NUCLEOPHILIC REACTIONS OF POLYDIALKYLCYCLOSILAZANES

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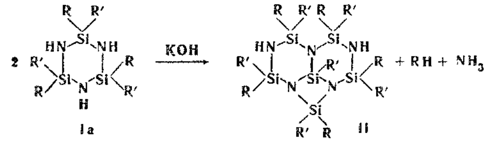
A study is made of the catalytic condensation polymerization of polydialkylcyclosilazanes $[RR'SiNH]_n$ (n = 3,4; R = CH_3, C_2H_5; R' = C_2H_5, C_4H_9, C_6H_{13}, C_9H_{19}) in the presence of small amounts of nucleophilic reagents, to give compounds of the general type $R_5R_6'Si_6N_3(NH)_2$ and oligomers. The reactivities of polydialkylsilazanes decrease with increase in aliphatic group chain length.

The reaction of organocyclosilazanes with nucleophilic reagents has been investigated for polydimethylcyclosilazanes [1] and polymethylphenylcyclosilazanes [2]. It is accompanied by evolution of methane or formation of benzene, depending on the framework of the starting ring, and by formation of high-melting polymers cyclic in structure [3]. To investigate the general laws governing this reaction, we have studied a number of polydialkylcyclosilazanes (I), general formula $[RR'SiNH]_n$ (n = 3,4; R = CH_3, C_2H_5; R' = C_2H_5, C_4H_9, C_6H_{13}, C_9H_{19}), which are of interest in that they allow the effect of size of organic group on the reactivities of these compounds, along with the properties of the products, to be followed.

It was found that polymethylethyl-, methylbutyl-, methylhexyl- and diethylcyclosilazanes react with KOH or EtONa at relatively high temperature only. While polydimethylcyclosilazanes start to give methane and ammonia at about 100° [4], the above compounds give those products at 250° and above. The reaction dies away after 10–15 hours, and raising the temperature to 300° and higher does not give any considerable evolution of gaseous products. Compounds II of composition $R_5R_6'Si_6N_3(NH)_2$ (R = CH_3, C_2H_5; R' = C_2H_5, C_4H_9, C_6H_{13}), whose properties are given in Table 1 can be isolated from the reaction products.

The equation for their formation from hexaalkylcyclotrisilazanes is:



Here obviously, as with polydimethylcyclosilazanes (I), an intermediate complex with alkali is first formed, this decomposing to give hydrocarbon and a negatively charged ion, the latter ion then attacking the neutral ring molecule with breaking of a S—N bond and subsequent cyclization to II. All this leads to elimination of a molecule of ammonia, and regeneration of a molecule of alkali. The total amount of ammonia recovered corresponds to that which should be eliminated by the stated reaction (Table 2), but the amount of methane formed is considerably greater than that given by the equation. So it can be assumed that the given reaction is accompanied by polymerization which takes place without ring opening, to give higher molecular weight oligomers. The chemical inertness of the compounds II when they are treated with catalytic quantities of alkali indicates that oligomers are formed by a mechanism previously suggested [1, 3], and not via these compounds. The negative ion formed in the first stage adds to the neutral ring, with separation of hydrocarbon, and formation of a new bicyclic ion.

In the case of octaalkylcyclotetrasilazanes, the reaction is complicated by rearrangement of the

Table 1

Products Formed by the Reaction of Polydialkylcyclosilazanes with Alkalies

II	Bp, °C (1 mm)	n_D^{20}	d_4^{20}	M		MR_D		Yield, %
				Found	Calculated	Found	Calculated	
$(CH_3)_5(C_2H_5)_6Si_6N_3(NH)_2$ (a)	150—152	1.4869	1.0044	440	490	140.27	140.67	52.5
$(CH_3)_5(C_4H_9)_6Si_6N_3(NH)_2$ (b)	219—224	1.4786	0.9586	600	658	194.57	194.23	46
$(CH_3)_6(C_6H_{13})_6Si_6N_3(NH)_2$ (c)	249—254	1.4790	0.9441	850	827	248.26	249.79	47.5
$(C_2H_5)_{11}Si_6N_3(NH)_2$ (d)	191—191.5*	—	—	540	560	—	—	28

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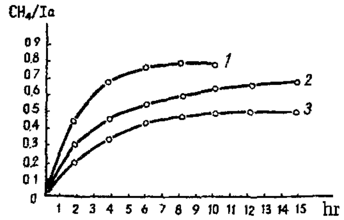
*Mp 41.5–42.5°

