teristics of the 3-bromooxindole. [For oxindole formation alone, 1% of water appears to be as useful as 5% (Table IV), but no experiments on a preparative scale have been performed in the former.]

When a sample of *t*-butyl alcohol was distilled and the collected fractions were used as the reaction medium, the value of *R* decreased as the fraction number increased. Moreover, many commercial samples of the alcohol showed an anomalous absorption maximum at 236 mμ, and the peak became more intense in the later fractions. The presence of benzene obscures this peak, but, as the benzene is removed in the first fractions, the new absorption peak becomes visible. Treatment with Darco reduced the peak to a slight shoulder, and NBS had a similar effect. However, a second treatment with Darco had no further effect on the absorption spectrum even though the value of *R* increased further (Table IV), and treatment of *t*-butyl alcohol with NBS followed by distillation yielded solvent with the same *R* value as that observed before the NBS treatment. Moreover, many samples of *t*-butyl alcohol do not show this anomalous absorption but do give low *R* values. Whether the impurity absorbing at 236 mμ is responsible for the low *R* values is, therefore, a moot point at this time.

All attempts to concentrate the impurity by careful fractionation or to identify it by v.p.c. analysis have been unsuccessful. Samples of *t*-butyl alcohol rich in the impurity discharged the color of potassium permanganate and gave negative Beilstein tests for halogen and negative tests for thiophene. A number of substances suggested by the position of the absorption maximum or by the likelihood of their presence as contaminants of commercial *t*-butyl alcohol have been added to reaction mixtures of NBS and indole-3-butyric acid in small quantities, but without effect on the value of *R*. These included 2,5-dimethyl-2,4-hexadiene, diisobutylene, mesityl oxide, thiophene, and *n*-butyraldehyde.

The impurity is present in many, but not all, commercial samples of *t*-butyl alcohol, even those of the specially purified grade used in the analysis of corticosteroids (Matheson Coleman and Bell, Catalog No. BX 1800). From the lot analysis of the best samples, the impurity must be present in very small amounts (<0.1%). If this is the case, its effect on the product distribution is of a remarkable catalytic nature.

Preparation of Cyclic Siloxazanes

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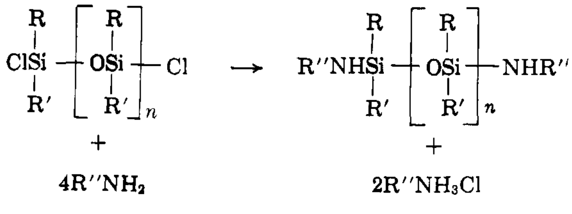
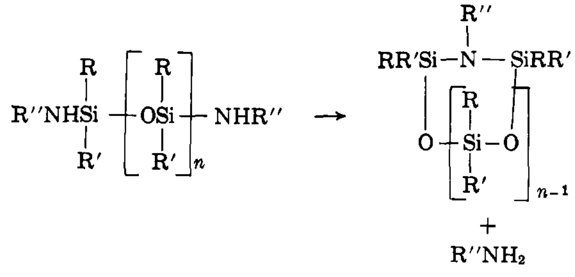
The preparation and characterization of a number of mixed cyclic siloxane–silazane compounds (*i.e.*, cyclic siloxazanes) is described.

This report describes the preparation and some properties of mixed cyclic silicon compounds having both siloxane and silazane bonds (*i.e.*, cyclic siloxazanes), which were of interest to us as intermediates for polymerization and condensation reactions. At the outset of this work, this class of compounds had not been isolated and characterized. Since then, Kruger and Rochow[1] have described the preparation and isolation of several of the compounds reported in this paper. The compounds prepared in this work are listed in Fig. 1 and their properties in Table I.

