

## NUCLEOPHILIC REACTIONS OF ORGANOCYCLOSILAZANES OF DIFFERENT STRUCTURE

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### SUMMARY

1. The catalytic polymerisation of phenylmethylcyclosilazanes and the effect of their configuration on reactivity have been studied.

2. New organocyclosilazanes with fixed configuration of the silazane ring were obtained.

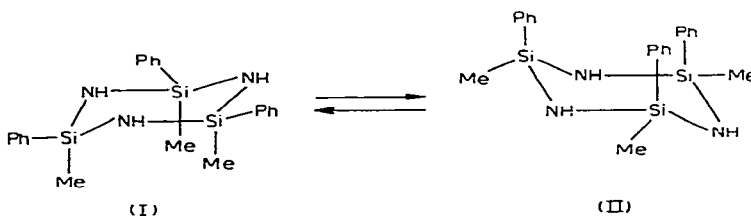
3. The catalytic co-polymerization of phenylmethylcyclosiloxanes and dimethylcyclosilazanes was achieved.

The effect of the molecular and electronic structure of organocyclosilazanes on some of their physical and chemical properties has been studied in earlier papers<sup>1-3</sup>. The peculiarities of the behaviour of this class of compounds compared to that of organocyclosiloxanes were considered on the basis of the interaction between organocyclosilazanes and nucleophilic reactants, and it was established that in these reactions they show a tendency to substitution in the organic radicals attached to the silicon atoms with formation of a new Si-N bond. It should be noted that silicon-nitrogen-containing heterocycles have some aromatic properties. This characteristic is especially strong in methylphenyl- and dimethylcyclosilazanes<sup>4-6</sup>. In the case of methylethyl-, methylbutyl-, methylhexyl- and diethyl-cyclosilazanes, a side reaction of Si-N bond fission begins to play an important part. This reaction yields complex cyclic systems<sup>1,7</sup>. The temperature for the start of alkyl radical substitution reactions increases to 70-80° for the latter cycles. These facts agree with the spectroscopic characteristics of the Si-N bond in organocyclosilazanes and in particular with the change of the Si-N bond force constant with increasing total effective electronegativity of the organic radicals surrounding the cycle<sup>2</sup>. However it is insufficient to consider only the electron distribution in organocyclosilazanes, because their reactions follow statistical laws and the reactivity in nucleophilic reactions will be determined also by the configurational properties and by spatial filling in cyclic molecules. The configuration of organosilicon heterocycles has been studied<sup>3,8</sup> and it was established that the configuration of the silazanic ring in simple cycles is not fixed, *i.e.*, a rapid conversion of the ring takes place resulting in approximately equal amounts of the two configurations. For example, the following equilibrium is attained

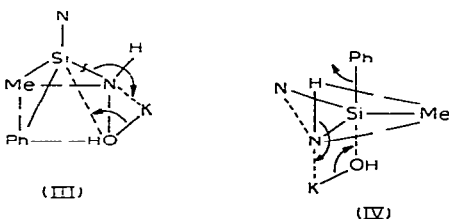
TABLE I  
REACTION OF PHENYL METHYL CYCLOSILAZANES

Compounds	Benzene moles yielded/mole initial cycle	Methane moles yielded/mole initial cycle	Ammonia moles yielded/mole initial cycle	$K\beta$ ( $10^{-4} \text{ sec}^{-1}$ )	Temp. polymer vitrification	Yield of oligomer
$\{(\text{C}_6\text{H}_5\text{CH}_3\text{SiNH})(\text{CH}_3)_2\text{SiNH}\}_2$	0.72	0.15	0.30	9.13	174	39
$\{(\text{C}_6\text{H}_5\text{CH}_3\text{SiNH})_2(\text{CH}_3)_2\text{SiNH}\}$	0.85	0.14	0.19	2.36	139	0
<i>trans</i> - $[\text{C}_6\text{H}_5\text{CH}_3\text{SiNH}]_3$	0.75	0.12	0.14	0.77	115	0
<i>cis</i> - $[\text{C}_6\text{H}_5\text{CH}_3\text{SiNH}]_3$	0.71	0.00	0.07	0.96	148	0

