

# Ring-opening reactions of cyclic ethers with diiodo- and dibromodimethylsilane equivalents

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## Abstract

Ring-opening halosilation of cyclic ethers with reagents of  $(\text{Me}_2\text{N})_2\text{SiMe}_2/4\text{MeI}$  (**1a**) and  $(\text{Me}_2\text{N})_2\text{SiMe}_2/4\text{allylBr}$  (**1b**) was studied. Tetrahydrofuran and cyclohexene oxide reacted with **1a** and **1b** to give ring-opened di(haloalkoxy)dimethylsilanes in good yield. With less strained tetrahydropyran, however, only reagent **1a** gave the ring-opened product. Reactions of reagents **1a** and **1b** with propylene oxide also proceeded smoothly, although the regioselectivity was rather low. When similar reactions were carried out with  $(\text{Me}_2\text{N})_2\text{SiMe}_2/2\text{MeI}$  (**2a**) and  $(\text{Me}_2\text{N})_2\text{SiMe}_2/2\text{allylBr}$  (**2b**) in a ratio of cyclic ethers/**2a** or **2b** = 1/1, the corresponding 1:1 adducts were obtained. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Iodosilane; Bromosilane; Halosilation; Cyclic ether

## 1. Introduction

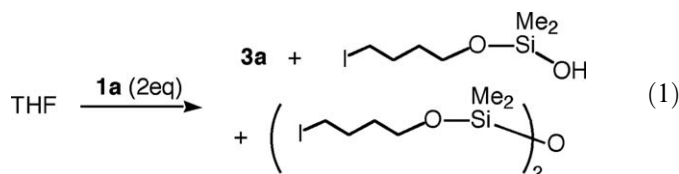
Iodo- and bromosilanes are important reagents in organic synthetic chemistry [1]. They react readily with cyclic ethers to give ring-opened halosilation products. However, iodo- and bromosilanes usually exhibit a strong tendency to undergo hydrolytic changes, and therefore, they must be handled with special care in contrast to chloro- and fluorosilanes.

Recently, we found that 1:2 mixtures of (diethylamino)trimethylsilanes with methyl iodide and allyl bromide ( $\text{Et}_2\text{NSiMe}_3/2\text{RX}$ ,  $\text{RX} = \text{MeI}$ , allylBr) behave as the synthetic equivalents of iodo- and bromotrimethylsilane, respectively, and react readily with cyclic ethers giving ring-opened halosilation products [2,3]. They react also with ketones [4], acetals [5,6], and amins [6]. In an extension to this work, we now describe the ring-opening halosilation of cyclic ethers by dihalosilane equivalents,  $(\text{Me}_2\text{N})_2\text{SiMe}_2/4\text{MeI}$  (**1a**) and  $(\text{Me}_2\text{N})_2\text{SiMe}_2/4\text{allylBr}$  (**1b**), and amino-

halosilane equivalents,  $(\text{Me}_2\text{N})_2\text{SiMe}_2/2\text{MeI}$  (**2a**) and  $(\text{Me}_2\text{N})_2\text{SiMe}_2/2\text{allylBr}$  (**2b**).

## 2. Results and discussion

When tetrahydrofuran (THF) was treated with reagent **1a** in a ratio of  $\text{THF}/\mathbf{1a} = 3/1$  in toluene at 50–60 °C for 35 h, a ring-opened product bis(4-iodobutoxy)dimethylsilane (**3a**) was obtained in 76% isolated yield (Table 1). Increasing the ratio of  $\text{THF}/\mathbf{1a}$  to 6/1 did not considerably affect the results giving a 79% yield of **3a**. However, decreasing the ratio to  $\text{THF}/\mathbf{1a} = 2/1$  resulted in incomplete transformation. In fact, when the reaction mixture was hydrolyzed after 38 h-reaction, a mixture consisting of **3a**, (4-iodobutoxy)dimethylsilanol, and di(4-iodobutoxy)-



tetramethyldisiloxane in an approximate ratio of 1:2:1 was obtained (Eq. (1)), indicating that some side reactions

