acid solution.

TABLE 4

α-TRIORGANOSILYLALKYLAMINES, $R^1_3Si\overset{R^5}{\overset{|}{C}}HN\begin{smallmatrix}R^2\\R^3\end{smallmatrix}$ (III)

	R^1	R^2	R^3	R^5	B.p. (°C/mmHg) [m.p.]	M.p. (°C)	Formula	Analysis found (calcd.) (%)		
								C	H	N
IIIa	Me	Me	Me	H	114–116 [a]					
IIIb	Me	Et	Et	H	145–146 [b]					
IIIc	Me	Et	Et	Me	89–90/67	107–108 [c] (picrate)	$C_9H_{23}NSi \cdot C_6H_3N_3O_7$	44.58 (44.76)	6.50 (6.51)	13.62 (13.92)
IIId	Me	n-Pr	n-Pr	Et	84–86/16		$C_{12}H_{29}NSi$	66.45 (66.90)	13.20 (13.57)	6.18 (6.50)
IIIf	Me	n-Bu	n-Bu	H	98–99/18	120–122 [d] (oxalate)	$C_{12}H_{29}NSi \cdot C_2H_2O_4$	54.82 (55.04)	10.18 (10.02)	4.49 (4.59)
IIIg	Me	–(CH$_2$)$_4$–		H	65–68/25 [e]					
IIIh	Me	–(CH$_2$)$_5$–		H	74–76/22 [f]					
IIIi	Me	Ph	Me	H	112–118/13		$C_{11}H_{29}NSi$	68.21 (68.33)	9.75 (9.90)	7.01 (7.24)
IIIj	Ph	Me	Me	H	[111–113] [g]		$C_{21}H_{23}NSi$	79.35 (79.04)	7.24 (7.30)	4.36 (4.41)
IIIk	Ph	Me	i-Pr	H	150–155/0.1		$C_{23}H_{27}NSi$	79.81 (79.94)	7.90 (7.88)	4.00 (4.05)
IIIl	Ph	Et	Et	H	150–152/0.1		$C_{23}H_{27}NSi$	79.96 (79.94)	7.81 (7.88)	4.02 (4.05)
IIIm	Ph	Ph	Me	H	[73–74] [h]		$C_{26}H_{25}NSi$	82.40 (82.32)	6.66 (6.60)	3.47 (3.70)

[a] Lit. b.p. 115–118°C [9b]. [b] Lit. b.p. 145–150°C [9a]. [c] Recrystallized from ethanol. [d] Recrystallized from an ethanol/ether mixture. [e] Lit. b.p. 65–67°C/25 mmHg [9b]. [f] Lit. b.p. 59°C/9 mmHg [9a]. [g] Recrystallized from petroleum ether. [h] Recrystallized from n-hexane.

of the neutral part, because IIIm was not extracted with 10% hydrochloric acid solution.

Trimethyl- (or triphenyl-)vinylsilane (V), trimethyl-(or triphenyl-)-n-butylsilane (VI), and hexamethyldisiloxane (or triphenylsilanol) (VII) were detected and determined by GLC analysis (30% dioctyl sebacate or 5% DC-550 column) of the ether layer. Their yields were based on GLC analysis using an internal standard (trimethyl-n-propylsilane or dimethyldiphenylsilane).

The potassium bicarbonate (or ammonium chloride) solution was concentrated unde reduced pressure and extracted with hot chloroform. After removal of the solvent, 300 ml of ether was added to the residue to give unreacted II.

The experimental results are summarized in Tables 1, 3, 4, and 5.

Mixing experiment. In a similar manner as described above, a mixture of trimethyl(2-trimethylsilylethyl)ammonium iodide (IIa) (0.86 g, 3 mmol) and diethylmethyl (2-triphenylsilylethyl)ammonium iodide (III) (1.51 g, 3 mmol) was allowed to react with n-butyllithium (6.6 mmol) in a mixture of HMPA (30 ml) and ether (30 ml), and the reaction mixture was treated. From the acid extract, (dimethylaminomethyl)trimethylsilane (IIIa, 35.1%) and (diethylaminomethyl)triphenylsilane (IIIl, 15.4%) were detected and determined by GLC.

