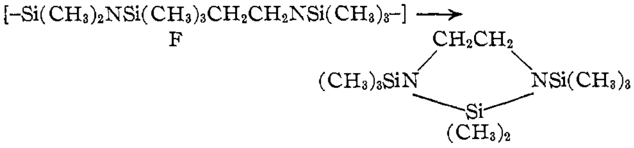
Apparently this reaction occurs in the first step (amine hydrochloride is formed), but in a second step cleavage and cyclization of F take place


F
G

When the polymeric reaction product is heated *in vacuo* to remove low-boiling compounds, a liquid is isolated which consists in large part of compound G. The chain units of the original material thus are removed to a high degree, and a ring structure of the approximate composition of E is left (product VII).

The results of this investigation show the strong tendency of silylethylenediamine compounds to form cyclic structures with the 1,3-diaza-2-silacyclopentane basic skeleton, in agreement with earlier results.[4,5] The failure to obtain a purely linear species $[-Si(CH_3)_2-NHCH_2CH_2NH-]_n$ (A), even in the presence of excess ethylenediamine, underlines the stability of this ring system and the previously discussed ring closure effect.[8]

Acknowledgments.—The authors wish to thank Dr. J. D. Baldeschwieler of this department for his assistance and for many interesting discussions in connection with this work.

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(8) In a recent paper Yoder and Zuckerman (*Inorg. Chem.*, **3**, 1329, 1964) erroneously suggest that we indicated that the presence of $NSi(CH_3)_3$ groups was necessary for the formation of five-membered rings and claim to have found a more general reaction for the formation of cyclic compounds with various alkyl or aryl groups on the nitrogen atoms. We desire to emphasize that the first cyclic silylethylenediamine compounds carrying alkyl as well as silyl substituents on the nitrogen atoms had already been prepared by Lienhard[5] in 1959. Thus it was known quite early that the formation of cyclic silylethylenediamines does not depend upon the presence of the $NSi(CH_3)_3$ group.

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N-Methylcyclosiloxazanes

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When 1,3-dichlorotetramethyldisiloxane or 1,5-dichlorohexamethyltrisiloxane was treated with methylamine, mixtures of silylamines and cyclosiloxazanes were obtained. The corresponding methylphenylsiloxanes gave only silylamines. All these silylamine derivatives could be converted to cyclosiloxazanes with heat in the presence of ammonium sulfate, and several stereoisomers were separated from the phenyl-substituted cyclosiloxazanes. Like the cyclosilazanes, the cyclosiloxazanes could be polymerized with aromatic diols.

Introduction

Several recent publications have described the synthesis of cyclic siloxazanes derived from ammonia.[1-6] As an extension of the interest of this laboratory in N-substituted cyclosilazanes as intermediates in polymer preparation, the synthesis of N-methylcyclosiloxazanes has been investigated. N-Ethyl-[7,8] and N-butylsiloxazanes[6] have been reported, but it has been observed in the literature that 1,3-bis(methylamino)tetramethyldisiloxane and 1,5-bis(methylamino)hexamethyldisiloxane, which are obtained in good yield from methylamine and the corresponding chlorosilane, resist thermal condensation to ring compounds.[1,2]

Results

The properties and characterization of the siloxazanes and the intermediates in their preparation are reported in Table I. Rather than a single product, methylamine and 1,3-dichlorotetramethyldisiloxane (I) and 1,5-dichlorohexamethyltrisiloxane (II) gave mixtures of cyclic and linear compounds. The reactions were carried out by treating the chlorosilanes in petroleum ether with methylamine at 5–10° and heating the resulting mixtures at reflux for 1 hr.

