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THE PREPARATION AND PROPERTIES OF *N,N'*-BIS(CHLORODIMETHYLSILYL)TETRAMETHYLCYCLODISILAZANE AND ITS DERIVATIVES

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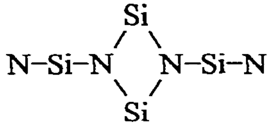
SUMMARY

N,N'-Bis(chlorodimethylsilyl)tetramethylcyclodisilazane, which is obtained along with minor proportions of 1,3-dichloro-1,1,3,3-tetramethyldisilazane, 1,5-dichloro-1,1,3,3,5,5-hexamethyltrisilazane, and *N*-(chlorodimethylsilyl)-*N'*-(3-chloro-1,1,3,3-tetramethyldisilazanyl)tetramethylcyclodisilazane by heating dichlorodimethylsilane and 2,2,4,4,6,6-hexamethylcyclotrisilazane at 175°, can be converted to its amino, methylamino, dimethylamino, diethylamino, piperidino, anilino, hydride, methyl, phenyl, methoxy, ethoxy, isopropoxy, phenoxy, phenyldimethylsiloxy, hydroxy, and acetoxy derivatives. Substances in this series are readily characterized by the Si_2N asymmetric stretch frequencies in the IR and the methylsilyl proton chemical shifts in the NMR spectra. They do not undergo thermal disproportionation reactions, but the hydroxy, amino, and methylamino derivatives undergo thermal decomposition with the cleavage of the cyclodisilazane ring, particularly in the presence of an acid catalyst.

INTRODUCTION

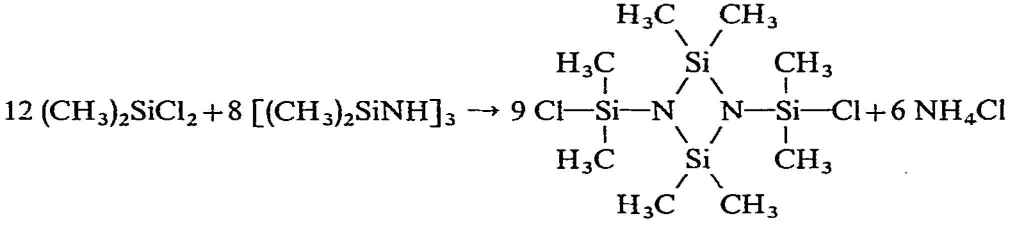
Some time ago we reported the preliminary results of our work on the synthesis of functional derivatives of *N,N'*-bis(dimethylsilyl)tetramethylcyclodisilazane[1]. A satisfactory route to the necessary intermediate, *N,N'*-bis(chlorodimethylsilyl)-tetramethylcyclodisilazane (I) had not been available until Wannagat found that it was obtained directly by heating mixtures of dichlorodimethylsilane and 2,2,4,4,6,6-hexamethylcyclotrisilazane or 2,2,4,4,6,6,8,8-octamethylcyclotetrasilazane[2]. The cyclodisilazanes, in turn, are useful in preparing functional trisilylamine derivatives[3]. The methods by which the functionally substituted cyclodisilazanes and the functionally substituted trisilylamines are prepared depend in a large part on the differences in reactivity of the various silicon–ligand bonds in the cyclodisilazane structures. For example, in the skeletal structure



the terminal Si–N bond is most easily broken by nucleophilic reagents, the Si–N bonds in the ring are more slowly cleaved, and the Si–N bonds in the resulting trisilylamine structures least readily broken. The products are determined by reagents and conditions. Although the synthesis of a number of derivatives of (I) are reported in the literature[4–7], with the exception of some recent publications[5,6], few details of the methods have been described. We would like to provide the details of the work described in our earlier publication as well as some more recent findings.

RESULTS AND DISCUSSION

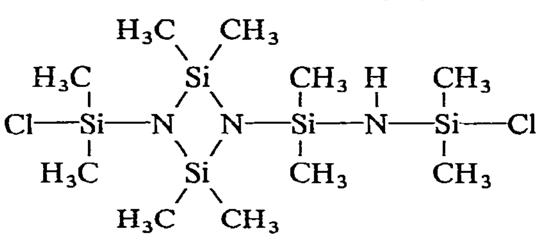
The procedure in which dichlorodimethylsilane and 2,2,4,4,6,6-hexamethylcyclotrisilazane or 2,2,4,4,6,6,8,8-octamethylcyclotetrasilazane are heated at 175° in the required stoichiometric proportions for at least 48 h has proved exceedingly convenient for the synthesis of laboratory quantities of (I). After the ammonium chloride by-product is removed, the cyclodisilazane can be obtained directly by distillation in yields of about 60%.



