

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC CO.]

Alkylsilazanes¹ and Some Related CompoundsBY STUART D. BREWER AND CHARLES P. HABER²

Organosilazanes of the type $R_3SiNHSiR_3$ and organoaminosilanes R_3SiNHR , have been described in the literature.³ We report here the preparation of two novel types of silazanes containing difunctional silicon. These include members of the series of cyclic polymers, $(R_2SiNH)_n$, and the linear polymers $R(R_2SiNH)_nSiR_3$. We have also prepared, for comparison with their imino analogs, the trimeric and tetrameric polyethylcyclopolysiloxanes. The properties of these compounds are summarized in Table I.

moles) of dimethyldichlorosilane was introduced beneath the surface of 500 ml. of liquid ammonia, contained in a 1-liter flask. The flask was provided with a stirrer and reflux condenser. The condenser and flask were cooled with Dry Ice-acetone mixtures. Stirring was continued for fifteen minutes after the addition of the chlorosilane. The product was extracted from the ammonium chloride with one 250-ml. portion and four smaller portions of benzene and, after distilling the benzene, amounted to 60 g. (76%). Fractionation gave 33 g. of hexamethylcyclotrisilazane and 20 g. of octamethylcyclotetrasilazane.

Polyethylcyclopolysilazanes.—An unsilvered Dewar flask of 1400-ml. capacity was provided with an ammonia inlet tube, a dropping funnel with a capillary tip and a Dry

TABLE I
NEW COMPOUNDS

	B. p. °C.	Mm.	M. p., °C.	n_D^{20}	d_4^{20}	Mol. wt. ^a		N, % ^b	
						Calcd.	Obs.	Calcd.	Found
$[(CH_3)_2SiNH]_3$	188	756	-10	1.4448	0.9196	219	208	19.15	19.08
$[(CH_3)_2SiNH]_4$	225	756	97	292	293	19.15	18.98
$[(C_2H_5)_2SiNH]_3$	150	10	-41	1.4670	.9287	303	292	13.84	13.75
$[(C_2H_5)_2SiNH]_4$	190-192	10	16	1.4769	.9521	404	393	13.84	13.21
$[C_2H_5(CH_3)_2Si]_2NH$	175	754	..	1.4212	.8079	7.40	7.24
$[(CH_3)_3SiNH]_2Si(CH_3)_2^c$	192-195	756	..	1.4281	.8366	11.95	12.12
$[(C_2H_5)_2SiO]_3^{d,e}$	117	10	14	1.4308	.9555
$[(C_2H_5)_2SiO]_4^d$	158-159	10	-50	1.4340	.9594

^a Molecular weights were determined cryoscopically in cyclohexane; $K = 20.6^\circ C./mole/1000 g.$ ^b Nitrogen was determined by digesting a weighed sample in 0.1 *N* hydrochloric acid for several hours and back-titrating with standard base. ^c Fraction 5, Table II. ^d Specific refraction, calculated (from Sauer's constants, reference 11) 0.2710; found: for trimer 0.2708, for tetramer 0.2714. ^e First reported by Hyde and Delong (THIS JOURNAL, 63, 1194 (1941)); their sample boiled at 140-148° (17 mm.), had cryoscopic molecular weight of 297.

Experimental

Polymethylcyclopolysiloxanes by Solvent Ammonolysis.—In a 5-liter, 3-necked flask, provided with mechanical stirrer, water-cooled condenser, and inlet tube, a solution of 903 g. (7 moles) of dimethyldichlorosilane in 3.5 liters of dry benzene was treated with dry ammonia. The gas was passed over the surface of the agitated solution which was held below 30° by external cooling. After four hours the precipitated ammonium chloride prevented further stirring. Treatment of the filtered solution, combined with the benzene washings from the ammonium chloride, was continued in a similar but uncooled vessel. The reaction mixture warmed to the reflux temperature of benzene and the ammonium chloride which separated now had a granular rather than a flocculent form. Treatment with ammonia was continued for two hours, after which the temperature dropped. The solution was filtered and the benzene distilled, leaving 415 g. (81%) of crude silazanes. By fractional distillation 185 g. of hexamethylcyclotrisilazane, $[(CH_3)_2SiNH]_3$, was separated. Distillation was continued from a simple distilling flask, yielding 210 g. octamethylcyclotetrasilazane which was purified by recrystallization from petroleum ether. The non-volatile residue amounted to 20 g.

