

Lithiation of (Dialkylaminomethyl)trimethylsilanes

Kiyotaka Marumo, Sumie Inoue, Yoshiro Sato* and Hideo Kato

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

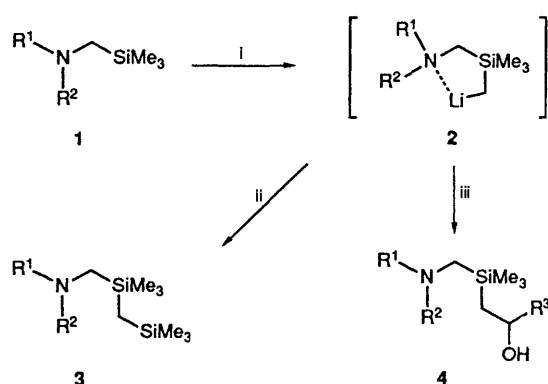
The silylmethyl groups of (dialkylaminomethyl)trimethylsilanes **1** undergo ready lithiation with butyllithium and the resulting mixtures when quenched with chlorotrimethylsilane or aldehydes afford *N,N*-dialkyl(2,2,4,4-tetramethyl-2,4-disilapentyl)amines **3** or (dialkylaminomethyl)(2-hydroxyalkyl)-dimethylsilanes **4**.

Since the α -hydrogens of organosilicon compounds are more acidic than the corresponding hydrogens of alkanes,¹ trimethylsilyl groups undergo ready lithiation with reagents such as butyllithium–*N,N,N',N'*-tetramethylethylenediamine (TMEDA)² or *tert*-butyllithium;³ the conversion yields are, however, usually low.

Selective lithiation occurs at the *ortho* position of *N,N*-dialkylbenzylamines.⁴ During our work with aminoalkylsilanes, we noticed that the treatment of *N*-methyl-*N*-(trimethylsilylmethyl)benzylamine with butyllithium followed by chlorotrimethylsilane gave *N*-methyl-*N*-(2,2,4,4-tetramethyl-2,4-disilapentyl)-*N*-methylbenzylamine as the main product instead of

the expected *N*-methyl-*N*-(trimethylsilylmethyl)-2-(trimethylsilyl)benzylamine.⁵ The lithiation of the silylmethyl group may be accelerated by the presence of a β -amino group. We then examined the reaction of (dialkylaminomethyl)trimethylsilanes with alkylolithium.

A solution of 1-(trimethylsilylmethyl)piperidine **1a** or *N*-(trimethylsilylmethyl)dibutylamine **1b** in ether was heated at reflux for 20 h with butyllithium (2 mol equiv.) and then quenched with chlorotrimethylsilane at 0 °C to room temperature to give *N,N*-dialkyl(2,2,4,4-tetramethyl-2,4-disilapentyl)amine (**3a** or **3b**) in moderate yield (entries 1 and 6). The quenching with aldehydes afforded (dialkylaminomethyl)(2-hydroxyalkyl)di-



Scheme 1 Reagents and conditions: i, BuLi (2 equiv.), Et₂O, reflux, 20 h; ii, Me₃SiCl (2 equiv.), 0–25 °C, 3 h; iii, RCHO (2.2 equiv.), 0–25 °C, 3 h

Table 1 Reaction of (dialkylaminomethyl)trimethylsilanes with BuLi followed by Me₃SiCl or RCHO^a

Entry	R ¹	R ²	Electrophile	Product (Yield, %) ^b	B.p. ^f (°C/mmHg)
1	–(CH ₂) ₅ –	Me ₃ SiCl		3a (85)	90–95/1
2	–(CH ₂) ₅ –	CH ₃ (CH ₂) ₆ CHO		4a (72)	95–105/0.4
3	–(CH ₂) ₅ –	<i>c</i> -C ₆ H ₁₁ CHO		4b (70)	95–105/0.4
4	–(CH ₂) ₅ –	Me ₃ CCHO		4c (57)	100–110/1
5	–(CH ₂) ₅ –	PhCHO		4d (85) ^c	150–155/0.4
6	Bu	Bu	Me ₃ SiCl	3b (61)	100–105/1
7	Bu	Bu	CH ₃ (CH ₂) ₆ CHO	4e (46) ^d	150–160/0.4
8	Bu	Bu	<i>c</i> -C ₆ H ₁₁ CHO	4f (48) ^d	140–150/0.4
9	Bu	Bu	Me ₃ CCHO	4g (50) ^e	105–115/0.5

^a All products exhibited NMR, IR and elemental analyses consistent with the assigned structures; details of these are available as a Supplementary publication [SUP 56839 (4 pp.)]. For details of the Supplementary publications scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, 1991, Issue 1. ^b Isolated yields. ^c PhCHO was added at –78 °C. ^d **1b** (24%) was recovered. ^e **1b** (30%) was recovered. ^f B.p.s are the oven temperature of the Büchi Kugelrohr distillation apparatus.

methylsilanes **4a–g** (entries 2–5 and 7–9). Use of equimolar amounts of butyllithium or treatment with 2 mol equiv. at room temperature resulted in a decrease of the yields of **3** or **4**.

The lithiation of the silylmethyl groups may be accelerated by the chelation between the lithium and the amino group **2**. No lithiation was observed by a similar treatment of (2-dialkylaminoethyl)trimethylsilanes with butyllithium.

Experimental

Diethyl ether was distilled under nitrogen from sodium–benzophenone.

Typical Procedure.—A solution of **1** (3 mmol) and butyllithium (1.6 mol dm^{–3} in hexane; 4 ml, 6.6 mmol) in diethyl ether (10 ml) was refluxed under nitrogen for 20 h. A solution of chlorotrimethylsilane (716 mg, 6.6 mmol) or aldehyde (6.6 mmol) in diethyl ether (5 ml) was then added to the reaction mixture at 0 °C. The mixture was stirred for 3 h at room temperature, after which the reaction was quenched with saturated aqueous NH₄Cl and extracted with ether. The ethereal extract was washed with water, dried (MgSO₄), and concentrated. The residue from the reaction with chlorotrimethylsilane was distilled under reduced pressure. The product from the reaction with aldehyde was purified on an alumina column (hexane–ether, 5:1). The compounds so prepared are listed in Table 1.

References

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