and $(CF_3)_2C{=}NSF_3$ which subsequently rearranges to $(CF_3)_2CFN{=}SF_2$.

The disulfide also reacts with fluorinating agents as shown below.

$$(CF_3)_2C{=}NSSN{=}C(CF_3)_2 + 6AgF_2 \xrightarrow[8\ hr]{25°} 2(CF_3)_2CFN{=}SF_2 + 6AgF$$

$$(CF_3)_2C{=}NSSN{=}C(CF_3)_2 + 6ClF \xrightarrow[2\ hr]{25°} 2(CF_3)_2CFN{=}SF_2 + 3Cl_2$$

Correlation of the ^{19}F nmr chemical shifts or of the infrared stretching frequencies of the C=N moiety with the substituent group attached to the $(CF_3)_2C{=}NS$ group cannot be made based on first-order effects, such as electronegativity. However, a similar lack of apparent order is osberved for compounds containing the CF_3S moiety, *e.g.*, CF_3SCl, CF_3SNH_2, etc.

It is interesting to note that in the case of $(CF_3)_2C{=}NSCl$ and $(CF_3)_2C{=}NSN(CH_3)_2$, the trifluoromethyl groups are magnetically nonequivalent, giving rise to two ^{19}F nmr resonances in the CF_3 region for each compound. Apparently the other new compounds do not behave similarly because the temperature (about 30°) at which the nmr spectra are determined is above that of coalescence, where the CF_3 groups become magnetically equivalent. An ongoing study involves the determination of coalescence temperatures and inversion energies. Ruff[12] reported that the CF_3 groups in $(CF_3)_2C{=}NF$ are magnetically nonequivalent and that the CF_3 group trans to the imine fluorine is shifted to lower field. Based on this, the resonance bands at 60.8 and 65.4 ppm in $(CF_3)_2C{=}NSCl$ and $(CF_3)_2C{=}NSN(CH_3)_2$ are assigned to the CF_3 group trans to Cl and $N(CH_3)_2$, respectively. No fluorine–hydrogen coupling is found and the proton nmr spectra are typical of the functional groups involved.

The infrared spectra of these compounds are reasonably simple, with C=N stretching frequencies being lowered only by 35 cm^{-1} (1640–1605 cm^{-1}) when the substituent is changed from dimethylamino to cyano. The C=N stretching frequency in the $(CF_3)_2C{=}NSCl$ and $((CF_3)_2C{=}N)_2S_2$ are the same (1630 cm^{-1}) which illustrates the insensitivity of the bond to substituents on the sulfur. The mass spectra are helpful in confirming the syntheses of these new compounds since, with the exception of $[(CF_3)_2C(Cl)N]_2S$ where $(M - Cl^+)$ is the highest *m/e*, all spectra show rather intense molecule ion peaks.

Acknowledgment.—Fluorine research at the University of Idaho is supported by the Office of Naval Research and the National Science Foundation. We are indebted to Mr. R. A. De Marco for mass spectra and to Dr. D. T. Sauer and Mr. R. F. Swindell for nuclear magnetic resonance spectra.

[12] J. K. Ruff, *J. Org. Chem.*, **32**, 1675 (1967).

Contribution from Midwest Research Institute,
Kansas City, Missouri 64110

New Cyclodisilazane Derivatives

By L. W. Breed* and J. C. Wiley, Jr.

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Cyclodisilazanes with mixed silicon-substituted groups $\{Cl(CH_3)RSi[SiR(CH_3)N]_2SiR(CH_3)Cl\}$ can be prepared either by heating mixtures of $[R(CH_3)SiNH]_3$ and $R(CH_3)SiCl_2$ or by treating $HN[Si(CH_3)RCl]_2$ with butyllithium and heating the product. One or both of the methods are shown to be applicable where R is ethyl, vinyl, phenyl, or 3,3,3-trifluoropropyl as well as methyl. The properties of the intermediate cyclotrisilazanes and disilazanes as well as the dialkylamino derivatives of the cyclodisilazanes are described.

