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FUNCTIONALLY SUBSTITUTED TRISILYLAMINE DERIVATIVES

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INTRODUCTION

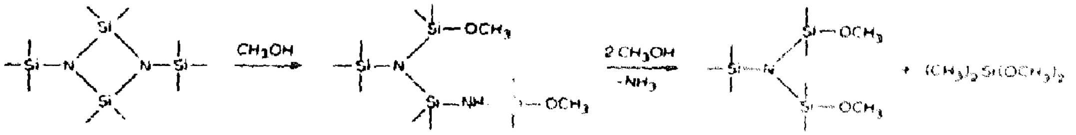
Recently, we described a preparative method for the synthesis of *N,N'*-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (I) and reported procedures for the conversion of (I) into other functionally substituted cyclodisilazanes as well as tetramethyl-*N,N'*-bis(trimethylsilyl)cyclodisilazane[1] (II). For example, *N,N'*-bis(aminodimethylsilyl)tetramethylcyclodisilazane (III), which was prepared from (I) and ammonia, afforded *N,N'*-bis(dimethylmethoxysilyl)tetramethylcyclodisilazane when it was treated with two moles of methanol in a petroleum ether/acetone mixture. Similar synthetic procedures have also been reported recently by Silbiger, Fuchs, and Gesundheit[2] and by Wannagat[3].

Among the properties of the cyclodisilazane derivatives that we have examined are their reactions with alcohols and water. In the course of solvolysis studies, it became apparent that although the cyclodisilazane ring could be cleaved by these reagents, the derivative trisilylamine was much more stable. This finding provided a synthetic access to di- and trifunctionally substituted trisilylamines. It has also been recently reported by others that (I) can be cleaved with a stoichiometric quantity of hydrogen chloride at low temperature to obtain tris(chlorodimethylsilyl)amine[4].

In this paper, the preparation of a number of functionally substituted trisilylamines by the cleavage of cyclodisilazanes and cyclotrisilazanes by a variety of reagents is described, and the properties of these compounds are reported.

RESULTS

When (III) was refluxed with a large molar excess of methanol (16 : 1), the chief product was tris(dimethylmethoxysilyl)amine (IV). A similar alcoholysis procedure proved successful in preparing the unsymmetrical bis(methoxydimethylsilyl)(trimethylsilyl)amine (V) from (II). Stoichiometric quantities of phenol and acetic acid in homogeneous solutions with (II) were also used to prepare bis(dimethylphenoxysilyl)(trimethylsilyl)amine (VI) and bis(acetoxydimethylsilyl)(trimethylsilyl)amine (VII). The cleavage of (II) with methanol can be represented as follows:



Difunctional trisilylamines, (V) and bis(ethoxydimethylsilyl)(trimethylsilyl)amine (VIII), were equally well obtained by the methanolysis and ethanolysis of *N*-(trimethylsilyl)hexamethylcyclotrisilazane (IX), which can be prepared by a single step procedure from hexamethylcyclotrisilazane and chlorotrimethylsilane in the presence of sodium and styrene[5]. When the stoichiometry was very carefully controlled, hydrogen chloride cleavage was effective in preparing bis(chlorodimethylsilyl)(trimethylsilyl)amine (X) from either (II) or (IX). (X) was readily converted to bis(dimethylsilyl)(trimethylsilyl)amine (XI) with lithium aluminum hydride and to bis[(dimethylamino)dimethylsilyl](trimethylsilyl)amine (XII) with dimethylamine.

Similarly, the hydrogen chloride cleavage of *N*-(dimethylphenylsilyl)hexamethylcyclotrisilazane (XIII) gave bis(chlorodimethylsilyl)(dimethylphenylsilyl)amine (XIV). Presumably, (XIV) could also have been prepared by the cleavage of *N*,*N'*-bis(dimethylphenylsilyl)tetramethylcyclodisilazane (XV), but condensation of phenyllithium and (I) had afforded only very low conversions to (XV). (XIII) could readily be obtained in high yields from hexamethylcyclotrisilazane and chlorodimethylphenylsilane in the presence of sodium and styrene, but the products were frequently contaminated with 1,4-diphenylbutane, which could not always be completely removed by fractional distillation. (XIV) and dimethylamine gave *N*,*N'*-bis[(dimethylamino)dimethylsilyl](dimethylphenylsilyl)amine (XVI).

