Thermolysis Reactions of 2-Methoxy-2-(*o*-*N*,*N*-dimethylaminomethyl)-phenyl-3-trimethylsilyl-5,5-dimethyl-2-silahexane

Myong Euy Lee,* Hyeon Mo Cho, and Chang Hwan Kim

Department of Chemistry, Graduate School, Yonsei University, Seoul 120-749, Korea
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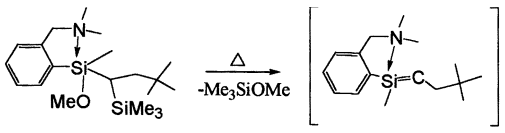
In the neat flow vacuum pyrolysis of 2-methoxy-2-(*o*-*N*,*N*-dimethylaminomethyl)phenyl-3-trimethylsilyl-5,5-dimethyl-2-silahexane (**4**) at 600 °C and its static thermolysis at 350 °C, 2,3-benzo-5-aza-1-silacyclohexane (**5**) has been obtained in 97% and 46% yields, respectively. Product **5** might have been formed *via* an intramolecular rearrangement involving a zwitterionic species generated from the pentacoordinated silene Si-atom. From trapping experiments with an excess of Me_3SiOMe or MeOH, we have obtained 2-(*o*-*N*,*N*-dimethylaminomethyl)phenyl-5,5-dimethyl-2-trimethylsiloxy-2-silahexane (**6**) and 2-(*o*-*N*,*N*-dimethylaminomethyl)phenyl-2-methoxy-5,5-dimethyl-2-silahexane (**7**) formed *via* an intermolecular protodesilylation reaction rather than through trapped products of the silene.

Introduction

Silenes have been the subject of considerable interest over the last 30 years.[1] Most of them have been generated as reactive intermediates in the photolyses[2-4] and thermolyses of organosilicon compounds,[5-7] and several stable silenes[8-11] have also been synthesized.

The Si = C bond is strongly polarized, in the sense of $Si^{\delta+}$-$C^{\delta-}$, as expected from the different electronegativities of carbon and silicon atoms. The increased negative charge expands the valence orbitals at the carbon, whereas the positive charge contracts the orbitals at the silicon. This induces the "mismatching" of π-atomic orbitals on C and Si, which has been thought to be a main reason for the weakening of the Si-C π-bond.[12] We attempted to stabilize silenes through compensation for the electronic deficiency of the silicon atom with intramolecular electron-donor substituents such as (*o*-*N*,*N*-dimethylaminomethyl)phenyl group,[13] which has been used extensively to synthesize a variety of the hyper-valent organosilicon compounds, and which has also shown effectiveness in stabilizing the low valent silicon centers in highly reactive species like silylenes[14] and silyl cations[15] by the intramolecular donation of electrons.



Scheme 1

Experimental Section

In reactions where air-sensitive chemicals were used, the reagents and solvents were dried before use. Hexane and diethylether were distilled from Na/Ph_2CO. MeOH and EtOH were distilled from Mg-turnings/I_2. Other starting materials were purchased in reagent grade and used without further purification. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 250 FT-NMR spectrometer and a Bruker AMX 500 NMR spectrometer. Analyses of the thermolysates were accomplished using HP 5890 II with FID (HP-1, 15 m column) and with TCD (OV-1, 1/8 inch 6 ft column). Mass spectra were recorded on a low resolution Shimadzu GCMS QP-2000A mass spectroscopy and high resolution VG ANALYTICAL 70-VSEQ mass spectroscopy. Flow Vacuum Pyrolysis (FVP) reactions were carried out in a quartz tube, 12 mm (OD) × 330 mm thick wall (1.0 mm) with or without glass wool inside the tube. Vacuum Sealed Tube Thermolysis (VSTT) reactions were also carried out using a tube similar to the one mentioned above. All thermolyses were executed at 1.0×10^{-2}-1.5×10^{-2} torr using dried decane as an internal standard.