Polymethylcyclopolysilazanes by Direct Ammonolysis.—Through a capillary-tipped dropping funnel 140 g. (1.08

Ice-acetone cooled reflux condenser. To 300 ml. of absolute ether sufficient ammonia was added to increase the volume to about 400 ml. A mixture of diethyldichlorosilane and diethylmethylchlorosilane, 515 g. (the 118-132° fraction from the treatment of diethyldichlorosilane and methylmagnesium bromide) was diluted to 1200 ml. with absolute ether. Three equal portions of this solution were added to ether-ammonia solutions prepared as indicated. After allowing the reaction mixtures to stand for fifteen minutes the ammonium chloride was removed by filtration and the ether washings combined with the filtrates. After removal of ether, flash distillation of the solution gave 143 g. of distillate boiling below 235°. Attempts to isolate constant-boiling material from the flash distillate were unsuccessful. Fractional distillation of the residue at reduced pressure gave first 24 g. of uncharacterized material which boiled over a wide range and which probably contained tetraethyltrimethylsilazane, and then 88 g. of hexaethylcyclotrisilazane and 41 g. of octaethylcyclotetrasilazane. Distillation was stopped because of decomposition. The residue amounted to 20 g.

In the hope of obtaining a better sample of the tetrasilazane, 157 g. (1.00 mole) diethyldichlorosilane, dissolved in 1000 ml. ether in a 2-liter, 2-nickel flask, provided with gas inlet tube, stirrer, and Dry Ice-acetone cooled condenser, was treated with ammonia until the solution became saturated. No cooling was provided for the flask; the addition of ammonia was continued until the flask began to frost from the refluxing of the excess ammonia. The separation of ammonium chloride from the solution occasioned considerable difficulty because of its extreme fineness. It was never completely removed and contaminated the silazanes, subliming with them during the fractionation. From the 64 g. of silazanes recovered, 44.6 g. of hexaethylcyclotrisilazane was separated by fractional distilla-

(1) The nomenclature used in this paper follows the recommendation of the A. C. S. Committee, *Chem. Eng. News*, 24, 1233 (1946).

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(3) (a) Kipping, *J. Chem. Soc.*, 91, 209 (1907); (b) Kraus and Rosen, *THIS JOURNAL*, 47, 2739 (1925); (c) Kraus and Nelson, *ibid.*, 56, 195 (1934); (d) Sauer, *ibid.*, 66, 1707 (1944); (e) Sauer and Hasek, *ibid.*, 68, 241 (1946); (f) Sommer, Bailey and Van Strien, 109th American Chemical Society Meeting, April, 1946.

tion, leaving a residue which the temperature readings at various locations in the still indicated to be mostly trimer. Complete separation was not feasible; we estimate that 85% of the silazanes produced was trimer.

The first preparation was questionable because of the possibility of forming linear polymeric polymers of the series $\text{CH}_3[(\text{C}_2\text{H}_5)_2\text{SiNH}]_n\text{Si}(\text{C}_2\text{H}_5)_2\text{CH}_3$. Analysis leaves no doubt as to the purity of the trimer, but the low nitrogen content of the sample of tetramer suggests that it may have been contaminated by a member of the linear series.

Diethyltetramethyldisilazane.—A mixture of diethyldimethylsilane and ethyldimethylchlorosilane was prepared by the treatment of dimethyldichlorosilane with ethylmagnesium bromide. A solution of 284 g. of this material (b. p. 85–100°) in two volumes of ether was added to an ether–ammonia solution following the procedure used in the first preparation of the polyethylcyclopolysilazanes. The greater part of the ether was removed by flash distillation and discarded. The material boiling above 45° was fractionally distilled. After the residual ether had distilled, the vapor temperature fell to 23° and then rose to 95° with the still at total reflux. Simultaneously the still pot temperature rose from 104 to 157° and the evolution of a considerable amount of ammonia was noted. Crude diethyldimethylsilane,⁴ 26 g., was first collected, followed by *sym*-diethyltetramethyldisilazane, 33 g. The residue, 35 g., was composed for the most part of the latter material.