The general reactions for the preparation of the cyclic siloxazanes are indicated in eq. 1 and 2. Most of the dichlorosiloxanes used in reaction 1 were prepared by the partial hydrolysis of the dialkyldichlorosilane followed by distillation to separate the individual members of the homologous series of materials formed. These products have been described previously.[2,3] The intermediate for the preparation of IX (1,5-dichloro-1,1,5,5-tetramethyl-3,3-diphenyltrisiloxane) was prepared by the condensation of diphenylsilanediol and dimethyldichlorosilane in pyridine–benzene solution.

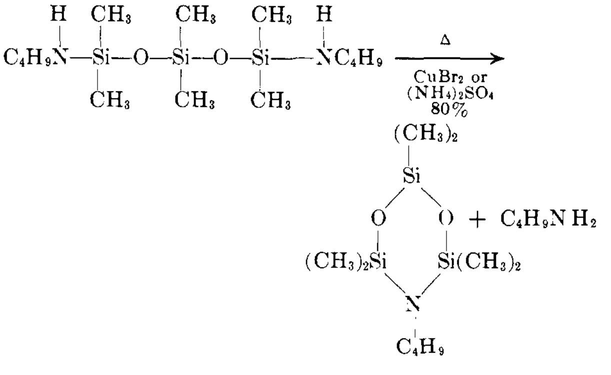


$$\mathrm{Cl}\underset{\mathrm{R'}}{\overset{\mathrm{R}}{\mathrm{Si}}}\!-\!\left[\mathrm{O}\underset{\mathrm{R'}}{\overset{\mathrm{R}}{\mathrm{Si}}}\right]_n\!-\!\mathrm{Cl} + 4\mathrm{R''NH_2} \longrightarrow \mathrm{R''NH}\underset{\mathrm{R'}}{\overset{\mathrm{R}}{\mathrm{Si}}}\!-\!\left[\mathrm{O}\underset{\mathrm{R'}}{\overset{\mathrm{R}}{\mathrm{Si}}}\right]_n\!-\!\mathrm{NHR''} + 2\mathrm{R''NH_3Cl} \qquad (1)$$



$$\mathrm{R''NH}\underset{\mathrm{R'}}{\overset{\mathrm{R}}{\mathrm{Si}}}\!-\!\left[\mathrm{O}\underset{\mathrm{R'}}{\overset{\mathrm{R}}{\mathrm{Si}}}\right]_n\!-\!\mathrm{NHR''} \longrightarrow \mathrm{RR'Si}\!-\!\overset{\mathrm{R''}}{\mathrm{N}}\!-\!\mathrm{SiRR'}\ \ \left(\mathrm{O}\!-\!\left[\underset{\mathrm{R'}}{\overset{\mathrm{R}}{\mathrm{Si}}}\!-\!\mathrm{O}\right]_{n-1}\right)_{\text{ring}} + \mathrm{R''NH_2} \qquad (2)$$

The products of reaction 1 were not isolated when R'' was H, but the presence of these diaminosiloxanes in the crude reaction products was indicated in some cases by the NH_2 band splitting (near 3390 cm.$^{-1}$) in the infrared spectra. On heating, this splitting disappeared. When R'' was butyl, only the diaminosiloxane was formed, with no cyclization occurring even during the distillation of the product. In the presence of an acidic catalyst, however, cyclization and elimination of butylamine took place readily, as indicated in eq. 3 for the preparation of VII.



$$\mathrm{C_4H_9\overset{H}{N}\!-\!\underset{CH_3}{\overset{CH_3}{Si}}\!-\!O\!-\!\underset{CH_3}{\overset{CH_3}{Si}}\!-\!O\!-\!\underset{CH_3}{\overset{CH_3}{Si}}\!-\!\overset{H}{N}C_4H_9} \xrightarrow[\substack{\mathrm{CuBr_2\ or}\\ \mathrm{(NH_4)_2SO_4}\\ 80\%}]{\Delta} \mathrm{(CH_3)_2Si(O\!-\!Si(CH_3)_2)_2N\!-\!C_4H_9}\ (\text{ring}) + \mathrm{C_4H_9NH_2} \qquad (3)$$

The yield of the low cyclic isolated varied from 21–81%. No attempt was made to optimize yields. Most of the reactions were run by passing ammonia into a moderately concentrated solution of the dichloropolysiloxane; this procedure might be expected to favor the formation of the larger cyclics and linear polymers at the

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(1) C. R. Kruger and E. G. Rochow, *Angew. Chem.*, **74**, 491 (1962).