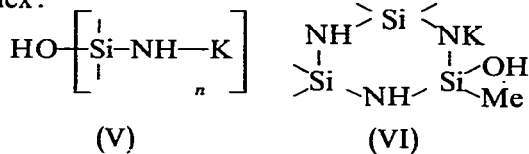
for the *cis*-isomer of triphenyl(methyl)cyclotrisilazane



This fact has to be taken into account in the probability approach to the reaction of catalytic polymerization of organocyclosilazanes, because the possibilities of substitution of corresponding organic groups of configurations I and II are different. We have investigated the polymerization of phenylmethylcyclosilazanes of different structure in the presence of catalytic amounts of KOH (Table 1). The reaction order was determined from the kinetics of benzene liberation.  $K\beta$  rate constants were calculated according with a first-order reaction. First, let us consider the polymerization of the *cis*- and *trans*-isomers of triphenyl(methyl)cyclotrisilazane, taking into account some features of this reaction mechanism. The polymerization process starts with dissolution of alkali. Its molecules attack neutral molecules of the cycle forming a transition complex in conformity with the  $S_Ni$ -Si mechanism. The  $S_N1$ -Si; and  $S_N2$ -Si mechanisms are of low probability because this would require dissociation of alkali molecules and the conditions for such dissociation are unfavourable. As to the structure of the transient state for the  $S_Ni$ -Si mechanism, a tetragonal pyramid or a trigonal bipyramid



can be formed depending on the direction of attack at the Si-X bond, where X is the group detached. In case of a trigonal bipyramid (IV) both  $-N<$  and  $-Ph$  can be the group detached. However from an energy stand-point, cleavage of the Si-Ph bond rather than of the Si-N bond seems to be preferable provided the position of at least one proton in the adjacent NH-groups is such that it can be of electrophilic assistance to the Ph-group, having regard to its geometrical position. When a tetragonal pyramid (III) is formed, the Si-C bond cleavage is impossible from geometrical considerations and only  $-N<$  will be the group detached, potassium giving electrophilic assistance. The electronic transitions taking place under such conditions are shown in the Figure. Since both processes are theoretically possible, two types of nucleophilic particles can be present in the mixture after decay of the transitional complex:



These carry on the process. The nature and rate of the process will be determined by the number of possible collisions of these particles with the reaction centres, by the direction of attack and the energy of the broken bonds. For example, the probability of attack of any *cis*-isomer of triphenyl (methyl)cyclotrisilazane by a nucleophilic particle resulting in the formation of a trigonal bipyramid with a phenyl group at the top, is  $P_1 = \frac{1}{4}$ . The screening effect of the methyl groups is not taken into account here because it is negligible. The screening effect of the phenyl groups in a *trans*-isomer should be allowed for. Let us denote this effect for the group connected with a reactive silicon atom by  $\beta$  and the adjacent group by  $\alpha$ . Then the following value is obtained for the *trans*-isomer.

$$P_2 = (\frac{1}{12} - 2\alpha) + 2(\frac{1}{12} - \alpha) = \frac{1}{4} - 4\alpha$$

On formation of a trigonal bipyramid with a methyl group at the top in the *cis*- and *trans*-isomers, the probability values will be  $P'_1 = \frac{1}{4} - 3\beta - 6\alpha$  and  $P'_2 = \frac{1}{4} - 3\beta - 4\alpha$ , respectively. It may be seen from these formulae that the process yielding benzene is more probable than that resulting in methane liberation, especially for the *cis*-isomer as

$$\frac{\frac{1}{4}}{\frac{1}{4} - 3\beta - 6\alpha} > \frac{\frac{1}{4} - 4\alpha}{\frac{1}{4} - 3\beta - 4\alpha}$$

It is easy to understand also that the  $\alpha$ - and  $\beta$ -values will be different for various attacking nucleophilic particles. For instance, they will be considerably lower for alkali molecules than for particles that carry on the process at the chain growth stage.