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Table 1  
Ring-opening halosilation of cyclic ethers with reagents **1a** and **1b**<sup>a</sup>

Ether	Reagent	Temperature (°C)	Product	Yield (%) <sup>b</sup>
	<b>1a</b>	50–60	$(\text{X}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2\text{SiMe}_2$	<b>3a</b> (X = I) 76
	<b>1b</b>	80–90		<b>3b</b> (X = Br) 79
	<b>1a</b>	50–60	$(\text{X}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2\text{SiMe}_2$	<b>4a</b> 60
	<b>1a</b>	rt	$(\text{X}-\text{C}_6\text{H}_{10}\text{O})_2\text{SiMe}_2$	<b>5a</b> (X = I) 68
	<b>1b</b>	50–60		<b>5b</b> (X = Br) 73
	<b>1a</b>	50–60	$(\text{X}-\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_2\text{SiMe}_2$ $\text{X}-\text{CH}_2\text{CH}(\text{CH}_3)\text{O}-\text{SiMe}_2$ $(\text{X}-\text{CH}(\text{CH}_3)\text{CH}_2\text{O})_2\text{SiMe}_2$ $\text{X}-\text{CH}(\text{CH}_3)\text{CH}_2\text{O}-\text{SiMe}_2$	<b>6a</b> (X = I) 70
	<b>1b</b>	50–60		<b>6b</b> (X = Br) 66

<sup>a</sup> Reactions were carried out in benzene or toluene, using **1a** ((Me<sub>2</sub>N)<sub>2</sub>SiMe<sub>2</sub>/4MeI) or **1b** ((Me<sub>2</sub>N)<sub>2</sub>SiMe<sub>2</sub>/4allylBr). The substrate/reagent ratio was 3/1.

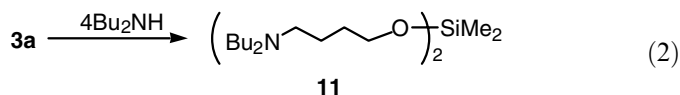
<sup>b</sup> Isolated yield based on the diaminosilane used.

consuming THF were involved. Similar treatment of tetrahydropyran (THP) with **1a** gave bis(5-iodopentoxy)dimethylsilane (**4a**) in 60% yield. Reagent **1b** reacted with THF to give bis(3-bromobutoxy)dimethylsilane (**3b**) in 79% yield, while no reaction occurred with less strained THP. Cyclohexene oxide underwent smooth ring-opening both with **1a** and **1b** to give bis(*trans*-2-halocyclohexyloxy)silanes **5a** and **5b**, respectively. In these reactions, no *cis*-isomers were produced, similar to the reaction of cyclohexene oxide with Et<sub>2</sub>NSiMe<sub>3</sub>/2MeI, reported previously [2]. Reactions of unsymmetrical propylene oxide with **1a** and **1b** proceeded again smoothly, but with rather low regioselectivity, to afford isomeric mixtures. The NMR spectrometric analysis of the mixtures indicated the existence of XCH<sub>2</sub>MeCHO- and XMeCHCH<sub>2</sub>O- units in a ratio of 76:24 for X = I and 86:14 for X = Br in the mixtures, respectively, indicating that cleavage of the less hindered CH<sub>2</sub>-O bond had occurred mainly. This is in contrast to similar iodination of propylene oxide with reagent of Et<sub>2</sub>NSiMe<sub>3</sub>/2MeI, which proceeded more selectively than the present reactions to give ICH<sub>2</sub>MeCHO-SiMe<sub>3</sub> and IMeCHCH<sub>2</sub>O-SiMe<sub>3</sub> in a ratio of 92:8 [2].

