

Short communication

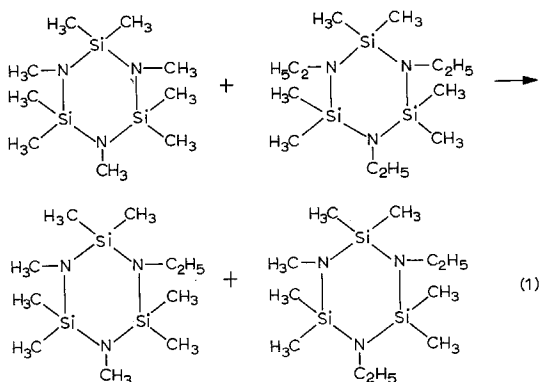
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Redistribution reactions of N-alkylcyclotrisilazanes

In recent years there has been a growing interest in silicone heterocycles in which silicon atoms alternate with heteroatoms. Redistribution reactions of this type of compound involving ring-chain equilibria have been studied in some detail¹. However, apart from ring expansions and contractions^{1,2} (usually acid or base catalyzed), little work has been presented relating to ring-ring equilibria. The redistribution of nonamethylcyclotrisilazane with hexamethylcyclotrisilthiazanes to form two new cyclotrisilthiazanes was reported recently³, and full quantitative data were obtained for this reaction⁴.

This communication presents evidence for the interchange of N-alkyl groups between cyclotrisilazanes to form new mixed N-alkylcyclotrisilazanes. This type of reaction is analogous to the exchange of labile B-alkyl groups between borazoles observed by NEWSON *et al.*⁵.

Redistribution of N-alkyl groups was found to occur when equimolar quantities of tris-(N-methyl)-hexamethylcyclotrisilazane ($N^1N^1N^1$) and tris-(N-ethyl)-hexamethylcyclotrisilazane ($N^2N^2N^2$) were heated together in chloroform in sealed tubes for several hours at 140° (Eqn. 1).



Analysis of the reaction products was carried out using a Pye F. 104 gas chromatograph, with a flame ionization detector, and 6 ft. \times $\frac{1}{4}$ in. O.D. column containing as a stationary phase 12% w/w Silicone Gum SE-30 on treated Celite. The column temperature was 180°. The chromatogram of the redistributed mixture showed the formation of two new compounds with retention volumes intermediate between those of ($N^1N^1N^1$) and ($N^2N^2N^2$). These new compounds were not formed when either ($N^1N^1N^1$) or ($N^2N^2N^2$) were heated alone (Fig. 1). A plot of log retention time *vs.* carbon number for the four compounds resulted in a straight line, as expected for an homologous series of this nature.

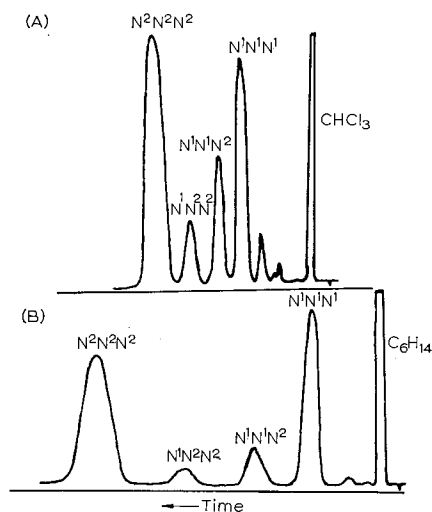
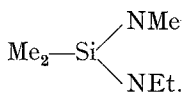


Fig. 1. Chromatograms obtained from the $N^1N^1N^1$ - $N^2N^2N^2$ redistribution in chloroform (A) and hexane (B).

The GLC data were supported by the proton resonance spectrum of the redistributed mixture. The original mixture of ($N^1N^1N^1$) and ($N^2N^2N^2$) gave rise to five resonances, with values corresponding to those given in the literature⁵. After equilibration, new resonances were observed, due to silyl methyl protons in the environment



This type of reaction has also been found to occur in systems involving tris-(*N*-propyl)-hexamethylcyclotrisilazane ($N^3N^3N^3$). Preparation of cyclotrisilazanes with large *N*-alkyl groups is difficult or in some cases impossible^{6,7}, and it was not possible to obtain ($N^3N^3N^3$) in an extremely pure condition. However, mixtures containing this compound underwent redistributions with both ($N^1N^1N^1$) and ($N^2N^2N^2$) giving predicted gas chromatogram patterns, and linear plots of log retention volumes *vs.* carbon number.

A detailed account of these redistribution reactions will be presented later.

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