REACTIONS OF ORGANOCYCLOSILAZANES WITH ELECTROPHILIC AND NUCLEOPHILIC REAGENTS

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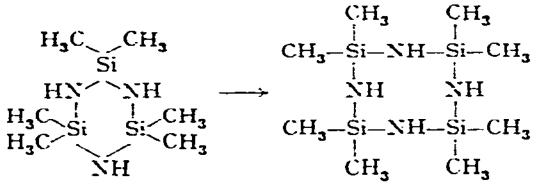
The reactions of dimethyl- and phenylmethylcyclosiloxanes in the presence of electrophilic and nucleophilic reagents lead to breakage of the rings and formation of polymers:

$$m(R_2SiO)_n \longrightarrow (R_2SiO)_{mn} \qquad (1)$$

The behaviour of organocyclosilazanes is radically different from that of organocyclosiloxanes. When hexamethylcyclotrisilazane is treated with a catalytic quantity of an electrophilic reagent redistributions leading to enlargement and reduction in ring-size occur[1], together with polymerization.

Studies of the rearrangements of hexamethylcyclotrisilazane and octamethylcyclotetrasilazane proved that the yields of rearrangement and polymerization products depend essentially on the nature of the electrophile and nucleophile used, as well as on the reaction conditions. Thus, treatment of hexamethylcyclotrisilazane with 0.3 % aluminium chloride at 140° results in ring-enlargement, with formation of more than 8 % of octamethylcyclotetrasilazan, whereas at 160° over 14 % of the latter compound is produced; the yield of polymers in this case exceeds 16 %.


(2)

Further addition of aluminium chloride and raising of the reaction temperature to 240° increases the yield of octamethylcyclotetrasilazane to 19.8 % and the yield of polymer to 69 %.

With titanium tetrachloride or tin tetrachloride, hexamethylcyclotrisilazane rearranges to give octamethylcyclotetrasilazane in 5.5 % and 29 % yields, respectively. Hexamethylcyclotrisilazane when treated with phenyltrichlorosilane gives 31 % of octamethylcyclotetrasilazane.

In presence of aluminium chloride, octamethylcyclotetrasilazane at 160° gives hexamethylcyclotrisilazane in 28.6 % yield (3).

Change of ring-size of organocyclosilazanes also occurs when they are treated

TABLE 1

DATA CONCERNING THE REARRANGEMENTS OF DIMETHYLCYCLOSILAZANES

Initial silazane	*Reagents*	*Quantity of catalyst* (%)	*Reaction time* (*h*)	*Reaction temp.* (°C)	*Yield of rearrangement product* (%)	*Rearrangement product*	*Yield of polymer* (%)	*Ref.*
$[(CH_3)_2SiNH]_3$	$(CH_3)_3SiCl + NH_3$	—	—	20–40	36.6	$[(CH_3)_2SiNH]_4$	12.3	1
$[(CH_3)_2SiNH]_3$	NH_4Cl	0.5	48	220–250	3	$[(CH_3)_2SiNH]_4$	—	1
$[(CH_3)_2SiNH]_3$	$AlCl_3$	0.29	5	140	8.2	$[(CH_3)_2SiNH]_4$	16.2	
$[(CH_3)_2SiNH]_3$	$AlCl_3$	0.3	5	160	14.3	$[(CH_3)_2SiNH]_4$	16.7	
$[(CH_3)_2SiNH]_3$	$AlCl_3$	3.8	5	240	19.8	$[(CH_3)_2SiNH]_4$	69.1	
$[(CH_3)_2SiNH]_3$	$TiCl_4$	1.9	6	240	5.5	$[(CH_3)_2SiNH]_4$	65	
$[(CH_3)_2SiNH]_3$	$SnCl_4$	1.1	8	195	29	$[(CH_3)_2SiNH]_4$	13.2	
$[(CH_3)_2SiNH]_3$	$C_6H_5SiCl_3$	2.0	5	230	31	$[(CH_3)_2SiNH]_4$	8	
$[(CH_3)_2SiNH]_3$	H_2SO_4	0.5	216	20	79.2	$[(CH_3)_2SiNH]_4$	—	2
$[(CH_3)_2SiNH]_3$	H_2SO_4	1.5	24	20	90	$[(CH_3)_2SiNH]_4$	—	
$[(CH_3)_2SiNH]_3$	H_2SO_4	1.5	3	175	8.3	$[(CH_3)_2SiNH]_4$	16.5	
$[(CH_3)_2SiNH]_4$	$AlCl_3$	0.54	6	160	28.6	$[(CH_3)_2SiNH]_3$	3.2	
$[(CH_3)_2SiNH]_4$	H_2SO_4	1.5	3	175	38	$[(CH_3)_2SiNH]_3$	11.8	