Table 2

Yields of RH and NH_3 Formed by Reaction of Ia with KOH

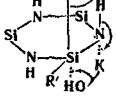
Starting Ia	Quantity of hydrocarbon evolved mole RH/mole Ia	Quantity of ammonia evolved mole RH/mole Ia	Quantity of ammonia evolved mole NH_3/mole II
$[CH_3C_2H_5SiNH]_3$	0.79	0.36	0.96
$[CH_3C_4H_9SiNH]_3$	0.69	0.22	0.97
$[CH_3C_6H_{13}SiNH]_3$	0.52	0.30	1.10
$[(C_2H_5)_2SiNH]_3$	0.53	0.17	1.10

8-membered ring to a 6-membered one. Thus when tetramethyltetraethylcyclotetrasilazane reacts with KOH, the reaction products are found to contain 19% trimethyltriethylcyclotrisilazane, 55% pentamethylhexaethyltricyclohexasilazane, and 26% oligomers.



Amount of methane evolved in mole per mole starting cyclotrisilazane.

On passing from methylethyl-substituted rings to methylhexyl-substituted ones, at 250° the rate of evloution of methane drops (Fig. 1) and this is obviously due to a steric effect. In the case of trimethyl-trinonylcyclotrisilazane, there is no reaction, even at over 300°. With hexaethylcyclotrisilazane gaseous products start to be evolved at an appreciable rate at about 300°. It is difficult to explain such low reactivity of the compounds investigated as compared with polydimethyl-cyclosilazanes by steric shielding of the S—N bonds by aliphatic groups. It is possible that in the particular case an important part is played by the existence of polydialkylcyclosilazanes in some or other different geometrical conformations and their reciprocal conversion. The structure of the intermediate complex is also connected with a certain conformation of the cyclic part of the molecule, e.g. a planar one, where a synchronous electron transfer, resulting in breaking of some bonds and formation of new ones, is more probable.



Increase in length of the organic group on the silicon atom will stabilize the conformation of the starting cyclosilazane, likewise rendering difficult its conversion to the activated state. Obviously this also results in a sharp drop in chemical reactivity on replacing a methyl group in hexamethylcyclotrisilazane by ethyl, butyl, etc.

The high reaction temperature for polydiethylcyclosilazanes is, moreover, explained by the increase in energy of breaking of the Si—C bond on account of the great electron-donating properties of the ethyl group compared with methyl.

To confirm the structures of the polymerization products given in Table 1, their IR spectra were determined. They have an absorption band at about 900 cm^{-1}, lacking in the starting rings, and obviously this can be ascribed to valence vibrations of the Si—N bond in the 4-membered ring. The intensity of the band at 3400 cm^{-1} is considerably lowered, this band being characteristic of N—H bond vibrations, and this decrease is in agreement with structure II.

It is of interest to note that these compound were inert not only towards alkalies, but also towards catalytic amounts of proton acids, e.g. sulfuric acid. They were also stable towards water in heterogeneous systems, and even in acids underwent only very slight hydrolysis.

EXPERIMENTAL

The reactions between polydialklcyclosilazanes and catalytic amounts of alkalies were run in 50 ml flask, with a reflux condenser and flask for absorbing the ammonia, and provided with a graduated cylinder, full of water, for catching the hydrocarbon evolved in the reaction. The hydrocarbon was identified by means of a KhL-4 gas chromatograph.

Reaction of trimethyltriethylcyclotrisilazane with KOH. 14.3 g $[CH_3C_2H_5SiNH]_3$ bp 66–69° (1 mm) and 0.15 g KOH were heated together to 200°, then the temperature gradually raised to 250°. There was appreciable evolution of ammonia and methane. After 10 hr 0.7 g CH_4 and 0.3 g NH_3 were evolved. Distillation of 12.6 g reaction products gave 10.4 g compounds, bp 150–265° (1 mm). Repeated fractional distillation of this gave IIa bp 150–152° (1 mm). 1.3 g oligomers bp 210–220° (1 mm) was also isolated, giving: C 40.67; 40.63; H 9.27; 9.30; Si 35.91; 35.75; N 14.40; 14.67%; M 640.