From the product of treating I with methylamine was isolated 40% of 1,3-bis(methylamino)tetramethyldisiloxane (V), 11% of the linear dimer, methylbis(3-(1-methylamino)tetramethyldisiloxanyl)amine (X), and 31% of the cyclic dimer decamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane (XI). II and methylamine afforded a mixture from which 32% of 1,5-bis(methylamino)hexamethyltrisiloxane (VII) and 45% of the cyclic derivative, octamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane (XII), were separated. When the phenyl-substituted siloxanes 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisiloxane (III) and 1,5-dichloro-

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(1) C. R. Krueger and E. G. Rochow, *Angew. Chem.*, **74**, 491 (1962).
(2) C. R. Krueger and E. G. Rochow, *Inorg. Chem.*, **2**, 1295 (1963).
(3) K. A. Andrianov, I. Khaiduk, and L. M. Khananashvili, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1701 (1963).
(4) J. G. Murray and R. K. Griffith, *J. Org. Chem.*, **29**, 1215 (1964).
(5) Compagnie Francaise Thomson-Houston (by J. G. Murray), French Patent 1,356,767 (1964).
(6) K. A. Andrianov, L. M. Volkova, and V. N. Talanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2045 (1963).
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TABLE I

PROPERTIES OF SILOXAZANES AND THEIR INTERMEDIATES

	Compound	B.p. or m.p., °C.	n^t_D	Calcd., %		Found, %	
				N	Si	N	Si
I[a]	$O[Si(CH_3)_2Cl]_2$	136–138					
II[a]	$(CH_3)_2Si[OSi(CH_3)_2Cl]_2$	79–81 (20 mm.)					
III[b]	$O[Si(CH_3)(C_6H_5)Cl]_2$	133–136 (0.6 mm.)					
IV[b]	$(CH_3)(C_6H_5)Si[OSi(CH_3)(C_6H_5)Cl]_2$	189–195 (0.4 mm.)					
V[c]	$O[Si(CH_3)_2NH(CH_3)]_2$	63–65 (20 mm.)	1.4085 (27°)				
VI	$O[Si(CH_3)_2NH(C_6H_5)]_2$	60–63 (10 mm.)	1.5742 (23°)	8.85	17.75	8.72	17.85
VII[c]	$(CH_3)_2Si[OSi(CH_3)_2NH(CH_3)]_2$	97–98 (20 mm.)	1.4070 (27°)				
VIII	$O[Si(CH_3)(C_6H_5)NH(CH_3)]_2$	146–153 (0.8 mm.)	1.5281 (22°)	8.85	17.75	8.48	17.88
IX	$(CH_3)(C_6H_5)Si[OSi(CH_3)(C_6H_5)NH(CH_3)]_2$	195–200 (0.5 mm.)	1.5338 (27°)	6.19	18.61	5.72	18.41
X	$(CH_3)N[Si(CH_3)_2OSi(CH_3)_2NH(CH_3)]_2$	90–94 (0.8 mm.)	1.4280 (24°)	11.88	31.76	10.98	31.85
XI	$[Si(CH_3)_2OSi(CH_3)_2N(CH_3)]_2$	82–85 (0.2 mm.)	1.4315 (26°)	8.68	34.82	8.70	34.59
XII	$\overline{Si(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2N}(CH_3)$	65–70 (20 mm.)	1.4059 (27°)	5.94	35.78	5.92	35.95
XIII	$[Si(CH_3)(C_6H_5)OSi(CH_3)(C_6H_5)N(CH_3)]_2$						
	Mixed isomers[d]	228 (0.4 mm.)		4.91	19.68	4.80	19.55
	Isomer 1[e]	136–137 (m.p.)		4.91	19.68	4.90	19.74
	Isomer 2[f]	115–118 (m.p.)		4.91	19.68	4.88	19.85
XIV	$\overline{Si(CH_3)(C_6H_5)OSi(CH_3)(C_6H_5)OSi(CH_3)(C_6H_5)N}(CH_3)$						
	Mixed isomers[g]	184–189 (10.5 mm.)		3.32	19.98	3.39	19.81
	Isomer 1[h]	111–112 (m.p.)		3.32	19.98	3.26	20.05

[a] W. Patnode and D. Wilcock, *J. Am. Chem. Soc.*, **68**, 358 (1946). [b] W. H. Daudt and J. F. Hyde, *ibid.*, **74**, 386 (1952). [c] C. R. Krueger and E. G. Rochow, *Inorg. Chem.*, **2**, 1295 (1963). [d] Mol. wt.: calcd. 571; found 572 (VPO in toluene), 539 (cryoscopically in benzene). [e] Mol. wt.: calcd. 571; found 568 (VPO in toluene), 531 (cryoscopically in benzene). [f] Mol. wt.: calcd. 571; found 576 (VPO in toluene), 524 (cryoscopically in benzene). [g] Mol. wt.: calcd. 422; found 428 (VPO in toluene), 411 (cryoscopically in benzene). [h] Mol. wt.: calcd. 422; found 417 (VPO in toluene), 411 (cryoscopically in benzene).