Synthesis of Chloro(*o*-*N*,*N*-dimethylaminomethyl)phenylmethylvinylsilane (2). To dichloromethylvinylsilane (13 mL, 0.10 mol) at 0 °C was slowly added (*o*-*N*,*N*-dimethylaminomethyl)phenyllithium (**1**) (14.0 g, 0.10 mol) in 200 mL of ether. The reaction mixture was stirred for approximately 12 h at room temperature. The precipitated LiCl was removed by filtration, and volatiles were distilled off under vacuum. The residue was distilled to yield **2** (16.4 g, 70%). Bp: 88-92 °C (0.15 torr), MS (*m/z*; EI): 239 (M^+, 9), 224 (15), 212 (3), 204 (16), 196 (100), 159 (19). ^1H NMR (CD_2Cl_2, 500 MHz): δ 0.80 (s, 3H), 2.17 (s, 6H), 3.50-3.67 (m, 2H), 5.82-6.47 (m, 3H), 7.19-8.31 (m, 4H). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 2.94 ($\underline{C}H_3Si$), 45.39 ($N(\underline{C}H_3)_2$), 64.15 ($\underline{C}H_2N$), 126.96, 126.99, 127.34, 130.45, 134.16, 137.87, 138.85, 145.36 (aryl and vinyl). HRMS (EI): Calcd for $C_{12}H_{18}NSiCl$, 239.0897; Found, 239.0907.

Synthesis of Methoxy(*o*-*N*,*N*-dimethylaminomethyl)phenylmethylvinylsilane (3). A mixture of MeOH (1.5 mL, 0.037 mol) and Et_3N (6.0 mL, 0.043 mol) was slowly dropped into 8.5 g (0.036 mol) of **2** in Et_2O (100 mL) at 0 °C. After addition was completed, the mixture was heated at reflux condition for 6 h. The reaction mixture was cooled down to room temperature, and the precipitated $Et_3NH^+Cl^-$ was

removed by filtration, and volatiles were stripped off under vacuum. The residue was distilled to afford **3** in 78% yield (6.6 g) as a colorless oil. Bp: 62-65 °C (0.15 torr) MS (*m/z*; EI): 235 (M^+, 5), 220 (4), 234 (4), 192 (85), 58 (100), 44 (48). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.49 (s, 3H), 2.17 (s, 6H), 3.42-3.61 (dd, 2H), 3.52 (s, 3H), 5.81-6.40 (m, 3H), 7.27-7.79 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 2.80 ($SiCH_3$), 45.41 ($N(CH_3)_2$), 51.01 (OCH_3), 64.68 (CH_2N), 126.50, 126.73 (vinyl), 128.77, 129.80, 136.16, 136.84, 139.48, 145.36 (C_6H_4). HRMS (EI): Calcd for $C_{13}H_{21}NOSi$, 235.1392; Found, 235.1393.

Synthesis of 2-Methoxy-2-(*o-N,N*-dimethylaminomethyl)-phenyl-3-trimethylsilyl-5,5-dimethyl-2-silahexane (4). A solution of 7.0 g (0.030 mol) of **3** in 120 mL of *n*-hexane was treated dropwise at -78 °C with 17.6 mL (0.030 mol) of *t*-BuLi (1.7 M in *n*-hexane). After stirring for 2 h at -78 °C, chlorotrimethylsilane (3.9 mL, 0.030 mol) was dropped slowly into the reaction mixture at the same temperature. After the dropping was completed, stirring was continued for 6 h, keeping the temperature at -30 ~ -20 °C. Following the removal of $Et_3NH^+Cl^-$ by filtration, volatiles were distilled off under vacuum. The residue was distilled to give the thermolysis precursor **4** in 45% yield (4.9 g) as a colorless oil. Bp: 112-118 (0.15 torr) MS (*m/z*; EI) 365 (M^+, 9), 350 (39), 308 (76), 292 (81), 208 (100), 165 (63), 73 (55), 58 (67). HRMS (EI): Calcd for $C_{20}H_{39}NOSi_2$, 365.2570; Found, 365.2578. **4a**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.05 (s, 9H), 0.39 (t, 1H), 0.45 (s, 3H), 0.62 (s, 9H), 1.43 (m, 2H) 2.28 (s, 6H) 3.34 (s, 3H) 3.61 (m, 2H), 7.19-7.50 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ -3.04 ($SiCH_3$), 0.60 ($Si(CH_3)_3$), 9.92 (SiCHSi), 29.61 ($C(CH_3)_3$), 31.56 ($C(CH_3)_3$), 37.42 (CH_2t-Bu), 45.77 (NMe_2), 50.31 (OMe), 63.71 (CH_2N), 125.82-145.00 (C_6H_4). **4b:** ^{1}H NMR ($CDCl_3$, 500 MHz): δ -0.05 (s, 9H), 0.39 (t, 1H), 0.50 (s, 3H), 0.72 (s, 9H), 1.45 (m, 2H) 2.28 (s, 6H) 3.30 (s, 3H) 3.61 (m, 2H), 7.19-7.50 (m, 4H). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ -2.03 (SiMe), 0.35 ($SiMe_3$), 10.10 (SiCHSi), 29.69 ($C(CH_3)_3$), 31.70 ($C(CH_3)_3$), 37.48 (CH_2t-Bu), 45.77 (NMe_2), 49.99 (OMe), 63.71 (CH_2N), 125.82-145.00 (C_6H_4).

