

# LITHIUM PERCHLORATE MEDIATED AMINATION REACTION OF ALDEHYDES: A NOVEL METHOD FOR SYNTHESIS OF N, N-DIALKYL- $\beta$ -SILYLATED AMINES\*

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## Abstract

$\beta$ -Silylated N,N-dialkyl amines (5) were easily synthesized in good to excellent yield from aldehydes (1), trimethylsilyldialkylamines (2), and trimethylsilylmethylmagnesium chloride (4) in the presence of 5 M lithium perchlorate solution in diethyl ether. The reaction of (2) with aldehyde proceeded smoothly in the LiClO<sub>4</sub> to give the iminium salt (3). Addition of trimethylsilylmethylmagnesium chloride (4) gave the desired product.

## Introduction

Development of new synthetic methods for the preparation of organosilicon compounds continues to attract much attention. Synthesis of  $\alpha$ -silylamines was reported recently, using trimethylchlorosilane (TMS-Cl), lithium, and imines in THF. The  $\gamma$ -silylamines were also prepared by the reduction of  $\beta$ -silylated amides. The  $\beta$ -silylated amides were prepared from  $\alpha,\beta$ -unsaturated amides with TMS-Cl and Li in THF at 0-10°C. To the best of our knowledge, there is no report on one pot preparation of  $\beta$ -silylated amines from aldehydes [1-5].

Iminium salts play an important role in organic

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\* Results of these investigations were presented in the 5th Belgian Organic Synthesis Symposium, Namur, July 11-15, (1994).

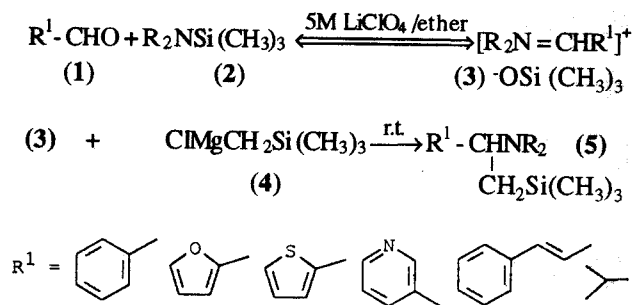
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chemistry, especially with regard to the development of synthetic approaches, using these species as polar and reactive intermediates [6-9]. The important discovery of using lithium perchlorate as a Lewis acid to mediate Mannich type reaction of aldehydes with tertiary amines, to produce the iminium salt (3), and the subsequent reaction with a nucleophile, is a very versatile synthetic method of preparing different types of compounds [10].

## Results

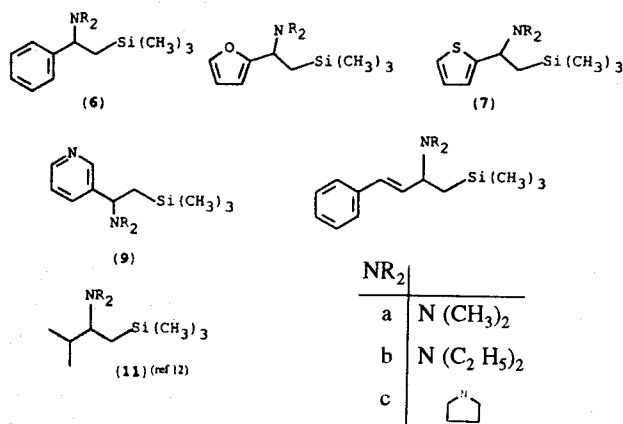
Despite previous extensive works on these important transformations, we would like to report a novel one pot preparation of  $\beta$ -silylated amines (6)-(10), by treatment of the iminium salt (3) with trimethylsilylmethylmagnesium chloride in high yields [9]. Aldehyde (1) (aliphatics or aromatics, enolizable or nonenolizable) react with trimethylsilyldialkylamines (2) in the presence of LiClO<sub>4</sub> (5 molar solution in diethyl ether) at r.t. to produce the iminium

salt (3) in about 30 min. Reaction of trimethylsilylmethylmagnesium chloride in diethyl ether with iminium salt (3) afforded the corresponding  $\beta$ -silylated amines (5) after stirring at r.t. for about 1 h.



