Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

SYNTHESIS AND PROPERTIES OF ORGANOCYCLOSILAZANES

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(Received May 13th, 1966)

The principal method for obtaining organocyclosilazanes is the ammonolysis of organochlorsilanes. Depending on the functional characteristics of the initial organochlorsilane, cyclic systems of two types may be obtained: cyclopolysilazanes $[RR'SiNH]_n$ and silsesquiazanes $[R^1Si(NH)_{1.5}]_n$. Compounds of the first type have been described in the literature, and some reactions of their conversion into high-molecular compounds have also been investigated. There is, however, a lack of data on the structure of this interesting class of substances and on the influence of the structure on the chemical reactivity in the: 7 interaction with electrophilic and nucleophilic reagents. No information is available on systems of the second type, the so-called silsesquiazanes.

We have synthesized a number of new dialkylcyclopolysilazanes and alkylsilsesquiazanes, the formation of which occurs according to the following equations:

$$RR'SiCl_2 + 3\ NH_3 \rightarrow \frac{1}{n}[RR'SiNH]_n + 2\ NH_4Cl\,,$$

where $n = 3$–4; $R = CH_3, C_2H_5$; $R^1 = C_2H_5, C_4H_9, C_6H_{13}, C_8H_{17}, C_9H_{19}$.

$$R^1SiCl_3 + 4.5\ NH_3 \rightarrow \frac{1}{n}[R^1Si(NH)_{1.5}]_n + 3\ NH_4Cl$$

where $n = 6$–8; $R^1 = CH_3, C_2H_5, C_6H_{13}, C_7H_{15}, C_8H_{17}, C_9H_{19}$.

The physical properties of the compounds isolated are given in Tables 1 and 2.

The initial dialkyldichlorsilanes and alkyltrichlorsilanes constitute a homologous series in which the number of methylene groups in one of the radicals increases from homologue to homologue. This lengthening of the aliphatic radical enables the effect of spatial factors on the ammonolysis of the corresponding organochlorsilanes to be investigated and also the dependence of the structure of the organocyclosilazanes obtained, on their organic grouping; to be established.

Ammonolysis of the lower and medium dialkyldichlorsilanes follows the above pattern. However, the reaction with ammonia of dialkyldichlorsilanes having octyl and nonyl radicals at the silicon atom, differs somewhat from that of the preceding members of the homologous series. In this case, the reaction results in the formation of linear condensation products, such as diaminotetraalkyldisilazanes and diaminohexaalkyltrisilazanes. When these products are isolated by distillation from the reaction mixture, they condense into cyclic systems. Nevertheless, we have been able to isolate 1,3-diamino-1,3-diethyl-1,3-dioctyldisilazane from the ammonolysis products of ethyloctyldichlorsilane. The compound isolated proved to be stable at

TABLE 1

DIALKYLCYCLOPOLYSILAZANES

	B.p. (°C/mm)	n_D^{20}	d_4^{20}	M		MR		Yield (%)
				Calcd.	Found	Calcd.	Found	
$(CH_3C_2H_5SiNH)_3$	91–93/3	1.4570	0.9258	261.5	256	76.74	76.92	75
$(CH_3C_2H_5SiNH)_4$	136–139/3	1.4688	0.9511	348.7	341	102.31	102.38	21
$(CH_3C_4H_9SiNH)_3$	126–128/1	1.4600	0.9074	345.7	342	104.52	104.48	73
$(CH_3C_4H_9SiNH)_4$	162–165/1	1.4677	0.9215	460.9	446	139.14	139.13	22
$(CH_3C_6H_{13}SiNH)_3$	171–173/1	1.4642	0.8938	429.8	432	132.30	132.73	68
$(CH_3C_6H_{13}SiNH)_4$	220–224/1	1.4689	0.9057	573.1	559	176.40	176.37	25
$(CH_3C_8H_{17}SiNH)_3$	185–189/1	1.4654	0.8942	514	504	160.08	159.97	60
$(CH_3C_9H_{19}SiNH)_3$	203–207/1	1.4680	0.8896	556	522	173.97	173.75	53
$(C_2H_5C_8H_{17}SiNH)_3$	224–228/1	1.4710	0.8970	556	525	173.97	173.88	53
$HN(C_2H_5C_8H_{17}SiNH_2)_2$	169–171/1	1.4620	0.8790	388	413	121.41	121.24	41

