

CONTRIBUTIONS TO GROUP IV ORGANOMETALLIC CHEMISTRY

XII*. PREPARATION AND PROPERTIES OF SOME BIS(1,3,2-DIAZASILACYCLOALKYL)DIMETHYLSILANES

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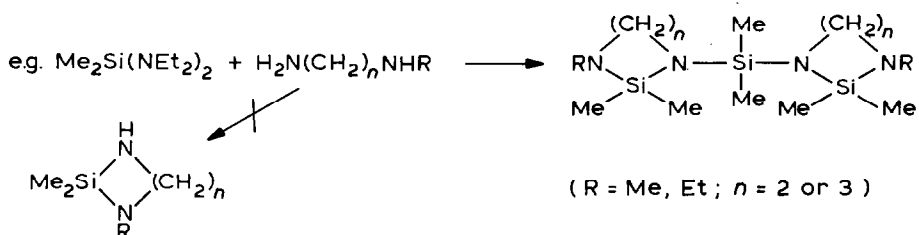
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Summary

The preparation of some bis(1,3,2-diazasilacycloalkyl)dimethylsilanes, via the interaction of bis(diethylamino)dimethylsilane and an *N*-alkyldiamine are reported and their ^{13}C and ^{29}Si NMR spectra discussed.

We have been interested, for a number of years, in the synthesis and properties of compounds containing silicon–nitrogen bonds [2] and have recently reported the results of a study concerning the preparation and properties of some organo-1,3,2-diazasilacycloalkanes [3]. The interaction of a bis(dialkylamino)dialkyl silane and an *N,N'*-dialkyldiamine results in the formation of the corresponding 2,2'-substituted-1,3,2-diazasilacycloalkane [4]. In contrast we have observed that the interaction of a bis(dialkylamino)dialkylsilane and an *N'*-alkyldiamine results in the formation of a bis(1,3,2-diazasilacycloalkyl)dialkylsilane.



Similar compounds have been prepared from the interaction of 1,2-diaminoethane and dichlorodimethylsilane or dimethylphenylsilane [5,6]. In all our studies we were unable to isolate a 2,2-dimethyl-1-alkyl-1,3,2-diazasilacycloalkane.

* For part XI see ref. 1.

Preparation

The titled compounds were prepared by a transamination reaction involving the interaction of bis(dimethylamino)dimethylsilane and an *N*-alkyldiamine. The reactants together with ammonium sulphate, as catalyst, were refluxed for two to three days. The compounds were purified by distillation under reduced pressure and characterised by mass spectrometry, ^{13}C and ^{29}Si NMR spectroscopy. It is interesting to note that from the interaction of an *N*-alkyldiamine and bis(diethylamino)methylphenylsilane we were only able to isolate polymeric products.

Results and discussion

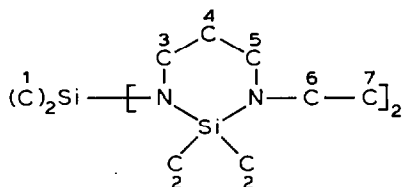
^{13}C NMR spectra

The chemical shifts for the compounds synthesised are given in Table 1. Two Si-Me peaks were observed in all the spectra (e.g. Fig. 1) which is consistent with

TABLE 1

NMR SHIFTS FOR BIS(1,3,2-DIAZASILACYCLOALKYL)DIMETHYLSILANES (δ in ppm)

Numbering of atoms:



(H atoms are omitted for clarity)

Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)
$\text{Me}_2\text{Si}-\left[\begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{Si} \\ \diagup \quad \diagdown \\ \text{Me} \quad \text{Me} \end{array} \right]_2$ (1)	-0.87	0.19	44.31	-	53.49	33.84	-
$\text{Me}_2\text{Si}-\left[\begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{Si} \\ \diagup \quad \diagdown \\ \text{Me} \quad \text{Me} \end{array} \right]_2$ (2)	-0.68	1.35	44.29	-	50.47	41.87	15.63
$\text{Me}_2\text{Si}-\left[\begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{Si} \\ \diagup \quad \diagdown \\ \text{Me} \quad \text{Me} \end{array} \right]_2$ (3)	1.49	-0.31	42.40	31.10	52.62	36.97	-
$\text{Me}_2\text{Si}-\left[\begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{Si} \\ \diagup \quad \diagdown \\ \text{Me} \quad \text{Me} \end{array} \right]_2$ (4)	1.38	1.66	43.26	31.25	48.15	42.37	14.67