Introduction

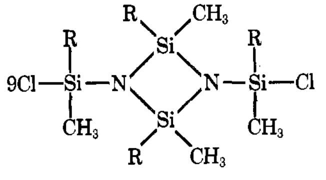
Recently, we reported the synthesis and properties of *N,N'*-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (1) and a number of its functional derivatives.[1,2] In that work, 1 was obtained in good yields by heating dichlorodimethylsilane and hexamethylcyclotrisilazane or octamethylcyclotrisilazane at 175°. The work described in this paper encompasses an examination of procedures applicable to the synthesis of cyclodisilazane derivatives with mixed silicon-substituted groups, $Cl(CH_3)RSi[SiR(CH_3)N]_2SiR(CH_3)Cl$, as well as certain intermediates and derivatives.

Results

The structures and physical properties of substances examined in the course of this work are summarized in Table I. The phenyl-, 3,3,3-trifluoropropyl-, vinyl-, and ethylcyclodisilazane derivatives could all be prepared by the method previously used to prepare **1**, provided higher temperatures were used when larger groups were present.

Although **4** and **5** could be satisfactorily obtained by

$12R(CH_3)SiCl_2 + 8[R(CH_3)SiNH]_3 \longrightarrow$



$+ 6NH_4Cl$ (1)

2, R = 3,3,3-trifluoropropyl
3, R = phenyl
4, R = vinyl
5, R = ethyl

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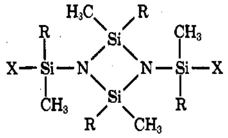
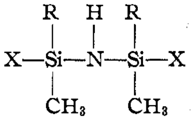
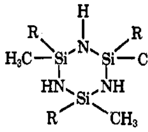
[1] L. W. Breed, R. L. Elliott, and J. C. Wiley, Jr., *J. Organometal. Chem.*, **24**, 315 (1970).

[2] L. W. Breed, W. L. Budde, and R. L. Elliott, *ibid.*, **6**, 676 (1966).

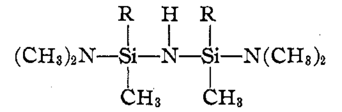
Table I

Structure and Properties of Cyclodisilazanes and Related Compounds

Compd no.		R	X	Bp, °C (mm)	Mp, °C	$n^{20}D$	Lit. value
2		$C_3H_4F_3$	Cl	130–132 (0.2)	60–73	...	
3		C_6H_5	Cl	220–221 (0.2)	...	...	
4		C_2H_3	Cl	120 (2)	...	...	
5		C_2H_5	Cl	114 (0.2)	...	...	
6		C_3H_4F	$N(CH_3)_2$	140–142 (0.1)	80–85	...	
7		C_6H_5	$N(CH_3)_2$	206–210 (0.01)	...	1.5728	
8		C_2H_3	$N(CH_3)_2$	104–106 (0.2)	...	1.4849	
9		C_2H_5	$N(CH_3)_2$	138–140 (0.2)	...	1.4722	
10		$C_3H_4F_3$	Cl	72–74 (0.3)	...	...	
11		C_6H_5	Cl	158–160 (0.2)	...	...	
12		C_2H_3	Cl	120–122 (18)	...	...	
13		C_2H_5	Cl	88–90 (3)	...	...	
14		CH_3	Cl	96–98 (48)	...	...	*a*
15		$C_3H_4F_3$	NH_2	82–84 (0.7)	...	1.4008	
16		$C_3H_4F_3$	$N(CH_3)_2$	104–107 (0.3)	...	1.4072	
17		C_6H_5	$N(CH_3)_2$	168–169 (0.4)	44–51	...	
18		$C_3H_4F_3$		134–136 (1)[b]	41–45		*c*
19		C_6H_5		212–214 (0.6)	...[d]	...	*e*
20		C_2H_3		100–102 (6)	...	1.4840	*f*
21		C_2H_5		104–106 (5)	...	1.4589	*g*