Flow Vacuum Pyrolysis (FVP) of 4. The FVP of **4** (0.04 g, 0.1 mmol) was conducted at 600 °C (1.0×10^{-2}-1.5×10^{-2} torr) by injection of **4** through glass chips packed in a quartz tube. The pyrolysate was condensed in a spiral trap cooled to -196 °C . Yields were determined by GC with decane as the internal standard and are corrected for the 24% recovery of **4**. The product **5** obtained in 97% yield (GC area % yield) was isolated by preparative GC and identified by GC-MS, ^{1}H NMR, ^{13}C NMR, DEPT 135° and HRMS.

2,3-Benzo-1-(2,2-dimethylbutyl)-1-methyl-5-methylaza-1-silacyclohexane (5). MS (*m/z*; (EI): 261 (M^+, 5), 246 (14), 176 (100), 162 (21), 58 (3). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.30 (s, 3H), 0.70-0.77 (m, 2H) 0.87 (s, 9H), 1.18-1.28 (m, 2H) 2.20 (s, 2H), 2.53 (s, 3H) 3.56 (s, 2H), 7.08-7.51 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ -3.01 ($SiCH_3$), 9.65 ($SiCH_2$), 29.45 ($C(CH_3)_3$), 31.80 ($C(CH_3)_3$), 38.25 (CH_2t-Bu), 46.57 ($SiCH_2N$), 51.38 (NMe), 63.10 (CH_2N), 127.00, 127.75, 129.76, 133.00, 134.58, 145.71 (C_6H_4). HRMS (EI): Calcd for $C_{16}H_{27}NSi$, 261.1913; Found, 261.1937.

Vacuum Sealed Tube Thermolysis (VSTT) of 4. The VSTT of **4** (0.052 g, 0.14 mmol) without solvent was conducted at 350 °C for 0.6 h in the sealed tube. The thermolysis of **4** afforded Me_3SiOMe, **5** (46% yield) and **6** (23% yield), which were isolated by preparative GC.

2-(*o-N,N*-Dimethylaminomethyl)phenyl-5,5-dimethyl-2-trimethylsiloxy-2-silahexane(6). MS (*m/z*; (EI): 351 (M^+, 13), 336 (27), 294 (60), 266 (52), 58 (100). ^{1}H NMR (CD_2Cl_2, 250 MHz): δ 0.15 (s, 9H), 0.35 (s, 3H), 0.81 (m, 2H), 0.84 (s, 9H), 1.12-1.22 (m, 2H), 2.17 (s, 6H), 3.49 (s, 2H), 7.20-7.63 (m, 4H). ^{13}C NMR (δ; CD_2Cl_2): 0.48 ($SiCH_3$), 2.20 ($SiMe_3$), 12.85 ($SiCH_2$) 28.99 ($C(CH_3)_3$), 31.20 ($C(CH_3)_3$), 37.74 (CH_2t-Bu), 45.38 (NMe_2), 64.62 (CH_2N), 126.38, 129.00, 129.42, 135.49, 136.28, 143.64 (C_6H_4). HRMS (EI): Calcd for $C_{19}H_{37}NOSi_2$, 351.2414; Found, 351.2417.

