Journal of Organometallic Chemistry, 153 (1978) 193—207

SYNTHESES OF 1-SUBSTITUTED 4,4-DIMETHYL-1,2,3,4-TETRAHYDRO-BENZO[b]-1,4-AZASILINES AND 1-SUBSTITUTED 3,3-DIMETHYL-1,2,3,4-TETRAHYDROBENZO[e]-1,3-AZASILINES

TOYOHIKO AOYAMA, YOSHIRO SATO*, TOORU SUZUKI and HIDEAKI SHIRAI

Faculty of Pharmaceutical Sciences, Nagoya City University, Tanabe-dori, Mizuho-ku, Nagoya 467, (Japan)

(Received January 17th, 1978)

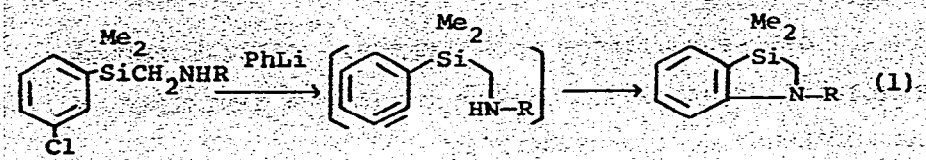
Summary

1-Substituted 4,4-dimethyl-1,2,3,4-tetrahydrobenzo[b]-1,4-azasilines (X) and 1-substituted 3,3-dimethyl-1,2,3,4-tetrahydrobenzo[e]-1,3-azasilines (XIII) were synthesized by the intramolecular benzyne reaction of the corresponding N-substituted 2-(3-chlorophenyl)dimethylsilylethylamines (IX) and N-substituted (3-chlorobenzyl)dimethylsilylmethylamines (XII).

Introduction

It is well known that the intramolecular addition of nucleophiles to benzyne intermediates has provided a useful method for the synthesis of heterocyclic systems [1]. In an earlier paper, we reported the synthesis of a new ring system, 1-substituted 3,3-dimethylbenzo[d]-1,3-azasiloline, by the

benzyne reaction of N-substituted (3-chlorophenyl)dimethylsilylmethylamine [2] (eq. 1).



(1)

On continuation of this work, we describe here the syntheses of 1-substituted 4,4-dimethyl-1,2,3,4-tetrahydrobenzo[b]-1,4-azasiline (X) and 1-substituted 3,3-dimethyl-1,2,3,4-tetrahydrobenzo[e]-1,3-azasiline (XIII) by such benzyne routes.