TABLE II

N.M.R. SPECTRA OF CYCLOSILOXAZANES[a]

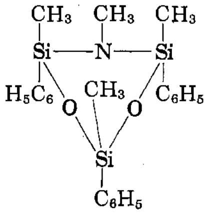
	Compound	δ $SiCH_3$, p.p.m.	Area ratio	δ NCH_3, p.p.m.	Area ratio	δ SiC_6H_5, p.p.m.	Area ratio
XIII	Isomer 1	0.32		2.33		7.20–7.60[b]	
			12.0		5.7		21.0
	Isomer 2	0.22		2.34		7.20–7.60[b]	
			12.0		6.0		19.8
	Remaining isomer mixture	0.26		2.31		7.15–7.70[b]	
		0.29		2.35			
		0.30		2.37			
		0.39					
		0.44					
		0.47					
			12.0		5.6		21.1
XIV	Isomer 1	0.45	(3.0)	2.31		7.15–7.50[b]	
		0.55	(6.0)				
			9.0		2.9		
	Remaining isomer mixture	0.38		2.31		7.17–7.75[b]	
		0.44		2.35			
		0.47					
		0.49					
		0.56					
			9.0		2.5		15.5

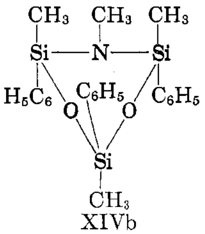
[a] 60-Mc. n.m.r. spectra. [b] Multiplet.

1,3,5-trimethyl-1,3,5-triphenyltrisiloxane (IV) were treated with methylamine, no cyclization occurred and 1,3-bis(methylamino)-1,3-dimethyl-1,3-diphenyldisiloxane (VIII) and 1,5-bis(methylamino)-1,3,5-trimethyl-1,3,5-triphenyltrisiloxane (IX) were isolated in yields of 84 and 74%, respectively. Similarly, no condensed products were obtained when I was treated with aniline, but 1,3-dianilinotetramethyldisiloxane (VI) was produced in a 58% yield.

Compounds V, IX, and X were cyclized at 120–180° in the presence of ammonium sulfate, but in every experiment a significant part of the starting material was recovered as a nondistillable liquid residue. V and X produced XI in yields of 33–45% and VII produced XII in a yield of 43%. Cyclization of the phenyl-containing derivatives occurred in higher yield. The cyclic dimer hexamethyl-2,4,6,8-tetraphenyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane (XIII) was obtained from VIII in a 68% yield and tetramethyl-2,4,6-triphenyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane (XIV) from IX in a 69% yield.

Compounds XIII and XIV were mixtures of solid and liquid stereoisomers. One component which melted at 111–112° was isolated from XIV by separating the liquid and solid phases by filtration and recrystallizing the solid component. The n.m.r. spectrum (Table II) of the solid contained two methyl proton peaks, with an area ratio of 2:1, which is consistent with either structure XIVa or XIVb. A similar separation procedure for XIII afforded two solid components, one melting at 136–137° and the other at 115–118°. Both of these components exhibited a single methyl proton peak on n.m.r. The liquid portions of both mixtures showed a series of six resolved methyl proton peaks, which suggests that each of the above components was a pure isomer.