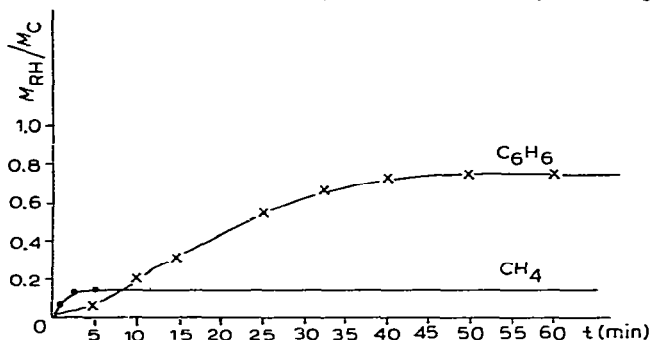
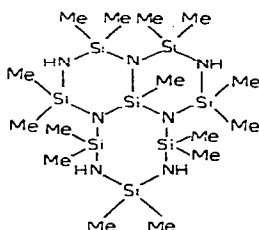


Fig. 1. Curves for benzene and methane evolution (moles/moles of initial cycle) on catalytic polymerization of *trans*-triphenyl(methyl)cyclotrisilazane.

For this reason the liberation of a relatively large amount of methane is possible at the initial stage. This is confirmed experimentally (Fig. 1). In spite of the high probability of the tetragonal pyramid formation leading to possible cleavage of the Si-N bond, this process is not essential for triphenyl(methyl)cyclotrisilazane. This may be seen from the small amounts of ammonia liberated in polymerization. Force constants, and thus the Si-N bond energy for phenylmethylcyclosilazanes, are somewhat higher than for dialkylcyclosilazanes<sup>2</sup>. Consequently, only an insignificant number of collisions will result in opening of the silazan cycle at the reaction temperature. Conversely, for dialkylcyclosilazanes that polymerize at higher temperature, the side reaction of Si-N bond cleavage becomes appreciable and has an effect on the structure of the products obtained<sup>1,7</sup>.

Table 1 lists the data referring to the phenylpentamethylcyclotrisilazane and diphenyltetramethylcyclotrisilazane polymerization. Asymmetric distribution of electron density due to higher concentration of positive charge at one or two silicon atoms is an essentially new element in the structure of these compounds. Here the probability of nucleophilic attack on sensitized silicon considerably increases and this leads to a sharply increasing rate constant,  $K\beta$ , in these cycles (Table 1). The Si-N bond cleavage takes place in this case. A relatively high yield of these oligomers is obtained by phenylpentamethylcyclotrisilazane polymerization. The molecular weight, elemental analysis, absence of the phenyl group in the NMR spectra and IR spectral data warrant the following tentative structure for these substances:

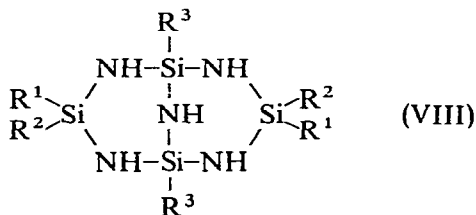


VII

Similar cycles have already been obtained<sup>1,7</sup> and they were all found to be inert to alkali up to a temperature of 300°.

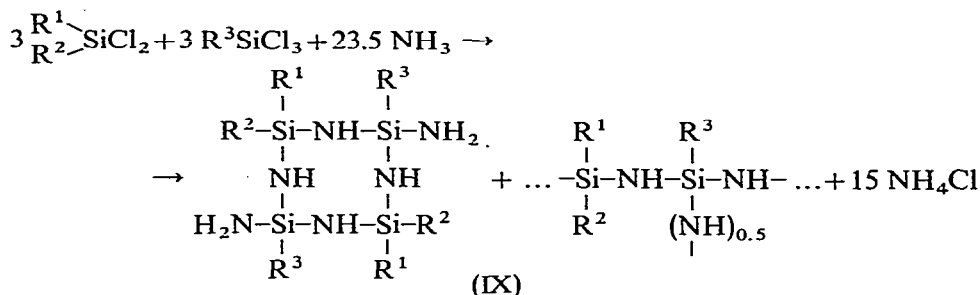
Since synchronous electronic transition that leads to the decay of the organosilazane transition complex with alkali, yielding carbon, takes place at a strictly fixed geometric position of the relevant bonds, it will naturally be determined by ready transition of a neutral molecule of the cycle to the activated state. Taking into consideration the above-mentioned conversion of the ring, this state will be obtained periodically at a high rate in simple cycles. However, rotation around the bonds seems to be rather difficult in complex polycyclic systems and as a result of it the cycle configuration may appear to be partially fixed. The energy of transition to an activated state must then increase considerably and this in its turn will lead to a decrease of the reactivity of these cycles with respect to nucleophilic reagents. A similar situation was observed for organoalkoxycyclosilazanes. The reason for slow rotation around Si-N-bonds appeared to be the formation of *intramolecular hydrogen bonds*<sup>3</sup>.