[a] Reported[3] bp 64° (11 mm). [b] Normal bp 290–294° (differential thermal analysis). [c] Reported mp 74–82°; G. Ya. Rumba and Ya. E. Rozhkaln, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.*, 507 (1968); *Chem. Abstr.*, **70**, 28,989 (1969). [d] Contains two isomers, one mp 115–116°, the other a liquid isomer. [e] Reported mp 115–116°: K. Hizawa and E. Nojimoto, *Kogyo Kagaku Zasshi*, **59**, 1445 (1956); *Chem. Abstr.*, **53**, 4176 (1959). [f] Reported bp 63–65° (1); $n^{20}D$ 1.482: D. Ya. Zhinkin, N. V. Markova, and M. V. Sobolevskii, *Zh. Obshch. Khim.*, **33**, 2638 (1963); *Chem. Abstr.*, **60**, 540 (1964). [g] Reported bp 112–115° (13); $n^{20}D$ 1.4564: Hizawa and Nojimoto, footnote *e*.

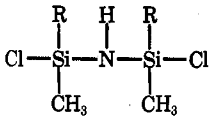
the same procedure that had been employed for **1** (heating at about 175°), considerably higher temperatures were required for **2** and **3**. Cyclodisilazane formation proceeded satisfactorily when the condensations were carried out at 290°. When the reaction was attempted at 175° and the immediate condensation products were treated with dimethylamine, the only substances that could be separated from mixtures were disilazane derivatives.



$$(CH_3)_2N-\overset{R}{\underset{CH_3}{Si}}-\overset{H}{N}-\overset{R}{\underset{CH_3}{Si}}-N(CH_3)_2$$

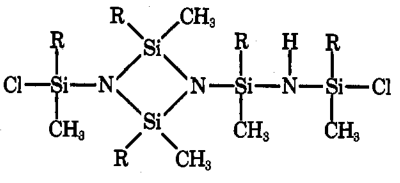
16, R = 3,3,3-trifluoropropyl
17, R = phenyl

In the preparation of **2**, **4**, and **5**, small quantities of higher and lower boiling by-products were also separated.



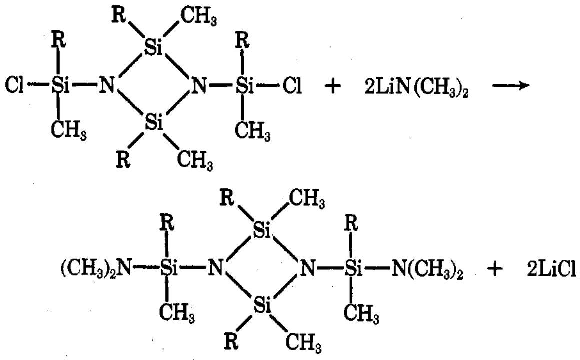
$$Cl-\overset{R}{\underset{CH_3}{Si}}-\overset{H}{N}-\overset{R}{\underset{CH_3}{Si}}-Cl$$

10, R = 3,3,3-trifluoropropyl
12, R = vinyl
13, R = ethyl



R = vinyl

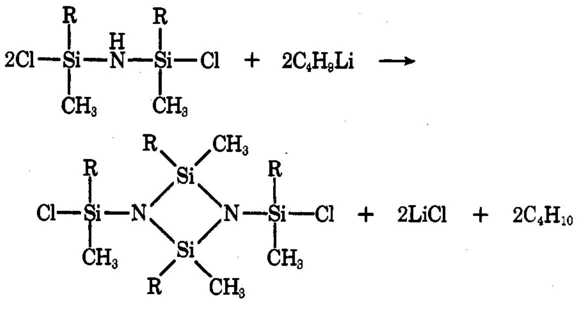
The four chlorine-substituted cyclodisilazanes were readily converted to their dimethylamino derivatives with the lithium salt of dimethylamine.