An ammonia derivative of (X) could not be prepared. When (X) was treated with ammonia, the only product that could be unequivocally identified was hexamethylcyclotrisilazane. On the other hand methylamine gave unexpectedly as a part of the product a four-membered ring compound, pentamethyl-*N*-(trimethylsilyl)cyclodisilazane (XVII), in yields between 30 and 50% at temperatures between −20° and −60°. A higher boiling product with an elemental analysis corresponding to bis[dimethyl(methylamino)silyl](trimethylsilyl)amine was obtained, but its NMR spectrum did not verify this structural assignment. Similar procedures gave *N*-ethyltetramethyl-*N'*-(trimethylsilyl)cyclodisilazane (XVIII), tetramethyl-*N*-phenyl-*N'*-(trimethylsilyl)cyclodisilazane (XIX), and *N*-(dimethylphenylsilyl)pentamethylcyclodisilazane (XX). A higher boiling by-product was isolated in each experiment.

Two trisilylamine derivatives were prepared by a method described by Lehn[6], the condensation of lithium nitride and a silicon chloride in tetrahydrofuran. Lithium nitride and chlorodimethylethoxysilane gave tris(ethoxydimethylsilyl)amine (XXI), and lithium nitride and chlorodimethylphenylsilane gave tris(dimethylphenylsilyl)amine (XXII).

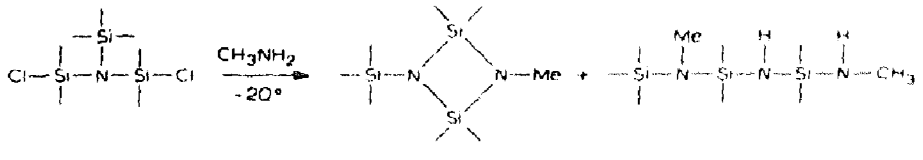
DISCUSSION

The conversion of (IX) to bis(alkoxydimethylsilyl)(trimethylsilyl)amines in yields above 80% by refluxing the compound for an extended period in the presence of a molar excess of alcohols clearly confirms the much greater solvolytic stability of the Si_3N group over the Si_2NH group. Comparative rates of alcoholysis of various silicon–nitrogen compounds were reported and discussed earlier[7]. The alcoholysis reactions of the cyclodisilazanes, however, indicate a lesser solvolytic stability for the trisilylamine structure when it occurs as a part of the cyclodisilazane ring. Thus, the first trisilylamine group is cleaved rapidly with consequent ring opening, but the remaining trisilylamine group in the open chain product is cleaved more slowly. The interpretation of reactions of silicon–nitrogen bonds involving protonation of cyclodisilazane nitrogen was discussed recently in terms of the high electron density on nitrogen in cyclodisilazane rings[8], particularly in the *N,N'*-dimethyl derivative. It is not surprising that the presence of the trisilylamine group in the highly strained ring also leads to a decrease in solvolytic stability. Moreover, it should be concluded that the reported stability of compound (II) against hydrolysis[8] is largely due to insosolubility in water.

Although the silyl halide group is rarely preferentially reduced in the presence of the silylamine group with lithium aluminum hydride, (X) could be reduced to (XI) in a 68 % yield. (I) can also be reduced to the corresponding hydride under similar conditions, but the yields in a number of experiments did not exceed 35 %.

Compound (X) reacted normally with dimethylamine to give the bis(dimethylamine) derivative. The chief product from methylamine, however, was a cyclodisilazane derivative, which was obtained when the condensation was carried out as low as −60°. Although cyclodisilazanes can be prepared at low temperatures by the condensation of the alkali metal derivatives of silicon–nitrogen compounds with appropriate chlorosilanes, their formation is frequently associated with higher temperature processes, thermolysis reactions of appropriate precursors or equilibrations of chlorine and nitrogen containing organosilicon derivatives[8]. The formation of the cyclodisilazane by the action of a free amine on a chlorosilicon compound at low temperatures has not been previously observed. The novelty of ring formation under these conditions is further emphasized by the fact that the product of condensing alkylamines and diorganodichlorosilanes at room temperature and below are silylamines, and although minor amounts of disilazanes have been observed, four-, six- or eight-membered ring compounds are not formed under these conditions. Ring formation is peculiarly associated with the $R_3SiN[Si(CH_3)_2Cl]_2$ structure, since $CH_3NSi(CH_3)_2Cl_2$ gives bis[dimethyl(methylamino)silyl]methylamine under the same conditions and no cyclic derivative.

