PREPARATION OF ORGANOCYCLOSILAZANES BY AMMONOLYSIS OF DIALKYLDICHLOROSILANES

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A study is made of ammonolysis of dialkyldichlorosilanes of the RR'SiCl$_2$ series, where R = Me, Et, and R' = Me(CH$_2$)$_n$ (n = 1, 3, 5, 7, 8). With the lower members of the homologous series it takes place in accordance with a previously known equation. Ammonolysis of dialkyldichlorosilanes with big R' radicals on the silicon atom gives both cyclic and linear ammonolysis products.

At the present time ammonolysis of diorganodichlorosilanes is widely used for preparing organocyclosilazanes. From the ammonolysis products of dimethyldichlorosilane, first described in 1948 [1], hexamethyltrisilazane and octamethylcyclotetrasilazane have been isolated, the equation for their formation being

$$(CH_3)_2SiCl_2 + 3NH_3 \rightarrow 1/n[(CH_3)_2SiNH]_n + 2NH_4Cl,$$

where n = 3, 4.

Ammonolysis of the following compounds proceeds in the same way: diethyldichlorosilane [1], methylethyldichlorosilane, methylphenyldichlorosilane [2], diphenyldichlorosilane [3], di-n-butyldichlorosilane [4], methylvinyldichlorosilane and methylallyldichlorosilane [5]. There it was not possible to isolate reaction products with primary amino groups, e.g., diorganodiaminosilanes and tetraorganodiaminodisilazanes. However, ammonolysis of alkylchlorosilanes with a tertiary butyl group on the silicon atom led to the isolation of [4] the following diorganodiaminosilanes: $(t\text{-}C_4H_9)_2Si(NH_2)_2$, $t\text{-}C_4H_9(CH_3)Si\text{-}(NH_2)_2$, $t\text{-}C_4H_9(C_6H_5)Si(NH_2)_2$, $t\text{-}C_4H_9(C_{16}H_{31})Si(NH_2)_2$. Their stability is due to the steric effect of the tertiary butyl group which hinders further condensation of the primary amino groups.

We have synthesized a number of organocyclosilazanes and 1,3-diamino-1,3-diethyl-1,3-dioctyldisilazanes, hitherto undescribed in the literature. The starting dialkyldichlorosilanes RR'SiCl$_2$ had R = CH$_3$, C$_2$H$_5$; R' = C$_2$H$_5$, C$_4$H$_9$, C$_6$H$_{13}$, C$_8$H$_{17}$, C$_9$H$_{19}$. They were ammonolyzed in benzene solution with ammonia gas at room temperature. The individual compounds isolated and their properties are given in the table.

The chosen subjects of research are of interest in that they form the homologous series R[CH$_3$(CH$_2$)$_n$]SiCl$_2$. Increase in length of group R' makes it possible to follow the effect of steric factors on the ammonolysis of RR'SiCl$_2$, and also to establish a connection between the structures of the organocyclosilazanes prepared and their organic frameworks.

Ammonolysis of the lower and middle dialkyldichlorosilanes does not differ from that described in the literature for diorganodichlorosilanes, and proceeds according to the equation given above. However, reaction of the higher dialkyldichlorosilanes with ammonia proceeds somewhat differently, and we consider this to be due to the steric effect of large aliphatic groups. In such cases reaction results in formation of linear condensation products, e.g., 1,3-diamino-1,1,3,3-tetraorganyldisilazanes and 1,5-diamino-1,1,3,3,5-hexaorganotrisilazanes. When these compounds are