(2)

6, R = 3,3,3-trifluoropropyl
7, R = phenyl
8, R = vinyl
9, R = ethyl

An alternate procedure proved satisfactory and in some ways advantageous for the synthesis of the cyclodisilazane derivatives. When 1,3-dichloro-1,1,3,3-tetraorganodisilazanes were cooled in a Dry Ice bath,

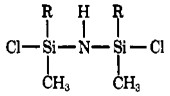
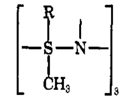
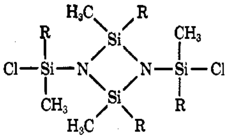
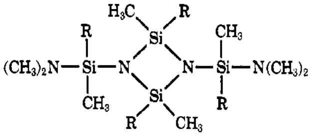
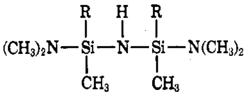
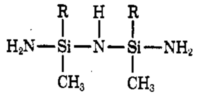


(3)

1, R = methyl
2, R = 3,3,3-trifluoropropyl
3, R = phenyl
5, R = ethyl

TABLE II

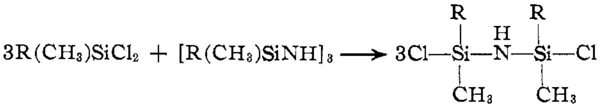
SELECTED INFRARED AND NMR ABSORPTIONS

	Nmr spectra Chemical shifts (τ) for methyl protons					Infrared spectra Absorption frequencies (cm^{-1}) for Si_2N, Si_2NH, NH, and Si_4N_2				
	R					R				
	CH_3	$C_3H_4F_3$	C_6H_5	C_2H_3	C_2H_5	CH_3	$C_3H_4F_3$	C_6H_5	C_2H_3	C_2H_5
	9.50	9.46	9.44 9.33	9.47	9.55	954 1200 3370	954 $\sim$1190^a 3300	950 1187 3310	952 1195 3310	948 1184 3270
	9.93	9.98	9.53^{b,c} 9.67 (doublet) 9.62	9.86	10.00	923 1060 3410	940 $\sim$1175^a 3490	930 (br)^{b,d} 1186 (br)^{b,d} 3350	926 1069 3390	917 1058 3300
	9.64	9.56 9.59	9.27–9.54 (multiplet) 9.65–9.73 (multiplet)	9.56 9.59	9.68	877 1038	868 1022	850 1019 (1030 ?)	860 1038	855 1032
	9.78 10.01	9.69 9.93	9.34–9.48 (multiplet) 9.94–10.09 (multiplet)	9.65 9.98	9.81 10.02	880 1032	863 1012	854 1018	862 1030	858 1028
	9.98	9.92	9.68 9.73 (doublet)			925 1183 3400	929 1175 3300	925 1182 3410		
		9.95					936 $\sim$1180^a 3400 NH_2 1540			

[a] Obscured by CF band at 1205 cm^{-1}. [b] The isomeric mixture. [c] τ 9.53 in the 115–116° melting isomer. [d] In the 115–116° melting isomer, 950, 920, 1181, 3390 cm^{-1}.

treated with an equivalent quantity of butyllithium, and subsequently heated briefly at the temperatures required for the other procedure, the cyclodisilazanes were obtained in good yield (eq 3). Infrared spectra of the products prior to purification by distillation indicated that the conversions were nearly quantitative. The procedure is applicable to the preparation of **1**, which can be obtained in a 73% yield after distillation. By-products, usually obtained by the other procedure, are not evident in the product obtained by this method.

Two of the 1,3-dichlorotetraorganodisilazanes required for the syntheses with butyllithium were satisfactorily obtained by the equilibrium redistribution of a 5:1 molar excess of the diorganodichlorosilane with the corresponding cyclotrisilazane (eq 4). Neither group interfered with this reaction, which has been previously described by Wannagat for the synthesis of 1,3-dichlorotetramethyldisilazane.[3]



$$3R(CH_3)SiCl_2 + [R(CH_3)SiNH]_3 \longrightarrow 3Cl-\underset{CH_3}{\overset{R}{Si}}-\overset{H}{N}-\underset{CH_3}{\overset{R}{Si}}-Cl \qquad (4)$$