(I)

Since the reaction involves the equilibrium redistribution of silicon–nitrogen and silicon–chlorine groups, a number of other products can be shown to be present in the mixtures. Under appropriate conditions, the immediate cleavage products of dichlorodimethylsilane and hexamethylcyclotrisilazane, 1,3-dichloro-1,1,3,3-tetramethyldisilazane (II) and 1,5-dichloro-1,1,3,3,5,5-hexamethyltrisilazane (III), can be identified. When the equilibration products were distilled directly, significant amounts of (II) could be separated as the lower boiling component of the mixture. In order to obtain evidence for the presence of (III) in the mixtures, it was necessary to remove the silicon–chlorine groups by treating the mixture with an amine and separating the amine derivative of the trisilazane by distillation. It is entirely possible that in the chlorine-containing mixtures, redistribution continued during distillation with the separation of the lower boiling (II) even though (III) may have been the primary redistribution product. When the equilibration was carried out at 150°, the chief lower boiling component of the equilibration mixture was the trisilazane.

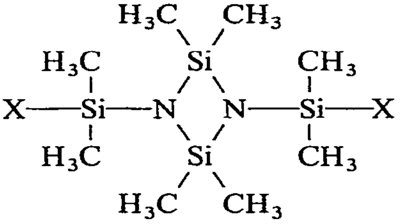
A higher boiling component, (IV), was also separated as an amine derivative.

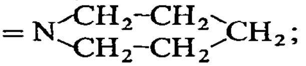


(IV)

Although this product could arise directly by the condensation of a disilazane and a trisilazane, it seems more likely that it also forms as one of the equilibrium redistribution products. Its formation in this way was observed in an experiment in which 0.03 mole of (I) was heated with 0.01 mole of 2,2,4,4,6,6-hexamethylcyclotrisilazane at 175° for 48 h and the product was distilled (83% recovery). GLC analysis indicated that the distillate contained 25% of (IV).

(I) can be readily converted to a variety of amine derivatives, either through the use of an excess of the amine as an acid acceptor or through the use of the lithium salt of the amine by a method already described[6]. The amine derivatives prepared in this work include the following:

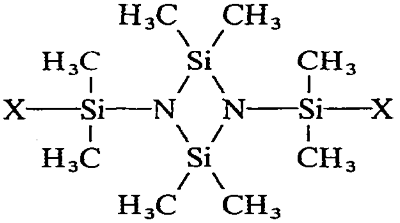


[(V), X = NH_2; (VI), X = $NHCH_3$;
(VII), X = $N(CH_3)_2$; (VIII), X = $N(C_2H_5)_2$;
(IX), X =

$N(CH_2CH_2)_2CH_2$;
(X), X = NHC_6H_5]

Compound (X) could also be obtained in the sodium hydride-catalyzed condensation of aniline with *N,N'*-bis(dimethylsilyl)tetramethylcyclodisilazane (XI), the latter substance being obtained by a lithium aluminum hydride reduction of (I).

Condensation of (I) with organometallic reagents did not proceed readily. Unless forcing conditions or an excess of the reagent were used, the products contained considerable chlorine. Excess methyllithium or methylmagnesium bromide could be used to prepare *N,N'*-bis(trimethylsilyl)tetramethylcyclodisilazane (XII). However, use of an excess of phenylmagnesium bromide led to a 75% recovery of (I). *N,N'*-Bis(dimethylphenylsilyl)tetramethylcyclodisilazane (XIII) could be obtained with phenyllithium, but the conversions were low, and the separation of the products cyclodisilazane from the biphenyl by-product was difficult.

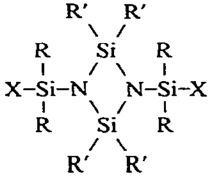
The amine functional groups were readily displaced by hydroxyl-containing reagents, and the following, with the exception of compound (XX), were prepared in this manner:



[(XIV), X = OCH_3; (XV), X = OC_6H_5;
(XVI), X = O-i-C_3H_7; (XVII), X = OC_6H_5;
(XVIII), X = $OSi(CH_3)_2C_6H_5$;
(XIX), X = OH; (XX), X = $OCOCH_3$]

The good conversions in the synthesis of many of these substances confirm the much greater solvolytic stability of the Si–N bonds in which silicon is attached to a nitrogen in the cyclodisilazane ring. Rates of cleavage of the pendant Si–N bonds is sufficiently rapid that very little ring cleavage occurs under the conditions of the experiments. It is noteworthy that an excess of ethanol was required to completely displace the amine substituents, but even under these conditions, the ethoxy derivative was obtained in a 73% conversion. The hydroxy derivative was somewhat unstable, and was most conveniently prepared in small quantities by hydrolysis of an amine intermediate under heterogeneous conditions.

