REACTION OF DIALKYLDICHLORO- AND ALKYLDICHLORO-SILANES WITH METHYLAMINE

E. A. Semenova, D. Ya. Zhinkin, and K. A. Andrianov

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It is known from the literature that dialkyldichloro- and diaryldichloro-silanes react with ammonia with formation of alkylcyclosilazanes and alkylaminosilanes. In this way silanediamines [1, 2] and cyclic silazanes of general formula $[R_2SiNH]_n$ were prepared. From dimethyl- and diethyl-dichlorosilanes cyclosilazanes having n = 3 and 4 have been prepared [3]. By the ammonolysis of diphenyl- [4], ethylmethyl-, and methylphenyl-dichlorosilanes [5] cyclotrisilazanes have been prepared. The reaction of dialkyl- and diaryl-dichlorosilanes with primary and secondary amines leads to the formation of silanediamines [2, 4, 6, 7]. The reaction with methylamine was studied for the case of dichlorodimethylsilane [6] and dichlorodiphenylsilane [4]. The reaction led to the formation of silanediamines: N,N',1,1-tetramethylsilanediamine and N,N'-dimethyl-1,1-diphenylsilanediamine. As yet there are no data on the products of the aminolysis of alkyldichlorosilanes.

In the present investigation we studied the reaction of dialkyldichloro- and alkyldichloro-silanes with methylamine. For investigation we took dichloromethylsilane, dichlorodimethylsilane, dichloroethylsilane, and dichlorodiethylsilane. The synthesis was carried out by the general method: amination of the alkylchlorosilane with gaseous methylamine in benzene solution. After the introduction of the calculated amount of methylamine the solution was filtered from the precipitate of methylamine hydrochloride. Benzene was distilled from the filtrate, and the residue was fractionated through a column of 17- or 24-plate efficiency. Our experiments showed that the reaction of these chlorosilanes with methylamine proceeds with formation of cyclic silazanes, disilazanes, and silanediamines. In the reaction of methylamine with an alkyldichlorosilane, a disilazane and cyclosilazanes were formed by the reaction

$$RHSiCl_{2} + CH_{3}NH_{2} \rightarrow \begin{bmatrix} H \\ CH_{3} \end{bmatrix} N - Si \begin{pmatrix} H \\ R \end{bmatrix}_{2} NCH_{3} + [RHSiNCH_{3}]_{3} + [RHSiNCH_{3}]_{4} + CH_{3}NH_{2} \cdot HCl$$

A cyclotetrasilazane was obtained only in the aminolysis of dichloromethylsilane.

Thus, from the products of the aminolysis of dichloromethylsilane we isolated three individual products: N,N',1,2,3-pentamethyl-1,3-disilazanediamine, 1,2,3,4,5,6-hexamethylcyclotrisilazane, and 1,2,3,4,5,6,7,8-octamethylcyclotetrasilazane in the proportions of 1:6:4. The content of the first silazane in the mixture of reaction products after the distillation of benzene from the filtrate was 2-5%, that of the second was 35-40%, and that of the third was 20-25%. The over-all yield of alkylsilazanes was 60% on the dichloromethylsilane taken. As the result of the aminolysis of dichloroethylsilane we obtained two compounds: 1,3-diethyl-N,N',2-trimethyl-1,3-disilazanediamine and 2,4,6-triethyl-1,3,5-trimethylcyclotrisilazane in the proportions of 1:1. The content of each compound in the mixture of liquid reaction products was 38-40%. In this case the yield of alkylsilazanes reached 75%. Under our conditions the aminolysis of dialkyldichlorosilanes went in accordance with the equation

$$\mathbf{R_{2}SiCl_{3}} + \mathbf{CH_{3}NH_{2}} \rightarrow \begin{bmatrix} \mathbf{H} \\ \mathbf{CH_{3}} \end{pmatrix} \mathbf{N} - \mathbf{Si} \begin{pmatrix} \mathbf{R} \\ \mathbf{R} \end{bmatrix}_{2} \mathbf{NCH_{3}} + \mathbf{R_{2}Si} (\mathbf{NHCH_{3}})_{2} + \mathbf{CH_{3}NH_{2}} \cdot \mathbf{HCH_{3}} + \mathbf{R_{3}Si} (\mathbf{NHCH_{3}})_{2} + \mathbf{CH_{3}NH_{3}} \cdot \mathbf{HCH_{3}} + \mathbf{HCH_{3}}$$