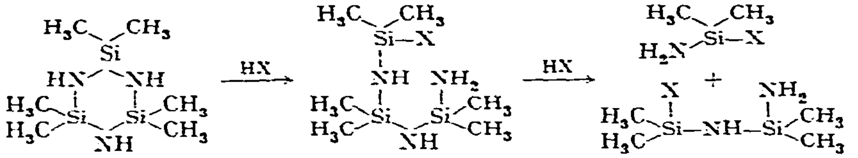
with sulfuric and nitric acids[2]. The reaction with sulfuric acid proceeds vigorously and the products depend on the conditions and the proportions of the starting materials. The addition of small quantities of concentrated sulfuric acid to hexamethylcyclotrisilazane causes almost quantitative ring-enlargement, even at room temperature. It is interesting to note that when hexamethylcyclotrisilazane is allowed in react with sulfuric acid for 3 h at 175°, the yield of octamethylcyclotetrasilazane is only 8.3 %, whereas octamethylcyclotetrasilazane under the same conditions gives hexamethylcyclotrisilazane in 38 % yield.

Data concerning the rearrangements of dimethylcyclosilazanes are contained in Table 1.

Krüger and Rochow[3] treated hexamethylcyclotrisilazane with ammonium bromide and obtained (together with polymers) 24–32 % of distillable oligomers, but the authors did not describe the physical properties of the products.

The rearrangement reaction in the presence of electrophilic reagents probably proceeds as follows:

(a) the electrophilic reagent breaks a silicon-nitrogen bond to open the ring:



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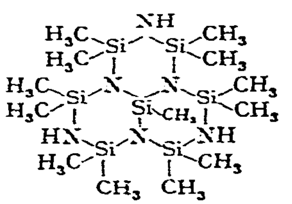
(b) the resulting intermediates recombine to form hexamethylcyclotrisilazane together with octamethylcyclotetrasilazane. Owing to the strong tendency of organosilylamines to cyclize, these reactions produce not only polymers but also considerable quantities of cyclic compounds.

Experiments were carried out to confirm this mechanism for catalysis by sulfuric acid. In these experiments the reaction of bis(trimethylsilyl) sulfate with triethylsilylamine took place as follows:

$$[(CH_3)_3SiO]_2SO_2 + 6\,(C_2H_5)_3SiNH_2 \longrightarrow 2\,(CH_3)_3SiNHSi(C_2H_5)_3 +$$
$$2\,(C_2H_5)_3SiNHSi(C_2H_5)_3 + (NH_4)_2SO_4$$

The products were trimethyltriethyldisilazane in 28 % yield, ammonium sulfate and hexamethyldisilazane. (To confirm the identity of the trimethyltriethyldisilazane, it was also made by co-ammonolysis of trimethyl- and triethyl-chlorosilane.) Formation of trimethyltriethylsilazane in this reaction proves that the intermediate products indicated in the rearrangement reaction mechanism can recombine.

The mechanism of polymerization of organocyclosilazanes by nucleophilic reagents also differs from that for organocyclosiloxanes. In the presence of catalytic



(5)

quantities of KOH, dimethylcyclosilazanes polymerize with evolution of methane and, at the initial stage, with formation of a crystalline product[4], m.p. 164–165°. The structure of this material, as determined by X-ray and chemical examinations, is as shown in (5).