Characteristic bands in the IR and NMR spectra of these compounds are very useful in verifying the *N,N'*-disilylcyclodisilazane structure. The NMR spectra are characterized by two resonance peaks. One peak, which is observed at τ 9.95 to 10.05 [except in compounds (I), (X), (XIII), (XVII), and (XX); X=Cl, NHC_6H_5, C_6H_5, OC_6H_5, and $OCOCH_3$], which can be assigned to the pendant silylmethyl protons. The other peak occurs at τ 9.64 to 9.79, but is most often found between τ 9.76 and 9.79. The downfield shifts occur mostly in substances in which electron withdrawing groups are substituted on the pendant silicon atoms, requiring that the effect be transmitted through a silicon–nitrogen bond to the ring. Specific bands for each compound are summarized in Table 1.



(R=R'=CH_3)

TABLE 1

IR AND NMR DATA FOR *N,N'*-DISILYLCYCLODISILAZANES

Compound No.	X	Proton chemical shifts (ppm)		Si_2N asymmetric stretch frequencies (cm^{-1})
		τ(Si–R)	τ(Si–R')	
(I)	Cl	9.64	9.64	878, 1038
(V)	NH_2	10.02	9.76	895, 1033
(VI)	$NHCH_3$	10.05	9.77	833, 1028
(VII)	$N(CH_3)_2$	10.01	9.78	881, 1034
(VIII)	$N(C_2H_5)_2$	10.02	9.78	875, 1008 and/or 1037
(IX)	NC_5H_{10}	10.02	9.77	889, 1008 and/or 1036
(X)	$NH(C_6H_5)$	9.79	9.77	898, 1026
(XI)	H	9.95[a]	9.77	896, 1040
(XII)	CH_3	10.02	9.79	885, 1028
(XIII)	C_6H_5	9.88	9.72	878, 1020 and/or 1032
(XIV)	OCH_3	10.03	9.76	882, 1027
(XV)	OC_2H_5	10.03	9.76	879, 1021
(XVI)	$OCH(CH_3)_2$	10.00	9.73	885, 1008 and/or 1040(sh)
(XVII)	OC_6H_5	9.80	9.70	876, 1038
(XVIII)	$OSi(CH_3)_2(C_6H)_5$	10.02	9.78	894, 1012
(XIX)	OH[b]	10.05	9.77	891, 1028
(XX)	$OCOCH_3$	9.80	9.70	872, 1013 and/or 1038

[a] Doublet, $J=3.5$ Hz. [b] In diethyl ether.

Two asymmetric stretch frequencies were observed as very strong bands in the IR at about 880–895 cm^{-1} and at 1010–1040 cm^{-1}. The consistency with which these bands are observed justifies their assignment to the group. The two bands have been assigned by Buerger[8] as two of the six possible vibrational modes for the Si_4N_2 structure. No absorptions, except those assignable to other groups, were observed in the 900–1000 cm^{-1} region. In several of the substances, two bands were observed in the 1000–1040 cm^{-1} region. One or both of these bands may be related to the cyclodisilazane structure. Buerger[8] and Fink[9] have reported considerably different IR absorption peaks for compound (XII) (X=CH_3). In this work, a spectrum was obtained that was in close agreement to the one reported by Buerger.

Should compound (I) (X=Cl) undergo an equilibrium redistribution reaction, it could be expected to thermally disproportionate with the formation of dichlorodimethylsilane and a cyclodisilazane oligomer. However, when (I) was heated at 245° for 240 h, no dichlorodimethylsilane distilled, and most of the (I) could be recovered. Many of the other cyclodisilazane derivatives showed exceedingly good heat stability when they were heated at a temperature close to their normal boiling point, both in the presence and absence of catalysts. When compounds (XIV), (XV), (XVI), and (XVII) (X=OCH_3, OC_2H_5, OC_3H_7, and OC_6H_5) were heated in the presence of 1 wt.% of ammonium sulfate for 24 h, no change occurred. Compound (XI) (X=H) did not change under similar conditions in the presence of quinoline.

When (V) (X=NH_2) was heated with ammonium sulfate for 24 h at 200°, decomposition occurred with the formation of a mixture of products of which 15% was identified as 2,2,4,4,6,6-hexamethylcyclotrisilazane. Although the pure compound could be heated rapidly to its normal boiling point (236°) under the conditions of differential thermal analysis with no evidence for decomposition, some decomposition occurred when compound was heated at 200° for 24 h as evidenced by the formation of a weak absorption band at 940 cm^{-1} in the IR spectrum. Even after this period, however, relatively little change had occurred in the spectrum, and the 940 cm^{-1} was weak with respect to 880 cm^{-1} band. When *N,N'*-bis[dimethyl(methylamino)silyl]-tetramethylcyclodisilazane was heated at 175° with ammonium sulfate, ring expansion accounted for a larger portion of the product. About 38% of the monomer was converted to 1,2,2,4,4,5,6,6,8,8-decamethylcyclotetrasilazane.

