

Study of the Reaction of Methyltris(dimethylamino)silane with Diamines

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ABSTRACT

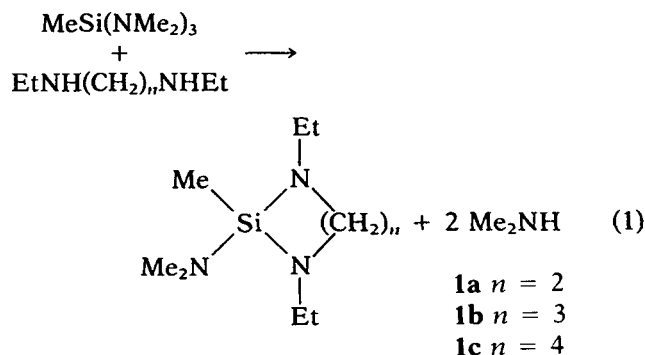
Tris(dimethylamino)methylsilane reacts with *N,N'*-dialkyldiamines to give the corresponding substituted 1,3,2-diazasilacycloalkanes. In contrast, the reaction with an *N*-alkyldiamine yields the corresponding polycyclic silazane.

INTRODUCTION

We have previously reported the synthesis of polycyclic borazines from the reaction of a trisdialkylaminoborane with an *N*-alkyl diamine [2] and now wish to report the syntheses of the analogous polycyclic silazanes.

There is considerable interest in the synthesis and properties of 1,2,3-organo-1,3,2-diazasilacycloalkanes due to their use as synthetic intermediates, for example, in the synthesis of macrocyclic amides [3].

The general method of synthesis of organo-1,3,2-diazasilacycloalkanes is via the reaction of a bisdialkylaminosilane with the corresponding diamine [4]. We observe that the reaction of tris(dimethylamino)methylsilane with an *N,N'*-dialkyldiamine results in the formation of the corresponding 2-alkyl-2-dimethylamino-1,3,2-diazasilacycloalkane (Equation 1).



The compounds were characterized by analysis, ^1H , ^{13}C and ^{29}Si NMR spectroscopy. Although organo-1,3,2-diazasilacyclopentanes and hexanes are well established, this is the first report of a fully characterized organo-1,3,2-diazasilacycloheptane. An increase in ring size from five to six atoms is accompanied by an upfield shift of $\delta^{29}\text{Si} = 10.82$ and is of the same order as that reported for the corresponding diorgano-1,3,2-diazasilacycloalkanes [4]. The polysilazanes were obtained by refluxing tris(dimethylamino)methylsilane and the corresponding *N*-methyl diamine in the presence of ammonium sulfate (Equation 2).

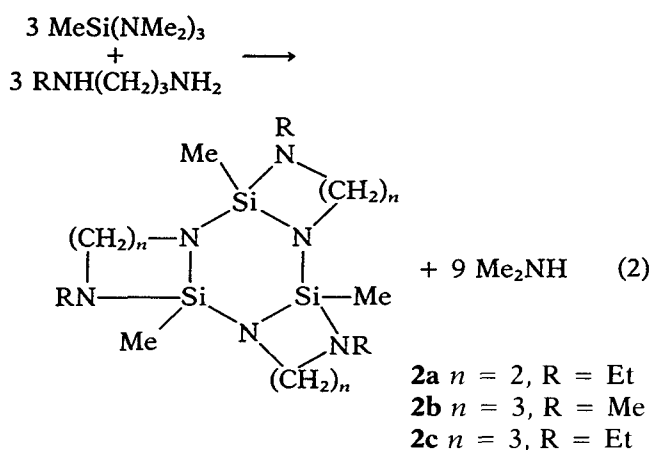
The ^1H and ^{13}C NMR spectra were consistent with the proposed structure, and three Me-Si peaks were observed in the ^{13}C spectrum. For example, in the ^{13}C NMR spectrum of **2b** three Me-Si peaks, at $\delta = 1.45, -3.15$ and -3.30 , were observed.

The ^{29}Si NMR spectrum of each compound contained three peaks with the effect of ring size ($\delta = 14$) being far greater than the effect of the nitrogen substituent ($\delta = 1$); see Table 1.

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TABLE 1

Compound	Formula	Yield (%)	bp (°C mmHg)	mol wt	Analysis, found (calcd)			$\delta^{29}\text{Si}$
					C	H	N	
1a	$\text{C}_9\text{H}_{23}\text{N}_3\text{Si}$	51	68–74/10	—	53.5(53.7)	11.9(11.5)	20.9(20.9)	–14.96
1b	$\text{C}_{10}\text{H}_{25}\text{N}_3\text{Si}$	50	74–6/5.5	—	56.0(55.80)	12.3(11.7)	19.8(19.5)	–25.78
1c	$\text{C}_{11}\text{H}_{27}\text{N}_3\text{Si}$	56	78–80/3.0	—	58.3(57.6)	12.4(11.9)	18.5(18.3)	–17.21
2a	$\text{C}_{15}\text{H}_{36}\text{N}_6\text{Si}_3$	23	144/0.2	384	44.0(46.9)	9.9(9.4)	20.8(21.9)	–6.76 –8.22 –10.72
2b	$\text{C}_{15}\text{H}_{36}\text{N}_6\text{Si}_3$	48.9	126–30/0.18	384	46.6(46.9)	9.8(9.4)	22.2(21.9)	–20.83 –21.09 –22.77
2c	$\text{C}_{18}\text{H}_{42}\text{N}_6\text{Si}_3$	45.4	160.2/0.15	426	50.5(50.7)	10.6(9.9)	20.4(19.7)	–21.68 –22.70 –23.30



The mass spectra of the polycyclic silazanes contained molecular ion peaks although, in the case of the polycyclic derivative of *N*-ethylethanediamine, there was evidence of a tetrameric compound.

EXPERIMENTAL

NMR spectra were recorded on a JEOL-PS-100 NMR spectrometer with the instrument in the CW mode for proton spectra and in the FT mode for ^{13}C and ^{29}Si spectra. Samples used were as solutions in either CDCl_3 or CCl_4 with internal TMS as standard.

Molecular weights were determined by mass spectrometry using an AEI MS902 mass spectrometer at 70 eV. The source was maintained at 170° and the compounds were introduced using a variable-temperature direct-insertion probe.

Tris(dimethylamino)methylsilane was prepared by an established method [5]. As the experimental procedure was the same in all cases, only two examples are discussed in detail and all analytical and physical data are given in Table 1.

1,3-Diethyl-2-dimethylamino-2-methyl-1,3,2-diazasilacycloheptane (**1c**)

Tris(dimethylamino)methylsilane (5.2 g, 0.03 mol) and *N,N'*-diethyl-1,4-diaminobutane (4.3 g, 0.03 mol) together with ammonium sulfate (0.21 g) were heated under reflux using a heating mantle. The reaction was completed in 3h as indicated by the loss of the calculated amount of dimethylamine. Distillation of the liquid residue under reduced pressure afforded **1c** (3.8 g, 56%) as a colorless liquid.

Tris(1,2-dimethyl-1,3,2-diazasilacyclohexane) (**2b**)

Tris(dimethylamino)methylsilane (4.95 g, 0.028 mol) and *N*-methyl-1,3-diaminopropane (2.46 g, 0.028 mol) together with ammonium sulfate (0.19 g) were refluxed for 3h, during which time the theoretical amount of dimethylamine was lost through the drying tube. Distillation of the liquid residue yielded **2b** (1.75 g, 48.9%).

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