VSTT of 4 in an Excess of Me_3SiOMe. The VSTT of a mixture of **4** (0.052 g, 0.14 mmol) and Me_3SiOMe (240 μL, 2.0 mmol) were carried out at 350 °C for 6 h in the same manner as above. The recovery of **4** is 49%, and the products **6** (35% yield) and **7** (53% yield) were obtained.

2-(*o-N,N*-Dimethylaminomethyl)phenyl-2-methoxy-5,5-dimethyl-2-silahexane (7). MS (*m/z*; (EI): 293 (M^+, 13), 278 (21), 246 (61), 236 (100), 58 (45). ^{1}H NMR (CD_2Cl_2, 250 MHz): δ 0.39 (s, 3H), 0.84-0.89 (m, 2H), 0.92 (s, 9H), 1.18-1.34 (m, 2H), 2.19 (s, 6H) 3.47-3.56 (dd, 2H) 3.49 (s, 3H), 7.28-7.70 (m, 4H). ^{13}C NMR (δ; $CDCl_3$): -2.90 (SiMe), 10.29 ($SiCH_2$), 29.28 ($C(CH_3)_3$), 31.50 ($C(CH_3)_3$), 37.53 (CH_2t-Bu), 45.69 (NMe_2), 50.92 (OMe), 64.81 (CH_2N), 126.72, 129.33, 129.832, 135.966, 136.297, 145.69 (C_6H_4). HRMS (EI): Calcd for $C_{17}H_{31}NOSi$, 293.2175; Found, 293.2175.

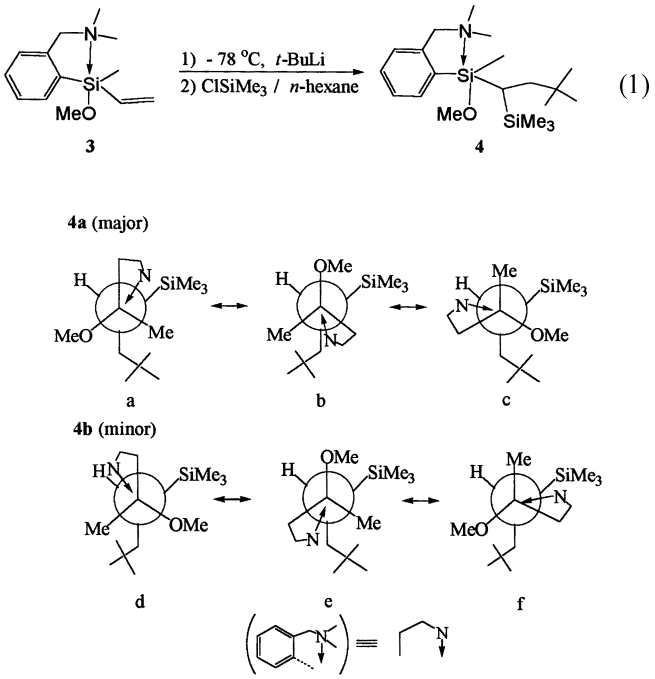
VSTT of 4 in an Excess of MeOH. The VSTT of a mixture of **4** (0.052 g, 0.14 mmol) and MeOH (150 μL, 2.8 mmol) were carried out at 340 °C for 6 h in the same manner as mentioned above. The recovery of **4** was 11%, and the products **6** (42% yield) and **7** (13% yield) were obtained.

FVP and VSTT of 4 in Various Trapping Agents. The FVP or VSTT of **4** in the presence of an excess of 2,3-dimethyl-1,3-butadiene, isoprene, 1,3-butadiene, anthracene, H_2O and CCl_4 was carried out at various temperatures, respectively, in the same manner as mentioned above. In these experiments, only products, **5**, **6** and **7** were obtained without any silene-trapped adduct or silene dimers.

Results and Discussion

Presumably penta-coordinated organosilicon compounds **4a**, **b** as the thermal precursor for the 1-methyl-1-(*o-N,N*-dimethylaminomethyl)phenyl-2-neopentylsilene were synthesized as a diastereomeric mixture in 45% yield *via* the silylation of α-lithiomethoxysilane.