TABLE 2

ALKYLSILSESQUIAZANES

	B.p. (°C/mm)	M.p. (°C)	n_D^{20}	d_4^{20}	M		MR		Yield (%)
					Calcd.	Found	Calcd.	Found	
$[CH_3Si(NH)_{1.5}]_6$	—	260	—	—	—	—	—	—	11
$[C_2H_5Si(NH)_{1.5}]_6$	—	146–147	—	—	478	480	—	—	15
$[C_6H_{13}Si(NH)_{1.5}]_6$	314–320/2	—	1.5005	1.0028	814	847	240.32	239.10	52
$[C_7H_{15}Si(NH)_{1.5}]_6$	324–330/1.5	—	1.4978	0.9830	898	894	267.79	267.60	43
$[C_8H_{17}Si(NH)_{1.5}]_8$	345–350/1	—	1.2929	0.9712	1310	1290	394.79	395.62	56
$[C_9H_{19}Si(NH)_{1.5}]_6$	330–347/2	—	1.4940	0.9629	1067	1057	323.56	322.60	53

the distillation temperature and the yield was relatively high.

An investigation of the ammonolysis of methyl- and ethyl-trichlorsilane showed that low-melting or liquid (at normal temperature) polymeric products containing crystals are formed. By fractional solution of the crude product, we isolated large quantities of crystalline substances the properties of which are given in Table 2.

The products of ammonolysis of the higher alkyltrichlorsilanes are clear viscous liquids of low molecular weight.

The presence in the infrared spectra of the 1550-cm^{-1} absorption band characteristic of the deformation oscillations of the primary amino-group, the easy hydrolysis of the ammonolysis products even in the presence of alkalis in heterogenous environment and the evolution of relatively large quantities of ammonia on heating in a nitrogen atmosphere, point to the presence of a large number of amino-groups in these products. When the condensation process of these products was investigated, it was noted that evolution of ammonia was not accompanied by an increase in their viscosity or molecular weight. This indicates that the condensation process occurs not between the amino-groups of different molecules (which would result in an increase in their molecular weight) but inside the molecules with the formation of closed cyclic systems that can be distilled in a vacuum.

Particularly interesting is the study of the chemical properties of the compounds synthesized. It was demonstrated earlier[1,2] that the behaviour of organocyclosilazanes with nucleophilic reagents differs sharply from that of organocyclosiloxanes. For example, polymerization of hexamethylcyclotrisilazane and trimethyltriphenylcyclotrisilazane in the presence of catalytic quantities of alkalis occurs without rupturing the ring and results in the production of a hydrocarbon and the formation of a new Si–N bond, as a result of which, the cyclic structure of the chain of macromolecules is preserved. This suggests that organocyclosilazanes are more prone to ring substitution reactions than to cycle-rupturing reactions, *i.e.*, they display certain properties similar to those of organic aromatic compounds. This characteristic of organosilazanes is due to the special features of the Si–N bond, *viz.*, a certain delocalization of free electron-pairs of nitrogen along the contour of the cycle. It should be noted, however, that the aromaticity of these compounds is quite unlike that of homomorphic cycles and the term itself seems to be conditional. Electron distributions in these molecules include separate allyl areas which begin and end on silicon atoms. Approximately the same picture is observed in phosphornitrile- and borazole-cycles for which quantum-mechanics calculations have been carried out, and it has been demonstrated that in them the delocalization energy in per electron terms increases smoothly with increasing cycle dimensions[5]. This stabilizes the bond, increases its power constant and, therefore, results in a corresponding change of the frequencies of valence vibrations in the infrared spectra.

In the organocyclosilazanes synthesized, the frequency of valence vibrations of the Si–N bond is also shifted on passing from six-membered to eight-membered cycles (Table 3). In octalkylcyclotetrasilazanes, the absorption band typical of valence vibrations of the N–H bond is shifted towards lower frequencies compared with hexaalkylcyclotrisilazanes, which is to be expected considering the reduced electron density on nitrogen. The frequency shift is greater still in the case of alkylsilsesquiazanes where the frequency of asymmetric valence vibrations of the Si–N bond attains