EXPERIMENTAL

Reactions were carried out in glass equipment that had been flame-dried and flushed with dry nitrogen before use. Reactants were protected from atmospheric moisture with Drierite-packed tubes or a positive pressure of dry nitrogen as needed. Analysis were by Spang Microanalytical Laboratory. IR spectra were determined with a Perkin–Elmer Infracord spectrophotometer and NMR spectra were determined with a Varian Associates Model A60 spectrometer with cyclohexane as an internal standard.

Preparation of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (I)

After a mixture of 158 g (0.72 mole) of 2,2,4,4,6,6-hexamethylcyclotrisilazane and 139 g (1.08 moles) of dichlorodimethylsilane was heated at 175° for 77 h and cooled, the residue crystallized. To this residue was added 200 ml of petroleum ether, b.p. 30–60° and the soluble portion was decanted away from the insoluble ammonium chloride. Fractional distillation gave a series of fractions, 160 g (60%), between 151–166° (45 mm) having an overall purity of 96% *N,N'*-bis(chlorodimethylsilyl)-tetramethylcyclodisilazane by GLC. A centercut, b.p. 153–154° (45 mm), m.p. 66–67°, was characterized. (Found: C, 28.82; H, 7.26; Cl, 21.42; N, 8.51; Si, 33.97. $C_8H_{24}Cl_2$-

N_2Si_4 calcd.: C, 28.98; H, 7.30; Cl, 21.39; N, 8.45; Si, 33.89%.) [Lit.[7]: b.p. 116–118° (10 mm), m.p. 69–70°.] 1,3-Dichloro-1,1,3,3-tetramethyldisilazane (II), b.p. 94° (45 mm) could be separated from the lower boiling portion of the distillate, but 1,5-dichloro-1,1,3,3,5,5-hexamethyltrisilazane could not be separated. 2,2,4,4,6,6,8,8-Octamethylcyclotetrasilazane was used equally well in the synthesis, provided the stoichiometry was suitably adjusted.

Isolation of 1,5-bis(methylamino)-1,1,3,3,5,5-hexamethyltrisilazane

In a similar equilibration reaction of 35.0 g (0.16 mole) of 2,2,4,4,6,6-hexamethylcyclotrisilazane and 31.0 g (0.24 mole) of dichlorodimethylsilane, in which the reactants were heated at 150° for 43 h, the petroleum ether-soluble portion of the product was added to 33.5 g (excess) methylamine in petroleum ether, which was cooled in an acetone/Dry Ice bath, the mixture was warmed to room temperature, the amine salts were filtered off, the solvent was evaporated and the remaining material was fractionally distilled. In addition to *N,N'*-bis[dimethyl(methylamino)silyl]-tetramethylcyclodisilazane, 12.8 g of 1,5-bis(methylamino)-1,1,3,3,5,5-hexamethyltrisilazane, b.p. 64° (8 mm), n_D^{20} 1.4409, NMR peaks (CCl_4) at τ 7.54 (6 H doublet, *J* 6 Hz, NCH_3) and at τ 9.96 and 10.01 [two singlets, 18 H total, $Si(CH_3)_2$], was separated. (Found: C, 36.19; H, 10.82; N, 21.17; Si, 31.45. $C_8H_{28}N_4Si_3$ calcd.: C, 36.31; H, 10.66; N, 21.17; Si, 31.85%.)

Isolation of N-[3-(dimethylamino)-1,1,3,3-tetramethyldisilazanyl]-N'-[(dimethylamino)-dimethylsilyl]tetramethylcyclodisilazane

A residue (32.3 g), which had been obtained from a distillation of *N,N'*-bis-(chlorodimethylsilyl)tetramethylcyclodisilazane after the compound was prepared by the usual equilibration procedure, was dissolved in 50 ml of petroleum ether, b.p. 35–60°, and added to 50 ml of condensed dimethylamine in 50 ml of petroleum ether cooled in an acetone/Dry Ice bath. After an additional 100 ml of petroleum ether was added, the mixture was warmed to room temperature, filtered, the solvent was evaporated, and the remaining material was fractionally distilled to obtain 12.5 g of *N*-[3-(dimethylamino)-1,1,3,3-tetramethyldisilazanyl]-*N'*-[(dimethylamino)dimethylsilyl]tetramethylcyclodisilazane, b.p. 108–109° (0.5 mm), n_D^{20} 1.4554. (Found: C, 40.00; H, 10.31; N, 16.67; Si, 33.18; mol.wt. cryoscopically in benzene, 425. $C_{14}H_{43}N_5Si_5$ calcd.: C, 39.84; H, 10.27; N, 16.60; Si, 33.29%; mol.wt., 422.)