Next, we examined (Me<sub>2</sub>N)<sub>2</sub>SiMe<sub>2</sub>/2MeI (**2a**) and (Me<sub>2</sub>N)<sub>2</sub>SiMe<sub>2</sub>/2allylBr (**2b**) as the aminoalcohol equivalents. As summarized in Table 2, reactions of **2a** and **2b** with cyclic ethers in a ratio of 1:1, followed by treatment of the resulting mixtures with alcohols in excess, gave 1:1 adducts in fairly good yield, except for the reaction of THF with **2b** that gave the product only in low yield. The GC-MS analyses of the reaction mixture of THF and **2b** revealed a peak of the 1:1 adduct in about 30% yield without any other detect-

able peaks. Some other reactions of THF leading to non volatile products, such as ring-opening polymerization seemed to be involved. The reaction of propylene oxide afforded a mixture of regioisomers in an approximate ratio of 82:18, similar to its reaction with reagent **1a** (see Table 1). Attempts to isolate (haloalkoxy)(dimethylamino)dimethylsilanes by direct distillation of the reaction mixtures were unsuccessful. Presumably, they were at equilibrium with their ammonium salts that would decompose at elevated temperature.

In summary, on the basis of the above mentioned results, we demonstrated that combinations of bis(dimethylamino)silane with alkyl halides behaved as dihalo- and aminoalcohol equivalents, depending on the ratios of bis(dimethylamino)silane and alkyl halide employed. The products seem to be potentially useful as the building units of organosilicon compounds, as exemplified by that amination of **3a** gave bis(aminobutoxy)silane **11** in 83% yield (Eq. (2)). Synthesis of organosilacycles by using bis(bromoalkoxy)silane as the starting compound has been reported, previously [7].




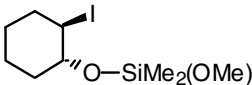

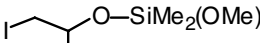
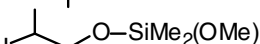


### 3. Experimental

#### 3.1. General

All reactions were carried out under an atmosphere of dry nitrogen. Toluene, benzene, and ether were dried over

Table 2  
Halosilation of cyclic ethers with reagents **2a** and **2b**, followed by alcoholysis<sup>a</sup>

Ether	Reagent	Product	Yield (%) <sup>b</sup>
	<b>2a</b>	$X-CH_2CH_2CH_2CH_2O-SiMe_2(OR)$	<b>7a-1</b> (X = I, R = Me) 61 <b>7a-2</b> (X = I, R = Et) 54
	<b>2b</b>		<b>7b</b> (X = Br, R = Me) 27
	<b>2a</b>	$I-CH_2CH_2CH_2CH_2CH_2O-SiMe_2(OMe)$	<b>8a</b> 48
	<b>2a</b>		<b>9a</b> 73
	<b>2a</b>	 	<b>10a</b> } <b>10a'</b> } 58 (10a:10a' = 82:18)

<sup>a</sup> Reactions were carried out in benzene or toluene, using **2a** ((Me<sub>2</sub>N)<sub>2</sub>SiMe<sub>2</sub>/2MeI) or **2b** ((Me<sub>2</sub>N)<sub>2</sub>SiMe<sub>2</sub>/2allylBr). The substrate/reagent ratio was 1/1.

<sup>b</sup> Isolated yield.

sodium. Dimethylbis(dimethylamino)silane was obtained from Shin-Etsu Co. Ltd.

