

JOM 23157PC

## Preliminary Communication

### Direct and sequential synthesis of polysilazanes using lithiated (n-butylamino)silanes \*

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(Received August 12, 1992)

#### Abstract

Mono- and poly-lithiated derivatives of (n-butylamino)silanes react cleanly with chlorosilanes  $\text{Me}_n\text{SiCl}_{4-n}$  ( $n = 0, 2, 3$ ) to give chain, cyclic, and spiro polysilazanes. When the chain polysilazane products contain terminal NHBu groups, these may be further lithiated and then coupled with chlorosilanes to produce successively longer chains; thus  $\text{Me}_2\text{Si}(\text{NHBu})(\text{NLiBu})$  reacts with  $\text{Me}_2\text{SiCl}_2$  to give  $[(\text{BuNH})\text{SiMe}_2\text{NBu}]_2\text{SiMe}_2$ , which after monolithiation reacts further with  $\text{Me}_2\text{SiCl}_2$  to yield the heptasilazane  $[(\text{BuNH})(\text{SiMe}_2\text{NBu})_3]_2\text{SiMe}_2$ .

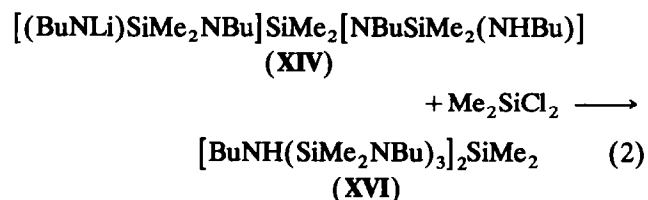
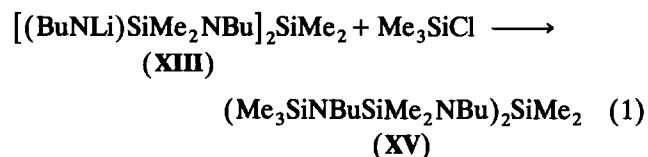
In a previous paper [1] we described the synthesis and characterisation of a number of lithiated (*Si*-n-butylamino)methylsilanes  $\text{Me}_{4-n}\text{Si}(\text{NLiBu})_n$  ( $n = 1, \text{I}; 2, \text{II}; 3, \text{III}; 4, \text{IV}$ ) and partially-lithiated derivatives such as  $\text{Me}_2\text{Si}(\text{NHBu})(\text{NLiBu})$  (V) and  $\text{Si}(\text{NHBu})_2(\text{NLiBu})_2$  (VI). We now report the use of these N–Li derivatives to prepare a range of polysilazanes of defined structure, forming an extension to the pioneering work of Fink, Andrianov, Rochow, Wannagat, Bürger, and others [2–5].

Table 1 shows that the dilithio derivative  $\text{Me}_2\text{Si}(\text{NLiBu})_2$  (II) reacted as expected with  $\text{Me}_3\text{SiCl}$  and  $\text{Me}_2\text{SiCl}_2$  to give the trisilazane VII and the cyclic disilazane VIII, respectively. The *spiro* compound IX was formed both from II +  $\text{SiCl}_4$  and from the tetralithio derivative IV +  $\text{Me}_2\text{SiCl}_2$ . A branched tetrasilazane X resulted from the reaction between the tri-lithio compound III and  $\text{Me}_3\text{SiCl}$ . Neither  $\text{Si}(\text{NLiBu})_4$  (IV) +  $\text{Me}_3\text{SiCl}$  nor  $\text{Me}_3\text{SiNLiBu}$  +  $\text{SiCl}_4$  gave the fully-substituted pentasilazane, doubtless for

steric reasons; in both cases, mixtures of partially-substituted products were observed.

When partially-lithiated aminosilanes are used as starting materials, the products can contain potentially reactive N–H bonds. Thus the mono-lithiated diamino compound V gave with  $\text{Me}_2\text{SiCl}_2$  a chain trisilazane XI with one n-butylamino group at each end position, but the di-lithiated tetra-amino compound VI with  $\text{Me}_2\text{SiCl}_2$  produced an unsymmetrical cyclodisilazane XII with two n-butylamino groups on one silicon.

Either two or one of the n-butylamino groups in the trisilazane XI could be lithiated to give symmetrical XIII or unsymmetrical XIV, respectively (Scheme 1). As shown in eqns. 1 and 2, the di-lithio compound XIII then reacted with  $\text{Me}_3\text{SiCl}$  to give the pentasilazane XV, while the mono-lithio derivative XIV with  $\text{Me}_2\text{SiCl}_2$  yielded the chain heptasilazane XVI.



It appears that this process can continue, so that mono-lithiation of XVI (an *n*-silazane  $\text{H}(\text{NBuSiMe}_2)_n\text{NHBu}$  where  $n = 7$ ) followed by reaction with a dichlorosilane leads to a  $(2n + 1)$ -silazane. As  $n$  increases, however, it becomes increasingly more difficult to characterise such polysilazanes.