TABLE 3

Alkylcyclosilazanes	*V SiNSi*	*γ NH*	*V NH*
$[(CH_3)_2SiNH]_3$	928	1169	3402
$[(CH_3)_2SiNH]_4$	939	1183	3395
$(CH_3C_2H_5SiNH)_3$	926	1170	3400
$(CH_3C_2H_5SiNH)_4$	940	1180	3385
$(CH_3C_4H_9SiNH)_3$	930	1170	3405
$(CH_3C_4H_9SiNH)_4$	940	1180	3390
$(CH_3C_6H_{13}SiNH)_3$	930	1170	3405
$(CH_3C_9H_{19}SiNH)_3$	930	1170	3405
$[CH_3Si(NH)_{1.5}]_6$	915, 960–980	1150, 1210	3320, 3385
$[C_2H_5Si(NH)_{1.5}]_6$	915, 955, 980	1150, 1215	3320, 3385
$[C_6H_{13}Si(NH)_{1.5}]_6$	950	1190	3390
$[C_7H_{15}Si(NH)_{1.5}]_6$	950	1190	3390
$[C_8H_{17}Si(NH)_{1.5}]_8$	960	1195	3390

960 cm^{-1}. The split of the corresponding absorption bands in methyl- and ethylsilsesquiazanes may be explained by the crystallinity effect. Such regular variation of spectra obtained on passing from six-membered to eight-membered cycles and to silsesquiazanes is due to changes in the electron structure of the molecules and agrees with the basic principles of the structure of heteromorphic aromatic systems.

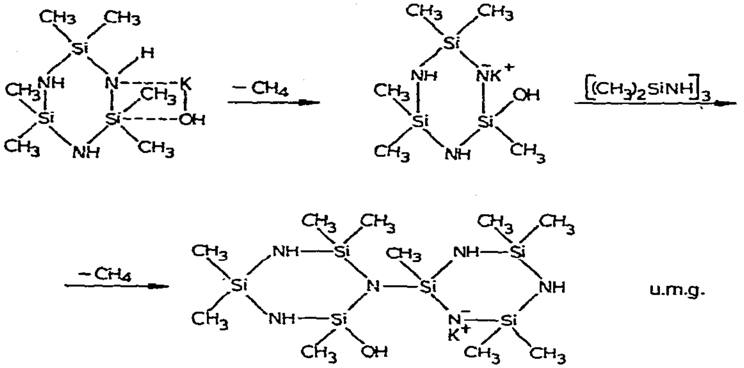
In alkylsilsesquiazanes, apart from an increase in the dimensions of the cycle, a change occurs in the ratio between nitrogen and silicon atoms together with an increase in the number of free nitrogen pairs per vacant *d*-orbit of silicon. The latter circumstance may result in an increase in linkage multiplicity in silsesquiazanes compared with polycyclosilazanes, which in turn will result in a shift of the frequency of valence vibrations of the Si–N bond towards higher frequencies.

TABLE 4

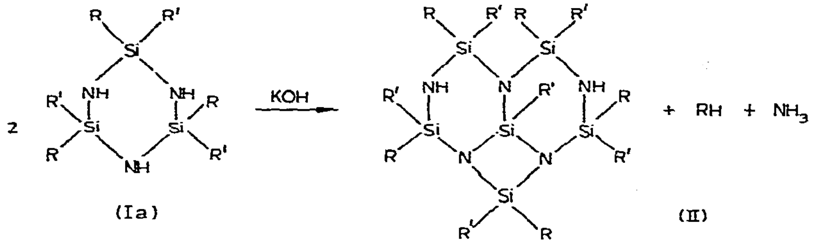
Alkylcyclosilazanes	*% Hydrolysis*
$(CH_3C_4H_9SiNH)_3$	53
$(CH_3C_4H_9SiNH)_4$	40
$(CH_3C_6H_{13}SiNH)_3$	43
$(CH_3C_6H_{13}SiNH)_4$	31
$(CH_3C_9H_{19}SiNH)_3$	36
$[C_6H_{13}Si(NH)_{1.5}]_6$	20
$[C_8H_{17}Si(NH)_{1.5}]_8$	13

Spectroscopic data agree well with the information obtained of alkylcyclosilazanes. Thus, hydrolytic stability increases from six-membered to eight-membered cycles and to silsesquiazanes. Table 4 shows the percentage of hydrolysis of alkylcyclosilazanes obtained in a heterogenous environment in the presence of hydrogen ions which accelerate the hydrolysis of these compounds. In this case, hydrolytic stability varies with the basicity of these compounds which declines as the number of structural units in the cycle increases. The results obtained give also some indication of the spatial effect of aliphatic radicals.