Cyclic derivatives (XVIII), (XIX), and (XX) were also prepared under similar conditions from the corresponding compounds. Purification of the cyclic derivatives by fractional distillation afforded a second, higher boiling product, which in the condensation of (X) with methylamine, was identified as 1,1,3,3,4,5,5,5-octamethyl-1-(methylamino)trisilazane. Structurally, the compound is the silyl migration product



of bis[(methylamino)dimethylsilyl](trimethylsilyl)amine, which implies that the bis(methylamino) derivative was a part of the original reaction product. However, examination of the NMR spectra of undistilled products prepared at temperatures between −30° and +30° and by direct and inverse addition showed that the initial product was nearly entirely the cyclodisilazane. The linear product, then must have formed during the distillation by cleavage of the cyclodisilazane by residual methylamine hydrochloride. In the preparation of the *N*-phenylcyclodisilazane, aniline hydrochloride was extremely difficult to remove from the product mixture and only a small amount of the cyclodisilazane was isolated; however, a near quantitative yield was obtained by condensing (X) with the *N,N*-dilithium derivative of aniline.

Of the compounds examined, (XXII) was most stable against solvolysis by methanol. Although the compound could be prepared from lithium nitride and chlorodimethylphenylsilane, it could not be prepared via the metallation of 1,3-diphenyltetramethyldisilazane (XXIII). When (XXIII) was treated with butyllithium and subsequently with chlorodimethylphenylsilane, 73% of (XXIII) could be recovered.

(XXI) was also prepared by a lithium nitride condensation, but some cyclodisilazane, which could be detected in the infrared spectrum, contaminated the product. Although compound (IV) was decomposed by hydrolysis in aqueous alkali, a portion of (XXI), treated under the same conditions, could be recovered free of cyclodisilazane contamination.

Compounds (X) and (XII), like tris(trimethylsilyl)amine, were isolated as nearly transparent crystalline solids. Difficulties in obtaining satisfactory capillary melting points on these materials prompted an examination of their thermal characteristics by differential thermal analysis between $-100°$ and $+100°$. All three compounds exhibited, in addition to a melting transition with an abnormally low ΔS_m, a second transition at a lower temperature. ΔS_t was greater than ΔS_m by about an order of magnitude. The following are the observed transition and melting temperatures: Tris(trimethylsilyl)amine, $-29°$, $+62°$ to $+66°$; (X), $+3°$, $+68°$ to $+76°$; and (XII), $-10°$ to $-8°$, $+77°$ to $+85°$. The compounds therefore, in common with many other symmetrical substances, exhibit a meso-crystalline state (plastic crystals).

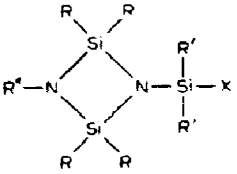
TABLE 1

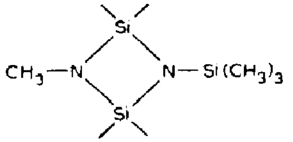
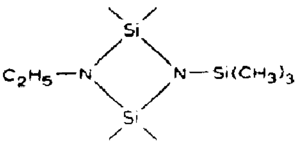
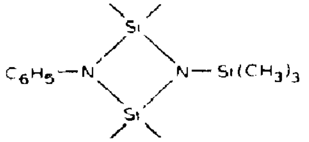
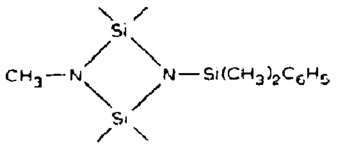
PROTON CHEMICAL SHIFTS IN TRISILYLAMINES $YR'_2SiN(SiR_2X)_2$
$R = R' = CH_3$

Compound	*Structure*	$\tau(R)$	$\tau(R')$	$\tau(X)$	$\tau(Y)$
	$N[Si(CH_3)_3]_3$	9.82			
(IV)	$N[Si(CH_3)_2OCH_3]_3$	9.87		6.66	
(V)	$(CH_3)_3SiN[Si(CH_3)_2OCH_3]_2$	9.84	9.84	6.63	
(VI)	$(CH_3)_3SiN[Si(CH_3)_2OC_6H_5]_2$	9.61	9.69	2.92–3.34 mult.	
(VII)	$(CH_3)_3SiN[Si(CH_3)_2OCOCH_3]_2$	9.60	9.67	8.00	
(VIII)	$(CH_3)_3SiN[Si(CH_3)_2OC_2H_5]_2$	9.86	9.86	8.83 trip. $J = 7$ cps	6.35 quad.
(X)	$(CH_3)_3SiN[Si(CH_3)_2Cl]_2$	9.38	9.67		
(XI)	$(CH_3)_3SiN[Si(CH_3)_2H]_2$	9.80 doub.	9.85	5.42 sept. $J = 3.5$ cps	
(XII)	$(CH_3)_3SiN[Si(CH_3)_2N(CH_3)_2]_2$	9.87	9.85	7.59	
(XIV)	$C_6H_5(CH_3)_2SiN[Si(CH_3)_2Cl]_2$	9.46	9.43	2.35–2.86 mult.	
(XVI)	$C_6H_5(CH_3)_2SiN[Si(CH_3)_2N(CH_3)_2]_2$	9.92	9.68	7.62	2.14–2.67 mult.
(XXI)	$N[Si(CH_3)_2OC_2H_5]_3$	9.84		8.50 trip. $J = 7$ cps	6.03 quad.
(XXII)	$N[Si(CH_3)_2C_6H_5]_3$	9.77		2.30–2.86 mult.	