Preparation of N,N'-bis(aminodimethylsilyl)tetramethylcyclodisilazane (V)

To a stirred solution of 30 ml (excess) of ammonia in 50 ml of petroleum ether, b.p. 35–60°, cooled in acetone/Dry Ice bath, was added 28.6 g (0.086 mole) of *N,N'*-bis-(chlorodimethylsilyl)tetramethylcyclodisilazane in 50 ml of petroleum ether. After the mixture was warmed to room temperature, stirred overnight, the salts filtered off, and the solvent evaporated, fractional distillation gave 14.9 g (69%) of *N,N'*-bis-(aminodimethylsilyl)tetramethylcyclodisilazane, b.p. 95° (5 mm). After redistillation on a spinning band column, the m.p. was 36–38°. (Found: C, 32.67; H, 9.48; N, 19.06; Si, 38.24. $C_8H_{28}N_4Si_4$ calcd.: C, 32.83; H, 9.64; N, 19.15; Si, 38.39%.) (Lit.[7]: m.p. 35–36°.)

Preparation of N,N'-bis[dimethyl(methylamino)silyl]tetramethylcyclodisilazane (VI)

By the procedure for the preparation of *N,N'*-bis(aminodimethylsilyl)-

tetramethylcyclodisilazane, 62.8 g (0.19 mole) of *N,N'*-bis(chlorodimethylsilyl)-tetramethylcyclodisilazane and excess methylamine gave 44.1 g (73%) of *N,N'*-bis-[dimethyl(methylamino)silyl]tetramethylcyclodisilazane, b.p. 108–109° (5 mm), n_D^{20} 1.4517. (Found: C, 37.37; H, 10.09; N, 17.52; Si, 35.16. $C_{10}H_{32}N_4Si_4$ calcd.: C, 37.45; H, 10.06; N, 17.47; Si, 35.03%.) [Lit.[7]: b.p. 122° (10 mm) n_D^{20} 1.4508.]

Preparation of N,N'-bis[(dimethylamino)dimethylsilyl]tetramethylcyclodisilazane (VII)

By the procedure for the preparation of *N,N'*-bis(aminodimethylsilyl)tetramethylcyclodisilazane, 27.3 g (0.083 mole) of *N,N'*-bis(chlorodimethylsilyl)tetramethylcyclodisilazane and excess dimethylamine gave 20.3 g (70%) of *N,N'*-bis-[(dimethylamino)dimethylsilyl]tetramethylcyclodisilazane, b.p. 113–114° (4 mm), n_D^{20} 1.4530. (Found: C, 41.37; H, 10.46; N, 16.04; Si, 32.08. $C_{12}H_{36}N_4Si_4$ calcd.: C, 41.32; H, 10.40; N, 16.06; Si, 32.21.) [Lit.[7]: b.p. 135° (10 mm), n_D^{20} 1.4510.]

Preparation of N,N'-bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane (VIII)

To 18.6 g (0.25 mole) of freshly distilled diethylamine in 75 ml of petroleum ether, b.p. 60–90°, was added 159 ml of 1.6 *M* butyllithium in hexane while the temperature was maintained below 30°. Subsequently, the mixture was treated with 42.0 g (0.127 mole) of *N,N'*-bis(chlorodimethylsilyl)tetramethylcyclodisilazane in 75 ml of petroleum ether, refluxed 2 h, cooled, and filtered. Evaporation of the solvent from the filtrate and fractional distillation gave 26.3 g (51%) of *N,N'*-bis[(diethylamino)-dimethylsilyl]tetramethylcyclodisilazane, b.p. 83° (0.1 mm), n_D^{20} 1.4590. (Found: C, 47.51; H, 10.80; N, 14.02; Si, 27.68. $C_{16}H_{44}N_4Si_4$ calcd.: C, 47.46; H, 10.95; N, 13.84; Si, 27.75%.) [Lit.[5]: b.p. 164° (12 mm), n_D^{20} 1.4584.]

Preparation of N,N'-bis(dimethylpiperidinosilyl)tetramethylcyclodisilazane (IX)

By a procedure similar to the one used in the preparation of *N,N'*-bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane, 10.2 g (0.12 mole) of piperidine in 50 ml of petroleum ether, 75 ml of 1.6 *M* butyllithium in hexane, and 20.0 g (0.61 mole) of *N,N'*-bis(chlorodimethylsilyl)tetramethylcyclodisilazane in 50 ml of petroleum ether gave 17.8 g (70%) of *N,N'*-bis(dimethylpiperidinosilyl)tetramethylcyclodisilazane, b.p. 142–144° (0.10 mm), m.p. 42–43°. (Found: C, 50.45; H, 10.20; N, 13.09; Si, 26.02. $C_{18}H_{44}N_4Si_4$ calcd.: C, 50.40; H, 10.34; N, 13.06; Si, 26.19%.)