Ammonolysis product	Bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	Found		Calculated		Found, %				Calculated, %				Yield, %
				M	MR_D	M	MR_D	C	H	Si	N	C	H	Si	N	
$[CH_3C_2H_5SiNH]_3$	91—93 (3)	1.4570	0.9258	256	76.92	261.5	76.74	41.36 41.40	10.50 10.22	32.15 32.38	15.07 14.95	41.33	10.40	32.18	16.07	75
$[CH_3C_2H_5SiNH]_4$	136—139 (3)	1.4688	0.9511	341	102.38	348.7	102.31	41.30 41.17	10.34 10.30	32.40 32.50	16.27 16.06	41.33	10.40	32.18	16.07	21
$[CH_3C_4H_9SiNH]_3$	126—128 (1)	1.4600	0.9074	342	104.48	345.7	104.52	51.63 51.92	11.30 11.30	24.33 24.49	11.79 11.89	52.12	11.37	24.35	12.16	73
$[CH_3C_4H_9SiNH]_4$	162—165 (1)	1.4677	0.9215	446	139.13	460.9	139.14	52.26 52.24	11.32 11.39	24.41 24.51	11.87 11.76	52.12	11.37	24.35	12.16	22
$[CH_3C_6H_{13}SiNH]_3$	171—173 (1)	1.4642	0.8938	432	132.73	429.8	132.30	58.60 58.75	12.08 12.23	19.21 19.51	9.88 9.65	58.67	11.96	19.58	9.78	68
$[CH_3C_6H_{13}SiNH]_4$	220—224 (1)	1.4689	0.9057	559	176.37	573.1	176.40	59.12 59.02	11.67 11.83	19.07 18.97	9.43 9.47	58.67	11.96	19.58	9.78	25
$[CH_3C_8H_{17}SiNH]_3$	185—189 (1)	1.4654	0.8942	504	159.97	514	160.08	63.03 63.17	12.11 12.16	16.30 16.52	7.52 7.66	63.08	12.36	16.38	8.18	60
$[CH_3C_9H_{19}SiNH]_3$	203—207 (1)	1.4680	0.8896	522	173.75	556	173.97	65.10 64.83	12.22 12.20	14.89 15.39	6.90 7.18	64.79	12.51	15.14	7.57	53
$[C_2H_5C_8H_{17}SiNH]_3$	224—228 (1)	1.4710	0.8970	525	173.88	556	173.97	64.94 64.71	12.27 12.25	15.69 15.85	7.90 8.12	64.79	12.51	15.14	7.57	53
$NH[C_2H_5C_8H_{17}SiNH_2]_2$	169—171 (1)	1.4620	0.8790	413	121.24	388	121.41	61.96 61.79	12.72 12.66	14.09 14.34	10.71 10.39	61.95	12.74	14.47	10.86	41

isolated from the reaction products by distillation, they condense to cyclosil azanes. Still, it proved possible to isolate from the ammonolysis products of ethyloctyldichlorosilane a comparatively high yield of the corresponding diaminodisilazane, which was stable when distilled.

It is of interest to note that as length of the organic group increases the yields of cyclotrisilazanes drops (see table). This is explained not by decreasing tendency to ring formation, but to more rapid change in chemical activity of the primary amino groups. In proportion as the length of the organic group increases, the capacity of these groups to undergo condensation decreases, leading to increase in yield of linear dimer, and decrease in yield of linear trimer. Since in the action of heat on the reaction mixture the linear trimer is the sole structural unit from which cyclotrisilazane can be formed, decrease in the amount of the former in the mixture leads to decrease in the yield of the latter

To check the structures of the compounds prepared, their IR spectra were determined, and absorption bands at 925–950, 1160–1190, and 3395–3420 cm^{-1} were found, characteristic of organosilazanes. The spectrum of 1,3-diethyl-1,3-dioctyl-1,3-diaminodisilazane was found to have an absorption band at 1550 cm^{-1}, belonging to deformation vibrations of a primary amino group. This band was absent with all the organocyclosilazanes which we prepared.

EXPERIMENTAL

The ammonolysis of methylethyldichlorosilane is described below, as an example of the general ammonolysis of $RR'SiCl_2$.

A 4-necked flask was fitted with a stirrer, reflux condenser, thermometer, and gas inlet tube for introducing the ammonia. It was charged with a solution of 43.9 g $CH_3(C_2H_5)SiCl_2$ in 200 ml benzene, and ammonia passed into the solution until the methylethyldichlorosilane was completely neutralized. The reaction temperature is maintained within the limits, 20–25°. At the end of the reaction the NH_4Cl was filtered off, the benzene distilled off, and the ammonolysis products vacuum-distilled. The properties and elementary analyses of the products isolated are given in the table.

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