TABLE 2

PROTON CHEMICAL SHIFTS IN *N*-SILYL-*N'*-ALKYLCYCLODISILAZANES



Compound	*Structure*	τ(*R*)	τ(*R'*)	τ(*R''*)	
(XVII)		9.85	10.04	7.55	
(XVIII)		9.83	10.05	7.18 quad *J* = 7 cps	8.97 trip
(XIX)		9.57	9.94	2.80–3.69 mult	
(XX)		9.87	9.72	7.53	

The proton chemical shifts observed in the NMR spectra of these compounds are reported in Tables 1 and 2. The value for the ring silyl-methyl protons in (XVII) (9.85) was intermediate between the value for (II) (9.79) and hexamethylcyclodisilazane (9.89)[8], and the value for (XX) (9.57) was intermediate between (II) (9.79) and *N*,*N'*-diphenyltetramethylcyclodisilazane (9.37)[8].

The infrared spectra of several of the unsymmetrical trisilylamines showed two discrete bands assignable to the two possible vibrational modes of the Si_2N asymmetric stretch. These bands were observed in the usual 900–950 cm^{-1} region. We had previously[1] observed two asymmetric stretch frequencies in *N*,*N'*-disilylcyclodisilazane derivatives, but both bands lay outside the 900–950 cm^{-1} region. A band at about 880–890 cm^{-1} seemed to be always associated with the cyclodisilazane ring and a second band at about 1025–1040 cm^{-1} seemed to be associated with the Si_2N group in which only the Si–N is part of a ring. The *N*-silyl-*N'*-alkylcyclodisilazanes show strong absorption at about 880 cm^{-1}, consistent with the presence of the cyclodisilazane ring, and exhibit a second strong band at 1060 cm^{-1}. Other *N*-alkyl silazane structures, for example nonamethylcyclotrisilazane, show a strong band in this region. We plan to publish the details of the infrared spectra of compounds in these series at a later date.

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. Analyses were by Spang Microanalytical Laboratory. Infrared 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 tris(methoxydimethylsilyl)amine, (IV)

After a solution of 16.6 g (0.057 mole) of *N,N'*-bis(aminodimethylsilyl)tetramethylcyclodisilazane in 40 ml of methanol was refluxed 16 h and fractionally distilled, 9.0 g (56%) of (IV), b.p. 71° (4 mm), m.p. −18°, n_D^{20} 1.4231, was obtained. (Found: C, 38.60; H, 9.62; N, 5.04; Si, 29.80. $C_9H_{27}NO_3Si_3$ calcd.: C, 38.39; H, 9.67; N, 4.97; Si, 29.92%.)

Preparation of bis(methoxydimethylsilyl)(trimethylsilyl)amine, (V)

After 17.9 g (0.062 mole) of tetramethyl-*N,N'*-bis(trimethylsilyl)cyclodisilazane was refluxed in 30 ml of methanol for 65 h, the cooled mixture was filtered to remove 0.2 g of ammonium chloride formed from chlorine-containing impurities in the starting material. Fractional distillation gave 6.3 g (38%) of (V), b.p. 84° (10 mm), m.p. −55°, n_D^{20} 1.4303. (Found: C, 40.64; H, 10.18; N, 5.33; Si, 31.50. $C_9H_{27}NO_2Si_3$ calcd.: C, 40.70; H, 10.25; N, 5.27; Si, 31.73%.)

When a solution of 22.5 g (0.077 mole) of hexamethyl-*N*-(trimethylsilyl)cyclotrisilazane and 37 ml of methanol was refluxed for 24 h, distillation gave 16.7 g (82%) of (V) boiling at 88–90° (12 mm), n_D^{20} 1.4322.