10, R = 3,3,3-trifluoropropyl
11, R = phenyl

The cyclotrisilazane intermediates could be obtained by the ammonolysis of the diorganodichlorosilanes at Dry Ice temperatures (eq 5). In the preparation of **18** at Dry Ice temperatures, the results were erratic, and in one experiment, a substantial proportion of the product isolated was 1,3-diamino-1,3(bis-3,3,3-trifluoropropyl)-1,3-dimethyldisilazane (**15**). Compound **18** could consistently be obtained in high yield when the ammonolysis was carried out at 50°.

$$R(CH_3)SiCl_2 + 9NH_3 \longrightarrow [R(CH_2)SiNH]_3 + 6NH_4Cl \qquad (5)$$

18, R = 3,3,3-trifluoropropyl
·**19**, R = phenyl
20, R = vinyl
21, R = ethyl

The infrared and nmr spectra of the cyclodisilazanes and their intermediates are summarized in Table II.

Discussion

Both procedures examined in the course of this work appear to be generally applicable to the synthesis of cyclodisilazane derivatives, including substances with aromatic substituents and substances with bulky alkyl substituents. Because vinylsilicon compounds are known to polymerize with butyllithium,[4] no attempt was made to prepare the vinyl-substituted cyclodisilazane from 1,3-dichloro-1,3-dimethyl-1,3-divinyldisilazane (**12**) and butyllithium. The vinyl group is quite stable under the conditions of thermal equilibration in that moderately good yields of the cyclodisilazane containing four vinyl substituents could be obtained after 48 hr of heating at 175°.

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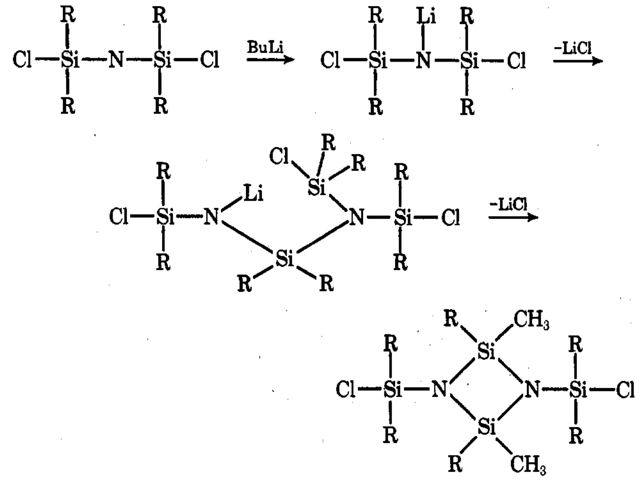
(3) U. Wannagat, *Angew. Chem., Int. Ed. Engl.*, **4**, 605 (1965).

(4) M. R. Stober, K. W. Michael, and J. S. Speier, *J. Org. Chem.*, **32**, 2740 (1967).

The formation of cyclodisilazanes under the conditions of treating a 1,3-dichlorotetraorganodisilazane with butyllithium requires primary metalation at nitrogen followed by a bimolecular condensation to a trisilylamine structure with subsequent ring closure.



The use of bases to effect cyclodisilazane ring closure is not new. Butyllithium is a satisfactory reagent for the cyclization of hexachlorodisilazane in the preparation of the perchlorocyclodisilazane derivative.[5] Greatly enhanced proton acidity would be expected in hexachlorodisilazane as well as greater reactivity of the intermediate metalation product in cyclodisilazane formation. Indeed, Wannagat found that near-quantitative conversion to the cyclodisilazane occurred at 85°.

Geymayer first reported that compound **1** could be obtained by treating 1,3-dichlorotetramethyldisilazane $\{[Cl(CH_3)_2Si]_2NH\}$ with an equivalent amount of sodium bis(trimethylsilyl)amide $\{[(CH_3)_3Si]_2NNa\}$; however, he postulated that condensation occurred at the silicon–halogen bond with subsequent disproportionation.[6] We have found that when 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisilazane (**11**) is treated with sodium bis(trimethylsilyl)amide, the product is not a cyclodisilazane but a direct substitution product, the 1,3-bis[bis(trimethylsilyl)amino] derivative, which does not disproportionate even at the rather high temperatures required for its distillation.[7]