Preparation of N,N'-bis(anilinodimethylsilyl)tetramethylcyclodisilazane (X)

After a solution of 17.7 g (0.19 mole) of aniline in 200 ml of petroleum ether, b.p. 60–90°, was treated with 15.7 g (0.048 mole) of *N,N'*-bis(chlorodimethylsilyl)-tetramethylcyclodisilazane in 60 ml of petroleum ether and the mixture was refluxed for 1 h and filtered, evaporation of the filtrate gave 17.6 g (84%) of a crude product containing considerable aniline hydrochloride. Three recrystallizations from petroleum ether afforded 5.0 g (24%) of *N,N'*-bis(anilinodimethylsilyl)tetramethylcyclodisilazane, m.p. 106–107°. (Found: C, 53.68; H, 7.97; N, 12.57; Si, 25.19. $C_{20}H_{36}N_4Si_4$ calcd.: C, 53.99; H, 8.16; N, 12.59; Si, 25.26%.)

By an alternate method, 2.62 g (0.010 mole) of *N,N'*-bis(dimethylsilyl)tetramethylcyclodisilazane, 1.86 g (0.020 mole) of aniline, and 30 mg of sodium hydride was heated to 110° over a 3 h period. Hydrogen evolution began vigorously at 46° and was complete at 110°. The mixture, dissolved in 10 ml of petroleum ether, was filtered, concentrated, and fractionally distilled to obtain 1.0 g (24%) of a fraction boiling at 170–174° (0.02 mm) that was chiefly *N*,*N'*-bis(anilinodimethylsilyl)tetramethylcyclodisilazane.

In a third procedure after 4.2 g (0.045 mole) of aniline in 50 ml of dry ether was treated with 28 ml of 1.6 *M* buthyllithium in hexane and then with 7.5 g (0.022 mole) of *N*,*N'*-bis(chlorodimethylsilyl)tetramethylcyclodisilazane in 50 ml of dry ether and the mixture was refluxed 1 h, filtration gave 2.2 g (calcd. 1.9 g) of lithium chloride. Evaporation of the filtrate gave 10.4 g (calcd. 10.0 g) of the impure anilino derivative, m.p. 85–100°, from which 6.5 g (65%) of *N*,*N'*-bis(anilinodimethylsilyl)tetramethylcyclodisilazane, m.p. 104–106°, was obtained after recrystallization from petroleum ether, b.p. 60–90°.

Preparation of N,N'-bis(dimethylsilyl)tetramethylcyclodisilazane (XI)

After 3.9 g (0.102 mole) of lithium aluminum hydride in 250 ml of dry ether was treated with 33.8 g (0.102 mole) of *N*,*N'*-bis(chlorodimethylsilyl)tetramethylcyclodisilazane in 100 ml of dry ether while the mixture was maintained below 30°, stirring was continued overnight, the mixture was filtered, and the ether was removed at reduced pressure. A preliminary distillation of the residue under reduced pressure gave 22.6 g of distillate boiling at 37–39°, which was redistilled to obtain 17.4 g (65 %) of *N*,*N'*-bis(dimethylsilyl)tetramethylcyclodisilazane, b.p. 79° (14 mm), n_D^{20} 1.4309. (Found: C, 36.50; H, 9.96; N, 10.77; Si, 42.51. $C_8H_{26}Si_4N_2$ calcd.: C, 36.58; H, 9.98; N, 10.67; Si, 42.77 %.) [Lit.[7]: b.p. 73° (10 mm), n_D^{20} 1.4308.]

Preparation of N,N'-bis(trimethylsilyl)tetramethylcyclodisilazane (XII)

A solution of 63.3 g (0.192 mole) of *N*,*N'*-bis(chlorodimethylsilyl)tetramethylcyclodisilazane in 150 ml of dry tetrahydrofuran was treated with 154 ml (0.463 ml) of 3 *M* methylmagnesium bromide in ether, the ether was distilled out, and the mixture was refluxed overnight. After the remaining solvent was distilled out, the residue was treated with 70 ml of petroleum ether, b.p. 60–90°, filtered, and the filtrate was evaporated. Fractional distillation gave 46.8 g (84%) of *N*,*N'*-bis(trimethylsilyl)tetramethylcyclodisilazane, b.p. 74° (5 mm), m.p. 42–44°. The product still contained a trace of chlorine. (Found: C, 41.35; H, 10.20; N, 9.50; Si, 38.48. $C_{10}H_{30}N_2Si_4$ calcd.: C, 41.31; H, 10.40; N, 9.64; Si, 38.65%.) [Lit.[5]: b.p. 85° (7 mm), m.p. 39°.]

The preparation was also carried out with excess methyllithium. When stoichiometric quantities of the organometallic reagents were used, the products contained a substantial proportion of unchanged chlorodimethylsilyl groups.