Preparation of bis(dimethylphenoxysilyl)(trimethylsilyl)amine, (VI)

A solution of 14.1 g (0.15 mole) of phenol in 25 ml of benzene was added in 1 h to 14.5 g (0.05 mole) of tetramethyl-*N,N'*-bis(trimethylsilyl)cyclodisilazane in 20 ml of benzene. The mixture, which was refluxed at 86° for 24 h, evolved ammonia after the first hour. Fractional distillation gave 11.9 g (61%) of (VI), b.p. 142–143° (0.03 mm), m.p. 38–40°. (Found: C, 58.69; H, 8.00; N, 3.62; Si, 21.49. $C_{19}H_{31}NO_2Si_3$ calcd.: C, 58.55; H, 8.02; N, 3.59; Si, 21.62%.)

Preparation of bis(acetoxydimethylsilyl)(trimethylsilyl)amine, (VII)

A solution of 14.4 g (0.05 mole) of tetramethyl-*N,N'*-bis(trimethylsilyl)cyclodisilazane in 25 ml of petroleum ether, b.p. 60–90°, was treated with 12.0 g (0.20 mole) of glacial acetic acid in 15 ml of petroleum ether in 0.5 h. The mixture was refluxed at 74° for 24 h. Filtration gave 2.8 g (73%) of ammonium acetate. After the filtrate was stripped of solvent, distillation gave 1.8 g of acetoxytrimethylsilane, b.p. 44–45° (79 mm), n_D^{20} 1.3890 (reported[10] n_D^{25} 1.3899), and 12.6 g of an impure product, b.p. 134–140° (12 mm). Redistillation gave 11.7 g (73%) of (VII), b.p. 138–140° (12 mm),

n_D^{20} 1.4422. (Found: C, 41.26; H, 8.58; N, 4.31; Si, 26.08. $C_{11}H_{27}NO_4Si_3$ calcd.: C, 41.08; H, 8.46; N, 4.36; Si, 26.20%.)

Preparation of bis(ethoxydimethylsilyl)trimethylsilylamine, (VIII)

A solution of 22.8 g (0.0785 mole) of *N*-(trimethylsilyl)hexamethylcyclotrisilazane in 35 ml of anhydrous ethanol was refluxed for 24 h. Distillation gave 19.4 g (84%) of (VIII) boiling at 98–100° (9 mm), n_D^{20} 1.4312. (Found: C, 45.04; H, 10.50; N, 4.88; Si, 28.80. $C_{11}H_{31}NO_2Si_3$ calcd.: C, 44.99; H, 10.64; N, 4.77; Si, 28.70%.)

Preparation of bis(chlorodimethylsilyl)(trimethylsilyl)amine, (X)

A solution of 14.5 g (0.05 mole) of tetramethyl-*N,N'*-bis(trimethylsilyl)cyclodisilazane in 75 ml of ether was cooled to −40°, and a solution of 7.3 g (0.20 mole) of anhydrous hydrochloric acid in 70 ml of dry ether was added in 0.5 h. After the mixture was maintained at −40° for an additional 1.5 h, it was allowed to warm to room temp. and stirred for 18 h. Filtration gave 3.6 g (133%) of ammonium chloride. The filtrate was stripped of ether and distilled to give 7.7 g (56%) of (X) boiling at 104–105° (12 mm); m.p. 68–70°. The yield in other experiments was 68–82%. (Found: C, 30.73, H, 7.69; Cl, 25.76; N, 4.94; Si, 30.52. $C_7H_{21}Cl_2NSi_2$ calcd.: C, 30.63; H, 7.7; Cl, 25.84; N, 5.11; Si, 30.71%.)

When 93.1 g (0.32 mole) of *N*-(trimethylsilyl)hexamethylcyclotrisilazane in 500 ml of ether was treated with 68.0 g (1.86 moles) of hydrogen chloride in 600 ml of ether at −40° in the same way and the product was distilled, 58.3 g (67%) of (X), b.p. 104–106° (12 mm), was obtained.

Preparation of bis(dimethylsilyl)(trimethylsilyl)amine, (XI)

To 1.9 g (0.05 mole) of lithium aluminum hydride in 100 ml of dry ether was added a solution of 13.7 g (0.05 mole) of bis(chlorodimethylsilyl)(trimethylsilyl)amine in 75 ml of ether in 1 h. After the mixture was stirred at 27° for 3 h, 150 ml of petroleum ether, b.p. 30–60°, was added, and the solid products were filtered off. The solvent was removed, and the liquid residue was distilled at reduced pressure and collected in an isopropyl alcohol/Dry Ice trap. Redistillation gave 7.0 g (68%) of (XI), b.p. 53° (12 mm), m.p. −48°, n_D^{20} 1.4309. (Found: C, 40.78; H, 11.16; N, 6.83; Si, 41.21. $C_7H_{23}NSi_3$ calcd.: C, 40.90; H, 11.28; N, 6.82; Si, 41.00%.)

