Substituted Tris(silyl)amines. Part III.[1] 1-Trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane

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The title compound (I) was prepared by ammonolysis of $Me_3Si{\cdot}N(SiMe_2Cl)_2$ and characterised. It rearranges in the presence of acids or bases to give principally $[Me_3Si{\cdot}NH{\cdot}Si(Me_2){\cdot}N{\cdot}SiMe_2]_2$ (III). Hydrolysis gave $[Me_3Si{\cdot}N{\cdot}Si(Me_2){\cdot}O{\cdot}SiMe_2]_2$ (V). Cyclodisilazanes are opened by methyl-lithium.

We have already briefly reported[2] the synthesis of 1-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane (I) by the ammonolysis of bis(chlorodimethylsilyl)trimethylsilylamine as a 10% solution in pentane at room temperature. The preparation of the required substrate by chlorination of bis(dimethylsilyl)trimethylsilylamine has now been described in more detail,[3] and it has also been prepared in other ways.[4]

$$Me_3Si{\cdot}N(SiMe_2Cl)_2 + NH_3 \longrightarrow Me_2\underline{Si{\cdot}N(SiMe_3){\cdot}Si(Me_2){\cdot}N}H + 2NH_4Cl \quad (1)$$

(I)

Compound (I) is the first example of a cyclodisilazane containing one NH group in the four-membered ring. Similar reactions to (I) were observed using primary amines (but not ammonia) by Breed and Elliott,[4] who commented upon the novel nature of these cyclisations.

The i.r. spectrum of our product (I) shows the following bands (cm.$^{-1}$): 3510m (NH str.), 2960s, 2800w (CH str.), 1430w, 1400w, 1252s ($SiCH_3$ deform.), 1080vs (NH deform.), 1002s (SiNSi), 928s, 870vs (SiNSi asymm. str.), 830s, 790s, and 680m. The strained ring results in a very high NH stretching and a very low NH bending frequency. The low SiNSi asymmetric stretch at 870 cm.$^{-1}$ is characteristic of cyclodisilazanes.[5] A further peak seems to arise from this vibration in *N*-silylated cyclodisilazanes[4,6] in the range 1025—1040 cm.$^{-1}$, which is thought to be due to an SiNSi vibration in which only one silicon atom is in the ring. In our compound it occurs at the low frequency of 1002 cm.$^{-1}$. We are unable to assign the peak at 928 cm.$^{-1}$; it may be due to the Si·NH·Si asymmetric stretch.

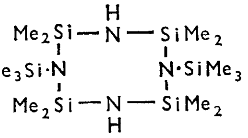
The n.m.r. spectrum shows two sharp peaks in the ratio 4 : 3 at 14 c./sec. and 0 c./sec. respectively downfield from tetramethylsilane. These are assigned, respectively, to the $SiMe_2$ and $SiMe_3$ protons. The spectrum is thus closely similar to that of 1,3-bis(trimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane.[7]

Further evidence for the structure of (I) comes from its silylation by bis(trimethylsilyl)acetamide at 170° to give the well characterised 1,3-bis(trimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane.[8] Although bis(trimethylsilyl)acetamide is a powerful silylating reagent, it does not react with linear disilazanes. The success of this reaction for compound (I) indicates the high acidity of the NH group in this structure.

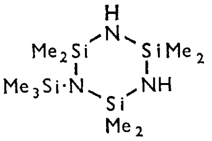
Silylation could not be achieved by metallation of the NH group by butyl-lithium followed by treatment with chlorotrimethylsilane. Instead, higher-boiling products, not containing cyclodisilazane units, were obtained. We ascribe this result to opening of the ring by the organolithium reagent, and we have shown that such a ring opening does occur in the case of 1,3-diethyl-2,2,4,4-tetramethylcyclodisilazane [reaction (2)]. This is the first reported case of cleavage of an Si–N bond by an organolithium reagent.