Results and discussion

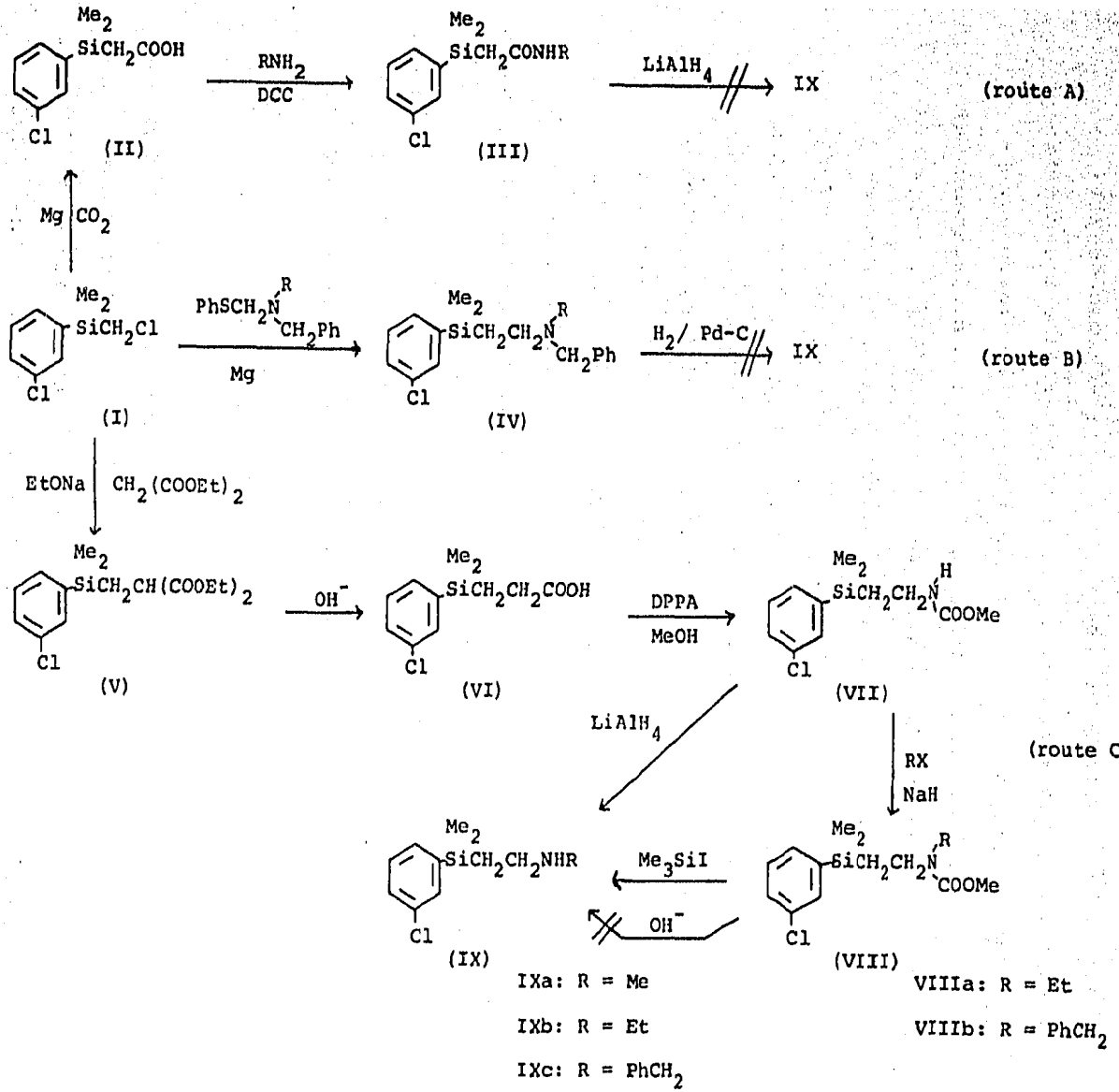
Synthesis of 1-Substituted 4,4-Dimethyl-1,2,3,4-tetrahydrobenzo[b]-1,4-azasiline (X)

Three routes to the synthesis of key compound, N-substituted 2-(3-chlorophenyl)dimethylsilylethylamine (IX), were examined as shown in Scheme 1.

N-Benzyl-2-(3-chlorophenyl)dimethylsilylacetamide (III, R = $PhCH_2$) was prepared by carboxylation of (3-chlorophenyl)-chloromethyldimethylsilane (I), followed by amidation. Lithium aluminum hydride reduction of III did not form N-benzyl-2-(3-chlorophenyl)dimethylsilylethylamine (IXc), but gave a complicated mixture which presumably resulted from competition of the reductive cleavage of Si-C bonds with the reduction of the carbonyl group (route A in Scheme 1).

Catalytic debenzylation of N-benzyl-N-methyl-2-(3-chlorophenyl)dimethylsilylethylamine (IV, R = Me), obtained by aminomethylation of I, also gave a complicated mixture which presumably was formed by debenzylation and dechlorination (route B in Scheme 1).

SCHEME 1

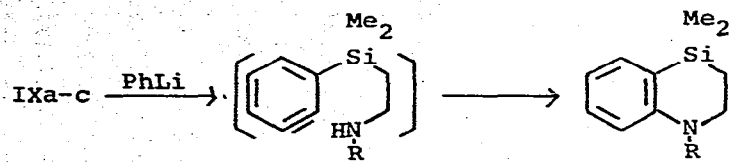

Me2SiCH2COOH
Cl
(II)
RNH2
DCC
Me2SiCH2CONHR
(III)
LiAlH4
IX
(route A)
Mg
CO2
Me2SiCH2Cl
(I)
PhSCH2NRCH2Ph
Mg
Me2SiCH2CH2NRCH2Ph
(IV)
H2/ Pd-C
IX
(route B)
EtONa
CH2(COOEt)2
Me2SiCH2CH(COOEt)2
(V)
OH-
Me2SiCH2CH2COOH
(VI)
DPPA
MeOH
Me2SiCH2CH2NHCOOMe
(VII)
LiAlH4
RX
NaH
(route C)
Me2SiCH2CH2NHR
(IX)
Me3SiI
OH-
Me2SiCH2CH2NRCOOMe
(VIII)
IXa: R = Me
IXb: R = Et
IXc: R = PhCH2
VIIIa: R = Et
VIIIb: R = PhCH2