Taking into consideration the dependence between configurational properties and the reactivity of organosilicon-nitrogen-containing heterocycles, specific synthesis of organocyclosilazanes with fixed ring configuration seemed to be necessary. Data referring to bi-cyclic systems of type VIII are given in this paper.



These compounds are formed by *intramolecular* condensation of the products of di- and tri-functional organochlorosilanes ammonolysis.

The reaction follows the scheme:



The properties of the low-molecular products are given in Table 2.

TABLE 2

PHYSICAL PROPERTIES OF ORGANOCYCLOSILAZANES, VIII

No	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	B.p. (°C/mm)	n <sub>D</sub> <sup>20</sup>	d <sub>4</sub> <sup>20</sup>	M		MR	
							Calcd.	Found	Calcd.	Found
1	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>4</sub> H <sub>9</sub>	194-197/4	1.4880	0.9919	361	357	102.27	103.00
2	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>4</sub> H <sub>9</sub>	158-161/1	1.4769	0.9771	389	370	111.43	111.31
3	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>13</sub>	188-190/1	1.4837	0.9971	417	410	121.07	120.90
4	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>9</sub> H <sub>19</sub>	224-227/1	1.4790	0.9720	502	517	154.18	153.50

Condensation of cyclic compounds, IX, takes place when the NH<sub>2</sub>-group is positioned towards the plane of the cycle. Thus, if the NH<sub>2</sub>-groups are in the *anti*-position, the *intramolecular* condensation is not possible for steric reasons, and the organocyclosilazanes condense *intermolecularly*. If radicals such as hexyl and nonyl are near neighbours of the amino-group attached to the silicon atom, the *intermolecular* condensation is greatly hindered. In the case of these groups in the *syn*-position, the *intramolecular* condensation takes place with formation of bi-cyclic structures, VIII. The results of elemental analysis and infrared spectroscopy show that additions of uncompleted cycles IX are present in the compounds 3, 4. The adsorption bands at 1550 cm<sup>-1</sup> characteristic of the deformation oscillations of the initial amino-group were found in the infrared spectra of 3, 4. Adsorption bands referring to the Si-N and N-H bonds in the organocyclosilazanes were detected in the spectra of all compounds. The possibility of formation of four-membered cycles in compounds VIII has not been spectroscopically confirmed.

Nuclear magnetic resonance spectra show that the synthesized bi-cyclic organosilazanes differ in their configurational properties from the dialkylcyclosilazanes obtained previously<sup>3</sup>. The proton signals of the methyl groups in the dialkylcyclosilazane spectra are single signals with chemical shift,  $\delta = 0.01 + 0.02 \cdot 10^{-6}$ ; also there is no complication from methyl proton spectra as a result of the unequivalent orientation of the methyl groups towards the bonds of the silazane ring and other

substituents. This can be explained by averaging the local magnetic fields due to internal rotation in a molecule (conversion of the ring). The peaks of the methyl group protons are evidently split in the spectra of compounds VIII (Fig. 2); this can

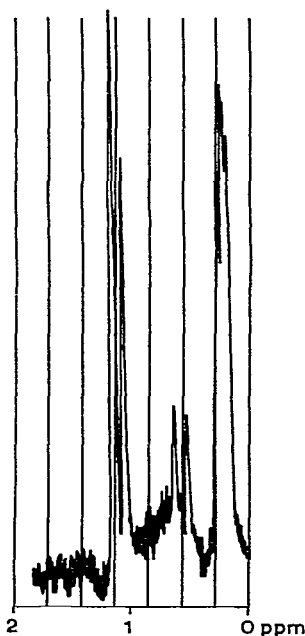


Fig. 2. NMR spectrum of compound VIII ( $R^1=R^2=CH_3$ ,  $R^3=C_4H_9$ ).