$$(Me_2Si{\cdot}NEt)_2 + MeLi \longrightarrow Me_3Si{\cdot}NEt{\cdot}Si(Me_2){\cdot}NEtLi \xrightarrow{Me_3SiCl} Me_3Si{\cdot}NEt{\cdot}Si(Me_2){\cdot}NEt{\cdot}SiMe_3 \quad (2)$$

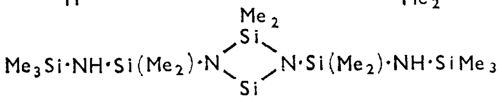
Although 1-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane (I) is stable at 190° when pure, in the presence of acids or bases, complex rearrangements occur. The main product of this temperature in the presence of an acid catalyst is not, as formerly reported,[2] 1,5-bis(trimethylsilyl)-2,2,4,4,6,6,8,8-octamethylcyclotetrasilazane (II), but the isomeric 1,3-bis(pentamethyldisilazanyl)-2,2,4,4-tetramethylcyclodisilazane (III). This structure was assigned on the basis of the i.r. spectrum which contained strong bands at 887 and 1032 cm.$^{-1}$, characteristic of an *N*-silylcyclodisilazane[4-6], and also at 927 cm.$^{-1}$, indicating a linear or unstrained silazane unit. Absorption due to NH was found at 3380 and 1178 cm.$^{-1}$. The n.m.r. spectrum contained three peaks in the SiMe region (see Experimental Section): this supports structure (III) rather than (II). This product is also formed when the cyclodisilazane (I) is set aside in the presence of pyridine or ammonium chloride. A number



(II)



(IV)



(III)

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[1] Part II, R. P. Bush and N. C. Lloyd, *J. Chem. Soc.* (*A*), 1969, 257.

[2] R. P. Bush, N. C. Lloyd, and C. A. Pearce, *Chem. Comm.*, 1967, 1269.

[3] Part I, R. P. Bush, N. C. Lloyd, and C. A. Pearce, *J. Chem. Soc.* (*A*), 1969, 253.

[4] L. W. Breed and R. L. Elliott, *J. Organometallic Chem.*, 1968, **11**, 447.

[5] K. Lienhard and E. G. Rochow, *Z. anorg. Chem.*, 1964, **331**, 316.

[6] R. P. Bush, N. C. Lloyd, and C. A. Pearce, to be published.

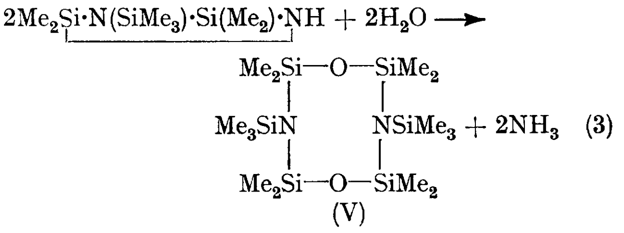
[7] H. Schmidbaur, *J. Amer. Chem. Soc.*, 1963, **85**, 2336.

[8] W. Fink, *Chem. Ber.*, 1963, **96**, 1071.

of other products are also formed, under these conditions, among which we identified 1-trimethylsilyl-2,2,4,4,6,6-hexamethylcyclotrisilazane (IV) and 1,3-bis(trimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane. These rearrangements sometimes occurred during the preparation or purification of the cyclodisilazane (I), and samples of the above compounds were isolated from one preparation. Yields of (I) are thus variable, and care should be taken in its preparation to use pure materials and remove ammonium chloride thoroughly before distillation.

Breed and Elliott[4] have pointed out that the cyclodisilazane system is much more readily solvolysed than the Si_3N system, and have taken synthetic advantage of the fact. In our compound we have an even greater difference in reactivity between the labile Si·NH·Si grouping and the tris(silyl)amine residue which remains after the ring has been opened.