The aromatic properties of organocyclosilazanes are even more pronounced in their behaviour in the presence of catalytic quantities of alkaline reagents. Thus, in the presence of 1% KOH, polydimethylcyclosilazanes react as follows:



Our study has demonstrated that the magnitude and nature of the organic radicals linked to silicon materially affect these reactions. Thus, methylethyl-, methylbutyl- and methylhexyl-cyclosilazanes interact with KOH or C_2H_5ONa only at a relatively high temperature. Whereas in the case of polydimethylcyclosilazanes the evolution of methane and ammonia begins at about 100°[4], the compounds mentioned above evolve the same reaction products at 250° and higher; after 10–15 h the process subsides and increasing the temperature to 300° or more does not result in any significant evolution of gaseous products. From the reaction mixture were isolated compounds of composition II, $R_5R^1_6Si_6N_3(NH)_2$ ($R = CH_3$; $R^1 = C_2H_5$; C_4H_9, C_6H_{13}), the properties of which are given in Table 5. Their formation from hexaalkylcyclotrisilazanes (Ia) takes place as follows:



Apparently in this case, as in the case of polydimethylcyclosilazane[1], a transitional complex with the alkali which is formed at first dissociates into a hydrocarbon

TABLE 5

	B.p. (°C/mm)	n_D^{20}	d_4^{20}	*M Calcd. (Found)*	*MR Calcd. (Found)*	*Yield (%)*
$(CH_3)_5(C_2H_5)_6Si_6N_3(NH)_2$(IIa)	150–152	1.4869	1.0044	490 (440)	140.67 (140.27)	52.5
$(CH_3)_5(C_4H_9)_6Si_6N_3(NH)_2$(IIb)	219–224	1.4786	0.9586	658 (600)	194.23 (194.57)	46
$(CH_3)_5(C_6H_{13})_6Si_6N_3(NH)_2$(IIc)	249–254	1.4790	0.9441	827 (850)	249.79 (248.26)	47.5

and a negatively-charged ion. This ion then attacks the neutral molecule of the cycle rupturing the Si–N bond with subsequent cyclization into II. As a result, a molecule of ammonia is evolved and a molecule of alkali regenerated. The total quantity of ammonia collected corresponds to that which should be formed as a result of the above reaction (Table 6). The quantity of methane formed, however, greatly exceeds that calculated from the above equation. Therefore, it may be assumed that this reaction is accompanied by polymerization which ocurs without breaking the cycle and with formation of higher-molecular oligomers. The chemical inertness of II when treated with catalytic quantities of alkali shows that oligomers are not formed *via* these compounds but according to the mechanism suggested earlier[1,3]. The negatively-charged ion produced at the first stage joins the neutral cycle with the evolution of a hydrocarbon and the formation of a new bicyclic ion.

TABLE 6

	Quantity of hydrocarbon evolved (mole RH/mole Ia)	*Quantity of ammonia evolved (mole NH_3/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

As we pass from methylethyl-substituted to methylhexyl-substituted cycles, the rate of methane evolution at 250° declines (Fig. 1) which, it seems, is due to the spatial effect. In the case of trimethyltrinonylcyclotrisilazane, the reaction does not occur even at temperatures above 300°. The low reactivity of the compounds investigated compared with polydimethylcyclosilazanes can hardly be explained by spatial screening of the Si–N bonds by aliphatic radicals. It is possible that in the given case an important role is played by the existence of an equilibrium between polydialkylcyclosilazanes of different geometrical conformations. The structure of the transitional complex is also associated with a definite (*e.g.*, flat) conformation of the cyclic part

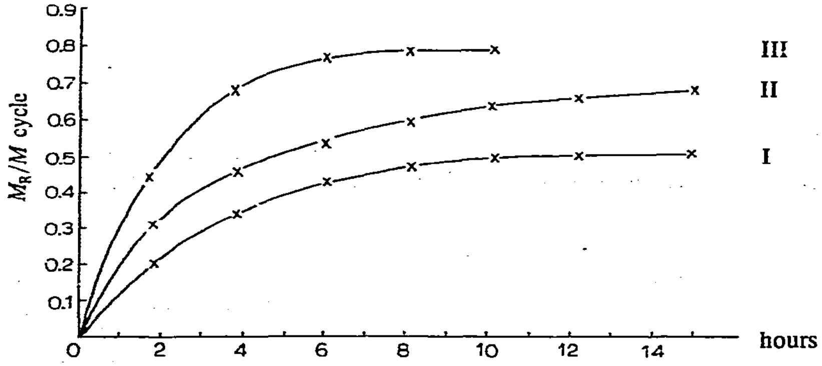
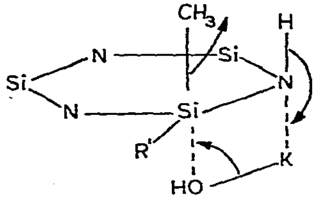