The ratio of diastereomers **4a** to **4b** estimated from their NMR spectra and GC analyses was ca. 70 to 30. The assignment of the diastereomeric isomers was made on the basis of the ^{1}H- and ^{13}C NMR spectra for the isomers. The difference in the chemical shifts for methylene carbon of neopentyl



(1)

Figure 1. Posible structures of diasteremer **4**.

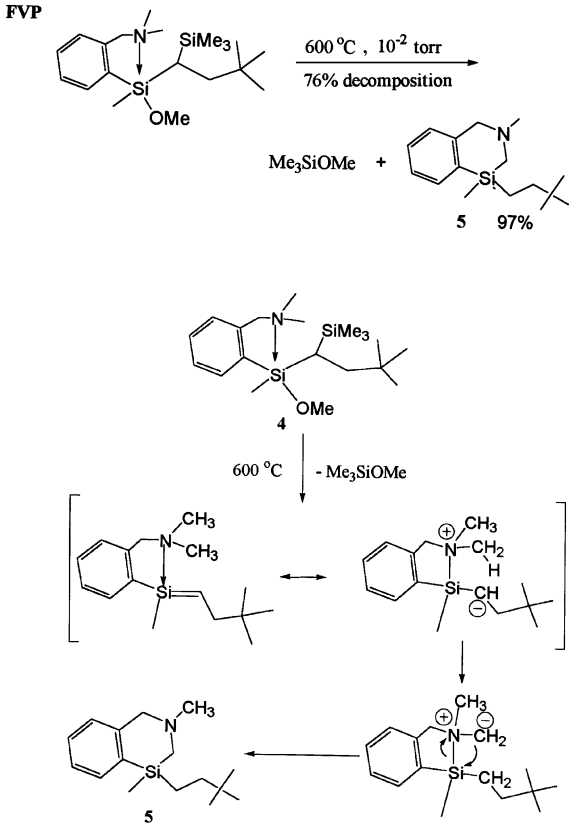
Table 1. NMR data for the diastereomeric compounds **4a**, **b**

NMR ($CDCl_3$)	diastereomer	SiMe	$SiMe_3$	CMe_3	CMe_3	OMe
^1H (ppm)	**4a**	0.45	0.05	0.62		3.34
(500 MHz)	**4b**	0.50	-0.05	0.72		3.30
^{13}C (ppm)	**4a**	-3.04	0.60	29.61	31.56	50.31
(124 MHz)	**4b**	-2.03	0.35	29.69	31.70	49.99

group between **4a** and **4b** is very small (0.06 ppm) compared to other substituents, such as SiMe (1.01 ppm), $SiMe_3$ (0.25 ppm), and OMe (0.32 ppm) in ^{13}C-NMR spectra. It implys that the neopentyl group has shielding effects similar to those of adjacent groups in **4a** and **4b**. Considering bulk shieldings as shown in Figure 1, since the methyl group of SiMe is shielded by both the neopentyl and $SiMe_3$ groups in a, and by both the H and neopentyl groups in d, the chemical shift for the methyl group of **4a** is up field compared with that of **4b**. In similar manners, the ^1H NMR and ^{13}C NMR peaks of the $SiMe_3$, and OMe groups were properly assigned. (Table 1) They are consistent with the conformational structures of a and d in Figure 1.

In the neat flow vacuum pyrolysis of **4** at 600 °C, the unexpected compound **5** was obtained, unexpectantly, in 97% yield along with Me_3SiOMe.