2-Silylethylamine (IX) was successfully synthesized by the third route (route C in Scheme 1). 3-(3-Chlorophenyl)-dimethylsilylpropionic acid (VI) was prepared by the modification of Sommer's method [3] from I via diethyl (3-chlorophenyl)-dimethylsilylmethylmalonate (V). Curtius rearrangement [4] of VI to methyl N-[2-(3-chlorophenyl)dimethylsilylethyl]-carbamate (VII) was achieved in moderate yield by the use of diphenyl phosphorazidate (DPPA). N-Methyl-2-(3-chlorophenyl)dimethylsilylethylamine (IXa) was obtained by lithium aluminum hydride reduction of VII. N-Alkylated products, methyl N-substituted N-[2-(3-chlorophenyl)dimethylsilylethyl]-carbamates (VIIIa, R = Et and VIIIb, R = $PhCH_2$), were not hydrolyzed in dilute potassium hydroxide solution. Under more drastic conditions, hydrolysis of the methyl ester of VIII competed with cleavage of Si-C bonds to form a complicated mixture. Recently Jung et al. [5] have shown that alkyl carboxylic esters are converted under mild conditions to the corresponding carboxylic acid by treatment with trimethyliodosilane, followed by hydrolysis (eq. 2). This method was successfully applied

$$RCOOR' \xrightarrow{Me_3SiI} \left[RCOOSiMe_3\right] \xrightarrow{H_2O} RCOOH \qquad (2)$$

to VIIIa-b to give the corresponding N-substituted 2-(3-chlorophenyl)dimethylsilylethylamines (IXb, R = Et and IXc, R = $PhCH_2$).

The reaction of 2-silylethylamines (IXa-c) with phenyllithium in refluxing ether gave a single basic product. The ^1H NMR spectral and elemental analyses of these compounds confirmed the structures as those of the desired cyclization products, 1-substituted 4,4-dimethyl-1,2,3,4-tetrahydrobenzo[b]-1,4-azasilines (Xa, R = Me; Xb, R = Et and Xc, R = $PhCH_2$) (eq. 3).



(3)

(X)

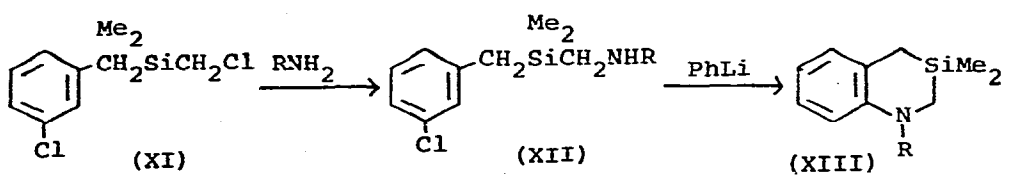
Xa: R = Me, 38%

Xb: R = Et, 35%

Xc: R = $PhCH_2$, 29%

Synthesis of 1-Substituted 3,3-Dimethyl-1,2,3,4-tetrahydrobenzo[e]-1,3-azasiline (XIII)

The key compounds, N-substituted (3-chlorobenzyl)dimethylsilylmethylamines (XIIa, R = Me; XIIb, R = Et and XIIc, R = $PhCH_2$), were prepared by the reaction of (3-chlorobenzyl)-chloromethyldimethylsilane (XI) with primary amines (methylamine, ethylamine and benzylamine). Under the same reaction conditions as were used for IX, compound XIIa-c gave the corresponding cyclization products, 1-substituted 3,3-dimethyl-1,2,3,4-tetrahydrobenzo[e]-1,3-azasilines (XIIIa, R = Me; XIIIb, R = Et and XIIIc, R = $PhCH_2$) in 40-61% yields (eq. 4).



(XI) (XII) (XIII) (4)

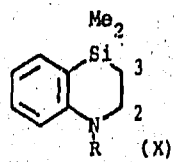
XIIIa: R = Me, 40%

XIIIb: R = Et, 41%

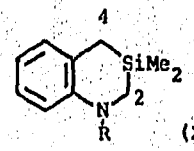
XIIIc: R = $PhCH_2$, 61%

The structures of these compounds were confirmed by the ^1H NMR spectral and elemental analyses (Table 1).