Further polymerization leads to hard products having melting points between 90° and 360°.

This great difference between the polymerization reaction of dimethylcyclosilazanes and those of dimethylcyclosiloxanes led us to study this reaction using other organocyclosilazanes. These experiments included the polymerization of trimethyltriphenylcyclotrisilazane which is particularly interesting because it contains both methyl and phenyl groups attached to silicon.

The experiments showed that the addition of 1 % of potassium hydroxide at 200° initiates a reaction in which benzene is formed together with trace quantities of ammonia. The quantity of benzene formed depends on the reaction time (Fig. 1) and the temperature (Table 2).

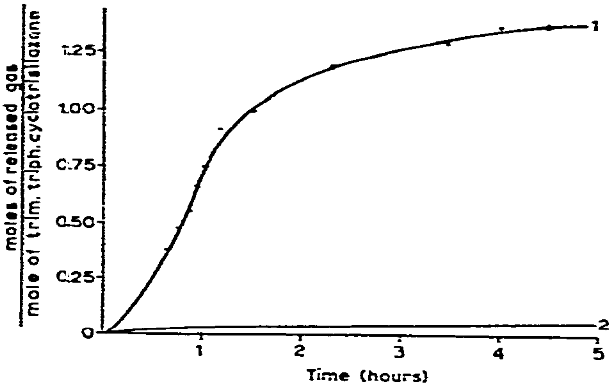


Fig. 1. Quantity of released benzene (curve 1) and ammonia (curve 2) in moles/mole of trimethyltriphenylcyclotrisilazane. Reaction temp., 280°.

The resultant polymers are readily soluble in organic solvents and their melting points depend on the conditions of the polymerization. Studies of the thermomechanical properties of the polymer obtained after heating for 5 h at a temperature

TABLE 2

PRODUCTS FROM TRIMETHYLTRIPHENYLCYCLOSILAZANE IN PRESENCE OF 1 % OF POTASSIUM HYDROXIDE

Reaction temp. (°)	*Time (h)*	*M.p. of polymers (°)*	*Moles benzene/mole reactant*
200	3.5	137	1.01
280	0.3	86	0.82
280	3.5	182–185	1.28
280	5	235	1.46
400	14	—	1.86

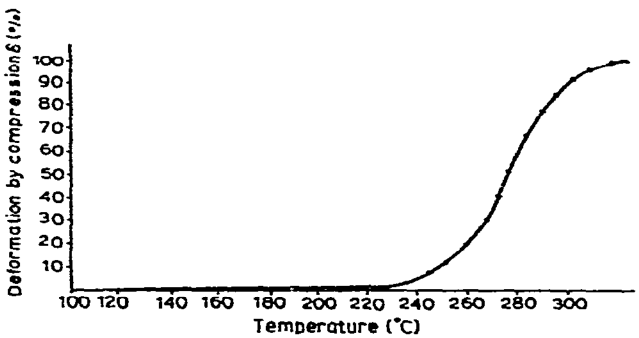
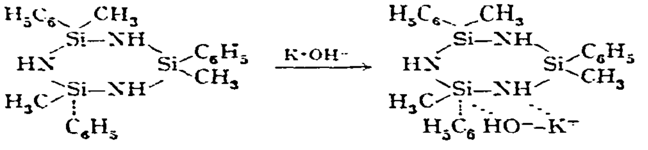


Fig. 2. Thermo-mechanical properties of polymer obtained by heating trimethyltriphenylcyclotrisilazane at 280°.

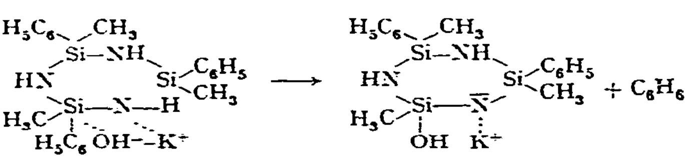
of 280° showed that it has no region of high elasticity in spite of its high melting point (Fig. 2).

