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# On the Preparation of Carbamoylsilanes

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## **On the Preparation of Carbamoylsilanes**

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## ABSTRACT

Various *N*,*N*-disubstituted carbamoyltrimethylsilanes can be prepared by the addition of LDA to a mixture of TMSCl and the appropriate formamide in THF at  $-78^{\circ}$ C. Slow (syringe pump) addition of LDA is crucial to obtaining good yields.

*Key Words:* Carbamoylsilane; Metalation-silylation; Amides; Lithiation; Coupling.

## 1963

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## 1964

## Cunico and Chen

The carbamoylsilane 3a has been shown to exhibit unique reactivity towards electrophilically-substituted C-H and C=C bonds<sup>[1]</sup> as well as aldehydic and ketonic  $C=O^{[2]}$  bonds. We previously reported the preparation of 3a from the in situ silvlation of the carbamovllithium 2 derived from formamide 1a, and ascribed this success to the possible stabilization of this species by chelation.<sup>[3]</sup> The reaction was carried out by dropping-funnel addition of LDA to a mixture of 1a and TMSCl over a 6–7 h period in a dropwise, but stop-and-start fashion. It has now been found that when the addition is closely monitored such that addition is continuous at the slowest rate possible under these conditions, addition is complete after only 4h at the scale previously reported and results in significant reductions in the yield of 3a. Upon adopting motorized syringe addition of LDA over an 8 h period, however, formerly obtained yields of 3a were reestablished. We then discovered that not only 3a, but a range of differently N,N-disubstituted carbamoylsilanes, including those lacking the possibility of chelation (Table 1) could be obtained in preparatively useful yields by this procedure. This observation significantly increases the scope and potential utility of this synthesis.



Several competing reactions may account for the low yields of **3f** and **3g**. Nudelman has shown that (at ambient temperatures) the reaction of lithium dialkylamides with *N*,*N*-disubstituted formamides produces a carbonyl adduct (**4**) which collapses to a dialkylamine and a carbamoyl-lithium **5** (Sch. 1).<sup>[4]</sup> If this scheme is applicable under present circumstances, **4g**, obtained by the addition of LDA to **1g**, could instead be expected to preferentially expel the more stable lithium diphenylamide (Sch. 1, R = Ph). In contrast to the known compatibility of LDA and TMSCl under the reaction conditions,<sup>[5]</sup> silylation of the lithium diphenylamide amide would ensue.<sup>[6]</sup> Indeed, *N*,*N*-diphenylformamide (**1g**) was found to afford the silylated derivative *N*-(trimethylsilyl)diphenylamine instead of the expected **3g**. Alternatively, if **5** (R = Ph) is initially formed, it may be unstable with respect to expulsion of CO to form lithium diphenylamide.<sup>[7]</sup>

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Table 1. Preparation of carbamoyl(trimethyl)silanes.

### Carbamoylsilanes

### 1965

	-	• • • • •	
H NR <sup>1</sup> R <sup>2</sup> LDA TMSCI - 78 °C TMS NR <sup>1</sup> R <sup>2</sup>			
Carbamoylsilane	$R^1$	$R^2$	Yield (%)
3a	CH <sub>3</sub>	CH <sub>2</sub> OCH <sub>3</sub>	70
3b	CH <sub>2</sub> OCH <sub>3</sub>	CH <sub>2</sub> OCH <sub>3</sub>	64
3c	CH <sub>3</sub>	CH <sub>3</sub>	67
3d	$CH(CH_3)_2$	$CH(CH_3)_2$	81
3e	$CH_3$	CH(CH <sub>3</sub> )Ph	77
3f	$CH_3$	Ph	40
3g	Ph	Ph	0



## **EXPERIMENTAL**

NMR spectra were obtained at 500 MHz in  $C_6D_6$  unless otherwise indicated. IR spectra are of neat samples. All reactions and workups involving carbamoylsilanes were carried out under strictly anhydrous conditions and an argon atmosphere. A manifold was used for evacuations and argon refills. Brief exposure of the carbamoylsilanes to air during transfer procedures was acceptable. Distillations employed a vacuumjacketed  $100 \times 5 \text{ mm}$  nickel-chromium wire spiral-packed column unless YYY

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## 1966

#### Cunico and Chen

otherwise noted. *n*-Butyllithium was obtained from ACROS Organics. THF was distilled from sodium-benzophenone as needed. "Anhydrous" pentane was obtained from Aldrich Chemicals. A KDS syringe pump driving a 50 mL gas-tight syringe was used for LDA introduction.