TABLE 1 1-SUBSTITUTED 4,4-DIMETHYL-1,2,3,4-TETRAHYDROBENZO[b]-1,4-AZASILINES (Xa-c) and 1-SUBSTITUTED 3,3-DIMETHYL-1,2,3,4-TETRAHYDROBENZO[e]-1,3-AZASILINES (XIIIa-c)



(X)



(XIII)

Compound	R	Reaction time (h)	b.p., °C (mmHg)	Yield(%)	NMR($CDCl_3$) δ (ppm)	Formula	Analysis found(calcd.)(%) C	H	N
Xa	Me	2.5	120-123 (22)	38	1.04 (t, 2H, J = 7 Hz, H-3) 3.36 (t, 2H, J = 7 Hz, H-2)	$C_{11}H_{17}NSi$	69.14 (69.05)	8.97 (8.96)	7.19 (7.32)
Xb	Et	8	127-129 (24)	35	0.96 (t, 2H, J = 7 Hz, H-3) 3.36 (t, 2H, J = 7 Hz, H-2)	$C_{12}H_{19}NSi$	70.60 (70.18)	9.32 (9.33)	7.16 (6.82)
Xc	$PhCH_2$	30	117-119 (0.15)	29	0.96 (t, 2H, J = 7 Hz, H-3) 3.48 (t, 2H, J = 7 Hz, H-2)	$C_{17}H_{21}NSi$	76.21 (76.35)	7.67 (7.91)	5.10 (5.24)
XIIIa	Me	2	115-117 (12)	40	1.90 and 2.20 (s×2, 2H×2, H-2 and H-4)	$C_{11}H_{17}NSi$	69.24 (69.05)	8.69 (8.96)	7.33 (7.32)
XIIIb	Et	2	124-125 (14)	41	1.88 and 2.20 (s×2, 2H×2, H-2 and H-4)	$C_{12}H_{19}NSi$	70.18 (70.18)	9.57 (9.33)	7.12 (6.82)
XIIIc	$PhCH_2$	2	119-121 (0.15)	61	2.00 and 2.16 (s×2, 2H×2, H-2 and H-4)	$C_{17}H_{21}NSi$	76.05 (76.35)	8.14 (7.91)	5.31 (5.24)

Experimental

NMR spectra were recorded using a JNM-MH-100 (JEOL) spectrometer with tetramethylsilane as internal standard. IR spectra were recorded on a IRA-2 (JASCO) spectrometer. All boiling points and melting points are uncorrected. Ether was dried by distillation from lithium aluminum hydride prior to use.

2-(3-Chlorophenyl)dimethylsilylacetic acid (II)

Carbon dioxide was bubbled into a solution of (3-chlorophenyl)dimethylsilylmethylmagnesium chloride [prepared from (3-chlorophenyl)(chloromethyl)dimethylsilane (I) [2] (6.57 g, 30 mmol) and magnesium turnings (0.80 g, 33 mg-atom) in diethyl ether (50 ml)] for 3 h at -30 to -35°C. The reaction mixture was hydrolyzed with water, and extracted with ether. The ethereal extracts were dried, concentrated, and recrystallized from n-hexane to give 4.07 g (60%) of II, m.p. 73-75°C. NMR ($CDCl_3$): δ 0.44 (s, 6H, $SiCH_3$), 2.08 (s, 2H, $SiCH_2$), 7.24-7.48 ppm (m, 4H, aromatic protons). IR (nujol): ν 1675 cm^{-1} (C=O). (Found: C, 52.61; H, 5.91. $C_{10}H_{13}ClO_2Si$ calcd.: C, 52.51; H, 5.73%.)

N-Benzyl-2-(3-chlorophenyl)dimethylsilylacetamide (III)

A mixture of II (684 mg, 3 mmol), benzylamine (321 mg, 3 mmol) and dicyclohexylcarbodiimide (680 mg, 3.3 mmol) in dichloromethane (6 ml) was stirred for 3 h at room temperature. The reaction mixture was filtered, and the filtrate was concentrated. The residue was recrystallized from benzene-n-hexane to give 380 mg (41%) of III, m.p. 100-102°C. NMR ($CDCl_3$): δ 0.40 (s, 6H, $SiCH_3$), 1.96 (s, 2H, $SiCH_2$), 4.28 (d, 2H, CH_2Ph), 7.05-7.48 ppm (m, 9H, aromatic protons).

IR (nujol): ν 1625 cm^{-1} (C=O). (Found: C, 64.48; H, 6.45; N, 4.33. $C_{17}H_{20}ClNOSi$ calcd.: C, 64.23; H, 6.34; N, 4.41%.)