Properties of the Alkylcyclos	ilazanes and Alkylsilanediamines Obtained							
	Compound	B.p., °C	, 20	1 20	Mol.	wt.	MR	
Formula	Name	(b, mm)	0 D	7	found	calc.	found	calc.
(CH ₃ SiHNHCH ₃) ₂ NCH ₃	N,N°,1,2,3-Pentamethyl-1,3-disilazane- diamine	48.5 (5)	1.4425	0.8871	176.6	177.0	52.92	52.99
(CH ₃ SiHNCH ₃) ₃ (CH ₃ SiHNCH ₃) ₄	1,2,3,4,5,6-Hexamethylcyclotrisilazane 1,2,3,4,5,6,7,8-Octamethylcyclotetrasil-	56 (5)	1.4580	0.9297	218	219	64.16	64.14
(C ₂ H ₅ SiHNHCH ₃) ₂ NCH ₃	azanediamine 1,3-Diethyl-N,N',2-trímethyl-1,3-disil-	88 (2)	1.4810	0.9776	290	292	85.00	85.52
(C ₂ H ₅ SiHNCH ₃) ₃	azanediamine 2,4,6-Triethyl-1,3,5-trimethylcyclotti-	68.5 (1, 5)	1.4520	0.8929	204.5	205	61.99	62.25
[(CH3)2SiNHCH3]2NCH3	silazane N.N.,1,1,2,3,3-Heptamethyl-1,3-disil-	74.5 (1, 5)	1.4680	0.9324	260	261	77.80	78.03
	azanediamine	34.5 (0, 5)	1,4435	0.8886	202	205	61.30	61.73
(C ₂ H ₅) ₂ Si(NHCH ₃) ₂	N,N, 1,1-1 ettamentytsuanediamine 1,1-Diethyl-N,N'-dimethylsilanediamine	156 (745) 156 (745)	1.4140	0.8421	119 146.2	118 146	35.87 44.97	35.98 45.24
• The literature [6] gives b.p	, 66° (165 mm).			-				

In the reaction of methylamine with dichloromethylsilane N,N',1,1,2,3,3-heptamethyl-1,3-disilazanediamine and N,N',1,1-tetramethylsilanediamine were formed in the proportions 1:3. The content of the first compound in the mixture of liquid reaction products after the removal of benzene was 20%, and that of the second was 70%. The over-all yield of nitrogen-containing compounds was 55-58%. In the reaction between dichlorodiethylsilane and methylamine we obtained only 1,1-diethyl-N,N'-dimethylsilanediamine; the yield of this product was 57%. The properties of the pure compounds obtained are given in the table.

EXPERIMENTAL

Aminolysis of Dichloromethylsilane. A fournecked flask fitted with stirrer, thermometer, reflux condenser, and bubbling tube for the introduction of the amine was charged with 165 g of dichloromethylsilane and 400 ml of benzene. Gaseous methylamine was passed through this solution at a rate of 1-1.5 liters/minute. The temperature in the flask was kept in the range 15-20° by cooling in an ice bath. After the introduction of the calculated amount of methylamine, the reaction mixture was filtered from the precipitate of methylamine hydrochloride. Benzene was distilled from the filtrate in a Wurtz flask. We obtained 92.5 g of product (yield 87.5%). The product was fractionated through a column of 24-plate efficiency at a residual pressure of 5 mm. We obtained 1.85 g (2.5%) of N,N',1,2,3-pentamethyl-1,3disilazanediamine. Found: C 33.5; H 10.5; Si 31.76; N 21.14%, C5H19Si2N3. Calculated: C 33.9; H10.73; Si 31.64; N 21.78%; 31.35 g (43%) of 1,2,3,4,5,6hexamethylcyclotrisilazane. Found: C 32.8; H 9.6; Si 38.46; N 18.8%, C₆H₂₁Si₃N₃, Calculated: C 32.87; H 9.58; Si 38.36; N 19.2%; 17.15 g (23.5%) of 1,2,3,-4,5,6,7,8-octamethylcyclotetrasilazanediamine. Found: C 32.9; H 9.3; Si 38.2; N 19.0%. C₈H₂₈Si₄N₄. Calculated: C 32.87; H 9.58; Si 38.36; N 19.2%; and 22.5 g (31%) of residue in the still, which contained 38.32% Si and 16-17% of N and had mol. wt. 1856.