Scheme 1

This synthetic method is much simpler and the experimental conditions are also milder than previously reported for the synthesis of  $\alpha$ - and  $\gamma$ -silylated amines [1-3]. The prepared  $\beta$ -silylated amines are summarized in Scheme 2. In all cases reported here, a clean product was obtained in good to excellent yield.



Scheme 2

### Experimental Section

IR spectra were recorded on Perkin Elmer model 883 and Matt Son 1000 Unicam FTIR spectrometers. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker Ac 80 spectrometer in CDCl<sub>3</sub>. MS spectra were recorded on a Finigan incos 500 spectrometer. LiClO<sub>4</sub> (Fluka) was heated at 160°C at 0.1 torr for 24 h, and was dissolved in dry diethyl ether (dried over Na/benzophenon). 1-(trimethylsilyl)imidazole (Fluka), N,N-dimethyltrimethylsilylamine (Merck), N,N-diethyltrimethylsilylamine and 1-(trimethylsilyl)pyrrolidine were synthesized according to the

literature procedures [11]. The aldehydes were distilled before they were used. Trimethylsilylmethylmagnesium chloride was prepared from chloromethyltrimethylsilane (Fluka) [12].

### General Procedure for the Preparation of N,N-dialkyl $\beta$ -silylated amines

Two mmol of aldehyde was placed in a 50 ml flask under argon. Then 3 ml of five molar lithium perchlorate solution in diethyl ether was added. After about 10 min of stirring at r.t. under argon, 3 mmol of dialkyltrimethylsilyl was added via a syringe, and the mixture was stirred for about 30 min. Then 3 mmol of trimethylsilylmethylmagnesium chloride in its diethyl ether solution was added via a syringe. After stirring for about 1.0 h at r.t., water (20 ml) and ether (20 ml) were added. After normal work up, the crude product was obtained. Extraction with cold 0.2 M aqueous HCl solution, and neutralization with 2 M solution of KOH [15], produced pure  $\beta$ -silylated dialkyl amines. The isolated yield for each product is given in parentheses.

**6b** (78%), IR(film);  $\nu = 1492, 1248, 863, 702 \text{ cm}^{-1}$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>, $\delta$ ); 7.4(m, 5H), 3.95(dd, 1H, J=5.6, 9.4 Hz), 2.8(m, 2H), 1.34(m, 2H), 1.14(t, 6H, J = 7.1), 0.06(s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ ); 134.38 (C-arom), 129.67-128.39 (CH-arom), 61.65(CH), 42.80(CH<sub>2</sub>), 20.92(CH<sub>2</sub>), 12.52(CH<sub>3</sub>), -1.26(CH<sub>3</sub>). MS(C<sub>12</sub>H<sub>27</sub>NSi, 249.1913), found 249.1942(M<sup>+</sup>), 162(base peak).

**7b** (75%), IR(film);  $\nu = 1250, 1150, 860 \text{ cm}^{-1}$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>, $\delta$ ); 7.4 (m, 1H), 6.1-6.4(m, 2H) 4.1 (dd, 1H, J=6.1, 9.5 Hz), 2.2-3.1 (m, 4H), 1.4(m, 2H), 1.2(t, 6H, J=7.0 Hz), 0.0(s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, $\delta$ ); 155.92(C), 140.72(CH), 109.54(CH), 106.83(CH), 54.12(CH), 43.37(CH<sub>2</sub>), 19.37(CH<sub>2</sub>), 13.57(CH<sub>3</sub>), -0.73(CH<sub>3</sub>).

**7c** (76%), IR(film);  $\nu = 1250, 1180, 860 \text{ cm}^{-1}$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>, $\delta$ ); 7.5(m, 1H), 6.4-6.7(m, 2H), 3.7(dd, 1H, J=6.6, 10.0 Hz), 2.7(m, 4H), 1.9(m, 4H), 1.4(m, 2H), 0.0(s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, $\delta$ ); 156.93(C), 142.01(CH), 108.93(CH), 107.21(CH), 64.35(CH), 51.21(CH<sub>2</sub>), 23.70(CH<sub>2</sub>), 22.85(CH<sub>2</sub>), -0.75(CH<sub>3</sub>).