These data indicate that the properties of these polymers are very different from those of polyphenylmethylsiloxanes. They are hard, fragile, glassy products with relatively high softening points. The difference between the properties of these polymers and those of polysiloxanes can hardly be attributed solely to the substitution of oxygen for the NH-group. It is known that the exchange of oxygen for the NH-group in compounds of low molecular weight does not essentially alter their physical properties[6]. Furthermore, the polymers obtained by polymerization of dimethylcyclosilazanes in the presence of electrophilic reagents (Table 1) are viscous at room temperature, and their properties resemble those of polydimethylsiloxanes. It is also known that if the polymerization reaction of dimethylcyclosilazanes proceeds with ring-cleavage, liquid polymethylsilazanes are produced[7]. The formation of intermediate crystalline products as well as of benzene during the reaction suggests that formation of polymers on treatment of trimethyltriphenylcyclotrisilazanes with catalytic quantities of alkalis proceeds not through ring-cleavage, but through some other mechanism. It is probable that a hydroxyl group coordinates with the silicon atom as follows:



(6)

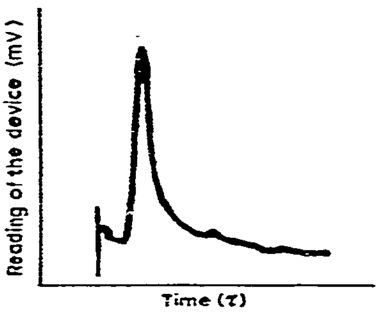
As a result of redistribution of electronic density in forming the transition-state complex, one of the bonds to silicon becomes weaker, and it has been shown that it is the Si–C bond and not the Si–N bond which breaks. Because of this, benzene splits off with the formation of a negatively charged ion.



(7)

The process then proceeds further through the co-ordination of the resultant ion with cyclic compounds to form another Si–N bond thereby producing the polymer, together with benzene.

To determine the general nature of this reaction, polymerization experiments were performed using non-cyclic compounds, such as hexamethyldisilazane and trimethyltriethyldisilazane in the presence of 1 % of potassium hydroxide. With hexamethyldisilazane the reaction proceeds with evolution of methane, whereas with trimethyltriethyldisilazane ethane is produced. The formation of methane and ethane was demonstrated by gas chromatography (Figs. 3, 4); it is due to splitting off of methyl and ethyl groups and their stabilization by the abstraction of hydrogen from nitrogen.



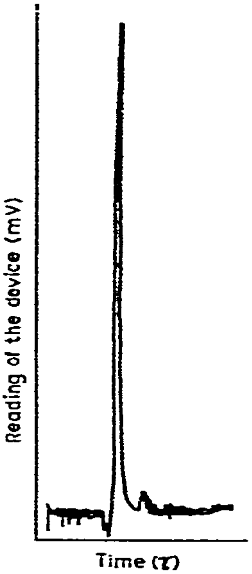


Fig. 3. Chromatogram of gas released during reaction of hexamethyldisilazane with potassium hydroxide. The gas is methane.

Fig. 4. Chromatogram of gas released during reaction of trimethyltriethyldisilazane with potassium hydroxide. The gas is ethane.

It is noteworthy that the chromatographic examination of the gaseous products of the reaction of dimethylcyclosilazanes and hexamethyldisilazane with potassium hydroxide sometimes revealed the presence of trace quantities of hydrogen and ethane (Fig. 5).

EXPERIMENTAL

(1) *Hexamethylcyclotrisilazane and aluminium chloride*

(*a*) 10.3 g (0.047 mole) of hexamethylcyclotrisilazane and 0.03 g of aluminium chloride were heated for 5 h at 140°. Distillation of the mixture yielded the following products: 7.74 g of hexamethylcyclotrisilazane, b.p. 32–40°/1.5 mm, n_D^{20} 1.4438;