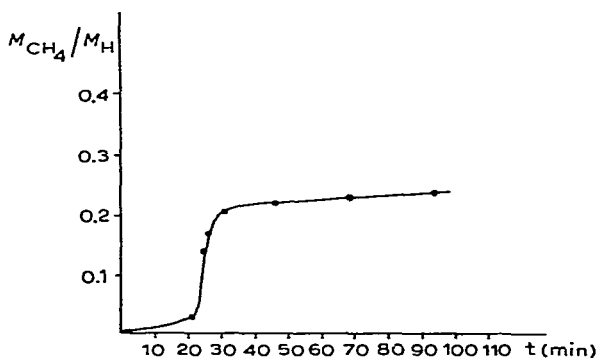


Fig. 3. Curve for methane evolution (moles/mole of initial cycle) on catalytic polymerization of compound VIII ( $R^1=R^2=CH_3$ ,  $R^3=C_4H_9$ ).

be connected only with slow internal rotation in the molecule. This points to the presence of isomers and congeners and must affect the reactivity of these cycles.

Indeed, the main parameters of catalytic polymerization<sup>1</sup> differ from those described previously<sup>6</sup>. As a result of the reaction, methane is evolved at 200°, which is much higher than the temperature for dimethyl cycles. The other peculiarity is a long-lasting induction period, (Fig. 3), which is apparently connected with some reconstruction of the bi-cyclic molecule. The evolution of a considerable quantity of

ammonia during this period is evidence of the cleavage of Si-N bonds in the complex cycle, probably the cleavage of the bridge bond, because this is the one that is least sterically protected against nucleophilic attack. Furthermore, the reconstructed cycle acquires a considerably larger number of degrees of freedom for different configurational transitions and thus a possibility for a favourable reaction procedure appears, owing to the formation of the transitional complex; the latter decomposes with production of a methane molecule.

The investigations carried out on the catalytic polymerization of phenyl-(methyl)cyclosilazanes enabled us to understand some peculiarities of the combined polymerization of triphenyl(methyl)cyclotrisiloxane and hexamethylcyclotrisilazane in the presence of catalytic quantities of KOH. On combined polymerization, a considerably larger quantity of benzene and ammonia is emitted and a brittle glass-like polymer is formed, the glass-forming temperature of which depends on the structure of the initial cycles and the conditions of the reaction. To stabilize detached phenyl groups it is necessary to obtain protons which can be taken from NH-groups of hexamethylcyclotrisilazane only under these conditions. Two principal routes for the reaction could be offered in this case: (i) a benzene molecule is evolved and a new Si-N bond is formed as a result of the encounter of siloxane and silazane molecules; (ii) a preliminary combined rearrangement of siloxanes and silazanes results in polymerization of the compounds obtained, the process following the mechanism characteristic of organocyclosilazanes. The first route is hardly possible; this can be confirmed by studying the kinetics of the reaction and determining the order of the reaction. Copolymerization has been carried out under milder conditions at 150° in order to establish possibilities for combined rearrangement. No hydrocarbon evolution was observed, because it is only the cleavage of Si-N and Si-O bonds with formation of oligomers that recombine to mixed organocyclosiloxanes that takes place in this case. The curve for distillation of the reaction mixture in the presence of alkali at 150° and that of the mixture without any heating (Fig. 4), gives some idea