(2) W. I. Patnode and D. F. Wilcock, *J. Am. Chem. Soc.*, **68**, 358 (1946).

(3) W. H. Daudt and J. F. Hyde, *ibid.*, **74**, 386 (1952).

TABLE I

PROPERTIES OF CYCLIC SILOXAZANES

Compound	B.p., °C. (mm.)	M.p., °C.	% yield	% N Calcd.	% N Found	Mole wt.[g] Calcd.	Mole wt.[g] Found
I	35–37 (5)[a]		34	6.32	6.25	221.49	230
II	78–79 (10)[b]		51	4.74	5.0	295.65	304
III	81–83 (3)		37	3.79	4.0	369.81	380
IV	64–65 (0.1)		30	3.16	3.6	443.96	451
V	98–101 (14)[c]	38.5–39.5	44	9.51	9.3	294.67	280
VI	72–75 (0.1)		d	6.3	6.25	442.98	446
VII	78 (5)		80[e]	(30.36)[f]	(30.3)[f]	277.60	290
VIII	95–98 (0.25)		38	6.89	7.1	406.88	403
IX	119–135 (0.05)	99–100	81	4.06	4.1	345.62	338
X	169–172 (0.25)		43	3.5	3.5	400	411
X-A		113–115	. . .	3.5	3.7	400	396
XI	192–202 (0.15)		58	2.6	2.5	544	554
XII	200–206 (0.1)		42	5.18	5.5	542.93	544

[a] Compound I, n^{20}_{D} 1.4088; lit.[1] b.p. 151–151.5° (760 mm.), n^{20}_{D} 1.4068. [b] Compound II, n^{20}_{D} 1.4156; lit.[1] b.p. 190–191° (760 mm.), n^{20}_{D} 1.4151. [c] Lit.[1] b.p. 206–208° (760 mm.), 82–83° (9 mm.); m.p. 37°. [d] Isolated as a by-product in preparation of I. [e] Yield in cyclization reaction. [f] Silicon analysis. [g] Ebullioscopic in benzene.

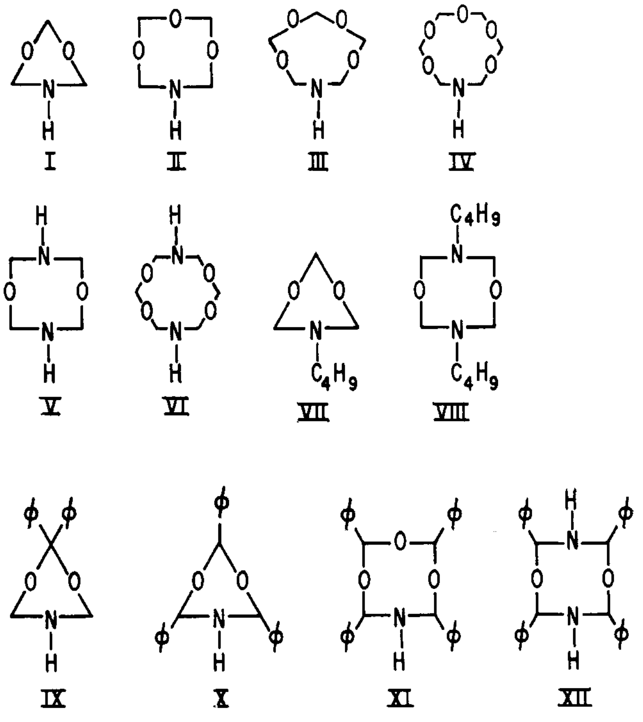
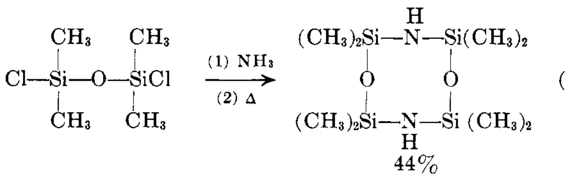