Preparation of N,N'-bis(dimethylphenylsilyl)tetramethylcyclodisilazane (XIII)

To a solution of 17.4 g (0.053 mole) of *N*,*N'*-bis(chloromethylsilyl)tetramethylcyclodisilazane in 60 ml of benzene was added a solution prepared from 12.9 g (0.11 mole) of *N*,*N*,*N'*,*N'*-tetramethylethylenediamine in 75 ml of benzene and 55 ml of 2 *M* (0.11 mole) phenyllithium in ether/benzene solution. After the mixture was refluxed for 2 h and filtered, the solvent was evaporated and fractional distillation gave 7.4 g (34%) of material, which after two recrystallizations from n-pentane afforded 2.3 g (18%) of *N*,*N'*-bis(dimethylphenylsilyl)tetramethylcyclodisilazane, m.p. 63–64°. (Found: C, 58.00; H, 8.26; N, 6.77; Si, 27.11. $C_{20}H_{34}N_2Si_4$ calcd.: C, 57.90; H, 8.27; N, 6.75; Si, 27.08%.) [Lit.[5]: b.p. 133° (0.03 mm), m.p. 62°.]

Similar results were obtained when the tetramethylethylenediamine was omitted from the procedure. Use of phenylmagnesium bromide resulted in a 75% recovery of the *N,N'*-bis(chlorodimethylsilyl)tetramethylcyclodisilazane.

Preparation of N,N'-bis(dimethylmethoxysilyl)tetramethylcyclodisilazane (XIV)

A solution containing 8.85 g (0.030 mole) of *N,N'*-bis(aminodimethylsilyl)-tetramethylcyclodisilazane and 1.94 g (0.061 mole) of methanol in 34 g of 95/10 mixture of petroleum ether and acetone was refluxed overnight. After the solvent was removed, fractional distillation gave 7.7 g (79%) of *N,N'*-bis(dimethylmethoxysilyl)-tetramethylcyclodisilazane, b.p. 104–106° (6 mm), n_D^{20} 1.4368. (Found: C, 37.32; H, 9.24; N, 8.90; Si, 34.61. $C_{10}H_{30}N_2O_2Si$ calcd.: C, 37.21; H, 9.37; N, 8.68; Si, 34.82%.) [Lit.[7]: b.p. 62° (0.2 mm), n_D^{20} 1.4340.]

Preparation of N,N'-bis(ethoxydimethylsilyl)tetramethylcyclodisilazane (XV)

After a solution of 9.95 g (0.034 mole) of *N,N'*-bis(aminodimethylsilyl)tetramethylcyclodisilazane and 3.14 g (0.068 mole) of ethanol in 54 g of petroleum ether, b.p. 60–90°, was refluxed overnight, fractional distillation gave a series of fractions still containing *N,N'*-bis(aminodimethylsilyl)tetramethylcyclodisilazane. The fractions were recombined and refluxed with an additional 3.14 g of ethanol in 39 ml of petroleum ether. A second fractional distillation gave 9.0 g (73 %) of *N,N'*-bis(ethoxydimethylsilyl)tetramethylcyclodisilazane, b.p. 115–116°, n_D^{20} 1.4332. (Found: C, 41.22; H, 9.91; N, 8.31; Si, 31.84. $C_{12}H_{34}N_2O_2Si_4$ calcd.: C, 41.09; H, 9.77; N, 7.99; Si, 32.03%.)

Preparation of N,N'-bis(dimethylisopropoxysilyl)tetramethylcyclodisilazane (XVI)

Impure *N,N'*-bis(chlorodimethylsilyl)tetramethylcyclodisilazane, dissolved in 250 ml of petroleum ether which through error contained isopropyl alcohol, was added to a solution of 50 ml of dimethylamine in 100 ml of petroleum ether while the mixture was cooled in a Dry Ice/isopropyl alcohol bath. After the salts were filtered off and the solvent evaporated, fractional distillation gave 14.9 g of *N,N'*-bis(dimethylisopropoxysilyl)tetramethylcyclodisilazane, b.p. 85° (1 mm), n_D^{20} 1.4298. (Found: C, 44.82; H, 10.07; N, 7.52; Si, 29.97. $C_{14}H_{38}N_2O_2Si_4$ calcd.: C, 44.38; H, 10.11; N, 7.39; Si, 29.66%.)

Preparation of N,N'-bis(dimethylphenoxysilyl)tetramethylcyclodisilazane(XVII)

To a solution of 23.7 g (0.068 mole) of *N,N'*-bis[(dimethylamino)dimethylsilyl]tetramethylcyclodisilazane in 150 ml of petroleum ether, b.p. 60–90°, was added 13.1 g (0.14 mole) of phenol in 40 ml of toluene and the mixture was refluxed for 2 h. After the solvent was distilled, fractional distillation gave 19.8 g (64%) of *N,N'*-bis-(dimethylphenoxysilyl)tetramethylcyclodisilazane, b.p. 147–149° (0.02 mm), m.p. 44–45°. (Found: C, 53.82; H, 7.52; N, 6.22; Si, 25.06. $C_{20}H_{34}N_2O_2Si_4$ calcd.: C, 53.76; H, 7.67; N, 6.27; Si, 25.14%.)