### 3.2. Reactions of cyclic ethers with **1a** and **1b**

A mixture of dimethylbis(dimethylamino)silane (1.46 g, 10.0 mmol), THF (2.16 g, 30.0 mmol), methyl iodide (5.68 g, 40.0 mmol), and benzene (20 mL) was stirred at 50–60 °C for 35 h. After the resulting mixture was hydrolyzed with water, the organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and dried over anhydrous magnesium sulfate. Evaporation of the solvent and volatile by-products under reduced pressure (1 mmHg) at room temperature gave 3.45 g of **3a** (76% yield). Attempted decomposition of **3a** by distillation resulted in partial decomposition of **3a**. Data for **3a** after evaporation: MS *m/z* 441 (M<sup>+</sup> – Me); <sup>1</sup>H NMR δ (CDCl<sub>3</sub>) 0.10 (s, 6H), 1.64 (br quintet, 4H, *J* = 6.9 Hz), 1.90 (br quintet, 4H, *J* = 7.2 Hz), 3.21 (t, 4H, *J* = 7.0 Hz), 3.68 (t, 4H, *J* = 6.3 Hz); <sup>13</sup>C NMR δ (CDCl<sub>3</sub>) –3.28, 6.81, 30.06, 33.28, 61.24. Anal. Calc. for C<sub>10</sub>H<sub>22</sub>I<sub>2</sub>O<sub>2</sub>Si: C, 26.33; H, 4.86. Found: C, 25.83; H, 4.80%.

Other reactions of cyclic ethers with reagents **1a** and **1b** were carried out as above. Compound **4a** could not be purified by distillation, similar to **3a**, and was analyzed just after evaporation of the solvent and volatile by-products at room temperature under reduced pressure (1 mmHg). Other halosilation products were purified by distillation. However, they underwent thermal decomposition when

distilled as usual, except for **3b** and **5b**. In these cases, the products were subjected to quick distillation with flame-heating under reduced pressure (1 mmHg) to avoid the decomposition and therefore we could not determine their exact boiling points.

Data for **3b**: b.p. 100–102 °C (1 mmHg); MS *m/z* 362 (M<sup>+</sup>); <sup>1</sup>H NMR δ (CDCl<sub>3</sub>) 0.10 (s, 6H), 1.68 (br quintet, 4H, *J* = 6.8 Hz), 1.93 (br quintet, 4H, *J* = 7.1 Hz), 3.43 (t, 4H, *J* = 6.8 Hz), 3.69 (t, 4H, *J* = 6.1 Hz); <sup>13</sup>C NMR δ (CDCl<sub>3</sub>) –3.30, 29, 34, 31.01, 33.70, 61.45. Anal. Calc. for C<sub>10</sub>H<sub>22</sub>Br<sub>2</sub>O<sub>2</sub>Si: C, 33.16; H, 6.12. Found: C, 32.96; H, 6.24%. Data for **4a** after evaporation of the solvent and volatile by-products: MS *m/z* 469 (M<sup>+</sup> – Me); <sup>1</sup>H NMR δ (CDCl<sub>3</sub>) 0.09 (s, 6H), 1.41–1.46 (m, 4H), 1.51–1.56 (m, 4H), 1.82 (br quintet, 4H, *J* = 7.2 Hz), 3.16 (t, 4H, CH<sub>2</sub>I, *J* = 7.0 Hz), 3.65 (t, 4H, CH<sub>2</sub>O, *J* = 6.4 Hz); <sup>13</sup>C NMR δ (CDCl<sub>3</sub>) –3.24, 6.94, 26.85, 31.39, 33.23, 62.10. Anal. Calc. for C<sub>12</sub>H<sub>26</sub>I<sub>2</sub>O<sub>2</sub>Si: C, 29.77; H, 5.41. Found: C, 29.91; H, 5.30%. Compound **5a** was obtained as a mixture of 1:1 diastereomers: MS *m/z* 508 (M<sup>+</sup>); <sup>1</sup>H NMR δ (CDCl<sub>3</sub>) 0.24 (s, 1.5H), 0.25 (s, 1.5H), 0.26 (s, 3H), 1.25–1.56 (m, 8H), 1.77–1.79 (m, 2H), 1.94 (tt, 1H, *J* = 10.6, 3.6 Hz), 1.98 (tt, 1H, *J* = 10.9, 4.1 Hz), 2.09–2.14 (m, 2H), 2.39–2.43 (m, 2H), 3.84–3.90 (m, 2H), 4.02 (td, 1H, *J* = 8.9, 4.1 Hz), 4.04 (td, 1H, *J* = 8.5, 4.1 Hz); <sup>13</sup>C NMR δ (CDCl<sub>3</sub>) –1.22, –1.11, –0.38, 23.94, 24.12, 27.23, 27.47, 34.92, 35.36, 37.65, 38.19, 39.61, 39.82, 76.13, 76.34. Anal. Calc. for C<sub>14</sub>H<sub>26</sub>I<sub>2</sub>O<sub>2</sub>Si: C, 33.08; H, 5.16. Found: C, 33.14; H, 5.12%. Compound **5b** was obtained as a mixture of 1:1 diastereomers: b.p. 117–120 °C (1 mmHg); MS *m/z* 414 (M<sup>+</sup>);