Andrianov has obtained *N*,*N*′-bis(dimethylsilyl)-tetramethylcyclodisilazane by treating 1,1,3,3-tetramethyldisilazane with potassium hydroxide,[8] and Fink has converted 1,3-dichlorotetramethyldisilazane to compound **1** in high yield with triethylamine.[9] On the other hand, Silbiger found that 1,3-dichlorotetramethyldisilazane and sodium methoxide gave simply 1,3-dimethoxytetramethyldisilazane $\{[CH_3O(CH_3)_2Si]_2NH\}$.[10] Normal substitution for halogen also occurs with dimethylamine.[11]

The use of butyllithium in this procedure probably provides the most convenient laboratory route to a variety of cyclodisilazane structures and also affords relatively pure products that require less extensive purification. The intermediate disilazanes and cyclotrisilazanes can be readily prepared.

Infrared and nmr characterization of the products and intermediates were consistent with the structures and require little explanation. All 1,3-dichlorotetraorganodisilazanes had relatively high asymmetric stretch frequencies for the Si_2NH group occurring at about 950–955 cm^{-1}. The cyclodisilazanes, regardless of substituents, exhibited the usual two bands associated with the Si_4N_2 skeleton at 850–880 and at 1010–1040 cm^{-1}.

In the nmr spectra of the methyl–silicon proton absorptions of the cyclodisilazane derivatives, the transmission of substituent effects throughout the entire Si_4N_2 system is evident. For the compounds with phenyl substituents, the nmr spectra are complicated by the existence of various isomeric structures, particularly for the phenyl-substituted cyclodisilazanes. The two isomers of 2,4,6-trimethyl-2,4,6-triphenylcyclotrisilazane (one mp 115–116° and the other a liquid) can be distinguished by a singlet at τ 9.54 assignable to the high-melting cis configuration and three peaks, a singlet at τ 9.61 and a doublet at τ 9.65 (J = 1 cps), assignable to the low-melting trans configuration, which have peak height ratios of about 2:1. 1.3-Bis(dimethylamino)-1,3-dimethyl-1,3-diphenyldisilazane shows an nmr pattern similar to the trans configuration of the cyclic compound with a singlet at τ 9.68 and a doublet at τ 9.73 (J = 1 cps). The doublet observed in these two substances provides evidence that long-range coupling can occur through silicon in the structure $C_6H_5SiCH_3$.

Experimental Section

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 and are summarized in Table III. Ir spectra were determined with a Perkin-Elmer Infracord spectrophotometer, and nmr spectra were determined in carbon tetrachloride solution with a Varian Associates Model A-60 spectrometer with cyclohexane as an internal standard. The following procedures are typical of the types of procedures employed for the various classes of compounds.

Synthesis of Disilazanes (Compounds 10–11).—After 14.4 g (0.031 mol) of 2,4,6-trimethyl-2,4,6-tris(3,3,3-trifluoropropyl)-cyclotrisilazane (**18**) and 32.7 g (0.115 mol) of dichloromethyl-3,3,3-trifluoropropylsilane were heated for 2 hr at 145°, fractional distillation gave 14.2 g of unchanged dichloromethyl-3,3,3-trifluoropropylsilane and 27.0 g (79%) of 1,3-bis(3,3,3-trifluoropropyl)-1,3-dichloro-1,3-dimethyldisilazane (**10**).

Similarly, a 5:1 molar ratio of dichloromethylphenylsilane and 2,4,6-trimethyl-2,4,6-triphenylcyclotrisilazane gave 69% of 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisilazane (**11**) after 2 hr at 150° and a 4:1 molar ratio gave 33% after 16 hr at 180°.

Synthesis of Cyclotrisilazines (Compounds 18–21). Method A.—To 100 ml of ammonia condensed in an isopropyl alcohol–Dry Ice bath and diluted with 800 ml of petroleum ether (bp 30–60°) was added over a period of 1.5 hr a solution of 191 g (1.00 mol) of dichloromethylphenylsilane. After the mixture was warmed to room temperature, the salts were filtered off and the solvent was evaporated. Fractional distillation gave 92% of 2,4,6-trimethyl-2,4,6-triphenylcyclotrisilazane (**19**).