An attempt to prepare the compound by treating *N,N'*-bis(chlorodimethylsilyl)tetramethylcyclodisilazane with phenol in the presence of pyridine resulted in the recovery of 43% of the *N,N'*-bis(chlorodimethylsilyl)tetramethylcyclodisilazane.

Preparation of N,N'-bis(tetramethyl-3-phenyldisiloxanyl)tetramethylcyclodisilazane (XVIII)

After 11.8 g (0.034 mole) of *N,N'*-bis[(dimethylamino)dimethylsilyl]tetramethylcyclodisilazane in 35 ml of toluene was added to 10.3 g (0.068 mole) of dimethylphenylsilanol in 35 ml of toluene, the solution was heated at 80° for 1 h, cooled, the solvent was evaporated, and the remaining material was fractionally distilled. There was collected 12.6 g (66%) of *N,N'*-bis(tetramethyl-3-phenyldisiloxanyl)tetramethylcyclodisilazane, b.p. 178–180° (0.02 mm), n_D^{20} 1.4869. (Found: C, 51.00; H, 8.12; N, 4.88; Si, 29.37. $C_{24}H_{46}N_2O_2Si_6$ calcd.: C, 51.18; H, 8.23; N, 4.98; Si, 29.93%.)

Preparation of N,N'-bis(hydroxydimethylsilyl)tetramethylcyclodisilazane (XIX)

A solution of 4.26 g (0.015 mole) of *N,N'*-bis(aminodimethylsilyl)tetramethylcyclodisilazane in 57 ml of ether saturated with water was refluxed 20 h and the solvent was evaporated. Recrystallization of the residue from petroleum ether, b.p. 60–90°, gave 1.5 g (36%) of *N,N'*-bis(hydroxydimethylsilyl)tetramethylcyclodisilazane, m.p. 123–124°. (Found: C, 32.94; H, 8.76; N, 9.48; Si, 38.20. $C_8H_{26}N_2O_2Si_4$ calcd.: C, 32.60; H, 8.89; N, 9.50; Si, 38.13%.)

The compound could also be conveniently prepared by spreading a film of *N,N'*-bis(aminodimethylsilyl)tetramethylcyclodisilazane on a glass plate and exposing the compound to atmospheric moisture. When the liquid solidified, the *N,N'*-bis(hydroxydimethylsilyl)tetramethylcyclodisilazane could be purified by recrystallization and obtained in yields of 40–50%.

Preparation of N,N'-bis(acetoxydimethylsilyl)tetramethylcyclodisilazane (XX)

When a solution of 10.1 g (0.031 mole) of *N,N'*-bis(chlorodimethylsilyl)tetramethylcyclodisilazane and 5.5 g (0.80 mole) of pyridine in 100 ml of dry ether was treated with 3.66 g (0.061 mole) of glacial acetic acid in 20 ml of ether and the mixture was refluxed 1 h, filtered, and the solvent was distilled, fractional distillation gave 5.4 g (47%) of *N,N'*-bis(acetoxydimethylsilyl)tetramethylcyclodisilazane, b.p. 95–97° (0.2 mm), m.p. 49–52°. (Found: C, 37.89; H, 7.92; N, 7.22; Si, 29.44. $C_{12}H_{30}N_2O_4Si_4$ calcd.: C, 38.05; H, 7.98; N, 7.39; Si, 29.67%.)

Preparation of 1,2,2,4,4,5,6,6,8,8-*decamethylcyclotetrasilazane*

When a mixture of 3.2 g (0.010 mole) of *N,N'*-bis[dimethyl(methylamino)silyl]tetramethylcyclodisilazane and 1 wt.% ammonium sulfate was heated at 175° for 20 h and the product was distilled, 1.2 g (38%) of 1,2,2,4,4,5,6,6,8,8-decamethylcyclotetrasilazane, b.p. 86–90° (12 mm), n_D^{20} 1.4479, NMR peaks (CCl_4) at 7.60 (6 H singlet, NCH_3) and 9.95 [24 H singlet, $Si(CH_3)_2$], IR bands at 3440 cm^{-1} (NH), 1247 ($SiCH_3$) 1158 cm^{-1} (Si_2NH), and 1060 cm^{-1} (CN) and 927 cm^{-1} (Si_2N), was obtained. (Found: C, 37.26; H, 10.16; N, 17.36; Si, 34.96. $C_{10}H_{32}N_4Si_4$ calcd.: C, 37.44; H, 10.06; N, 17.47; Si, 35.03%.)

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