Aminolysis of Dichlorodimethylsilane. This was carried out in an analogous way. The flask was charged with 447 g of dichlorodimethylsilane and 800 ml of benzene. Methylamine was passed at a rate of 1.5 liters/minute. Benzene was distilled off, and we then obtained 257.85 g (62.5%) of product. Fractionation of the product through a column of 17-plate efficiency gave 53.4 g (22.5%) of N,N',1,1,2,3,3-heptamethyl-1,3-disilazanediamine. Found: C 40.9; H 10.9; Si 27.9; N 20.3%. $C_7H_{23}Si_2N_3$. Calculated: C 40.97; H 11.22; Si 27.32; N 20.49%, and 171.4 g (72.5%) of N,N',1,1-tetramethylsilanediamine. Found: C 40.3; H 12.1; Si 23.5; N 23.5% $C_4H_{14}SiN_2$. Calculated: C 40.68; H 11.86; Si 23.7; N 23.7%. After these individual compounds had been distilled off we were left with 12.05 g (5%) of residue containing 32.78% Si and 6.87% N and having mol. wt. 445.6.

Aminolysis of Dichloroethylsilane. This was carried out by the above-described method. The flask was charged with 327.0 g of dichloroethylsilane and 500 ml of benzene. The rate of passage of methylamine was 1 liter/minute. After the removal of benzene we obtained 216.45 g (92%) of crude product. On fractionation of the product we obtained 66.51 g (38.0%) of 1.3-diethyl-N,N',2-trimethyl-1.3-disilazanediamine and 68.15 g (39%) of 2,4,6-triethyl-1.3,5-trimethylcyclotrisilazane. Found: C 40.80; H 11.70; Si 27.36; N 19.2%. $C_7H_{23}Si_2N_3$. Calculated: C 40.97; H 11.22; Si 27.32; N 20.49%. Found: C 41.30; H 10.2; Si 32.2; N 15.70%. $C_9H_{27}Si_3N_3$. Calculated: C 41.38; H 10.34; Si 32.18; N 16.09%. The residue remaining after the fractionation, which amounted to 41.6 g (23%), was a viscous liquid containing 32.99% Si and 14.25% N; the mol. wt. of the residue was 518.3.

Aminolysis of Dichlorodiethylsilane. This was carried out by an analogous method. The flask was charged with 157.5 g of dichlorodiethylsilane and 400 ml of benzene. Methylamine was passed at a rate of 1 liter/minute. After the removal of benzene we obtained 103.8 g (71%) of product, by the rectification of which we isolated 83.3 g (80.5%) of 1,1-diethyl-N,N'-dimethylsilanediamine. Found: C 49.1; H 12.3; Si 19.09; N 18.8%. C₆H₁₈SiN₂. Calculated: C 49.31; H 12.4; Si 19.17; N 19.17%. The residue from the rectification amounted to 20.5 g (19.5%) and contained 27.45% Si and 7.5% N; it had mol. wt. 491.

SUMMARY

1. The reaction of methylamine with alkyldichlorosilanes and with dialkyldichlorosilanes was investigated. By the action of dichloromethyl- and dichloroethyl-silanes on methylamine alkylcyclosilazanes and disilazanes were formed, but by the action of dichlorodimethyl- and dichlorodiethyl-silanes on methylamine only disilazanes and silanediamines were formed.

2. Seven new compounds were isolated and characterized.

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