Fig. 1.—Cyclic siloxazanes prepared (corners represent silicon with dimethyl substitution except where replacement of one or both methyl groups by phenyl is indicated).

expense of low cyclics. In spite of this, reasonably good yields were obtained in some cases. However, none of the four-membered ring cyclics were isolated in reactions of ammonia or amine with dichlorodisiloxanes. In these reactions the eight-membered ring compound was the product isolated, as indicated in eq. 4 for the preparation of V.



$$\mathrm{Cl{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}Cl} \xrightarrow[(2)\ \Delta]{(1)\ \mathrm{NH_3}} \begin{array}{c} \mathrm{H} \\ \mathrm{(CH_3)_2Si{-}N{-}Si(CH_3)_2} \\ \mathrm{O\qquad\quad O} \\ \mathrm{(CH_3)_2Si{-}N{-}Si\ (CH_3)_2} \\ \mathrm{H} \\ 44\% \end{array} \qquad (4)$$

Compounds X–XII were prepared as mixtures of stereoisomers. In the case of X, one of the pure isomers (X-A) was isolated and has been tentatively identified as the *meso* compound having methyl groups *cis* to each other (rather than the possible *trans–meso* or *trans–dl* configurations). This assignment was made by comparison of the infrared spectra of X-A and the liquid mixture of stereoisomers remaining after removal of X-A, with that of the two isomeric phenylmethyltrisiloxanes.[4] In the phenylmethylsiloxane trimers, the *cis* compound has a strong methyl absorption at 778 cm.$^{-1}$ which appears at 793 cm.$^{-1}$ in the *trans* isomer. Compound X-A has a strong methyl absorption at 770 cm.$^{-1}$ which correspondingly appears at 790 cm.$^{-1}$ in the liquid mixture of isomers of X remaining after removal of X-A. The proton magnetic resonance of X-A shows a slight splitting (*ca.* 1 cycle) and a 2:1 ratio of peak heights for the methyl hydrogen atoms, presumably as a result of configurational differences introduced by the adjacent nitrogen and oxygen atoms.

The infrared spectra of the products (Table II) are of interest. The silazane stretching and NH bending absorptions shift to longer wave lengths in the smaller rings in a manner analogous to the shift in siloxane stretching bands in small ring siloxane compounds.[5] The siloxane asymmetric stretching absorptions are different from cyclosiloxanes of the same ring size. This difference is due to the interruption of coupling between siloxane chain segments by the silazane linkage. Siloxazanes, therefore, have a siloxane stretching band with an absorption characteristic of a short siloxane chain held in the ring configuration rather than the absorption typical[5] of the analogous cyclosiloxane. Thus, for example, I and II have a siloxane stretching frequency split into two bands at 983 and 1022 cm.$^{-1}$ and at 1022 and 1069 cm.$^{-1}$, respectively, while the analogous hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane have only a single band at 1018 and 1075 cm.$^{-1}$, respectively.

Some qualitative comparisons were made of the relative hydrolytic stability of four of the cyclic siloxazanes and three cyclic silazanes. These observations were made by preparing 0.25 *M* solutions of the compounds in aqueous dimethylformamide (5% water) and observing the rate of disappearance of the silazane band in the infrared spectrum. The results are listed in Table III. It is apparent that the rates of hydrolysis differ by

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(4) C. W. Young, P. C. Servias, C. C. Currie, and M. J. Hunter, *J. Am. Chem. Soc.*, **70**, 3758 (1948).