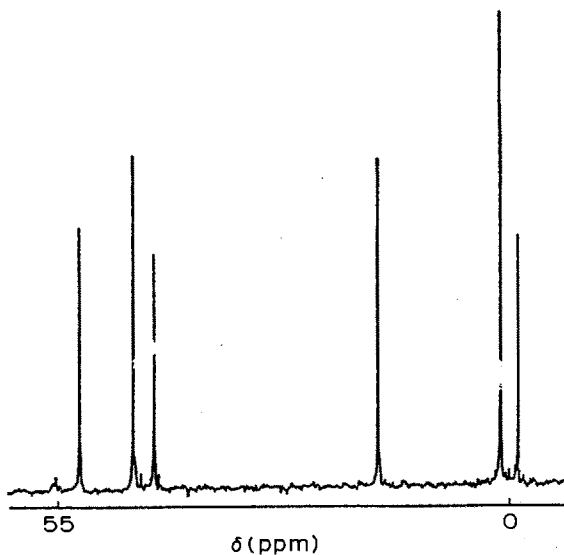


Fig. 1. ^{13}C NMR spectrum of **2**.

the proposed structure of the compounds. We observe that a change in ring size from a 5-membered to a 6-membered ring affects the shift of the ring Si-Me. By contrast changing the nitrogen substituent from a methyl group to an ethyl group has a greater affect on the ring Si-Me than the bridging Si-Me. In addition a 3 to 4 ppm upfield shift is observed in the nitrogen-carbon (C(5)) atom which we attribute to a γ *gauche* interaction between the *N*-ethyl group and the ring carbon atom. The nitrogen-carbon (C(3)) atom which is closer to the bridging SiMe₂ group is almost unaffected by the changes in the nitrogen substituents and an upfield shift of 1 to 2 ppm (5 → 6-membered ring) is observed.

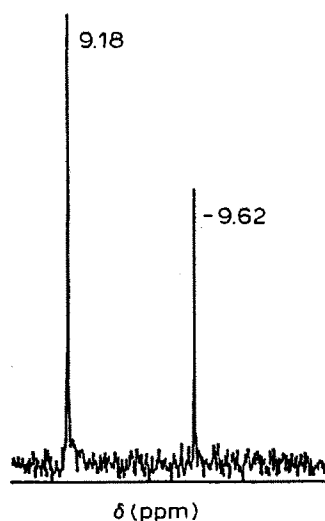
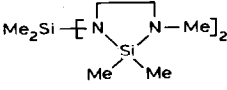
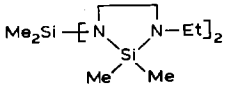
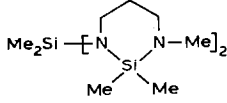
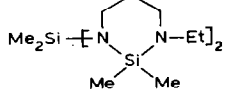


Fig. 2. ^{29}Si NMR spectrum of **2**.

TABLE 2

²⁹Si NMR SHIFTS FOR BIS(1,3,2-DIAZASILACYCLOALKYL)DIMETHYLSILANES (δ in ppm)^a

Compound	
	10.63, -9.51 (2/1)
	9.18, -9.62 (2/1)
	-3.64, -5.80 (2/1)
	-6.14, -6.38 (2/1)

^a (): ratio of intensity of the two peaks. The first value is assigned to the silicon atom contained in the ring while the second one is assigned to the silicon atom in the bridging position.

We suggest that the difference in shifts can be attributed to either a *gauche* steric interaction which will be more effective in a 6-membered ring than a 5-membered ring or a δ -*syn*-axial interaction which can operate in both the 5- and 6-membered ring with an *N*-ethyl substituent.