We attribute the fall in vapor temperature and the coincident evolution of ammonia which occurred after the separation of the ether to the deamination of ethyldimethylaminosilane with the formation of diethyltetramethyldisilazane. This aminosilane is evidently sufficiently stable to survive storage at room temperature but decomposes below its boiling point.

Octamethyltrisilazane.—A mixture of hexamethyldisilazane, 81 g. (0.5 mole), hexamethylcyclotrisilazane, 37 g. (0.17 mole), and ammonium chloride, 0.5 g., was heated in a 180-ml. Aminco bomb at 300 to 325° for twenty-six hours. The pressure rose from 2450 to 3100 p.s.i. during the heating period; at room temperature the pressure gage gave no reading but considerable gas, apparently ammonia, escaped when the bomb was opened.

The liquid product was distilled through a column of approximately fifteen theoretical plates, giving the fractions listed in Table II.

TABLE II
SEPARATION OF OCTAMETHYLTRISILAZANE

Fract.	B. p., °C.	Wt., g.	n_D^{20}	d_4^{20}	R_D^{20}
1	118.2–159.2	60.0
2	159.2–190.4	5.1
3	190.4–191.8	3.6	1.4292	0.8430	0.3059
4	191.8–192.2	7.2	1.4285	.8389	.3070
5	192.2–194.8	5.1	1.4281	.8366	.3076
Res.	28.2

The foregoing experiment was repeated, the reaction mixture being heated for fourteen hours at 410°, followed by seventy-two hours at 350°. The distillation curve coincided with that of the first experiment, indicating that equilibrium composition had been attained.

The direction of the change of the physical properties of the last three fractions indicates the presence of traces of the cyclic trimer, hexamethylcyclotrisilazane. The weight distribution is notable in that the type of random distribution of molecular size found in the analogous siloxane system^{5,6} does not apply here. In the present case 60 g. of hexamethyldisilazane and 19 g. of octamethyltrisilazane

(4) Bygden, *Z. physik. Chem.*, **90**, 243 (1915), reports for $(\text{C}_2\text{H}_5)_2\text{Si}(\text{CH}_3)_2$ b. p. 95.7–96.2° (759 mm.); n_D^{20} 1.39819; d_4^{20} 0.7129. The first of our two fractions, having a slight ammoniacal odor, showed b. p. 95.0–95.8°; n_D^{20} 1.4000; d_4^{20} 0.7190.

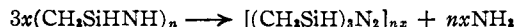
(5) Wilcock, *THIS JOURNAL*, **69**, 477 (1947).

(6) Scott, *ibid.*, **68**, 2294 (1946).

were isolated, while with random molecular size distribution these amounts would be 40 g. and 29 g., respectively.

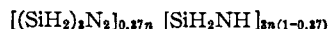
Ammonolysis of Methylchlorosilane.—Methyldichlorosilane, 230 g. (2 moles), was treated with ammonia, following the method used in the preparation of the polyethylcyclopolysilazanes. After evaporation of the ether, 60 g. of a viscous oil which did not boil below 195° remained. It was subjected to destructive distillation in a stream of nitrogen, giving a distillate of 28 g. of mobile liquid. Ammonia was evolved during the cracking. The residue was a porous, brittle resin, unaffected by further heating, which reacted very slowly with alcoholic potassium hydroxide. Fractional distillation of the condensate failed to give a pure compound. Ammonia escaped from the still during the attempted fractionation, and after the collection of 5.2 ml. of distillate, most of which boiled irregularly between 166 and 168°, the contents of the still pot set to a gel. This gel reacted much more rapidly with alcoholic potassium hydroxide than did the residue from the cracking. The boiling point of the distillate indicates that it was principally trimethylcyclotrisilazane, but, because of its obvious lack of purity, it was not examined further.

The evolution of ammonia during the cracking of the ammonolysis product of methylchlorosilane and also during the fractionation of the volatile cracking product is indicative of a rearrangement, which, at completion, is represented by the equation



No analyses of the residues are available, but their physical nature was typical of cross linked polymers.

