Journal of Organometallic Chemistry, 419 (1991) C1–C4
Elsevier Sequoia S.A., Lausanne
JOM 22260PC

Preliminary communication

A handy preparation of bis(trimethylsilyl)methylamine

Jean-Paul Picard *[,a], Stéphane Grelier [a], Jacques Dunoguès [a],
Jesus-Maria Aizpurua [b] and Claudio Palomo [b]

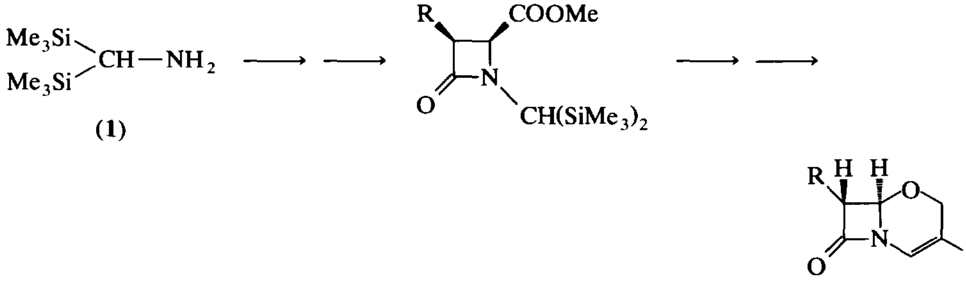
[a] *Laboratoire de Chimie Organique et Organométallique (URA 35 CNRS), Université Bordeaux I, 33405 Talence (France)*
[b] *Departamento de Química Orgánica, Facultad de Química, Universidad del País Vasco, Ado 1072, 20080 San Sebastián (Spain)*

(Received June 17th, 1991)

Abstract

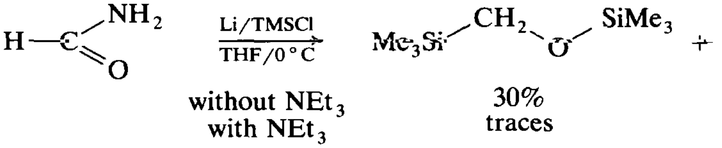
Reductive silylation of trimethylsilylcyanide provides a new and easy route to bis(trimethylsilyl)methylamine, a versatile synthon.

Bis(trimethylsilyl)methylamine, 1, was recently shown to play an efficient role in the synthesis of a series of original imines, phtalamides, 2-azadienes, azetidinones and oxacephems derivatives [1,2], e.g. [2]:

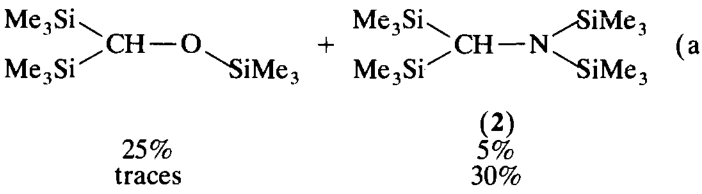


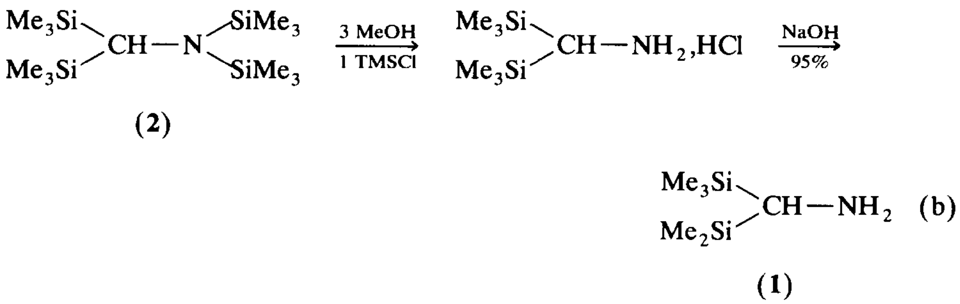
(1)

Compound **1** was first prepared [3] by protolysis of the tetrasilylated methylamine **2** by a technique we developed (see eq. a); **2** is produced by a reductive silylation of formamide [4]. However, this procedure gives only a low yield (30%) of **2**, even when the reductive silylation is carried out in the presence of NEt$_3$ (see eq. b).