(Dialkylaminomethyl)trimethylsilane (IIIa, IIIb and IIIf—IIIh)

A mixture of 0.1 mol of dialkylamine (dimethylamine, diethylamine, n-dibutylamine, pyrrolidine, or piperidine) and chloromethyltrimethylsilane (6.13 g, 0.05 mol) was heated in a sealed tube at 140°C for 8 h. After the addition of a saturated sodium carbonate solution (80 ml), the mixture was extracted with ether. The ethereal extract was dried, concentrated, and distilled to give the corresponding IIIa, IIIb, or IIIf—IIIh.

(Dimethylaminomethyl)triphenylsilane (IIIj)

A solution of triphenylsilyllithium (80 mmol) in THF (100 ml) was added to an ice-cold solution of dimethylaminomethyl phenyl sulfide (9.5 g, 56 mmol) in

TABLE 5

NMR SPECTRA OF α-TRIORGANOSILYLALKYLAMINES (III)

Compound	Chemical shift ($CDCl_3$) (δ, ppm), multiplicity, intensity, assignments
IIIc[a]	0.34 (s, 9H, $SiCH_3$), 1.54 (d, 3H, $SiCHC\underline{H}_3$), 1.50 and 1.53 (t, 6H, N—ethyl CH_3), 3.20—3.54 (m, 5H, NCH_2 and SiCHN)
IIId	0.08 (s, 9H, $SiCH_3$), 0.94 (t, 6H, N—n-Pr CH_3), 1.04 (t, 3H, SiC—Et_3 CH_3), 2.02 (t, 1H, SiCHN), 2.48 (t, 4H, NCH_2)
IIIf	0.08 (s, 9H, $SiCH_3$), 1.92 (s, 2H, $SiCH_2N$)
IIIi	0.08 (s, 9H, $SiCH_3$), 2.90 (s, 2H, $SiCH_2N$), 2.98 (s, 3H, NCH_3), 6.60—6.90 and 7.10—7.40 (m, 5H, aromatic protons)
IIIj	2.20 (s, 6H, NCH_3), 2.73 (s, 2H, $SiCH_2N$), 6.80—7.70 (m, 15H, aromatic protons)
IIIk	0.95 (d, 6H, N—i-Pr CH_3), 2.10 (s, 2H, $SiCH_2N$), 2.80 (s, 3H, NCH_3), 7.00—7.80 (m, 15H, aromatic protons)
IIIl	0.92 (t, 6H, N—Et CH_3), 2.50 (q, 4H, N—Et CH_2), 2.85 (s, 2H, $SiCH_2N$), 7.00—8.00 (m, 15 H, aromatic protons)
IIIm	2.72 (s, 3H, NCH_3), 3.66 (s, 2H, $SiCH_2N$), 6.60—7.80 (m, 20H, aromatic protons)

[a] Obtained in CF_3COOH.

THF (30 ml). After the addition, the mixture was stirred at room temperature for 3 h, and was then hydrolyzed with a saturated ammonium chloride solution. 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 10% hydrochloric acid solution. The acid extract was neutralized and extracted with ether. Distillation of the ethereal extract gave 8.7 g (48%) of IIIj: b.p. 172–174°C/0.6 mmHg; m.p. 111–113°C (recrystallized from petroleum ether).

(Diethylaminomethyl)triphenylsilane (IIIl)

In a similar manner as above IIIj, the treatment of triphenylsilyllithium (80 mmol) with diethylaminomethyl phenyl sulfide (11.1 g, 57 mmol) in THF (130 ml) gave 9.46 g (48.2%) of IIIl, b.p. 150–152°C/0.1 mmHg.

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