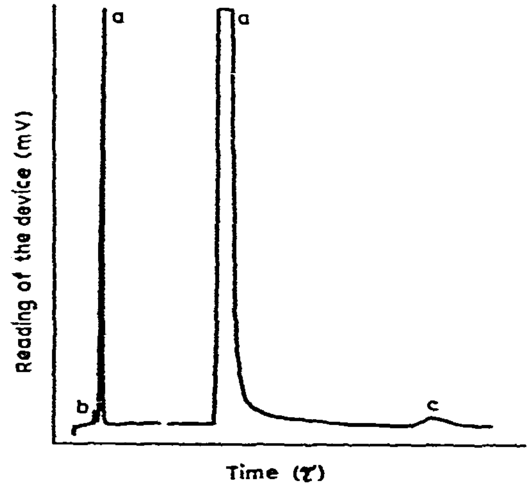


Fig. 5. Chromatograms of gas released during polymerization of dimethylcyclosilazanes. The higher peak (a) corresponds to methane. The lower peaks correspond to: (b), hydrogen; (c), ethane.

0.85 g (8.2 %) of octamethylcyclotetrasilazane, m.p. 96°, and 1.67 g (16.2 %) of polymer.

(*b*) 10 g (0.0456 mole) of hexamethylcyclotrisilazane and 0.03 g of aluminium chloride were heated for 5 h at 160°. Distillation of the mixture yielded the following products: 6.9 g of hexamethylcyclotrisilazane, b.p. 32–40°/1.5 mm, n_D^{20} 1.4438; 1.43 g (14.3 %) of octamethylcyclotetrasilazane, m.p. 96°, and 1.67 g (16.7 %) of polymer.

(*c*) 10 g (0.0456 mole) of hexamethylcyclotrisilazane, and 0.38 g of aluminium chloride were heated for 5 h at 240°. Distillation of the mixture yielded the following products: 1 g of hexamethylcyclotrisilazane, b.p. 32–40°/1.5 mm, n_D^{20} 1.4438; 1.98 g (19.8 %) of octamethylcyclotetrasilazane, m.p. 96°, and 6.90 g (69.0 %) of polymer.

(2) *Hexamethylcyclotrisilazane and titanium tetrachloride*

10 g (0.0456 mole) of hexamethylcyclotrisilazane and 0.19 g of titanium tetrachloride were heated for 6 h at 240°. Distillation of 9.4 g of the mixture yielded the following products: 2.27 g of hexamethylcyclotrisilazane, b.p. 32–40°/1.5 mm, n_D^{20} 1.4438; 0.55 g (5.5 %) of octamethylcyclotetrasilazane, m.p. 96°, and 6.5 g (65 %) of polymer.

(3) *Hexamethylcyclotrisilazane and tin tetrachloride*

10 g (0.0456 mole) of hexamethylcyclotrisilazane and 0.11 g of tin tetrachloride were heated for 8 h at 195°. Distillation of the mixture yielded the following products: 5.88 g of hexamethylcyclotrisilazane, b.p. 32–40°/1.5 mm, n_D^{20} 1.4438; 2.9 (29 %) of octamethylcyclotetrasilazane, m.p. 96°, and 1.32 g (13.2 %) of polymer.

(4) *Hexamethylcyclotrisilazane and phenyltrichlorosilane*

10 g (0.0456 mole) of hexamethylcyclotrisilazane and 0.2 g of phenyltrichlorosilane were heated for 5 h at 230°. Distillation of the mixture yielded the following

products: 6.07 g of hexamethylcyclotrisilazane, b.p. 32–40°/1.5 mm, n_D^{20} 1.4438; 3.1 g (31 %) of octamethylcyclotetrasilazane, m.p. 96°, and 0.8 g (8 %) of polymer.

(5) Octamethylcyclotetrasilazane and aluminium chloride

10.8 g (0.037 mole) of octamethylcyclotetrasilazane and 0.054 g of aluminium chloride were heated for 6 h at 160°. Distillation of the mixture yielded the following products: 3.1 g (28.6 %) of hexamethylcyclotetrasilazane, b.p. 32–40°/1.5 mm, n_D^{20} 1.4438; 7.2 g of octamethylcyclotetrasilazane, m.p. 96°, and 0.35 g (3.2 %) of polymer.