## *N*,*N*-Dimethylcarbamoyl(trimethyl)silane (3c) Typical Procedure

LDA was prepared by dropwise addition of *n*-butyllithium (16.5 mL of a 2.5 N in hexanes solution, 41 mmol) to a stirred solution of diisopropylamine (6.0 mL, 4.3 g, 43 mmol) in 28 mL THF at  $-78^{\circ}$ C. After warming to 25°C, the LDA solution was transferred to the syringe of the syringe pump and slowly introduced over 8 h to a stirred mixture of N,N-dimethylformamide (3.0 g, 41 mmol), chlorotrimethylsilane (7.0 mL, 6.2 g, 57 mmol) and 60 mL THF held at  $-78^{\circ}$ C. The reaction mixture was allowed to slowly warm to room temperature overnight, and volatiles removed at 10 mm Hg. Pentane (15 mL) was added, and the mixture stirred several hours, during which time a granular precipitate appeared. The mixture was filtered ("M" glass frit filter tube) under argon, solvent removed under vacuum, and the residue fractionally distilled to give 4.0 g (67%) of analytically pure 3c, bp 37-41°C (0.9 mm Hg). IR: 1574, 1377, 1250, 1115, 918, 845, 763 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta = 2.76$  (3H, s), 2.54 (3H, s), 0.30 (9H, s). <sup>13</sup>C NMR:  $\delta = 185.3$ , 36.1, 32.0, -1.2. Anal. calcd for C<sub>6</sub>H<sub>15</sub>NOSi: C, 49.61; H, 10.41; N, 9.64. Found: C, 49.45; H, 10.45; N, 9.50.

## *N*,*N*-*bis*(Methoxymethyl)carbamoyl(trimethyl)silane (3b)

From *N*,*N*-bis(methoxymethyl)formamide.<sup>[8]</sup> Bp 48–56°C (0.1 mm Hg). IR: 1678, 1560, 1389, 1251, 1185, 1099, 1072, 919, 847 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$ =5.02 (2H, s), 4.50 (2H, s), 3.33 (3H, s), 3.03 (3H, s), 0.34 (9H, s). <sup>13</sup>C NMR:  $\delta$ =190.0, 78.0, 73.2, 55.5, 54.5, -1.3. Anal. calcd for C<sub>8</sub>H<sub>19</sub>NO<sub>2</sub>Si: C, 46.79; H, 9.33; N, 6.82. Found: C, 46.70; H, 9.19; N, 7.30. HRMS calcd for C<sub>8</sub>H<sub>19</sub>NO<sub>2</sub>Si: 205.1135. Found: 205.1130.

## N,N-bis(2-Methylethyl)carbamoyl(trimethyl)silane (3d)

Kugelrohr distillation (110°C, 0.02 mm Hg) afforded an analytically pure soft white solid.

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#### Carbamoylsilanes

#### 1967

IR: 1671, 1569, 1435, 1369, 1302, 1253, 1208, 1107, 1042, 844 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta = 3.90$  (1H, septet, J = 7 Hz), 3.07 (1H, septet, J = 7 Hz), 1.65 (6H, d, J = 7 Hz), 0.91 (6H, d, J = 7 Hz), 0.33 (9H, s). <sup>13</sup>C NMR:  $\delta = 186.0$ , 48.9, 45.8, 20.83, 20.79, -1.3. Anal. calcd for C<sub>10</sub>H<sub>23</sub>NOSi: C, 59.64; H, 11.51; N, 6.95. Found: C, 59.41; H, 11.66; N, 6.95.

## N-Methyl-N-(1-phenylethyl)carbamoyl(trimethyl)silane (3e)

From *N*-methyl-*N*-(1-phenylethyl)formamide.<sup>[9]</sup> Bp 88–90°C (0.05 mm Hg). IR: 1567, 1384, 1250, 842 cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 7.3–7.5 (5H, m), 6.17 (1H, q, *J* = 7 Hz), 2.79 (3H, s), 1.52 (3H, d, *J* = 7 Hz), 0.376 (9H, s) and 7.3–7.5 (5H, m), 5.22 (1H, q, *J* = 7 Hz), 2.61 (3H, s), 1.70 (3H, d, *J* = 7 Hz), 0.379 (9H, s). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 186.2, 141.1, 128.3, 127.3, 126.9, 47.6, 29.7, 15.3, -1.3 and 186.7, 140.4, 128.6, 127.2, 126.7, 54.8, 25.7, 17.7, -1.0. Anal. calcd for C<sub>13</sub>H<sub>21</sub>NOSi: C, 66.33; H, 8.99; N, 5.95. Found: C, 66.62; H, 9.08; N, 6.11.

## N-Methyl-N-phenylcarbamoyl(trimethyl)silane (3f)

Short path distillation afforded analytically pure material, bp 74–78°C (0.1 mm Hg). <sup>1</sup>H NMR:  $\delta = 7.04$  (3H, m), 6.90 (2H, d, J = 6.5 Hz), 3.21 (3H, s), 0.09 (9H, s). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 187.2$ , 144.0, 129.4, 128.4, 127.8, 35.1, -1.3. Anal. calcd for C<sub>11</sub>H<sub>17</sub>NOSi: C, 63.72; H, 8.26; N, 6.76. Found: C, 63.78; H, 8.33; N, 6.71.

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