Preparation of bis[(dimethylamino)dimethylsilyl](trimethylsilyl)amine, (XII)

To a stirred solution of 35 ml (excess) of dimethylamine in 50 ml of petroleum ether, b.p. 35–60°, cooled in an acetone/Dry Ice bath was added 27.6 g (0.10 mole) of bis(chlorodimethylsilyl)(trimethylsilyl)amine in 50 ml of petroleum ether. After the amine salts were filtered off and the solvent was evaporated, fractional distillation gave 24.2 g (81%) of (XII), b.p. 109–110° (7 mm), m.p. 79–82°. (Found: C, 45.14; H, 11.25; N, 14.30; Si, 29.00. $C_{11}H_{33}N_3Si_3$ calcd.: C, 45.30; H, 11.40; N, 14.41; Si, 28.89%.)

Preparation of N-(dimethylphenylsilyl)hexamethylcyclotrisilazane, (XIII)

To a refluxing mixture of 9.7 g (0.42 g-atom) of sodium in 225 ml of dioxane was added a solution of 83.5 g (0.381 mole) of hexamethylcyclotrisilazane and 50 ml of freshly distilled styrene in about 2 h. After being heated for 4 h, the mixture was cooled to 25°, and 72.9 g (0.41 mole) of chlorodimethylphenylsilane was added in 1 h. Subsequently, the mixture was refluxed for 2 h, cooled, filtered, and stripped of solvent. Distillation gave 95.4 g (71 %) of crude (XIII) boiling at 124–128° (1.0 mm).

An analytical sample of (XIII), b.p. 136–138° (0.88 mm), n_D^{20} 1.5098, NMR peaks (CCl_4), τ 2.30–2.74 (5 H, multiplet, C_6H_5), τ 9.63 (6 H, singlet, pendant $(CH_3)_2Si$) and τ 9.90 [18 H total, singlet, ring $(CH_3)_2Si$], was obtained after a careful distillation in a spinning band column. (Found: C, 47.78; H, 8.84; N, 11.82; Si, 31.52. $C_{14}H_{31}N_3Si_4$ calcd.: C, 47.53; H, 8.83; N, 11.85; Si, 31.76%.)

Preparation of bis(chlorodimethylsilyl)(dimethylphenylsilyl)amine, (XIV)

A solution of 23.5 g (0.0664 mole) of *N*-(dimethylphenylsilyl)hexamethylcyclotrisilazane in 100 ml of ether at −60° was treated with 14.5 g (0.40 mole) of anhydrous hydrogen chloride in 150 ml of ether in 1 h, stirred at −60° for 1 h, allowed to warm up to 25°, and stirred an additional hour. The mixture was filtered and stripped of solvent. Distillation gave 15.2 g (68 %) of (XIV) boiling at 138–141° (3 mm). The compound, which contained some diphenylbutane, was characterized by its IR and NMR spectra.

Preparation of N,N′-bis(dimethylphenylsilyl)tetramethylcyclodisilazane, (XV)

To 35.4 g (0.107 mole) of *N,N′*-bis(chlorodimethylsilyl)tetramethylcyclodisilazane in 60 ml of benzene was added 115 ml (0.234 mole) of 2 *M* phenyllithium in ether/benzene solution in 2.5 h. The mixture was refluxed 19 h and filtered. After the solvent was stripped off, distillation of the residue gave 11.4 g of crude (XV) boiling at 130–154° (0.012 mm), m.p. 50–63°. Recrystallization from petroleum ether (b.p. 60–90°) gave 4.1 g (9 %) of XV, m.p. 63–65°, NMR peaks (CCl_4) at τ 9.88 [12 H singlet, pendant $Si(CH_3)$], 9.72 [12 H singlet, ring $Si(CH_3)$], and 2.48–2.87 (10 H multiplet, C_6H_5). (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%.)

Preparation of bis[(dimethylamino)dimethylsilyl](dimethylphenylsilyl)amine, (XVI)

A solution of 25 ml (excess) of dimethylamine in 30 ml of petroleum ether, b.p. 35–60°, was cooled in Dry Ice/isopropyl alcohol bath and treated with 15 g (0.045 mole) of crude bis(chlorodimethylsilyl)(dimethylphenylsilyl)amine in 30 ml of petroleum ether. After the amine salts were filtered off and the solvents evaporated, fractional distillation gave 6.0 g of (XVI), b.p. 113–117° (0.3 mm) and 6.3 g, b.p. 120–122° (0.7 mm). The total yield was 78 %. The compound, which contained some diphenylbutane, was characterized by its IR and NMR spectra.

