New Rearrangements of *N*-Lithiocyclosiloxazanes

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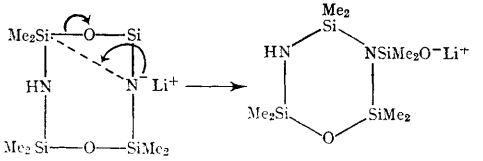
A number of cyclosiloxazanes are known,[1] and we report a novel rearrangement reaction undergone by some of their *N*-lithio-derivatives.

The eight-membered siloxazane ring (I) reacts with butyl-lithium (2 equiv.) in 1,2-dimethoxyethane at −60° to give the *NN'*-dilithium salt. At −60° this derivative reacts with chlorotrimethylsilane to give the expected disilyl derivative (II): if the solution is allowed to reach −30° and set aside for 1 hr. before reaction with the chlorosilane, the product is the isomeric six-membered ring compound (III). At room temperature a further "ring-contraction" is complete in 6 hr., and the product is the cyclodisilazane (IV).

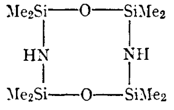
The monolithium salt of (I) rearranges in a similar manner at room temperature to give (V) on addition of chlorotrimethylsilane; attempts to couple it at −60° result in disproportionation to give a mixture of (I) and (II).

The product (V) is also lithiated, and coupling with chlorotrimethylsilane gives (III) at −30°, but the rearranged (IV) at room temperature.

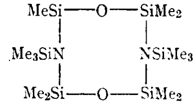
We attribute the formation of these products of smaller-ring size to a transannular nucleophilic rearrangement of the initially formed *N*-lithium salts, for example



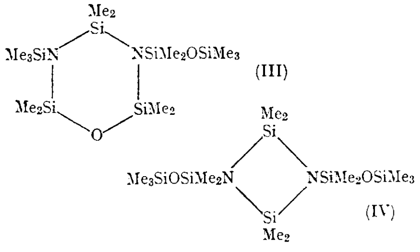
The rearrangement also occurs in tetrahydrofuran, but is very slow in diethyl ether or hexane.



(I)

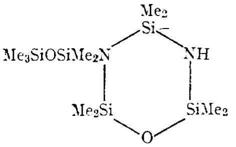


(II)

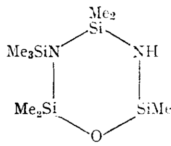


(III)

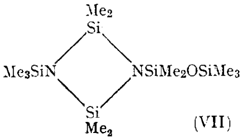
(IV)



(V)



(VI)



(VII)

The rearrangements seem only to take place when the ring geometry is favourable: the *N*-lithium derivatives of [$(Me_2SiO)_2Me_2SiNH$], [$(Me_2SiO)_2$

$Me_2SiNH]_2$, and $[Me_2SiO(Me_2SiNH)_2]$ do not rearrange in 24 hr. at 20° in 1,2-dimethoxyethane. The *N*-silyl derivative is obtained with retention of ring size. However, the *N*-lithio-derivative of (VI) [a system analogous to (V)] rearranges rapidly at room temperature, as expected, to give the cyclodisilazane (VII) on reaction with chlorotrimethylsilane.

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[1] C. Kruger and E. G. Rochow, *Inorg. Chem.*, 1963, **2**, 1295; K. A. Andrianov, I. Haiduc, and L.M. Khananashvili, *Zhur. obschchei. Khim.*, 1963, **33**, 2790; *Izvest. Akad. Nauk. S.S.S.R. Ser. khim.*, 1963, 1701; J. G. Murray and R. K. Griffith, *J. Org. Chem.*, 1964, **29**, 1215.