$^1\text{H}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) 0.21 (s, 2H), 0.22 (s, 4H), 1.26–1.45 (m, 6H), 1.60–1.85 (m, 6H), 2.04–2.11 (m, 2H), 2.30–2.34 (m, 2H), 3.81 (td, 2H,  $J = 8.4, 4.2$  Hz), 3.87–3.94 (m, 2H);  $^{13}\text{C}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) –1.76, –0.11, 23.33, 23.34, 25.44, 25.45, 34.61, 34.63, 35.40, 35.54, 58.30, 58.42, 75.00, 75.12. Anal. Calc. for  $\text{C}_{14}\text{H}_{26}\text{Br}_2\text{O}_2\text{Si}$ : C 40.59; H 6.33. Found: C 40.54; H 6.37%. Compounds **6a** and **6b** were obtained as mixtures of the regioisomers, respectively, as shown in Table 1. Each of the regioisomers was composed of 1:1 diastereoisomers. Data for **6a**: MS  $m/z$  428 ( $\text{M}^+$ );  $^1\text{H}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) 0.18 (s, 3.5H), 0.19 (s, 2.5H), 1.30 (d, 4.56H,  $J = 6.0$  Hz, Me–CHO), 1.87 (d, 1.44H,  $J = 6.7$  Hz, Me–CHI), 3.15–3.23 (m, 3.04H,  $\text{H}_2\text{C–I}$ ), 3.67–3.72 (m, 0.48H,  $\text{H}_2\text{C–O}$ ), 3.86–3.91 (m, 0.48H,  $\text{H}_2\text{C–O}$ ), 3.94–3.99 (m, 1.52H, HC–O), 4.08–4.17 (m, 0.48H, HC–I);  $^{13}\text{C}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) –2.91, –2.85, –2.21, 14.30, 14.45, 23.13, 23.98, 27.44, 67.87, 67.92, 69.49. Anal. Calc. for  $\text{C}_8\text{H}_{18}\text{I}_2\text{O}_2\text{Si}$ : C, 22.44; H, 4.24. Found: C, 22.41; H, 4.22%. Data for **6b**: MS  $m/z$  319 ( $\text{M}^+ - \text{Me}$ );  $^1\text{H}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) 0.14 (s, 1.5H), 0.18 (s, 4.5H), 1.29 (d, 5.1H, Me–CHO,  $J = 6.0$  Hz), 1.67 (d, 0.9H, Me–CHBr,  $J = 6.8$  Hz), 3.29 (dd, 1.7H,  $\text{H}_2\text{C–Br}$ ,  $J = 17.9, 5.8$  Hz), 3.35 (dd, 1.7H,  $\text{H}_2\text{C–Br}$ ,  $J = 9.9, 5.8$  Hz), 3.71–3.77 (m, 0.3H,  $\text{H}_2\text{C–O}$ ), 3.86–3.91 (m, 0.3H,  $\text{H}_2\text{C–O}$ ), 4.05–4.17 (m, 2.0H, HC–O and HC–Br);  $^{13}\text{C}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) –2.69, –2.62, –1.98, –1.93, 22.16, 39.05, 39.07, 49.21, 68.12, 68.22, 68.35. Anal. Calc. for  $\text{C}_8\text{H}_{18}\text{Br}_2\text{O}_2\text{Si}$ : C, 28.76; H, 5.43. Found: C, 28.73; H, 5.52%.