Preparation of pentamethyl-N-(trimethylsilyl)cyclodisilazane, (XVII)

A solution of 18.2 g (0.067 mole) of bis(chlorodimethylsilyl)(trimethylsilyl)amine in 25 ml of petroleum ether, b.p. 35–60°, was added dropwise to a solution of 20 ml (excess) of methylamine in 25 ml of petroleum ether, which was cooled in an isopropyl alcohol/Dry Ice bath. After the addition was complete, the mixture was warmed to room temperature, the amine salts were filtered off, and the solvent was evaporated. Fractional distillation gave 7.6 g (49 %) of (XVII), b.p. 52–53° (7 mm), n_D^{20} 1.4273, and 5.0 g (29 %) of 1,1,3,3,4,5,5,5-octamethyl-1-(methylamino trisilazane, b.p. 88° (7 mm), n_D^{20} 1.4437, NMR peaks (CCl_4) at τ 7.33 and 7.34 (6 H singlet and doublet, $J=6.5$ cps) and 9.92 and 9.97 (21 H total $SiCH_3$). (Found for fraction 1: C, 41.13; H, 10.47; N, 12.08; Si, 36.13; mol.wt., cryoscopically in benzene, 244. $C_8H_{24}N_2Si_3$ calcd.: C, 41.31; H, 10.40; N, 12.05; Si, 36.24%; mol.wt., 233.) (Found for fraction 2: C, 41.14; H, 11.16; N, 15.83; Si, 31.97. $C_9H_{29}N_3Si_3$ calcd.: C, 41.00; H, 11.09; N, 15.94; Si, 31.97%.)

Preparation of N-ethyltetramethyl-N'-(trimethylsilyl)cyclodisilazane, (XVIII)

A solution of 18.8 g (0.069 mole) of bis(chlorodimethylsilyl)(trimethylsilyl)amine in 25 ml of petroleum ether, b.p. 35–60°, was added to a solution of 18 ml (excess) of ethylamine in 25 ml of petroleum ether, which was maintained at −20° during the addition. After the mixture was warmed to room temp., the salts were filtered off and the solvent was evaporated. Fractional distillation gave 12.7 g (64%) of (XVIII), b.p. 61–62° (7 mm), n_D^{20} 1.4301. (Found: C, 43.76; H, 10.63; N, 11.42; Si, 34.17. $C_9H_{26}N_2Si_3$ calcd.: C, 43.83; H, 10.63; N, 11.36; Si, 34.17%.)

Preparation of tetramethyl-N-phenyl-N'-(trimethylsilyl)cyclodisilazane, (XIX)

A solution of 9.7 g (0.0354 mole) of bis(chlorodimethylsilyl)(trimethylsilyl)amine in 25 ml of ether was treated with a solution of 14.5 g (0.156 mole) of aniline in 25 ml of ether by dropwise addition. The precipitated aniline hydrochloride was filtered off and washed thoroughly with petroleum ether. The solvent was evaporated at room temperature. The solid residue was mixed with petroleum ether and filtered to remove the remaining aniline hydrochloride. The total weight of insoluble materials was 11.2 g. Evaporation of the petroleum ether extract gave 12.5 g of an oily residue, which was distilled, and about 1.0 g of crude (XIX) was collected at 100° (0.09 mm), m.p. 78–82°. The majority of the product distilled at 160–170° (0.2 mm). No cyclodisilazane could be isolated in a similar experiment when an attempt was made to effect purification by recrystallization.

A solution of 3.2 g (0.034 mole) of aniline in 50 ml of dry ether was treated with 43 ml (0.068 mole) of 1.6 *N* butyllithium in hexane. To the dilithium derivative of aniline was added 9.4 g (0.034 mole) of bis(chlorodimethylsilyl)(trimethylsilyl)amine in 50 ml of dry ether, then the mixture was refluxed 1.5 h. Filtration afforded 2.7 g (93%) of lithium chloride. When the filtrate was evaporated, 9.8 g (98%) of crude *N*-phenyl-*N'*-(trimethylsilyl)tetramethylcyclodisilazane, m.p. 82–89°, was obtained. Three recrystallizations from petroleum ether, b.p. 35–60°, afforded 6.1 g of (XIX), m.p. 95°. (Found: C, 53.12; H, 8.76; N, 9.49; Si, 28.48. $C_{13}H_{26}N_2Si_3$ calcd.: C, 52.99; H, 8.90; N, 9.51; Si, 28.60%.)