0022-328X/91/$03.50





Amine **1** was also obtained on a small scale in 76% yield, from bis(trimethylsilyl)methylchloride, via the corresponding azide [5*] as depicted below:

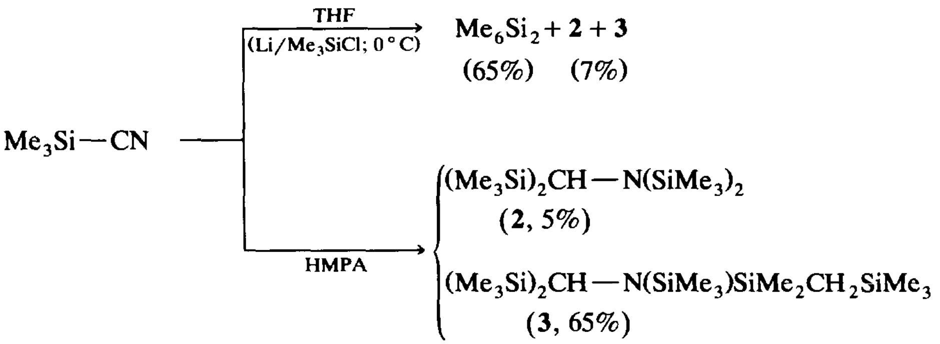
$$(Me_3Si)_2CHCl \xrightarrow[HMPA]{NaN_3} (Me_3Si)_2CHN_3 \xrightarrow[Et_2O]{LiAlH_4} (Me_3Si)_2CHNH_2$$

This method is limited by the cost of the starting chloride, which cannot be prepared efficiently in spite of the availability of the procedure described by Oliva et al. starting from trimethylsilylmethyl chloride [6]. We have therefore devised a new method starting from trimethylsilyl cyanide, a readily available reagent.

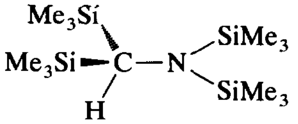
To our knowledge, all of the previously reported chemistry of silyl cyanides involves cleavage of the silicon–carbon bond (silylation, cyanation and cyanosilylation reactions [7]) and there is no example of a reaction involving the C≡N bond in these species. However, reductive silylation of unsaturated compounds is well known to give readily silylated saturated organic species [4,8–10]. Thus trimethylsilyl cyanide was submitted to reductive silylation by the trimethylsilylchloride/lithium reagent in an aprotic solvent at 0–5 ° C. In contrast to the outcome when tetrahydrofuran (THF) was used as the solvent, involving predominant formation of hexamethyldisilane (65% yield) and a trace ($\leqslant$ 7%) of polysilylated products [9], use of hexamethylphosphortriamide (HMPA) gave high yields ($\sim$ 70%) of the unexpected pentasilyl derivative **3**, accompanied by a small amount (5%) of the related tetrasilyl species **2** (see eq. below):

---

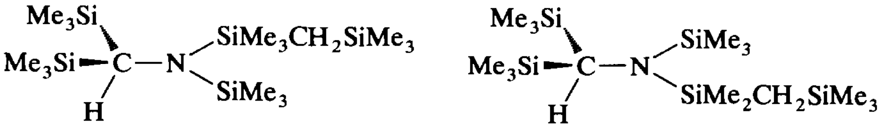
* Reference number with asterisk indicates a note in the list of references.