(5) A. Lee Smith, *Spectrochim. Acta*, **16**, 87 (1960).

TABLE II

INFRARED ABSORPTIONS OF CYCLIC SILOXAZANES

Compound	SiOSi stretch, cm.$^{-1}$	SiNSi[a] stretch, cm.$^{-1}$	NH bending,[a] cm.$^{-1}$
Hexamethylcyclotrisilazane		925	1158
Octamethylcyclotetrasilazane		941	1175
I	983 m, 1023 s	904	1147
II	1022 m, 1069 s	924	1176
III	1028 m, 1080 s	934	1180
IV	1020 sh, 1067 s, 1090 sh	939	1184
V	1059 s	947	1173
VI	1065 s, 1085 sh	945	1186
VII	1070 s	905	
VIII	1056 s	904	
IX	1015 s	898	1147
X	990 m, 1022 s	909	1157
XI	1078 s	927	1172
XII	1040 sh, 1072 s	941	1169

[a] See H. Kriegsmann and G. Englehardt, *Z. anorg. allgem. Chem.*, **310,** 321 (1961), for assignments of silazane infrared bands.

TABLE III

HYDROLYTIC STABILITY

Compound	Silazane stretching band position, cm.$^{-1}$	Rate of disappearance of silazane stretching band (solution allowed to stand at 25°)
Hexamethylcyclotrisilazane	925	Rapid loss during 1 hr.
IX	898	Rapid loss during 1 hr.
Octamethylcyclotetrasilazane	941	Rapid loss during 1 hr.
V	947	Slight loss in 13 hr.
XII	941	No change in 25 hr. Slight change after 7 days
VIII	904	No change in 7 days
Hexaphenylcyclotrisilazane	952	No change in 7 days

several orders of magnitude. Compounds having a phenyl substituent on the silicon atom adjacent to nitrogen, or a butyl substituent on the nitrogen atom, have improved stability.

Experimental[6]

The homologous dimethylsiloxanes chain-stopped with chlorine were prepared as described by Patnode and Wilcock,[2] and the phenylmethylsiloxanes chain-stopped with chlorine were prepared as described by Daudt and Hyde.[3]

Preparation of 1,5-Dichloro-1,1,5,5-tetramethyl-3,3-diphenyltrisiloxane.—Solid diphenylsilanediol (108.2 g., 0.5 mole) was added in portions during 1.5 hr. to a mixture of 129 g. (1.0 mole) of dimethyldichlorosilane, 79 g. (1.0 mole) of pyridine, and 1.5 l. of benzene contained in a 3-l. flask equipped with a stirrer and drying tubes to keep the temperature at 0–10°. The mixture was stirred overnight, being allowed to warm to room temperature. Pyridine hydrochloride was removed by filtration, the precipitate was washed with benzene, and the benzene was removed from the filtrate under reduced pressure. The residue was distilled through a short Vigreux column, and distillation was interrupted after the initial portion of product started distilling to remove sublimed pyridine hydrochloride. Distillation then was continued and there was collected 131.5 g. (66%) of product, b.p. 130–142° (0.3 mm.).

Condensation of Ammonia with Dichlorosiloxanes. General Procedure.—Ammonia was passed rapidly into benzene or ether solutions of the dichlorosiloxane with good stirring and with the mixture protected from moisture. The temperature was kept at 20–50° with cooling until ammonia absorption appeared to have stopped, and for 30 min. thereafter. The mixtures were filtered (protected from moisture), washed with fresh solvent, and the solvent was removed from the filtrate under reduced pressure. The residues then were distilled (X–XII were heated for an hour at 100° *in vacuo* to condense any unchanged silyl amine) under reduced pressure through a 3-ft. spinning band column.