**8b** (70%), IR(film);  $\nu = 1250, 1110, 850 \text{ cm}^{-1}$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>, $\delta$ ); 7.3-7.4(m, 1H), 6.8-7.1(m, 2H), 4.3(t, 1H, J=7.5 Hz), 2.1-2.9(m, 4H), 1.32(d, 2H, J=7.5 Hz), 1.1(t, 6H, J=7.1 Hz), 0.0(s, 9H). MS (C<sub>13</sub>H<sub>25</sub>NSSi); 255(M<sup>+</sup>), 240, 173, 168(base peak), 74.

**8c** (85%), IR(film);  $\nu = 1250, 1120, 860 \text{ cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3, \delta$ ); 6.9-7.3(m, 3H), 3.9(dd, 1H,  $J=5.5, 10.2$  Hz), 2.6(m, 4H), 1.8(m, 4H), 1.3(m, 2H), -0.1(s, 9H), MS ( $\text{C}_{13}\text{H}_{23}\text{NSSi}$ ); 253( $\text{M}^+$ ), 238, 166(base peak), 75,74.

**9b** (77%), IR(film);  $\nu = 1250, 1120, 860$   $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3, \delta$ ); 7.2-8.65(m, 4H), 4.05(dd, 1H,  $J=6.1, 9.5$  Hz), 2.2-2.9(m, 4H), 1.35(m, 2H), 1.18(t, 6H,  $J=7.1$  Hz), 0.0(s, 9H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3, \delta$ ); 149.78(CH), 147.88(CH), 137.19(C), 135.43(CH), 122.63(CH), 58.35(CH), 42.46( $\text{CH}_2$ ), 19.90( $\text{CH}_2$ ), 12.89( $\text{CH}_3$ ), -1.27( $\text{CH}_3$ ).  $\text{C}_{14}\text{H}_{26}\text{N}_2\text{Si}$ ; Cal. C 67.14%, H 10.46%; Found C 67.21%, 10.55%.

**9c** (65%), IR(film);  $\nu = 1250, 1120, 860$   $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3, \delta$ ); 7.2-8.5(m, 4H), 3.4(dd, 1H,  $J=5.4, 10.3$  Hz), 2.4(m, 4H), 1.7(m, 4H), 1.3(m, 2H), -0.2(s, 9H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3, \delta$ ); 149.48(CH), 148.75(CH), 137.90(C), 135.52(CH), 123.33(CH), 64.51(CH), 51.72( $\text{CH}_2$ ), 23.70( $\text{CH}_2$ ), 23.09( $\text{CH}_2$ ), -1.36( $\text{CH}_3$ ).

**10b** (72%), IR(film);  $\nu = 1600, 1250, 850, 750, 680$   $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3, \delta$ ); 7.3(m, 5H), 5.9-6.6(m, 2H), 3.3-3.7(m, 1H), 2.2-2.9(m, 4H), 1.05(t, 6H,  $J=7.1$ ), 1.0(d, 2H,  $J=9.0$ ), 0.0(s, 9H). MS( $\text{C}_{17}\text{H}_{29}\text{NSi}$ ); 275( $\text{M}^+$ ), 260, 203, 188(base peak), 74.

**10c** (81%), IR(film);  $\nu = 1600, 1245, 1120, 860, 840, 750, 690$   $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3, \delta$ ); 7.3(m, 5H), 5.9-6.6(m, 2H), 3.2(m, 1H), 2.7(m, 4H), 1.9(m, 4H), 1.2(m, 2H), 0.0(s, 9H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3, \delta$ ); 136.90(C), 132.03(CH), 131.19(CH), 128.51(CH), 127.36(CH), 126.29(CH), 64.27(CH), 50.87( $\text{CH}_2$ ), 23.29( $\text{CH}_2$ ), 22.77( $\text{CH}_2$ ), -0.77( $\text{CH}_3$ ).  $\text{C}_{17}\text{H}_{27}\text{NSi}$ ; Cal.

C 74.66%, H 9.95%; Found C 74.74%, H 10.06%.

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