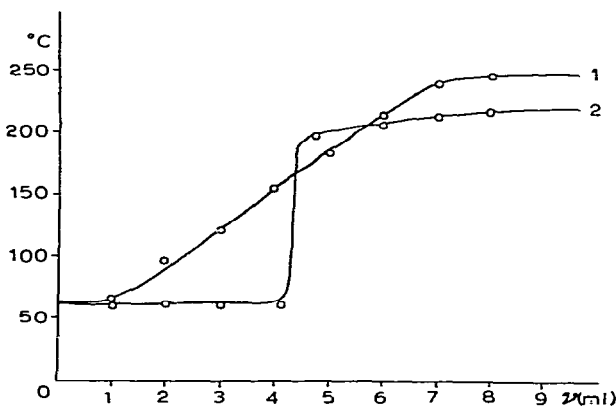


Fig. 4. Distillation curve for: (1), products of combined rearrangement of triphenyl(methyl)cyclotrisiloxane and hexamethylcyclotrisilazane in the presence of 1% KOH at 150°; (2) mixture of these products without the addition of KOH.

of the process. The combined rearrangement must result in a wide range of products that are separated with difficulty, and vary in structure and reactivity. Therefore,



TABLE 3  
 COPOLYMERIZATION OF PHENYLMETHYLCYCLOSILOXANES AND DIMETHYLCYCLOSILAZANES OF VARIOUS STRUCTURE

Initial monomers	Benzene moles yielded/mole initial siloxane	Methane moles yielded/mole initial silazane	Ammonia moles yielded/mole initial silazane	$K\beta$ ( $10^{-3} \text{ sec}^{-1}$ )	Induction period (min)	Vitri- fication temp. ( $^{\circ}\text{C}$ )
$[(\text{CH}_3)_2\text{SiNH}]_3$	1.6	0.00	0.11	0.08	18	60
$[(\text{CH}_3)_2\text{SiNH}]_3$ <i>trans</i> - $[\text{C}_6\text{H}_5\text{CH}_3\text{SiO}]_3$	2.4	0.00	0.04	1.75	13	175
$[(\text{CH}_3)_2\text{SiNH}]_4$ <i>cis</i> - $[\text{C}_6\text{H}_5\text{CH}_3\text{SiO}]_3$	1.8	0.26	0.18	0.75	7	123
$[(\text{CH}_3)_2\text{SiNH}]_3$ <i>cis</i> - $[\text{C}_6\text{H}_5\text{CH}_3\text{SiO}]_3$	2.9	0.00	0.09	0.36	14	180
$[(\text{CH}_3)_2\text{SiNH}]_4$ $[\text{C}_6\text{H}_5\text{CH}_3\text{SiO}]_4$	2.3	0.21	0.13	0.15	15	89

the process on the whole will be determined by the rate of rearrangement which depends on the initial cycle structure, and by the structure of products obtained at the rearrangement stage.

It should be mentioned that in a number of cases a small amount of methane is formed together with evolution of benzene and ammonia. A similar evolution occurred on the copolymerization of octamethylcyclotetrasilazane, and is apparently accounted for by a separate partial polymerization of silazane. The main parameters of the catalytic copolymerization for cycles of various structures are given in Table 3. The reactivity of the initial monomers in the reaction can be assessed by means of these data. The process proceeds more rapidly if *cis*-triphenyl(methyl)cyclotrisiloxane and hexamethylcyclotrisilazane take place in the reaction. A polymer with a high vitrification temperature is formed but its characteristic viscosity is low. The 930–950, 1020–1060, 1180 and 3400  $\text{cm}^{-1}$  adsorption bands characteristic of infrared arrangements were found in the Si–O–Si and Si–NH–S spectra of this polymer.

TABLE 4

COPOLYMERIZATION OF PHENYLMETHYLCYCLOSILOXANES AND DIMETHYLCYCLOSILAZANES AT VARIOUS CONCENTRATIONS OF THE INITIAL CYCLES

Mole ratio [C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> SiO] <sub>4</sub> : [(CH <sub>3</sub> ) <sub>2</sub> SiNH] <sub>4</sub>	Benzene moles/ mole initial siloxane	Methane moles/ mole initial silazane	Ammonia moles/ mole initial silazane	Kβ (10 <sup>-3</sup> sec <sup>-1</sup> )	Induction period (min)	Yield low molecular oligomers (%)
1:3	2.7	0.27	0.56	0.55	13	54
1:2	1.8	0.21	0.35	0.17	15	46
1:1	2.3	0.21	0.13	0.15	15	0

A change in the ratio of the initial reactants (Table 4) results in some increase of *Kβ* and ammonia yield, and in the formation of low-molecular oligomers of complex cyclic structure.