²⁹Si NMR spectra

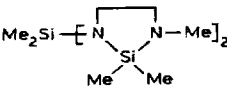
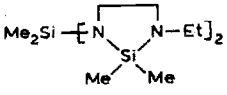
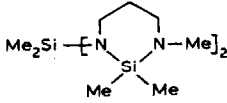
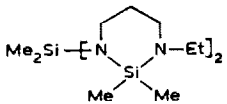
The chemical shift data and ratio of peak intensities are given in Table 2. In all the spectra two peaks were observed, (e.g. Fig. 2), which is in accordance with the proposed structure of the compounds. The assignments for the bridging silicon atom are consistent with those observed for a bis(dialkylamino)methylsilane (for example -5.52 ppm for bisdiethylsilane [3]) and for the ring silicon atom (for example 9.82 and -1.38 ppm for 1,2,2,3-tetramethyl-1,3,2-diazasilacyclopentane and hexane respectively [3]).

One interesting feature of the ²⁹Si NMR spectra is the observed large upfield shift of the ring silicon atom between the 5- and 6-membered rings which has recently been observed in the spectra of 2-substituted-1,3,2-diazasilacyclopentanes and hexanes [3]. We suggest that the large upfield shift is possibly due to a change in p_{π} - d_{π} bonding between nitrogen and silicon resulting in a change from a strained 5-membered ring to a relatively strain-free 6-membered ring.

Experimental

The NMR spectra were recorded on a JEOL-PS-100 NMR spectrometer with the instrument in the Fourier transform mode for ¹³C and ²⁹Si spectra. Samples used were as solutions in either CDCl₃ or CCl₄ with internal TMS as standard. For some

TABLE 3
ANALYTICAL AND PHYSICAL DATA FOR BIS(1,3,2-DIAZASILACYCLOALKYL)DIMETHYL-
SILANES

Compound	<i>m/e</i> (calcd.)	b.p. (°C/mmHg)	Yield (%)	Analysis (Found (calcd.) (%))		
				C	H	N
	-	86-90/0.25	52.3	44.8 (45.6)	10.7 (10.2)	17.4 (17.7)
	344(344)	92-96/0.1	18.0	48.1 (48.8)	11.0 (10.5)	16.2 (16.3)
	344(344)	120/0.2	39.5	48.5 (48.8)	11.0 (10.5)	16.1 (16.3)
	372(272)	130-133/0.3	17.0	51.1 (51.6)	10.8 (10.8)	15.3 (15.0)

²⁹Si spectra it was found necessary to add a trace of chromium-acetylacetonate as a relaxing agent. The mass spectra were recorded using an A.E.I. MS 902 mass spectrometer at 70 eV. The source was maintained at 170°C and the compounds were introduced using a variable-temperature, direct-insertion probe. As the experimental procedure was the same in all cases only one example is discussed in detail and all analytical and physical data of compounds are given in Table 3.

Preparation of bis(2,2-dimethyl-3-ethyl-1,3,2-diazasilacyclohexyl)dimethylsilane

Bis(diethylamino)dimethylsilane (4.84 g, 0.024 mol) and *N*-ethyl-1,3-propanediamine (1.62 g, 0.016 mol) together with ammonium sulphate (0.72 g) were refluxed for two days. After filtration the residue on distillation afforded bis(2,2-dimethyl-3-ethyl-1,3,2-diazasilacyclohexyl)dimethylsilane (0.5 g, 17%), b.p. 130-133°C/0.3 mmHg. (Found: C, 51.1; H, 10.8; N, 15.3; *M* 372. C₁₆H₄₀N₄Si₃ calcd.: C, 51.6; H, 10.8; N, 15.0% *M* 372).

Attempts to prepare similar compounds using bis(diethylamino)methylphenylsilane as starting material were unsuccessful and only polymeric products were obtained.

Acknowledgments

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References

- 1 R.H. Cragg and R.D. Lane, *Org. Mass Spec.*, submitted.
- 2 R.H. Cragg and M.F. Lappert, *J. Chem. Soc.*, (1966) 82.
- 3 R.H. Cragg and R.D. Lane, *J. Organomet. Chem.*, 294 (1985) 7.
- 4 C.H. Yoder and J.J. Zuckerman, *Inorg. Chem.*, 4 (1965) 116.
- 5 W. Fink, *Helv. Chim. Acta*, 50 (1967) 1131.
- 6 W. Fink, *Chem. Ber.*, 99 (1967) 2267.