Benzylmethylaminomethyl phenyl sulfide

Benzylmethylamine (13.2 g, 110 mmol) was added dropwise to thiophenol (11.0 g, 100 mmol) under cooling in an ice bath, and the mixture was stirred at room temperature for 10 min. To this mixture was added 37% formalin (8.9 g, 110 mmol) and stirring was continued for 2 h at 80°C. The mixture was extracted with ether. The ethereal extracts were dried, concentrated, and distilled to give 18.8 g (77%) of benzylmethylaminomethyl phenyl sulfide, b.p. 124-126°C/ 0.05 mmHg. NMR ($CDCl_3$): δ 2.26 (s, 3H, NCH_3), 3.56 (s, 2H, CH_2Ph), 4.36 (s, 2H, SCH_2), 7.01-7.40 ppm (m, 10H, aromatic protons). (Found: C, 74.15; H, 7.20; N, 5.69. $C_{15}H_{17}NS$ calcd.: C, 74.03; H, 7.04; N, 5.76%.)

N-Benzyl-N-methyl-2-(3-chlorophenyl)dimethylsilylethylamine (IV)

A solution of benzylmethylaminomethyl phenyl sulfide (6.96 g, 28.6 mmol) in ether (20 ml) was added dropwise to a solution of (3-chlorophenyl)dimethylsilylmethylmagnesium chloride prepared from I (6.26 g, 28.6 mmol) and magnesium turnings (0.75 g, 30.8 mg-atom) in ether (50 ml). After 4 h of stirring at room temperature, the reaction mixture was hydrolyzed with water, and extracted with ether. The ethereal extracts were extracted with 10% HCl. The acid extracts were made alkaline with 10% NaOH, and extracted with ether. The ethereal extracts were dried, concentrated, and distilled to give 7.24 g, (80%) of IV, b.p. 132-135°C/0.03 mmHg. NMR ($CDCl_3$): δ 0.28 (s, 6H, $SiCH_3$), 1.00 (t, 2H, J = 7 Hz, $SiCH_2$), 2.24

(s, 3H, NCH_3), 2.40 (t, 2H, J = 7 Hz, NCH_2), 3.36 (s, 2H, CH_2Ph) 6.88-7.36ppm (m, 9H, aromatic protons). (Found: C, 67.81; H, 7.50; N, 3.05. $C_{18}H_{24}ClNSi$ calcd.: C, 68.00; H, 7.61; N, 3.15%.)

Diethyl (3-Chlorophenyl)dimethylsilylmethylmalonate (V)

A solution of diethyl malonate (45 g, 205 mmol) in absolute ethanol (30 ml) was added to a solution of sodium ethoxide (215 mmol) in absolute ethanol (150 ml), and the mixture was stirred at room temperature for 30 min. Then a solution of I (34.5 g, 215 mmol) in absolute ethanol (30 ml) was added to the mixture and stirring was continued for 24 h at reflux. The reaction mixture was made acidic to litumus by addition of glacial acetic acid and then was concentrated. Water was added to the residual oil, and the mixture was extracted with ether. The ethereal extracts were dried, concentrated, and distilled to give 54.7 g (78%) of V, b.p. 133-136°C/0.2 mmHg. NMR ($CDCl_3$): δ 0.32 (s, 6H, $SiCH_3$), 1.24 (t, 6H, J = 7 Hz, $CH_2C\underline{H}_3$), 1.32 (d, 2H, J = 7 Hz, $SiCH_2$), 3.16 (t, 1H, J = 7 Hz, $CH_2C\underline{H}$), 4.06 (q, 4H, J = 7 Hz, $C\underline{H}_2CH_3$), 7.16-7.48 ppm (m, 4H, aromatic protons). IR (film): ν 1745, 1725 cm^{-1} (C=O). (Found: C, 56.18; H, 6.73. $C_{16}H_{23}ClO_4Si$ calcd.: C, 56.04; H, 6.76%.)

3-(3-Chlorophenyl)dimethylsilylpropionic acid (VI)

To a 50% potassium hydroxide solution (58 g) was added dropwise V (45 g, 131 mmol) at 90°C. After 1.5 h of stirring at this temperature, the reaction mixture was evaporated to dryness, and the residual salt was dissolved in water (73 ml). To the solution was added dropwise 35% HCl (58 ml) under cooling in an ice-salt bath. The mixture was heated for 8 h at reflux, and then extracted with benzene. The benzene

extracts were dried, concentrated, and distilled to give 28.0 g (88%) of VI, b.p. 145-147°C/0.4 mmHg. NMR ($CDCl_3$): δ 0.32 (s, 6H, $SiCH_3$), 1.12 (t, 2H, J = 7 Hz, $SiCH_2$), 2.32 (t, 2H, J = 7 Hz, CH_2CO), 7.24-7.40 ppm (m, 4H, aromatic protons). IR (film): ν 1710 cm^{-1} (C=O). (Found: C, 54.34; H, 6.32. $C_{11}H_{15}ClO_2Si$ calcd.: C, 54.42; H, 6.23%.)