Hydrolysis of (I) is very rapid and complicated in homogeneous solution in 1,2-dimethoxyethane, but in a heterogeneous system (pentane–water), 1,5-bis(trimethylsilyl)-2,2,4,4,6,6,8,8-octamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclo-octane (V)[2] is the product: no four-membered ring products were obtained.



$$2Me_2\underline{Si\cdot N(SiMe_3)\cdot Si(Me_2)\cdot N}H + 2H_2O \longrightarrow (Me_2Si{-}O{-}SiMe_2)(Me_3SiN)(NSiMe_3)(Me_2Si{-}O{-}SiMe_2) + 2NH_3 \quad (3)$$

(V)

EXPERIMENTAL

General.—Reactions were conducted under an atmosphere of argon with dried solvents and reagents. Their course was followed, where possible, by v.p.c. analysis with an F and M 810 gas chromatograph (6 ft. × $\frac{1}{4}$ in. columns of 10% SE 52 phenylmethyl silicone gum on 60—80 mesh diatoport S).

Fractional distillations were conducted with Nester-Faust spinning-band columns (18 in. or 2 ft.).

I.r. spectra were recorded on a Perkin-Elmer Model 237 spectrometer with pure liquids or 5% solutions in carbon tetrachloride. N.m.r. spectra were recorded on an A.E.I. RS2 60 Mc./sec. instrument with carbon tetrachloride as solvent and tetramethylsilane as internal standard.

Starting Materials.— Bis(chlorodimethylsilyl)trimethylamine was prepared as previously described.[3] 1,3-Bis-(trimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane,[8] 1,3-diethyl-2,2,4,4-tetramethylcyclodisilazane,[9] and 1-trimethylsilyl-2,2,4,4,6,6-hexamethylcyclotrisilazane[10] were prepared by literature methods.

Preparation of 1-*Trimethylsilyl*-2,2,4,4-*tetramethylcyclodisilazane.*—A current of ammonia was passed over a solution of bis(chlorodimethylsilyl)trimethylsilylamine (26·0 g.) in pentane (250 ml.) at room temperature until reaction was complete. The precipitated ammonium chloride was filtered off and washed with pentane. Distillation of the combined filtrate and washings gave pentane and 1-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane (11·6 g., 56%) b.p. 55°/10 mm. (Found: C, 39·3; H, 10·3; N, 12·6; Si, 38·5. Calc. for $C_7H_{22}N_2Si_3$: C, 38·6; H, 10·1; N, 12·85; Si, 38·5%).

In another preparation further fractionation of the residue gave a fraction containing 1,3-bis(trimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (separated by v.p.c. and identified by comparison of its i.r. spectrum with that of an authentic sample); 1-trimethylsilyl-2,2,4,4,6,6-hexamethylcyclotrisilazane, b.p. 90°/2·5 mm. (Found: C, 40·0; H, 10·3; N, 13·9; Si, 38·4. Calc. for $C_9H_{29}N_3Si_4$: C, 37·9; H, 10·3; N, 13·9; Si, 38·4%) whose i.r. spectrum was identical to that of an authentic sample; and a fraction containing two unidentified materials. The residue contained 1,3-bis(pentamethyldisilazanyl)-2,2,4,4-tetramethylcyclodisilazane, a sample of which was isolated by v.p.c. and shown to have the same i.r. spectrum as authentic material (reported below).

Silylation of 1-*Trimethylsilyl*-2,2,4,4-*tetramethylcyclodisilazane.*—(*a*) The cyclosilazane (1·6 g., 1 mol.) and bis(trimethylsilyl)acetamide (1·5 g., 1 mol.) were heated together to 170° during 5 hr. and then set aside at room temperature overnight. The main product was separated by v.p.c. and shown to have an identical i.r. spectrum to that of 1,3-bis(trimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane.