A comparison of these conclusions with those of Stock and Somieski⁷ is pertinent, since these workers reported that $(\text{SiH}_2\text{NH})_x$ is the product of the reaction of dichlorosilane and ammonia. When formed in benzene solution their product was a viscous oil having a degree of polymerization of 7.5, which set to a clear hard glass on standing by itself. When formed in the gas phase it was a non-volatile solid. Analysis was impossible because the latter silazane was inseparable from the ammonium chloride. Their postulation of the cyclic structure $(\text{SiH}_2\text{NH})_x$ was based on the material balance of the gases concerned with the reaction. Their formula conforms more closely to this datum than does any other simple structure. However, close inspection of their material balance indicates that their gas-formed silazane had the formula



This is a cross-linked structure which would be expected to have the properties which they describe, similar to those of our cracking residue, and thus probably structurally analogous.

Polyethylcyclopolysiloxanes.—Diethyldichlorosilane, 260 g. (1.55 moles), was introduced from a dropping funnel into 1.5 liters of vigorously stirred ice-water. The oil which separated was taken up in an equal volume of ether, washed twice with water, and dried over potassium carbonate. After evaporation of the ether, the oil was fractionally distilled. Hexaethylcyclotrisiloxane,⁸ 23.5 g., was collected at 117° (10 mm.) followed by octaethylcyclotetrasiloxane, 46.2 g. The purity of the latter was suspect because the vapor temperature fell during its distillation, indicating formation of trimer in the still pot by pyrolysis⁹ of the higher polymers. The still was drained and the residue, 70 g., was subjected to destructive distillation at atmospheric pressure in a stream of nitrogen. The distillate, 50 g., was combined with the tetramer which had been previously distilled and the mixture was fractionated in the same column. Trimer, 25.4 g., was followed by tetramer, 39.0 g., boiling at 158° (10 mm.). The residue, 22.5 g., contained some tetramer.

(7) Stock and Somieski, *Ber.*, **54**, 740 (1921).

(8) Hyde and DeLong, *THIS JOURNAL*, **63**, 1194 (1941), isolated hexaethylcyclotrisiloxane, b. p. 140–148° (17 mm.), mol. wt. 297 (benzene), from the hydrolyzate of diethyldichlorosilane.

(9) Patnode and Wilcock, *THIS JOURNAL*, **68**, 358 (1946).

Discussion

Comparison of Silazanes with Analogous Siloxanes.—Three different homologous series of siloxanes derived from dimethyldichlorosilane have been reported.⁹ These have the general formulas: $\text{CH}_3[(\text{CH}_3)_2\text{SiO}]_n\text{Si}(\text{CH}_3)_2$, $[(\text{CH}_3)_2\text{SiO}]_n$, and $\text{Cl}[(\text{CH}_3)_2\text{SiO}]_n\text{Si}(\text{CH}_3)_2\text{Cl}$. We have prepared the lower members of the silazane series which are analogous to the first two of these siloxane series. We have not attempted the preparation of α,ω -dichloropolysilazanes.

In the preparation of the linear siloxanes, sulfuric acid is used as catalyst at room temperatures in the equilibration of hexamethyldisiloxane with the hydrolysate of dimethyldichlorosilane.⁹ The analogous procedure for the preparation of linear silazanes was not practical. Instead, equilibrium was attained at elevated temperature and pressure with ammonium chloride as catalyst. As noted above, the composition of the equilibrated mixture was unlike that found in the siloxane series; considerably more than the statistical amount of the hexamethyldisilazane remained unincorporated in the higher molecular weight material. This difference in the distribution of molecular species indicates a greater tendency toward ring formation, as opposed to chain formation, in the silazane series than in the siloxane series. Another manifestation of the greater ring-forming tendency is found in the molecular size distribution of the products of the ammonolysis of dimethyldichlorosilane. Of these 45 to 55% is the cyclic trimer while in the siloxane series only 0.5% of the hydrolysis product is the cyclic trimer.⁹

Another interesting difference between the lower cyclic siloxanes and the corresponding silazanes is the reversal of the melting point relationships. As shown in Table III, the tetramer is higher melting than the trimer in the silazane series while the reverse is true in the siloxane series. This is also true of the derivatives of diethyldichlorosilane.