### 3.3. Reactions of cyclic ethers with reagents **2a** and **2b**

A mixture of dimethylbis(dimethylamino)silane (5.84 g, 40.0 mmol), THF (2.88 g, 40.0 mmol), methyl iodide (11.36 g, 80.0 mmol), and benzene (30 mL) was stirred at 50–60 °C for 2 h. To this was added methanol (2.56 g, 80.0 mmol) and the resulting mixture was hydrolyzed with water, the organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was distilled by a Kugelrohr apparatus under reduced pressure to give 6.90 g of **7a–1** (61% yield): b.p. 95–100 °C (oven temp.) (1 mmHg); MS  $m/z$  273 ( $\text{M}^+ - \text{Me}$ );  $^1\text{H}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) 0.10 (s, 6H), 1.64 (br quintet, 2H,  $J = 6.9$  Hz), 1.90 (br quintet, 2H,  $J = 7.2$  Hz), 3.21 (t, 2H,  $J = 7.0$  Hz), 3.47 (s, 3H), 3.69 (t, 2H,  $J = 6.0$  Hz);  $^{13}\text{C}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) –3.76, 6.74, 30.03, 33.26, 50.06, 61.19. Anal. Calc. for  $\text{C}_7\text{H}_{17}\text{IO}_2\text{Si}$ : C, 29.17; H, 5.95. Found: C, 29.13; H, 5.99%.

Other reactions of cyclic ethers with reagents **2a** and **2b** were carried out as above. The products were purified by quick distillation under reduced pressure (1 mmHg) as for bis(haloalkoxy)silanes described above, except for **7b** and **9a**.

Data for **7a–2**: MS  $m/z$  287 ( $\text{M}^+ - \text{Me}$ );  $^1\text{H}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) 0.11 (s, 6H), 1.21 (t, 3H,  $J = 7.1$  Hz), 1.64 (br quintet, 2H,  $J = 6.3$  Hz), 1.90 (br quintet, 2H,  $J = 6.9$  Hz), 3.21 (t, 2H,  $J = 6.9$  Hz), 3.69 (t, 2H,