#### EXPERIMENTAL

All catalytic polymerization reactions were carried out by the methods described earlier<sup>1,4</sup>.

#### *Polymerization of phenylpentamethylcyclotrisilazane*

11.05 g of {(C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>SiNH)[(CH<sub>3</sub>)<sub>2</sub>SiNH]<sub>2</sub>} and 0.11 g of KOH were heated for 2.5 h at 220°; 2.2 g of benzene, 0.097 g of methane and 0.2 g of ammonia were evolved. In the reaction flask, 8.6 g of viscous product remained from which the following fractions were separated on vacuum distillation: (I) 140–220°/1 mm, 0.89 g; (II) 220–243°/1 mm, 3.48 g. The residue was a brittle glass-like product with vitrification temperature, 170°. On repeated distillation of the second fraction a product with a boiling point of 225–230° was isolated. (Found: C, 33.51, 33.40; H, 8.21, 8.19; Si, 40.20, 40.01; N, 17.64, 17.82; mol. wt. 550. (CH<sub>3</sub>)<sub>15</sub>Si<sub>8</sub>N<sub>3</sub>(NH)<sub>4</sub> calcd.: C, 32.7; H, 8.9; Si, 40.80; N, 17.7%; mol. wt. 552.)

*Polymerization of diphenyltetramethylcyclotrisilazane*

9.1 g of  $\{(C_6H_5CH_3SiNH)_2[(CH_3)_2SiNH]\}$  and 0.1 g of KOH were heated under similar conditions; 1.76 g benzene, 0.058 g methane and 0.084 g ammonia were evolved.

*Polymerization of triphenyl(methyl)cyclotrisilazane*

The reactions of the *cis*- and *trans*-isomers were carried out separately under similar conditions. The quantities of low-molecular products evolved in molar ratio are given in Table 1.

The reactions of catalytic copolymerization were carried out by the same method as that for the polymerization of organocyclosilazanes.

*Copolymerization of triphenyltrimethylcyclotrisiloxane and hexamethylcyclotrisilazane*

7.22 g of  $(C_6H_5CH_3SiO)_3$  with a melting point of  $98^\circ$ , 3.55 g of  $[(CH_3)_2SiNH]_3$  with a boiling point of  $188$ – $192^\circ$  and 0.11 g of KOH were heated at  $220^\circ$  until the evolution of gaseous and liquid products ceased. The usual quantity of the benzene obtained was 3.32 g (2.4 mole per mole of the initial  $[C_6H_5CH_3SiO]_3$ ) and ammonia—0.012 g (0.04 mole per mole of the initial  $[(CH_3)_2SiNH]_3$ ). 7.45 g of a brittle polymer, soluble in organic solvents and with a characteristic viscosity in toluene of 0.15, remained in the reaction flask.

*Combined rearrangements of phenylmethylcyclosiloxanes and dimethylcyclosilazanes*

7.06 g of  $[C_6H_5CH_3SiO]_3$  and 3.76 g of  $[(CH_3)_2SiNH]_3$  were heated in the presence of 0.1 g of KOH at  $150^\circ$  for 10 h. A small amount of ammonia was formed but no evolution of benzene or methane was observed. The reaction products were dissolved in 30 ml of benzene, washed with water and, after benzene had been removed, distilled *in vacuo* at 1 mm Hg. The products boiled in the range,  $63$ – $250^\circ$ . For fractions with a boiling point of  $148$ – $165^\circ$  and  $n_D^{20} = 1.5150$ , the ratio between integral intensities for proton peaks in the NMR spectrum,  $H_{Me} : H_{Ph}$ , was 1.36 : 1; analysis for nitrogen was 4.61%.  $\{(C_6H_5CH_3SiO)_2[(CH_3)_2SiNH]\}$  calcd.:  $H_{Me} : H_{Ph}$ , 1.2 : 1; N, 4.10%.