Preparation of N-(dimethylphenylsilyl)pentamethylcyclodisilazane, (XX)

Excess methylamine was collected at −60°, and 100 ml of petroleum ether, b.p. 60–80°, was added. The temp. was maintained at −60° while 20.0 g (0.0595 mole) of bis(chlorodimethylsilyl)(dimethylphenylsilyl)amine in 100 ml of petroleum ether was added in 0.5 h. The reaction mixture was stirred at −60° for 0.5 h, warmed up to 26°, filtered, and stripped of solvent. Distillation gave 5.6 g (32%) of (XX), b.p. 86–87° (0.65 mm), n_D^{20} 1.4863. (Found: C, 52.77; H, 8.94; N, 9.45; Si, 28.81. $C_{13}H_{26}N_2Si_3$ calcd.: C, 52.99; H, 8.90; N, 9.51; Si, 28.60%.)

A second fraction, 3.6 g, which was collected at 115–116° (0.65 mm) was contaminated with 1,4-diphenylbutane.

Preparation of tris(ethoxydimethylsilyl)amine, (XXI)

A solution of 41.7 g (0.3 mole) of chloroethoxydimethylsilane in 60 ml of tetrahydrofuran was added slowly to a stirred slurry of 3.5 g (0.1 mole) of lithium nitride covered in 60 ml of tetrahydrofuran. The reaction was exothermic. After the addition was complete, the mixture was refluxed overnight, cooled and filtered. Lithium chloride, 11.7 g (96%), was recovered. Fractional distillation at 7 mm gave 5.6 g (17%) of (XXI), b.p. 111–113°, n_D^{20} 1.4231. (Found: C, 44.33; H, 10.30; N, 4.42; Si, 26.12. $C_{12}H_{33}NO_3Si_3$ calcd.: C, 44.53; H, 10.28; N, 4.33; Si, 26.04%.)

Preparation of tris(dimethylphenylsilyl)amine, (XXII)

When a stirred suspension of 1.2 g (0.033 mole) of lithium nitride covered with 20 ml of tetrahydrofuran was treated with 17.1 g (0.1 mole) of chlorodimethylphenylsilane in 20 ml of tetrahydrofuran, a slightly exothermic reaction was obtained. The mixture was refluxed for 3 h, 30 ml of tetrahydrofuran was distilled out, and 30 ml of petroleum ether, b.p. 35–60°, was added. Upon filtration 5.0 g (calcd. 4.3 g) of lithium chloride was obtained. (XXII) (4.9 g, 35%), m.p. 131–135°, crystallized from the filtrate. Additional recrystallization from petroleum ether raised the m.p. to 136–137°. (Found: C, 68.52; H, 7.97; N, 3.36; Si, 19.87. $C_{24}H_{33}NSi_3$ calcd.: C, 68.66; H, 7.93; N, 3.34; Si, 20.07%.)

Preparation of bis[dimethyl(methylamino)silyl]methylamine, (XXIII)

After a solution of 13.5 g (0.063 mole) of bis(chlorodimethylsilyl)methylamine in 25 ml of petroleum ether, b.p. 35–60°, was added to a solution of 20 ml (excess) of methylamine in 25 ml of petroleum ether, which was maintained at $-20°$ during the addition, the mixture was warmed to room temp., the salts were filtered off, and the solvent was evaporated. Fractional distillation gave 7.0 g (55%) of bis[dimethyl(methylamino)silyl]methylamine, b.p. 115° (55 mm), n_D^{20} 1.4452, NMR peaks (CCl_4) at τ 7.55 and τ 7.53 (total 9H, doublet and singlet, J 6.5 cps, $NHCH_3$) and τ 9.98 (12 H singlet, $SiCH_3$). [Lit.[7] b.p. 78° (11 mm), n_D^{27} 1.4393.]

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SUMMARY

N,N'-Disilylcyclodisilazanes are cleaved with methanol, ethanol, phenol, acetic acid, or hydrogen chloride to obtain the corresponding symmetrical or unsymmetrical trisilylamine derivatives. The unsymmetrical trisilylamines can equally well be prepared by the cleavage of *N*-silylcyclotrisilazanes. Bis(chlorodimethylsilyl)(trimethylsilyl)amine forms the amino and hydride derivatives with secondary amines and lithium aluminum hydride, resp., but gives *N*-alkyl(or aryl)-*N'*-silylcyclodisilazanes with primary amines at low temperatures. Properties of the new trisilylamines and cyclodisilazanes are discussed.

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