As shown in Scheme 2, **5** might be formed through an intramolecular rearrangement involving a zwitterionic species generated from the pentacoordinated silene Si-atom. In the zwitterionic species, α-silylated carbanion picks up the proton from the methyl group on the nitrogen atom to form ammonium ylide species, which can undergo nucleophilic attack to silicon atom to give the ring-expanded product **5**. This result suggests that an intramolecular electron-donor



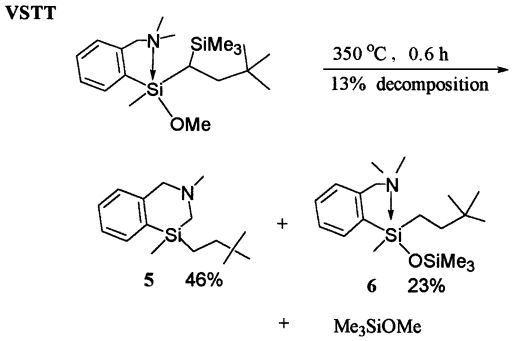
(2)

Scheme 2

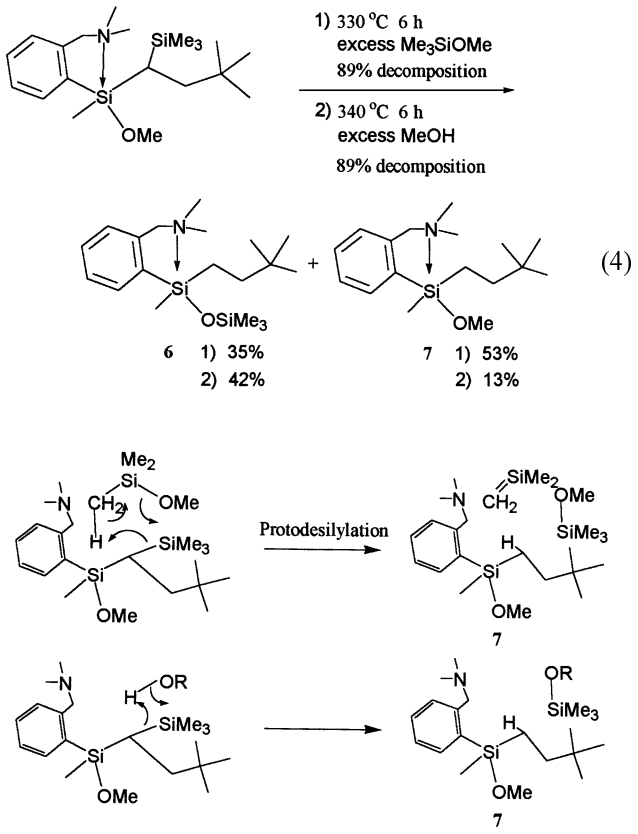
atom affects the formation of the zwitterionic species rather than affecting the stabilization of the silene. In 1992, Auner *et al.* also reported that the reaction of amino-substituted chlorovinylsilane with *t*-BuLi yielded the diazasilacyclopentane at 133 °C *via* the generation of zwitterionic species due to the N-Si bond formation, and this was followed by a migration of the trimethylsilyl group to the original sp^2 hybridized carbon atom of the silene.[16,17]

FVP experiments which lead to a decrease in the number of intermolecular collisions compared with VSTT experiments gave **5** in higher yield. This result might be indirect evidence that **5** is formed through the intramolecular reaction mechanism.

In the VSTT experiments under neat condition at 350 °C, compounds **5** and **6** were obtained. It is thought that **6** might be formed by the intermolecular elimination of Me_3SiOMe, followed by several reaction steps other than the intramole-



(3)



Scheme 3

cular reaction. An increase in the number of the intermolecular collisions in VSTT experiments resulted in the formation of **6,** which was not observed in FVP experiments.

In trapping reactions with an excess of Me_3SiOMe, MeOH and EtOH, we obtained **6** and 2-(*o-N,N*-dimethylaminomethylphenyl)-2-methoxy-5,5-dimethyl-2-silahexane (**7**) as the major products formed *via* the intermolecular protodesilylation mechanism,[18] which involves the electrocyclic reaction between **4** and Me_3SiOMe, MeOH and EtOH, respectively (Scheme 3).

Considering that there was no detection of compound **5**, it may be concluded that **5** is formed through the intramolecular reaction pathway. The FVP or VSTT of **4** gave **5**, **6**, **7** and other unidentified compounds in the presence of excess 2,3-dimethyl-1,3-butadiene, isoprene, 1,3-butadiene, H_2O and CCl_4. Nonetheless, no corresponding silene-trapped compounds were obtained.

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