Preparation of 3-*n*-Butyl-2,2,4,4,6,6-hexamethyl-1,5-dioxa-3-azacyclohexasilane (VII).[7]—The intermediate, 1,5-di-*n*-butylaminohexamethyltrisiloxane, was prepared by the addition of 58.5 g. (0.8 mole) of *n*-butylamine to a stirred mixture of 111 g. (0.4 mole) of 1,5-dichlorohexamethyltrisiloxane and 80.8 g. (0.8 mole) of triethylamine in 600 ml. of ether during 2 hr., with the temperature at 25–35°. The mixture was stirred for 2 hr. more and allowed to stand overnight. The product was filtered and washed with ether, the solvent was removed, and the residue was distilled under reduced pressure; 98.8 g. (70.6%) of product, b.p. 106–108° (1.0 mm.), was collected.

Cyclization of this diaminosiloxane to VII was carried out by slow distillation of 30.3 g. of this product from more than 0.5 g. of cupric bromide (or ammonium sulfate) in a 3-ft. spinning band column at 6 mm. using a liquid nitrogen trap to collect *n*-butylamine. There was obtained 19.5 g. (79%) of VII, b.p. 75–80° (6 mm.), which contained traces of lower boiling impurities (by v.p.c.) together with 6.0 g. of material in the trap. The product was redistilled for analysis and material with b.p. 78° (5 mm.) was collected.

Preparation of 3,7-Di-*n*-butyl-2,2,4,4,6,6,8,8-octamethyl-1,5-dioxa-3,7-diazacyclooctasilane (VIII).[8]—A mixture of 18.7 g. (0.064 mole) of V and 18.7 g. (0.256 mole) of *n*-butylamine together with 0.3 g. of copper bromide was refluxed for 17 hr. This reaction mixture then was distilled in the spinning band column, first removing 2.0 g. of material, b.p. 75° (atm.), lowering the pressure, and removing an additional 6.2 g. of material, b.p. 32° (132 mm.). Finally, the residue was distilled at 0.3 mm., and 9.9 g. of product, b.p. 88–98° (0.3 mm.), was collected. This material was about 90% pure (by v.p.c.), it was redistilled, and a sample of material, b.p. 95–98° (0.25 mm.), was collected for analysis.

Isolation of *cis*-2,4,6-Trimethyl-2,4,6-triphenyl-1,5-dioxa-3-azacyclohexasilane (X-A).—Fifty grams of the semisolid reaction product X was twice recrystallized from cyclohexane (in the drybox) and the product dried at 60° *in vacuo* yielding 11.1 g. of white crystals, m.p. 113–115°. The n.m.r. spectra of this product was run as a 10% solution in deuteriochloroform.

Acknowledgment.—The authors wish to thank Dr. J. F. Brown, Jr., for interpretations of infrared spectra.

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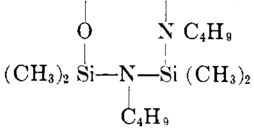
(6) Melting points are uncorrected and were taken on a Fisher-Johns apparatus. Infrared spectra were measured as 2% solutions in CS_2 on a Beckman Model IR7 spectrophotometer by Miss Dorothy McClung. N.m.r. absorption was recorded by Dr. C. M. Huggins with a 40-Mc. Varian high resolution spectrometer.

(7) These compounds are named using the oxa aza convention for organosilicon compounds [see *Chem. Eng. News*, **30**, 5517 (1952).

(8) One of the referees has suggested that VIII may contain the isomeric structure,



formed by a copper-catalyzed rearrangement of siloxane bonds. The possibility that this compound was present as an impurity in VIII cannot be ruled out, although the product isolated appeared to be essentially pure by analysis (9.3-min. retention time on a 2-ft. silicone rubber column programmed from 100–250° at 7.9°/min.). If the product isolated had the rearranged structure, we might expect to have observed a splitting of the siloxane band in the infrared spectrum.