Methyl N-[2-(3-Chlorophenyl)dimethylsilylethyl]carbamate (VII)

To a boiling solution of VI (17 g, 70 mmol) and triethylamine (7.14 g, 70.7 mmol) in dry benzene (150 ml) was added dropwise diphenyl phosphorazidate [4] (19.26 g, 70 mmol). After 1 h of stirring at reflux, absolute methanol (4.48 g, 140 mmol) was added and heating was continued for additional 6 h. The reaction mixture was washed with 5% NaOH and water, and then dried. The solvent was evaporated and the residual oil was distilled to give 15.7 g (83%) of VII, b.p. 124-126°C/0.1 mmHg. NMR ($CDCl_3$): δ 0.28 (s, 6H, $SiCH_3$), 1.04 (t, 2H, J = 7 Hz, $SiCH_2$), 3.08-3.36 (m, 2H, NCH_2), 3.64 (s, 3H, OCH_3), 7.20-7.52 ppm (m, 4H, aromatic protons). IR (film): ν 3340 (NH), 1705 cm^{-1} (C=O). (Found: C, 53.11; H, 6.66; N, 5.07. $C_{12}H_{18}ClNO_2Si$ calcd.: C, 53.02; H, 6.67; N, 5.15%.)

Methyl N-Ethyl-N-[2-(3-chlorophenyl)dimethylsilylethyl]carbamate (VIIIa)

A mixture of VII (11.76 g, 43 mmol) and sodium hydride (1.34 g, 56 mmol) in dry benzene (80 ml) was heated at reflux for 7 h. Then a solution of ethyl bromide (7.10 g, 65 mmol) in benzene (20 ml) was added to the mixture and stirring was continued for 4 h at reflux. The reaction mixture was hydrolyzed with water and then was extracted with benzene. The benzene extracts were dried, concentrated, and distilled to give 7.10 g (55%) of VIIIa, b.p. 126-128°C/0.25 mmHg.

NMR ($CDCl_3$): δ 0.28 (s, 6H, $SiCH_3$), 1.08 (t, 3H, J = 7 Hz, $CH_2\underline{CH_3}$), 1.00-1.24 (m, 2H, $SiCH_2$), 3.24 (q, 2H, J = 7 Hz, $\underline{CH_2}CH_3$), 3.08-3.40 (m, 2H, NCH_2), 3.68 (s, 3H, OCH_3), 7.28-7.56 ppm (m, 4H, aromatic protons). IR (film): ν 1700 cm^{-1} (C=O). (Found: C, 56.02; H, 7.45; N, 4.53. $C_{14}H_{22}ClNO_2Si$ calcd.: C, 56.07; H, 7.40; N, 4.67%.)

Methyl N-Benzyl-N-[2-(3-chlorophenyl)dimethylsilylethyl]-carbamate (VIIIb)

As described above for VIIIa, VII (11.20 g, 41 mmol), sodium hydride (1.10 g, 46 mmol) and benzyl chloride (6.70 g, 53 mmol) were allowed to react in dry benzene (100 ml), and then the reaction mixture was worked-up. Distillation of the benzene extract gave 8.67 g (58%) of VIIIb, b.p. 162-164°C/0.09 mmHg. NMR ($CDCl_3$): δ 0.24 (s, 6H, $SiCH_3$), 1.06 (t, 2H, J = 7 Hz, $SiCH_2$), 3.24 (t, 2H, J = 7 Hz, NCH_2), 3.72 (s, 3H, OCH_3), 4.44 (s, 2H, $PhCH_2$), 7.08-7.48 ppm (m, 9H, aromatic protons). IR (film): ν 1700 cm^{-1} (C=O). (Found: C, 62.92; H, 6.57; N, 3.82. $C_{19}H_{24}ClNO_2Si$ calcd.: C, 63.05; H, 6.68; N, 3.87%.)