(6) Hexamethylcyclotrisilazane and sulfuric acid

(*a*) 11.27 g of hexamethylcyclotrisilazane and 0.17 g of sulfuric acid were stirred for 30 min at room temperature. The mixture was allowed to settle for 24 h and the products obtained after vacuum distillation were as follows: 0.36 g (3.2 %) of hexamethylcyclotrisilazane, b.p. 85–95°/15–16 mm, n_D^{20} 1.4445; 10.1 g (90 %) of octamethylcyclotetrasilazane, m.p. 96°, mol. wt. 291 (cryoscopically in benzene), N, 18.6 and 18.4 % (found). Calculated for octamethylcyclotetrasilazane: mol. wt., 292; N, 19.2 %.

(*b*) 14.75 g of hexamethylcyclotrisilane and 0.22 g of sulfuric acid were heated for 3 h to yield the following products: 7.4 g of hexamethylcyclotrisilazane, b.p. 35–95°/15–16 mm, n_D^{20} 1.4450; 1.23 g (8.3 %) of octamethylcyclotetrasilazane, m.p. 96°, and 2.43 g (16.5 %) of polymer.

(7) Octamethylcyclotetrasilazane and sulfuric acid

13.54 g of octamethylcyclotetrasilazane and 0.2 g of sulfuric acid were heated for 3 h at 175° and gave the following products: 5.2 g (38 %) of hexamethylcyclotrisilazane, b.p. 182–196°, n_D^{20} 1.4445; 2.5 g of octamethylcyclotetrasilazane, m.p. 96°, and 1.6 g (11.8 %) of polymer.

(8) Co-ammonolysis of trimethylchlorosilane and triethylchlorosilane

Ammonia was passed through 41.8 g of trimethylchlorosilane and 58.5 g of triethylchlorosilane dissolved in benzene, and the precipitate of ammonium chloride was separated by filtration. The intermediate reaction products obtained after distilling off of the solvent were mainly hexamethyldisilazane and aminotriethylsilane, (22.4 g), b.p. 100–160°. The residual product (55.7 g) was vacuum distilled:

	Boiling range (°)	*Weight (g)*	*Refr. index*
I	45–70/15 mm	4.3	1.4302
II	70–76.5/13 mm	8.3	1.4339
III	76.5/13 mm	16.6	1.4349
IV	76.5–95/13 mm	11.1	1.4354
V	96–135/11 mm	13.1	1.4491
VI	Residual oil	2.3	

The repeated distillation of fractions I, II and IV resulted in 25.9 g of a product, b.p. 72–75°/11–13 mm, n_D^{20} 1.4346, d_4^{20} 0.8200, yield 41.7 %. (Found: MR, 64.56;

C, 53.97; H, 13.1, 12.7; N, 6.45, 6.7 %. Calcd.: MR, 65.31; C, 53.2; H, 12.3; N, 6.9 %.)

3.1 g of bis(trimethylsilyl) sulfate and 10 g of triethylaminosilane yielded 1.46 g of a product, b.p. 70–73°/10–12 mm, n_D^{20} 1.4326. The boiling point and the refractive index show that this product is identical with the trimethyltriethyldisilazane obtained earlier.

(9) *Polymerization of trimethyltriphenylcyclotrisilazane*

10 g trimethyltriphenylcyclotrisilazane and 0.1 g of potassium hydroxide were heated in a 50-ml flask. Benzene produced during the reaction was distilled off and collected in a graduated test tube and ammonia was absorbed in a Titohshenko bottle filled with dilute sulfuric acid. The temperature and duration of the reaction in various experiments are indicated in Table 2. The resultant polymers were tested for softening point using a thermo-mechanical curve and for melting point using the capillary method.

SUMMARY

Treatment of dimethylcyclosilazanes with catalytic quantities of electrophilic reagents leads to ring-expansion and ring-contraction.

In polymerization of trimethyltriphenylcyclotrisilazane catalysed by alkali, the polymer-forming reaction proceeds without ring opening.

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