XIVa


XIVb

In the infrared, the Si_2N asymmetric stretch occurred in the 900–910 cm.$^{-1}$ region for XI, XII, and XIV. The shift to lower frequency in smaller rings observed by Murray[4] in cyclosiloxazanes derived from ammonia was not observed in compounds XI and XII. Compound XIII (mixed isomers) exhibited a broad absorption band between 900 and 940 cm.$^{-1}$. The spectrum of the isomer that melted at 135° contained a principal absorption band at 905 cm.$^{-1}$, while the isomer melting at 115–118° absorbed at 930 cm.$^{-1}$ with a shoulder at 905 cm.$^{-1}$.

In the course of the synthesis of intermediates, a new and particularly convenient method was found for the synthesis of 1,3-dichlorotetramethyldisiloxane. This procedure, which gave a 69% conversion based on dimethyldichlorosilane, is reported in the Experimental section.

$$(CH_3)_2SiCl_2 \xrightarrow[2.\ FeCl_3]{1.\ C_2H_5OH} ClSi(CH_3)_2OSi(CH_3)_2Cl$$

Compound XI could be treated with 4,4′-isopropylidenediphenol in a manner similar to the procedure described elsewhere for cyclotrisilazanes[9] to produce a high molecular weight compound containing silazane linkages.

Experimental

1,3-Dichlorotetramethyldisiloxane (I).—Ethyl alcohol (30.6 g., 0.67 mole) was added to 258 g. (2.0 moles, 100% excess) of dichlorodimethylsilane in 30 min., and the mixture was purged with dry nitrogen for 30 min. About 1 g. of ferric chloride was added, and the mixture was slowly heated to reflux (67–83°). Ethyl chloride (40.9 ml., 86%) was collected in a cold trap over a 4-hr. period. The mixture was filtered and distilled to give 98.1 g. of unchanged dichlorodimethylsilane boiling at 66–70°, 87.0 g. (69% based on unrecovered dichlorodimethylsilane) of I boiling at 134–138°, and 19.1 g. (21%) of II boiling at 79–81° (20 mm.).

1,3-Bis(methylamino)-1,3-dimethyl-1,3-diphenyldisiloxane (VIII).—The following is typical of the procedure in which compounds I, II, III, and IV were treated with methylamine. Excess methylamine was introduced during 2 hr. over the surface of a solution of 120.2 g. (0.368 mole) of 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisiloxane in petroleum ether (b.p. 30–60°) which was cooled to 5°. The mixture was heated at reflux 1 hr., cooled, and filtered, and the solvent was stripped from the filtrate. Fractional distillation gave 97.9 g. (84%) of VIII boiling at 146–153° (0.8 mm.).

Hexamethyl-2,4,6,8-tetraphenyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane (XIII).—The following is typical of the experiments in which compounds V, VII, VIII, IX, and X were converted to cyclic siloxazanes. A mixture of 97.9 g. (0.31 mole) of VIII and 1 wt. % ammonium sulfate was heated at 150–180° for 29 hr. Methylamine (82%) was collected in an acid trap. Fractional distillation gave 60.4 g. (68%) of XIII boiling at 228° (0.4 mm.) and 23.9 g. of an undistillable liquid residue. The distillate partially crystallized on storage. After the crystals were separated by filtration, fractional crystallization in petroleum ether (b.p. 60–90°) gave two isomers, one melting at 136–137° and the other at 115–118°.

Polymer from XI and 4,4′-Isopropylidenediphenol.—When a mixture of 6.46 g. (0.02 mole) of XI and 4.56 g. (0.02 mole) of 4,4′-isopropylidenediphenol was heated in 10 ml. of refluxing toluene and the product was devolatilized to 150° (0.1 mm.), 9.9 g. (95%) of a rubbery polymer having an intrinsic viscosity of 2.70 in toluene at 30° was obtained. On thermogravimetric analysis (heating rate 3°/min., N_2 atmosphere) the temperature at which the weight loss exceeded 5%/hr. was 480°. Elemental analyses indicated that somewhat more than the calculated nitrogen was displaced in the polymerization reaction, but confirmed that the polymer retained silazane linkages.

Anal. Calcd. for $C_{24}H_{41}NO_4Si_4$: C, 55.44; H, 7.95; N, 2.69; Si, 21.61. Found: C, 47.52; H, 7.98; N, 1.84; Si, 21.22.

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