Fig. 1. Quantity of methane evolved, mole/mole of initial organocyclosilazane: (I) $(CH_3C_2H_5SiNH)_3$; (II), $(CH_3C_4H_9SiNH)_3$; (III), $(CH_3C_6H_{13}SiNH)_3$.

of the molecule, in which the synchronous electron transition which results in the breaking of certain links and the formation of new ones, is most probable:



The lengthening of the organic radical at the silicon atom will stabilise the conformation of the initial cyclosilazane thus hindering its transition into an activated state. It is this, apparently, that results in such a sharp decline of chemical reactivity when the methyl group in hexamethylcyclotrisilazane is substituted by ethyl, butyl or other groups.

The infrared spectra of the polymerization products given in Table 5, were taken to confirm their structure. They contain an absorption band at about 900 cm^{-1} which is lacking in the initial cycles; this can apparently be explained by the valence vibrations of the Si–N bond in a four-membered cycle. The intensity of the 3400 cm^{-1} band, characteristic of the valence vibrations of the n N–H bond is considerably reduced which is in conformity with structure II.

From the above results it is evident that the change in the geometric parameters of the molecules of organocyclosilazanes results in a new distribution of electron density in the cycle, which in turn materially affects the chemical reactivity of these compounds. In this case, however, we must take into account the spatial effect of organic radicals; this plays a noticeable role, particularly in those cases where the reaction of the silicoorganic cycle takes place *via* the formation of a transitional complex which requires a geometric reconstruction of the initial molecule.

EXPERIMENTAL

Ammonolysis of dialkyldichlorsilanes

A 15–20% solution of an appropriate dialkyldichlorsilane in benzene was placed in a four-necked flask equipped with a mixer, reflux condenser and a tube for introducing ammonia. Dry ammonia was passed until the dialkyldichlorsilane was completely neutralised. A temperature of 15–20° was maintained in the reaction flask. On completion of the reaction, ammonium chloride was filtered off, benzene was distilled off and the ammonolysis products vacuum fractionated.

Ammonolysis of methyl- and ethyl-trichlorsilane[6]

A benzene solution of an appropriate chlorsilane was amminated by the same method. The turbid viscous residue that remained after distilling off the benzene was dissolved in petroleum ether. The insoluble crystalline fraction was filtered off, washed with petroleum ether and dried. The petroleum ether was distilled from the filtrate and a clear brittle polymer with a melting point of about 50° was obtained.

Ammonolysis of higher alkyltrichlorsilanes[7]

The ammonolysis reaction was carried out by the method described above.