Reaction of trimethyltriethylcyclotrisilazane with EtONa. 11.4 g $[CH_3C_2H_5SiNH]_3$ and 0.06 g 30% NaOEt in EtOH were heated together for 15 hr, the temperature being gradually raised from 230 to 320°. Distillation of the reaction products gave two main fractions: bp 150–160° (1 mm), n_D^{20} 1.4856 (4.5 g) - IIa, and bp 160–225° (1 mm), n_D^{20} 1.4904 (2.8 g).

Table 3

Elementary Analytical Data for II

II	C, %		H, %		Si, %		N, %	
	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated
a	41.65 41.67	41.67	9.64 9 66	9.67	34.40 34.43	34.36	14.65 14.54	14.29
b	52.17 52 47	52.91	10.99 10.88	10.87	25.49 25.77	25.57	10.93 11.07	10.64
c	59.73 59.85	59.57	11.52 11.58	11.58	19.64 19.57	20.36	8.32 8.21	8.47
d	46.34 46.30	47.03	10.09 10.02	10.25	30.03 30.04	30.02	12.27 12.80	12.05

Reaction of tetramethyltetraethylcyclotetrasilazane with KOH. 4.9 g $[CH_3C_2H_5SiNH]_4$ bp 100–101° (1 mm) and 0.04 g KOH were heated together at 250° for 8 hr. Yield of methane 0.17 g (0.76 mole CH_4/mole cyclotetrasilazane), ammonia 0.09 g (0.39 mole NH_3/mole cyclotetrasilazane). Raising the temperature to 300° did not lead to any considerable further evolution of gaseous reaction products. After 2 hr at 300°, 15 ml methane in all was collected. Fractional distillation of the reaction products gave two main fractions 64–74° (1 mm), n_D^{20} 1.4560 (0.87 g) - Ia, and bp 148–158° (1 mm), n_D^{20} 1.4850 (2.5 g) - IIa.

Reaction of trimethyltributylcyclotrisilazane with KOH. 10.15 g $[CH_3C_4H_9SiNH]_3$ bp 126–128° (1 mm) and 0.1 g KOH were heated together at 250° for 15 hr. Yield of methane 0.33 g, of ammonia 0.11 g. Distillation of 9.54 g reaction products gave IIb.

Reaction of trimethyltrihexylcyclotrisilazane with KOH. 8.62 g $[CH_3C_6H_{13}SiNH]_3$ bp 171–173° (1 mm) and 0.09 g KOH were heated together at 250° for 15 hr. 0.166 g methane and 0.1 g ammonia were evolved. Repeated fractional distillation of the reaction products gave IIc.

Reaction of trimethyltrinonylcyclotrisilazane and KOH. 7.8 g $[CH_3C_9H_{19}SiNH]_3$ bp 203–207° (1 mm) and 0.08 g KOH were heated together, the temperature being gradually raised from 250 to 320°. After 10 hr 0.07 g ammonia (0.002 mole NH_3/mole cyclotrisilazane) was collected, but no methane. The starting cyclic compound was recovered quantitatively by distilling the reaction products.

Reaction of hexaethylcyclotrisilazane and KOH. 20.6 g $[(C_2H_5)_2SiNH]_3$ bp 91–93° (1 mm) and 0.2 g KOH were heated together, the temperature being gradually raised from 250 to 300°. Appreciable evolution of ammonia and ethane was found at 300°. In 19 hr there were evolved 1.1 g C_2H_6 and 0.19 g NH_3. Distillation of the reaction products gave 5.74 g IId.

Reaction of hexaethylpentamethyltricyclohexasilazane (IIa) and H_2SO_4. 5 g IIa and 0.05 g conc H_2SO_4 were heated together at 150° for 15 hr. No ammonia was evolved, and the relative viscosity of a 1% solution of the compound in benzene remained unchanged. Distillation gave unchanged starting material bp 145–149° (1 mm); n_D^{20} 1.4856.

Reaction of IIa with KOH. 5.34 g IIa and 0.06 g KOH were heated together at 250–320°. No ammonia or methane were evolved. Distillation of the reaction products gave the unchanged starting material, bp 149–155° (1 mm), n_D^{20} 1.4870.

Reaction of II with water. A 10% solution of II in benzene was boiled with excess distilled water for 24 hr. The degree of hydrolysis was calculated from the amount of ammonia formed. For all the II compounds listed in Table 2 it did not exceed 1%. When 0.1 N H_2SO_4 was used instead of distilled water, IIa was 10.6% hydrolyzed, IIb 8.3%, and IIc 7.5%.

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