(*b*) n-Butyl-lithium (1·6 ml., 22% solution in hexane; 1 mol.) was added to the disilazane (0·8 g., 1 mol.) at 50°. The solution was allowed to reach room temperature and tetrahydrofuran (2 ml.) and chlorotrimethylsilane (0·4 g., 1 mol.) were added. Filtration and evaporation of solvents gave a white crystalline solid, shown by v.p.c. to be a mixture of two high-boiling compounds, neither of which contained the cyclodisilazane unit (i.r.).

Interaction of 1,3-*Diethyl*-2,2,4,4-*tetramethylcyclodisilazane with Methyl-lithium and Trimethylchlorosilane.*—Methyl-lithium (22·4 ml. 2·3M-solution ether; 1 mol.) was added to disilazane (10·4 g., 1 mol.) in ether (50 ml.) when an exothermic reaction occurred. After 1 hr., chlorotrimethylsilane was added, to give a precipitate of lithium chloride. Filtration and distillation gave 2,4-*diethyl*-1,1,1,3,3,5,5,5-*octamethyltrisilazane* (5 g., 34%) b.p. 90°/9 mm. (Found: C, 49·4; H, 11·6; N, 9·4; Si, 28·8. $C_{12}H_{34}N_2Si_3$ requires C, 49·65; H, 11·7; N, 9·65; Si, 29·0%). ν(SiNSi), 915 cm.$^{-1}$: n.m.r. signals at τ 9·86 and 9·80, combined relative intensity 23·7 (SiMe); τ 8·90 (t) and 6·97 (quartet), intensities 4·0 and 6·3 (NEt).

Rearrangement of 1-*Trimethylsilyl*-2,2,4,4-*tetramethylcyclodisilazane.*—(*a*) A pure sample of the disilazane was heated at 190° for 4 hr., when no change could be detected by i.r. spectroscopy or v.p.c. analysis.

(*b*) The disilazane (3·5 g.) and sulphuric acid (1 drop) were heated together at 190° for 9 hr., when v.p.c. analysis showed complete conversion to a mixture of products, of which one predominated. Separation by preparative scale v.p.c. gave 1,3-*bis*(*pentamethyldisilazanyl*)-2,2,4,4-*tetramethylcyclodisilazane* (Found: C, 38·9; H, 10·1; N, 12·0; Si, 37·9. $C_{14}H_{44}N_4Si_6$ requires C, 38·6; H, 10·1; N, 12·85; Si, 38·55%), ν(NH) 3380 and 1178 cm.$^{-1}$; ν(SiNSi) 1032, 927, and 887 cm.$^{-1}$. N.m.r. signals at τ 10·00 ($SiMe_2$ in side-chain), 9·94 ($SiMe_3$), and 9·76 ($SiMe_2$ in ring).

(*c*) The same product, together with 1-trimethylsilyl-2,2,4,4,6,6-hexamethylcyclotrisilazane, 1,3-bis(trimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane, and other unidentified products were formed when 1-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane was set aside at room

[9] W. Fink, *Helv. Chim. Acta*, 1964, **47**, 498.

[10] L. W. Breed and R. L. Elliott, *Inorg. Chem.*, 1963, **2**, 1069.

temperature in the presence of pyridine or ammonium chloride.

Hydrolysis of 1-*Trimethylsilyl*-2,2,4,4-*tetramethylcyclodisilazane*.—Water (1·4 g., 1 mol.) was added to the silazane (17·2 g., 1 mol.) in pentane (150 ml.) and the mixture was shaken or stirred at intervals during 3 days. Excess of water was separated off and the organic layer was dried (molecular sieve) and distilled to give pentane and 1,5-bis-(trimethylsilyl)-2,2,4,4,6,6,8,8-octamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclo-octane (9·2 g., 54%), b.p. 126°/5 mm., n_D^{22} 1·4571 [Found: C, 39·0; H, 9·8; N, 6·1; Si, 36·3%; *M*, 438 (mass spectrum). Calc. for $C_{14}H_{42}N_2O_2Si_6$, C, 38·4; H, 9·6; N, 6·4; Si, 38·4%; *M*, 438].

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