Method B. An excess of ammonia was passed into a solution of 31.6 g (0.15 mol) of dichloromethyl-3,3,3-trifluoropropylsilane while the solution was maintained at 50°. Heating was continued 1 hr; then the mixture was cooled and filtered, and the filtrate was evaporated. Fractional distillation gave 79% of

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(5) U. Wannagat, P. Schmidt, and M. Schulze, *Angew. Chem., Int. Ed. Engl.*, **6**, 447 (1967).

(6) P. Geymayer and E. G. Rochow, *ibid.*, **4**, 592 (1965).

(7) L. W. Breed, R. L. Elliott, and J. C. Wiley, Jr., submitted for publication.

(8) K. A. Andrianov, V. M. Kapylov, L. M. Khananashvili, and T. V. Nesterova, *Dokl. Akad. Nauk SSSR*, **176**, 85 (1967).

(9) W. Fink, *Helv. Chim. Acta*, **51**, 1011 (1968).

(10) J. Silbiger and J. Fuchs, *Inorg. Chem.*, **4**, 1371 (1965).

(11) L. W. Breed, unpublished.

TABLE III

ELEMENTAL ANALYSES (%)[a]

Compd no.	C	H	Cl	N	F	Si
2	29.03	4.24	10.47	4.63	33.77	16.94
	(29.13)	(4.28)	(10.75)	(4.25)	(34.56)	(17.03)
3	57.93	5.57	12.29	4.92		19.19
	(58.00)	(5.56)	(12.23)	(4.83)		(19.38)
4	38.08	6.45	18.88	7.36		29.40
	(37.97)	(6.37)	(18.69)	(7.38)		(29.59)
5	36.27	8.05	18.49	7.41		29.90
	(37.18)	(8.32)	(18.29)	(7.23)		(28.98)
6	35.27	5.92	33.52	8.18		16.24
	(35.49)	(5.95)	(33.68)	(8.28)		(16.60)
7	64.37	7.43		9.38		18.82
	(64.19)	(7.82)		(9.36)		(18.96)
8	48.42	9.30		14.14		28.38
	(48.42)	(9.15)		(14.12)		(28.31)
9	47.41	10.92		13.88		27.80
	(47.46)	(10.95)		(13.84)		(27.75)
10	26.35	3.92	19.48	4.15	31.24	15.65
	(26.23)	(4.13)	(19.36)	(3.82)	(31.12)	(15.34)
11	51.35	5.32		4.26		16.92
	(51.52)	(5.25)		(4.29)		(17.21)
13	31.59	7.46	30.27	6.34		24.66
	(31.29)	(7.44)	(30.79)	(6.08)		(24.39)
15	29.47	6.09		12.51	34.56	16.87
	(29.34)	(5.85)		(12.83)	(38.82)	(17.16)
16	39.35	7.27		11.37	26.05	15.21
	(39.42)	(7.45)		(11.50)	(26.25)	(15.37)
17	62.84	8.49		12.14		16.24
	(62.91)	(8.51)		(12.23)		(16.23)
18	31.10	5.18		8.89	36.69	18.04
	(30.95)	(5.20)		(9.02)	(36.73)	(18.10)

[a] Calculated values are in parentheses.

TABLE IV

SYNTHESIS OF CYCLOTRISILAZANES (EQ 5)

			Product yield, %	
Compd no.	R	Method	$(R(CH_3)SiNH)_3$	$HN(Si(CH_3)RNH_2)_2$
18, 15	$C_3H_4F_3$	A	43	
		A	59	
		A	21	59
		A	54	15
		B	72	
19	C_6H_5	A	91	
20	C_2H_3	A	80	
21	C_2H_5	A	42	

2,4,6-trimethyl-2,4,6-tris(3,3,3-trifluoropropyl)cyclotrisilazane (**18**).

The results of other preparations are summarized in Table IV.