Compound **2** is a solid, easily separated from **3** by distillation [11*]. It was identified by comparison with the product obtained from formamide. Rotation around the C–N bond is prevented, presumably as a result of steric effects. The geometry at nitrogen is to be considered to be almost planar, as is generally the case with silazanes [12].



(**2**)



(**3**)

Compound **3** [13*], a liquid, was identified on the basis of its elemental analysis ($Si_5C_{16}H_{45}N$), mass spectrum (presence of the fragment $[Me_3SiCH_2SiMe_2]^+$) and ^1H, ^{13}C and ^{29}Si NMR data ($NSiCH_2Si$, Si_2CHN). It has a similar structure to **2** and exists as a 1/1 mixture of the two possible rotamers.

As previously described for **2** (eq. b), treatment of **3** in methanol with one equivalent of trimethylsilyl chloride also afforded (in 95% yield) the hydrochloride of the desired amine **1** (**1** · HCl), which was readily isolated by evaporation of the accompanying methoxysilanes:

$$\mathbf{3}\ \xrightarrow[1\ \mathrm{TMSCl}]{3\ \mathrm{MeOH}}\ \underset{(\mathbf{1}\cdot \mathrm{HCl})}{(Me_3Si)_2CH{-}NH_2 \cdot HCl} + 2\ MeOSiMe_3 + MeOSiMe_2CH_2SiMe_3$$

This salt can also be obtained directly from the mixture of **2** and **3** by the same procedure. After neutralization of its hydrochloride, amine **1** was obtained in a 65% overall yield from trimethylsilyl cyanide. By use of this route, 25 g of this amine could conveniently be prepared in one batch.

It is evident that the reductive silylation of trimethylsilyl cyanide by TMSCl/Li in HMPA at 0 ° C, provides an easy route to silylmethylamine **1**. To our knowledge this represents the first example of a reaction in which a silyl cyanide apparently behaves like an organic nitrile. The chemistry of amine **1** is under investigation.

References and notes

1 J. Lasarte, C. Palomo, J.P. Picard, J. Dunoguès and J.M. Aizpurua, J. Chem. Soc., Chem. Commun., (1989) 72.

2 C. Palomo, J.M. Aizpurua, J.M. Garcia, J.P. Picard and J. Dunoguès, Tetrahedron Lett., 31 (1990) 1921.

3 A. Ekouya, R. Calas, J. Dunoguès, C. Biran and N. Duffaut, J. Organomet. Chem., 177 (1979) 137.

4 J.P. Picard, J.M. Aizpurua, A. Elyusufi and P. Kowalski, J. Organomet. Chem., 391 (1990) 13.

5 C. Palomo, J.M. Aizpurua, J.M. Garcia and M. Legido, J. Chem. Soc., Chem. Commun., (1991) 524. This procedure is identical to the one reported for trimethylsilylmethylamine by M. Letellier, D.J. McPhee and D. Griller, Synth. Commun., 18 (1988) 1975.

6 A. Oliva, A. Molinari and G. Maulen, Bol. Soc. Chil. Quim., 27 (1982) 221.

7 W.P. Weber, Silicon Reagents for Organic Synthesis, Springer Verlag, Berlin, 1983.

8 see for instance: R. Calas and J. Dunoguès, J. Organomet. Chem. Libr., 2 (1976) 277.

9 A. Elyusufi, Thesis, University of Bordeaux no. 1771, 1982.

10 J.P. Picard, A. Elyusufi, R. Calas, J. Dunoguès and N. Duffaut, Organometallics, 3 (1984) 1660.

11 **2**: B.p.: 90 °C/0.05 torr; m.p.: 190 °C.

12 see for instance: J. Goubeau and J. Jiménez-Barberá, Z. Anorg. Allg. Chem., 303 (1960) 217.

13 **3**: B.p.: 120 °C/0.05 torr. Neither the isomeric $(Me_3Si)_3C{-}N(SiMe_3)_2$ nor the corresponding amine $(Me_3Si)_3CNH_2$ was observed.