Catalytic copolymerisation of phenylmethylcyclosiloxanes with dimethylcyclosilazanes of various molecular structures and with different concentrations of the initial reagents was carried out by the method described above. The quantities of gaseous and liquid products evolved, as well as some other parameters, are given in Tables 3 and 4. Low-molecular oligomers are formed on polymerization with excess silazane, an example of which is given below.

*Copolymerisation of tetraphenyltetramethylcyclo-tetrasiloxane with octamethylcyclo-tetrasilazane*

5.19 g of  $[C_6H_5CH_3SiO]_4$  with b.p.  $230$ – $240^\circ/1$  mm, 5 g of  $[(CH_3)_2SiNH]_4$ , m.p.  $97^\circ$ , and 0.11 g of KOH were heated at  $220^\circ$  until evolution of methane, benzene and ammonia ceased. The duration of the reaction was 3 h. The viscous liquid (8.8 g) that remained in the flask gave the following fractions on vacuum distillation: (I)  $145$ – $160^\circ/1$  mm—1.29 g. C, 32.40; H, 8.38; Si, 40.69; N, 13.20%. (II)  $160$ – $170^\circ/1$  mm—2.73 g. C, 31.98; H, 7.80; Si, 41.12; N, 13.16%. A glass-like polymer (4.54 g) remained in the still.

The co-ammonolysis of di- and tri-functional organochlorosilanes was carried out by gaseous ammonia in benzene. After removal of ammonium chlorate and benzene, the reaction mixture was distilled *in vacuo*. The quantity of the products distilled did not exceed 5%. Their physical properties are given in Table 2 and the

TABLE 5

ANALYSIS OF ORGANOCYCLOSILAZANES, VIII

R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Calcd (%)				Found (%)			
			C	H	Si	N	C	H	Si	N
CH <sub>3</sub>	CH <sub>3</sub>	C <sub>4</sub> H <sub>9</sub>	39.84	9.74	31.06	19.36	40.02	9.62	30.60	19.67
			39.94				39.94	9.57	30.78	19.50
CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>4</sub> H <sub>9</sub>	43.13	10.08	28.82	17.97	43.25	9.83	30.13	17.78
			43.05				43.05	9.87	29.61	17.82
CH <sub>3</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>13</sub>	45.98	10.37	26.89	16.76	45.49	9.91	26.97	17.65
			45.57				45.57	9.80	26.85	17.42
CH <sub>3</sub>	CH <sub>3</sub>	C <sub>9</sub> H <sub>19</sub>	52.63	11.04	22.38	13.95	51.32	10.96	21.41	14.54
			51.46				51.46	10.71	21.68	14.85

results of elemental analysis in Table 5. The residue consisted of solid polymers soluble in organic solvents.

## REFERENCES

- 1 K. A. ANDRIANOV AND G. V. KOTRELEV, *J. Organometal. Chem.*, 7 (1967) 217.
- 2 K. A. ANDRIANOV, V. P. BAZOV AND G. V. KOTRELEV, *Dokl. Akad. Nauk SSSR*, 176 (1967) 579.
- 3 K. A. ANDRIANOV, G. V. KOTRELEV, B. D. LAVRUKHIN AND L. N. OROBINSKAYA, *Izv. Akad. Nauk SSSR*, 10 (1967) 2275.
- 4 K. A. ANDRIANOV AND G. V. KOTRELEV, *Vysokomolekul. Soedin.*, 4 (1964) 691.
- 5 K. A. ANDRIANOV, B. A. ISMAILOV, A. M. KONONOV AND G. V. KOTRELEV, *J. Organometal. Chem.*, 3 (1965) 129.
- 6 K. A. ANDRIANOV AND G. J. RUMBA, *Vysokomolekul. Soedin.*, 4 (1962) 1010.
- 7 K. A. ANDRIANOV, G. V. KOTRELEV AND L. O. KOGAN, *Heterocycl. Soedin.*, (1967) 364.
- 8 K. A. ANDRIANOV, B. D. LAVRUKHIN, E. I. FEDIN AND A. A. ZHDANOV, *Dokl. Akad. Nauk SSSR*, 173 (1967) 331.

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