N-Methyl-2-(3-chlorophenyl)dimethylsilylethylamine (IXa)

A mixture of VII (5.4 g, 20 mmol), lithium aluminum hydride (1.0 g, 26 mmol) and ether (70 ml) was heated at reflux for 8 h and then hydrolyzed with water. The reaction mixture was extracted with ether. The ethereal extracts were dried, concentrated, and distilled to give 3.07 g (68%) of IXa, b.p. 141-143°C/12 mmHg. NMR ($CDCl_3$): δ 0.28 (s, 6H, $SiCH_3$), 1.00 (t, 2H, J = 7 Hz, $SiCH_2$), 2.40 (s, 3H, NCH_3), 2.60 (t, 2H, J = 7 Hz, NCH_2), 7.24-7.52 ppm (m, 4H, aromatic protons). IXa-oxalate; m.p. 190-192°C (decomp.) (from ethanol-ether). (Found: C, 49.12; H, 6.21; N, 4.49. $C_{11}H_{18}ClNSi \cdot C_2H_2O_4$

calcd.: C, 49.13; H, 6.34; N, 4.41%.)

N-Ethyl-2-(3-chlorophenyl)dimethylsilylethylamine (IXb)

A solution of VIIIa (7.66 g, 25.5 mmol) and trimethyliodosilane [5] (7.62 g, 38.1 mmol) in carbon tetrachloride (40 ml) was stirred at 50°C for 45 h, and then concentrated under reduced pressure. The residual oil was dissolved in 10% HCl and washed with ether. The acid layer was neutralized with 10% NaOH and extracted with ether. The ethereal extracts were dried, concentrated, and distilled to give 3.89 g (63%) of IXb, b.p. 125-127°C/10 mmHg. NMR ($CDCl_3$): δ 0.30 (s, 6H, $SiCH_3$), 1.00 (t, 2H, J = 7 Hz, $SiCH_2$), 1.08 (t, 3H, J = 7 Hz, $CH_2\underline{CH}_3$), 2.62 (q, 2H, J = 7 Hz, $\underline{CH}_2CH_3$), 2.66 (t, 2H, J = 7 Hz, NCH_2), 7.24-7.52 ppm (m, 4H, aromatic protons). IXb-oxalate; m.p. 207-209°C (decomp.) (from ethanol-ether). (Found: C, 50.74; H, 6.67; N, 4.36. $C_{12}H_{20}ClNSi \cdot C_2H_2O_4$ calcd.: C, 50.67; H, 6.68; N, 4.22%.)

N-Benzyl-2-(3-chlorophenyl)dimethylsilylethylamine (IXc)

As described above for IXb, VIIIb (8.62 g, 22.8 mmol) and trimethyliodosilane (6.84 g, 34.2 mmol) were allowed to react in carbon tetrachloride (40 ml), and then the reaction mixture was worked-up. Distillation of the ethereal extracts gave 5.29 g (76%) of IXc, b.p. 137-139°C/0.06 mmHg. NMR ($CDCl_3$): δ 0.28 (s, 6H, $SiCH_3$), 1.04 (t, 2H, J = 7 Hz, $SiCH_2$), 2.72 (t, 2H, J = 7 Hz, NCH_2), 3.76 (s, 2H, $PhCH_2$), 7.16-7.52 ppm (m, 9H, aromatic protons). (Found: C, 67.49; H, 7.35; N, 4.79. $C_{17}H_{22}ClNSi$ calcd.: C, 67.19; H, 7.30; N, 4.61%.)

(3-Chlorobenzyl)chloromethyldimethylsilane (XI)

A solution of chloromethyldimethylchlorosilane (23.6 g,

165 mmol) in ether (30 ml) was added dropwise to a solution of 3-chlorobenzylmagnesium bromide prepared from 3-chlorobenzyl bromide (30.8 g, 150 mmol) and magnesium turnings (3.65 g, 150 mg-atom) in ether (200 ml). After 6 h of stirring at reflux, the reaction mixture was hydrolyzed with water, and extracted with ether. The ethereal extracts were dried, concentrated, and distilled to give 20.6 g (59%) of XI, b.p. 149-151°C/17 mmHg. NMR ($CDCl_3$): δ 0.20 (s, 6H, $SiCH_3$), 2.24 (s, 2H, $SiCH_2$), 2.72 (s, 2H, CH_2Cl), 6.75-7.19 ppm (m, 4H, aromatic protons). (Found: C, 51.31; H, 5.83. $C_{10}H_{14}Cl_2Si$ calcd.: C, 51.50; H, 6.05%.)

N-Substituted (3-Chlorobenzyl)dimethylsilylmethylamine (XIIa-c)

A mixture of primary amine (methylamine, ethylamine, or benzylamine) (240 mmol) and XI (14.0 g, 60 mmol) was heated at 130°C for 4-6 h. After the addition of 10% NaOH (50 ml), the reaction mixture was extracted with ether. The ethereal extracts were dried, concentrated, and distilled to give XIIa (59%), XIIb (72%), and XIIc (80%), respectively. These compounds were characterized as follows.