TABLE III

MELTING POINTS OF POLYALKYLCYCLOPOLYSILAZANES AND ANALOGOUS SILOXANES

<i>n</i>	R	$(\text{R}_2\text{SiNH})_n$	$(\text{R}_2\text{SiO})_n$
3	CH ₃	-10	+64°
4	CH ₃	+97	+17.5°
3	C ₂ H ₅	-41	+14
4	C ₂ H ₅	+16	-50

° Reference 9.

Extent of Substitution on Nitrogen.—When silazanes are formed by the ammonolysis of chlorosilanes a single product usually predominates, and, depending upon the particular chlorosilane, there is a limit to the extent of the substitution upon the nitrogen. The simplest case is that of the monochlorosilanes. Of the silazanes derived from these, there is only one which has three silicons attached to nitrogen. This is silyldisilazane $(\text{SiH}_3)_3\text{N}$, the analog of trimethylamine, prepared by Stock and Somieski.⁷ The

same authors prepared disilazane, $(\text{SiH}_3)_2\text{NH}$, together with some silyldisilazane by using an excess of ammonia.

Sauer and Hasek,^{3e} by the ammonolysis of trimethylchlorosilane, prepared hexamethyldisilazane $[(\text{CH}_3)_3\text{Si}]_2\text{NH}$. That they are unable to detect trimethylaminosilane makes it appear unlikely that Stock and Somieski had any aminosilane in their reaction mixtures.

In the present work evidence for the existence of ethyldimethylaminosilane has been found; this material is unstable below its normal boiling point.

The greater part of the product of the ammonolysis of triethylchlorosilane^{3e} is triethylaminosilane, which is stable at its boiling point; considerable amounts of hexaethyldisilazane are also formed.

It is evident that the stability of these aminosilanes follows a consistent pattern. The greater the bulk of the inert substituents, the more stable is the aminosilane. Inspection of Fisher-Hirschfelder models indicates that this should be expected if the deamination follows the bimolecular nucleophilic ($\text{S}_{\text{N}}2$) reaction mechanism. The same sort of generalization applies in the case of the dehydration of the silanols and has been demonstrated quantitatively in the case of the attack of hydroxyl ion upon trialkylsilanes.¹⁰

The considerations which apply to the transition of a disilazane to a silyldisilazane are somewhat more obscure and already have been discussed in detail.^{3e} It seems likely that the reason that none but the simplest of the silyldisilazanes has been found is that the reaction by which they would be formed is blocked sterically.

When the ammonolysis products of dichlorosilanes are considered, the same considerations seem to apply. Thus, when the silicon atom bears only two hydrogen atoms, as in Stock's work, or a hydrogen atom and a methyl group, as in our work, products may be derived which contain nitrogen atoms attached to three silicons. When two methyl groups are attached to the silicon atom, only two such silicon atoms may be substituted upon nitrogen.

The Refractometric Constant for the Silazane Group.—There are now a sufficient number of silazanes to permit the deduction of the refractometric constant for the silazane (Si-NH-Si) group. By subtracting from the observed molar refractions the appropriate combination of the bond refractions determined by Sauer¹¹ for the silicon-alkyl groups, we have computed the following values for the refraction of the silazane group from the indicated compounds:

$[(\text{CH}_3)_3\text{Si}]_2\text{NH}^{3d}$	Ml.
$[\text{C}_2\text{H}_5(\text{CH}_3)_2\text{Si}]_2\text{NH}$	5.95
$[(\text{CH}_3)_2\text{SiNH}]_3$	6.07
$[(\text{C}_2\text{H}_5)_2\text{SiNH}]_3$	6.02
	6.05
Average	6.02

(10) F. P. Price, *THIS JOURNAL*, **69**, 2600 (1947).(11) Sauer, *THIS JOURNAL*, **68**, 954 (1946).

Because of their questionable purity, the other liquid silazanes reported in this paper have been omitted.