Synthesis of Cyclodisilazanes (Compounds 1–5). Method A.—After 64 ml (0.100 mol) of 1.6 *M* *n*-butyllithium in hexane was added to 20.2 g (0.100 mol) of 1,3-dichlorotetramethyldisilazane in 200 ml of petroleum ether (bp 35–60°), while the mixture was maintained at −65°, the mixture was heated and the solvent was allowed to distil. The residue was subsequently heated at 160° for 3 hr, cooled, dissolved in 50 ml of petroleum ether, and filtered. Evaporation of the solvent and distillation of the residue gave 73% of *N,N'*-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (**1**).

Method B.—After a mixture of 16.9 g (0.120 mol) of dichloromethylvinylsilane and 20.5 g (0.080 mol) of 2,4,6-trimethyl-2,4,6-trivinylcyclotrisilazane was heated at 175° for 48 hr, the mixture was cooled and the liquid portion was decanted from 5.6 g (calcd, 3.2 g) of ammonium chloride. Fractional distillation gave 7% of 1,3-dichloro-1,3 dimethyl-1,3-divinyldisilazane (**12**), 42% of *N,N'*-bis(chloromethylvinylsilyl)-2,4-dimethyl-2,4-divinylcyclodisilazane (**4**), and 12% of *N*-(chloromethylvinylsilyl)-*N'*-3-chloro-1,3-dimethyl-1,3-divinyldisilazanyl)-2,4-dimethyl-2,4-divinylcyclodisilazane, bp 132–140° (0.6 mm), which was identified by its infrared and nmr spectra.

TABLE V

SYNTHESIS OF CYCLODISILAZANES

Method A (Eq 3)

Compd no.	R	Heating period	Yield, %
2	$C_3H_4F_3$	1.5 hr at 270–300°	81
3	C_6H_5	1 hr at 285°	72
5	C_2H_5	1 hr at 175°	41

Method B (Eq 1)

			Yield, %	
Compd no.	R	Heating period	Cyclodisilazane	$HN(SiCH_3RCl)_2$ by-product
2, 10, 16	$C_3H_4F_3$	175° for 48 hr	...	13[a]
		230° for 6 hr and 290° for 3 hr	56	11
3, 17	C_6H_5	175° for 72 hr		14[a]
		175° for 48 hr and 295° for 4 hr	45	...
5, 13	C_2H_5	140° for 16 hr and 180° for 10 hr	34	16

[a] The mixture was treated with dimethylamine prior to distillation and the product isolated as the dimethylamino derivative.

Repetitions of the procedures in the preparation of other cyclodisilazanes are summarized in Table V. In two of the experiments, the unpurified product was treated with an excess of dimethylamine, and the products were isolated upon distillation as their dimethylamino derivatives.

Synthesis of Dimethylamino Derivatives of Cyclodisilazanes (Compounds 6–9).—After 2.4 g (0.053 mol) of dimethylamine in 100 ml of petroleum ether (bp 35–60°) was treated with 22.8 ml (0.053 mol) of 1.6 *N* *n*-butyllithium in hexane at −50°, a solution of 10.0 g (0.026 mol) of *N,N'*-bis(chloromethylvinylsilyl)-2,4-dimethyl-2,4-divinylcyclodisilazane in 50 ml of petroleum ether was added; the mixture was allowed to warm to room temperature and was refluxed 2 hr. Subsequent filtration of the mixture, evaporation of the solvent, and fractional distillation gave 65% of *N,N'*-bis[(dimethylamino)methylvinylsilyl]-2,4-dimethyl-2,4-divinylcyclodisilazane (**8**).

The following were similarly prepared: *N,N'*-bis[(dimethylamino)methylphenylsilyl]-2,4-dimethyl-2,4-diphenylcyclodisilazane (**7**) (57% yield); *N,N'*-bis[(dimethylamino)ethylmethylsilyl]-2,4-diethyl-2,4-dimethylcyclodisilazane (**9**) (23% yield); and *N,N'*-bis[(dimethylamino)methyl-3,3,3-trifluoropropyl]-2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethylcyclodisilazane (**6**) (73% yield).

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