There is always a delicate balance in silazane chemistry between linear and cyclic species [6]. The intermediate steric requirements of the n-butyl group may enable these compounds to avoid both condensation between NHR groups to give amine (always easy when R is small) and the reduction in reactivity which results when R is large.

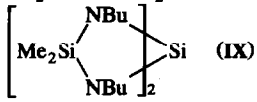
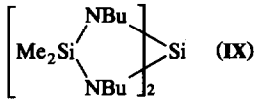
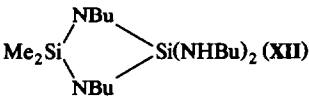
#### Experimental details

The general techniques and specific preparations of the lithio derivatives are described in ref. 1. Chloro-

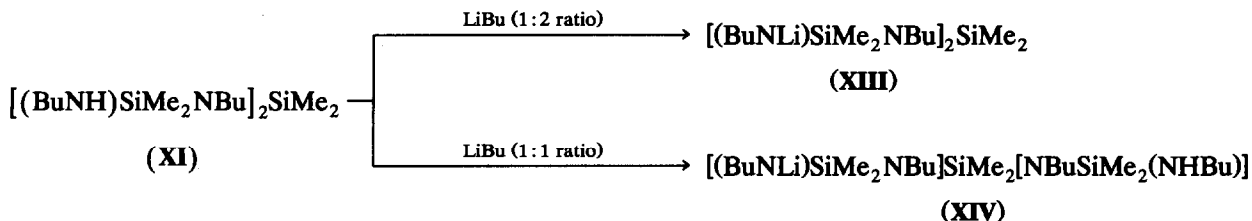
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\* This paper is dedicated by B.J.A. to Academician Mikhail G. Voronkov, in recognition of his outstanding contributions to organosilicon chemistry and his personal courage.

TABLE 1

Reactants		Products <sup>a</sup>
$\text{Me}_2\text{Si}(\text{NLiBu})_2$ (II)	+ $\text{Me}_3\text{SiCl}$ + $\text{Me}_2\text{SiCl}_2$	$\text{Me}_2\text{Si}(\text{NBuSiMe}_3)_2$ (VII) $\text{Me}_2\text{Si}(\text{NBuSiMe}_2\text{NBu})$ (VIII) <sup>b</sup>
	+ $\text{SiCl}_4$	 (IX)
$\text{MeSi}(\text{NLiBu})_3$ (III)	+ $\text{Me}_3\text{SiCl}$	$\text{MeSi}(\text{NBuSiMe}_3)_3$ (X)
$\text{Si}(\text{NLiBu})_4$ (IV)	+ $\text{Me}_2\text{SiCl}_2$	 (IX)
	+ $\text{Me}_2\text{SiCl}_2$	$[(\text{BuNH})\text{SiMe}_2\text{NBu}]_2\text{SiMe}_2$ (XI)
$\text{Si}(\text{NHBu})_2(\text{NLiBu})_2$ (VI)	+ $\text{Me}_2\text{SiCl}_2$	 (XII)

<sup>a</sup> Satisfactory analytical data and NMR, IR, and mass spectra were obtained. <sup>b</sup> cf. W. Fink, *Helv. Chim. Acta*, 47 (1964) 498.



Scheme 1

silanes (Aldrich Chemical Co.) were distilled *in vacuo* before use; all solvents were rigorously dried.

In a typical preparation, a mixture of  $\text{Li}^n\text{Bu}$  (0.746 g, 11.6 mmol) and  $\text{Me}_2\text{Si}(\text{NH}^n\text{Bu})_2$  (2.356 g, 11.6 mmol) in *n*-hexane (7.6 ml) was stirred at 20°C for 3 h. To the resulting solution of mono-lithio derivative V were added  $\text{Me}_2\text{SiCl}_2$  (0.751 g, 5.82 mmol) and THF (2 ml); the mixture was then stirred for a further 8 h. Precipitated LiCl was removed by filtration, and the resulting clear solution distilled to give  $[(\text{NHBu})\text{SiMe}_2\text{NBu}]_2\text{SiMe}_2$  (XI) as a colorless liquid (1.39 g, 52%; b.p. 96–97°C/ $1 \times 10^{-2}$  torr). Next a mixture of XI (1.20 g, 2.61 mmol) and  $^n\text{BuLi}$  (0.334 g, 5.21 mmol) in *n*-hexane (3.40 ml) and THF (2.0 ml) was stirred for 12 h at 20°C, and then  $\text{Me}_3\text{SiCl}$  (0.651 g, 5.99 mmol) was distilled under vacuum, and the mixture stirred for a further 6 h at 20°C. Filtration, removal of solvent, and fractionation yielded  $[\text{Me}_3\text{SiNBuSiMe}_2\text{NBu}]_2\text{SiMe}_2$  (XV) as a colorless liquid (0.252 g, 16%; b.p. 104°C/ $1 \times 10^{-2}$  torr).

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