The value of 2.00 ml. has been proposed by Warrick¹² for the silicon-nitrogen bond refraction. Application of Denbigh's¹³ nitrogen-hydrogen bond refraction, 1.81 ml., to our silazane bond refraction indicates that the silicon-nitrogen bond refraction is 2.11 ml. It is possible that our value holds only for silazane bonds in compounds of the type from which it was derived.

(12) Warrick, *THIS JOURNAL*, **68**, 2455 (1946).

(13) Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

Acknowledgment.—We are indebted to Mr. L. B. Bronk for the nitrogen analyses and to Mr. R. Northrup for some of the molecular weight determinations.

Summary

1. Alkyl-substituted cyclic and linear low polymers of the silazane series are described and compared with their siloxane analogs.

2. A refractometric constant for the silazane group has been derived.

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Composition of Butadiene-Styrene Copolymers from Sodium-Catalyzed Polymerization

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The composition of butadiene-styrene copolymers as a function of conversion in the GR-S emulsion polymerization system has been investigated thoroughly in connection with the synthetic rubber program. The styrene content of copolymer from this process is relatively low at the start of the reaction¹ (17.2% styrene in copolymer from a 75/25 butadiene-styrene charge) increasing at higher conversions as the butadiene is depleted from the system. This presumably indicates that the butadiene is the more reactive monomer in this peroxide-catalyzed emulsion reaction; however, due to the complexity of the emulsion system and the uncertainty of the concentrations of the monomers at the reaction loci, no definite conclusion can be drawn as to the rate constants of the reactions of each of the monomers with growing polymer chains.

In their study of the sodium-catalyzed copolymerization of butadiene and styrene, Marvel, Bailey and Inskeep² observed copolymers at all conversions to have styrene contents higher than that of the monomer charge, but no definite trend of composition with conversion was noted. Compositions of the copolymers were determined by means of ultraviolet absorption. In a further study of the sodium-catalyzed reaction, using catalyst preparation, polymerization and polymer recovery techniques somewhat different from those of Marvel and co-workers, we have employed refractive index measurements³ to determine the composition of the copolymers with results showing styrene contents to be highest at low conversions and to decrease regularly as the reaction proceeds. Obviously, styrene is the more reactive monomer in this alkali metal-catalyzed reaction in contrast to the peroxide-catalyzed emulsion

process in which the opposite has been shown to be the case.

It was of interest that the refractive indices of copolymers prepared by the sodium-catalyzed reaction are considerably lower than for polymers of the same composition prepared by the emulsion reaction. This was substantiated with samples of known compositions prepared by reacting to complete conversion charges of various proportions of butadiene and styrene. Results are presented graphically in Fig. 1 in which the refractive indices are shown as a function of styrene contents of polymers from both processes, the line for GR-S being from data of Madorsky and Wood.⁴ From this correlation of refractive index with styrene

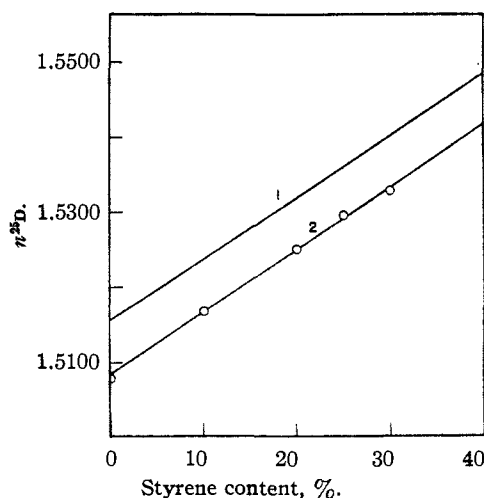


Fig. 1.—Refractive index of copolymers: 1, from emulsion reaction (data of ref. 4); 2, sodium-catalyzed reaction.

(1) Meehan, *J. Polymer Sci.*, **1**, 318 (1946).

(2) Marvel, Bailey and Inskeep, *ibid.*, **1**, 275 (1946).

(3) W. O. Baker and J. H. Heiss, Jr., private communication.

(4) Irving Madorsky and L. A. Wood, National Bureau of Standards, private communication.