N-Methyl-(3-chlorobenzyl)dimethylsilylmethylamine (XIIa); b.p. 142-144°C/14 mmHg. NMR ($CDCl_3$): δ 0.03 (s, 6H, $SiCH_3$), 2.04 (s, 2H, $SiCH_2N$ or $ArCH_2Si$), 2.10 (s, 2H, $SiCH_2N$ or $ArCH_2Si$), 2.42 (s, 3H, NCH_3), 6.72-7.24 ppm (m, 4H, aromatic protons). XIIa-oxalate, m.p. 186-187°C (decomp.) (from ethanol). (Found: C, 49.24; H, 6.25; N, 4.67. $C_{11}H_{18}ClNSi \cdot C_2H_2O_4$ calcd.: C, 49.13; H, 6.34; N, 4.41%.)

N-Ethyl-(3-chlorobenzyl)dimethylsilylmethylamine (XIIb); b.p. 149-151°C/16 mmHg. NMR ($CDCl_3$): δ 0.04 (s, 6H, $SiCH_3$), 1.04 (t, 3H, J = 7 Hz, $CH_2\underline{CH_3}$), 2.06 (s, 2H, $SiCH_2N$ or $ArCH_2Si$), 2.11 (s, 2H, $SiCH_2N$ or $ArCH_2Si$), 2.60 (q, 2H, J = 7 Hz, $\underline{CH_2}CH_3$), 6.80-7.24 ppm (m, 4H, aromatic protons). XIIb-oxalate,

m.p. 180-181°C (decomp.) (from methanol). (Found: C, 50.51; H, 6.56; N, 4.30. $C_{12}H_{20}ClNSi \cdot C_2H_2O_4$ calcd.: C, 50.67; H, 6.68; N, 4.22%.)

N-Benzyl-(3-chlorobenzyl)dimethylsilylmethylamine (XIIc); b.p. 134-136°C/0.1 mmHg. NMR ($CDCl_3$): δ 0.02 (s, 6H, $SiCH_3$), 2.06 (s, 2H, $SiCH_2N$ or $ArCH_2Si$), 2.12 (s, 2H, $SiCH_2N$ or $ArCH_2Si$), 3.76 (s, 2H, $PhCH_2$), 6.72-7.36 ppm (m, 9H, aromatic protons). (Found: C, 67.45; H, 7.44; N, 4.76. $C_{17}H_{22}ClNSi$ calcd.: C, 67.19; H, 7.30; N, 4.61%.)

Reaction of IXa-c or XIIa-c with Phenyllithium

General procedure: A solution of phenyllithium [6] prepared from bromobenzene (3.61 g, 23 mmol) and lithium clippings (0.64 g, 92 mg-atom) in ether (25 ml) was added dropwise to a boiling solution of silylalkylamine (IXa-c or XIIa-c) (15 mmol) in ether (35 ml). After 2—30 h of stirring at reflux, the reaction mixture was hydrolyzed with water, and extracted with ether. The ethereal extracts were extracted with 5% HCl. The acid extracts were made alkaline with 5% NaOH, and extracted with ether. The ethereal extracts were dried, concentrated, and distilled to give corresponding Xa-b and XIIIa-b. Compounds Xc and XIIIc were obtained by distillation of the first ethereal extract without acid extraction.

The yields and properties of these compounds are summarized in Table 1.

Acknowlegement This work was supported by the Matsunaga Research Grant from Matsunaga Science Foundation. The authors are also grateful to the Shin-Etu Chemical Industry Co., Ltd. for a generous gift of chlorosilanes.

References

1 H. Heaney, Chem. Rev., 62 (1962) 81.

2 T. Aoyama, Y. Sato and H. Shirai, J. Organometal. Chem., 118 (1976) 1.

3 L. H. Sommer, G. M. Goldberg, G. H. Barnes and L. S. Stone, Jr., J. Amer. Chem. Soc., 76 (1954) 1609.

4 K. Ninomiya, T. Shioiri and S. Yamada, Tetrahedron, 30 (1974) 2151.

5 M. E. Jung and M. A. Lyster, J. Amer. Chem. Soc., 99 (1977) 968.

6 R. G. Jones and H. Gilman, in R. Adams, (Ed.), Organic Reactions, Vol. VI, John Wiley and Sons, Inc, New York, N. Y., 1951, p. 353.