$J = 6.3$  Hz), 3.73 (q, 2H,  $J = 6.9$  Hz);  $^{13}\text{C}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) –3.25, 6.72, 18.36, 30.05, 33.26, 58.03, 61.12. Anal. Calc. for  $\text{C}_8\text{H}_{19}\text{IO}_2\text{Si}$ : C, 31.79; H, 6.34. Found: C, 31.89; H 6.16%. Data for **7b**: b.p. 60–62 °C (1 mmHg); MS  $m/z$  227 ( $\text{M}^+ - \text{Me}$ );  $^1\text{H}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) 0.10 (s, 6H), 1.68 (br quintet, 2H,  $J = 6.9$  Hz), 1.93 (br quintet, 2H,  $J = 7.1$  Hz), 3.42 (t, 2H,  $J = 6.9$  Hz), 3.47 (s, 3H), 3.69 (t, 2H,  $J = 6.3$  Hz);  $^{13}\text{C}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) –3.75, 29.33, 31.00, 33.65, 50.03, 61.40. Anal. Calc. for  $\text{C}_7\text{H}_{17}\text{BrO}_2\text{Si}$ : C, 34.86; H, 7.10. Found: C, 34.88; H, 7.09%. Data for **8a**: MS  $m/z$  302 ( $\text{M}^+$ );  $^1\text{H}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) 0.11 (s, 6H), 1.41–1.50 (m, 2H), 1.56 (br quintet, 2H,  $J = 6.8$  Hz), 1.84 (br quintet, 2H,  $J = 7.2$  Hz), 3.18 (t, 2H,  $J = 7.3$  Hz), 3.48 (s, 3H), 3.67 (t, 2H,  $J = 6.5$  Hz);  $^{13}\text{C}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) –3.73, 6.86, 26.84, 31.39, 33.25, 50.04, 62.12. Anal. Calc. for  $\text{C}_8\text{H}_{19}\text{IO}_2\text{Si}$ : C, 31.79; H, 6.34. Found: C, 31.78; H, 6.25%. Data for **9a**: b.p. 90–95 °C (1 mmHg); MS  $m/z$  299 ( $\text{M}^+ - \text{Me}$ );  $^1\text{H}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) 0.15 (s, 3H), 0.16 (s, 3H), 1.17–1.50 (m, 4H), 1.75–1.77 (m, 1H), 1.89–2.06 (m, 2H), 2.38–2.42 (m, 1H), 3.50 (s, 3H), 3.76 (td, 1H,  $J = 8.9, 4.4$  Hz), 3.97 (ddd, 1H,  $J = 11.2, 8.9, 4.1$  Hz);  $^{13}\text{C}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) –3.11, –2.82, 23.84, 27.20, 34.99, 37.90, 39.16, 50.32; 75.98. Anal. Calc. for  $\text{C}_9\text{H}_{19}\text{IO}_2\text{Si}$ : C, 34.40; H, 6.09. Found: C, 34.31; H, 6.09%. Compounds **10a** and **10a'** could not be separated from each other and were analyzed as a mixture: MS  $m/z$  274 ( $\text{M}^+$ );  $^1\text{H}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) 0.14 (s, 6H), 1.30 (d, 2.4H, Me–CHO,  $J = 6.5$  Hz), 1.87 (d, 0.6H, Me–CHI,  $J = 6.8$  Hz), 3.14–3.21 (m, 1.6H,  $\text{CH}_2\text{I}$ ), 3.49 (s, 3H,  $\text{CH}_3\text{O}$ ), 3.64–3.69 (m, 0.2H,  $\text{H}_2\text{C–O}$ ), 3.85–3.90 (m, 0.2H,  $\text{H}_2\text{C–O}$ ), 3.92–3.98 (m, 0.8H, HC–O), 4.09–4.14 (m, 0.2H, HC–I,  $J = 6.7$  Hz);  $^{13}\text{C}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) –3.66, –3.24, –3.16, 14.50, 23.33, 24.27, 27.60, 50.25, 68.14, 69.72. Anal. Calc. for  $\text{C}_6\text{H}_{15}\text{IO}_2\text{Si}$ : C, 26.28; H, 5.51. Found: C, 26.22; H, 5.58%.

### 3.4. Amination of **3a**

A mixture of dibutylamine (5.16 g, 40.0 mmol), **3a** (4.56 g, 10.0 mmol), and ether (5 mL) was stirred at 40 °C for 20 h. After the resulting ammonium salts were filtrated and the solvent was evaporated, the residue was subjected to flash distillation by flame-heating under reduced pressure (1 mmHg) to give 3.81 g of **11** (83% yield): MS  $m/z$  458 ( $\text{M}^+$ );  $^1\text{H}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) 0.09 (s, 6H), 0.89 (t, 12H,  $J = 7.2$  Hz), 1.28 (sextet, 8H,  $J = 7.5$  Hz), 1.38–1.55 (m, 16H), 2.37 (br q, 12H,  $J = 7.7$  Hz), 3.66 (t, 4H,  $J = 6.2$  Hz);  $^{13}\text{C}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) –3.21, 14.09, 20.75, 23.42, 29.26, 30.63, 53.87, 53.97, 62.45. Anal. Calc. for  $\text{C}_{26}\text{H}_{58}\text{N}_2\text{O}_2\text{Si}$ : C, 68.06; H, 12.74; N, 6.11. Found: C, 67.76; H, 12.72; N, 6.05%.

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