TABLE 7

Cyclosilazane	Calcd.				Found			
	C	H	Si	N	C	H	Si	N
$(CH_3C_2H_5SiNH)_3$	41.33	10.40	32.18	16.07	41.36	10.50	32.15	15.07
					41.40	10.22	32.38	14.95
$(CH_3C_2H_5SiNH)_4$	41.33	10.40	32.18	16.07	41.30	10.34	32.40	16.27
					41.17	10.30	32.50	16.06
$(CH_3C_4H_9SiNH)_3$	52.12	11.37	24.35	12.16	51.63	11.30	24.33	11.79
					51.92	11.30	24.49	11.86
$(CH_3C_4H_9SiNH)_4$	52.12	11.37	24.35	12.16	52.26	11.32	24.41	11.87
					52.24	11.39	24.51	11.76
$(CH_3C_6H_{13}SiNH)_3$	58.67	11.96	19.58	9.78	58.60	12.08	19.21	9.88
					58.75	12.23	19.51	9.65
$(CH_3C_6H_{13}SiNH)_4$	58.67	11.96	19.58	9.78	59.12	11.67	19.07	9.48
					59.02	11.83	18.97	9.47
$(CH_3C_8H_{17}SiNH)_3$	63.08	12.36	16.38	8.18	63.03	12.11	16.30	7.52
					63.17	12.16	16.52	7.66
$(CH_3C_9H_{19}SiNH)_3$	64.79	12.51	15.14	7.57	65.10	12.22	14.89	6.90
					64.83	12.20	15.39	7.18
$(C_2H_5C_8H_{17}SiNH)_3$	64.79	12.51	15.14	7.57	64.71	12.27	15.69	7.90
					64.94	12.25	15.85	8.12
$(C_2H_5C_8H_{17}NH_2Si)_2NH$	61.95	12.74	14.47	10.86	61.90	12.72	14.09	10.71
					61.79	12.66	14.34	10.39
$[CH_3Si(NH)_{1.5}]_6$	18.31	6.92	42.76	32.02	19.07	6.60	42.52	31.42
					18.88	6.83	42.34	31.05
$[C_2H_5Si(NH)_{1.5}]_6$	30.16	8.22	35.23	26.38	30.51	8.15	35.37	26.38
					30.35	8.28	35.39	26.18
$[C_6H_{13}Si(NH)_{1.5}]_6$	53.08	10.77	20.67	15.47	54.14	10.76	20.27	12.75
					54.23	10.49	20.38	12.99
$[C_7H_{15}Si(NH)_{1.5}]_6$	56.06	11.10	18.73	14.08	56.77	10.84	19.56	11.74
					56.64	10.83	19.27	11.82
$[C_8H_{17}Si(NH)_{1.5}]_8$	58.72	11.38	17.13	12.83	59.48	11.20	17.29	10.73
					59.28	11.21	17.37	10.97
$[C_9H_{19}Si(NH)_{1.5}]_6$	60.78	11.62	15.78	11.82	60.07	11.09	16.80	10.47
					59.96	11.18	16.66	10.58
$(CH_3)_5(C_2H_5)_6Si_6N_3(NH)_2$	41.67	9.67	34.36	14.29	41.65	9.64	34.40	14.64
					41.67	9.66	34.43	14.54
$(CH_3)_5(C_4H_9)_6Si_6N_3(NH)_2$	52.91	10.87	25.57	10.64	52.17	10.99	25.49	10.93
					52.47	10.83	25.77	11.07
$(CH_3)_5(C_6H_{13})_6Si_6N_3(NH)_2$	59.57	11.58	20.36	8.47	59.73	11.52	19.64	8.32
					59.83	11.58	19.57	8.21

After removal of ammonium chloride and benzene, a clear viscous liquid was obtained. This was vacuum fractionated. A small quantity of an insoluble brittle polymer remained in the retort.

Elementary analysis data for the fractions isolated and the crystalline products are given in Table 7.

Reaction of dialkylcyclosilazanes with alkalis

The reaction of dialkylcyclosilazanes with catalytic quantities of KOH or C_2H_5ONa (1% of the weight of the initial quantity of dialkylcyclosilazane) was carried out in a 50-ml flask with a reflux condenser series-connected with a flask for ammonia absorption, and a graduated water-filled cylinder in which the hydrocarbon evolved during the reaction was collected. Hydrocarbon identification was carried out on a gas chromatograph CL-4. The reaction products were vacuum fractionated. The elementary analysis for the fractions isolated is given in the table In the case of trimethyltriethylcyclotrisilazane on oligomer with a boiling point of 210–220° of the following composition was isolated: C, 40.67, 40,63; H, 9.27, 9.30; S, 35.71, 35,75; N, 14.40, 14.67%; mol. wt. 640.

Hydrolysis of alkylcyclosilazanes

A 10% benzene solution of the cyclosilazane was boiled for 24 h with an excess of a decinormal solution of sulphuric acid. The ammonia evolved was absorbed in water in a separate flask, filtered off and the hydrolysis percentage calculated from the quantity of ammonia evolved.

SUMMARY

1. As a result of the ammonolytic reaction of dialkyldichlorsilanes and alkyltrichlorsilanes a number of new dialkylpolycyclosilazanes and alkylsilsesquiazanes were obtained.

2. The infrared spectra and the reactivity with nucleophilic reagents of the organocyclosilazanes synthesized indicate that these compounds possess a certain aromaticity which varies with the dimensions of the cycles as with other heteromorphic aromatic systems.

3. It has been established that the magnitude of the organic radical linked to the silicon atom materially affects the reactivity of the organocyclosilazanes in their conversion in the presence of catalytic quantities of alkalis. This, apparently, is due to specific features in the structure of these cyclic systems.

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