

N-Substituted Alkyltriaminosilanes

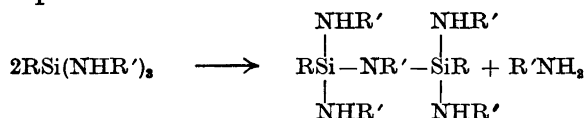
IV. On Intermolecular Condensation

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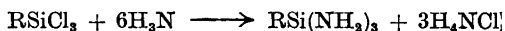
Ammonolysis of methyl-, ethyl-, and *n*-propyltrichlorosilane gave no distillable products. Alkyltriaminosilanes were presumably first formed but condensed intermolecularly with evolution of ammonia to give polymers. The corresponding N-substituted alkyltriaminosilanes, however, were obtained in good yields. In the presence of a small amount of a proton donor also these compounds condensed intermolecularly, the reactivity being greatly depending upon the nature of the groups attached to the silicon and nitrogen atoms.

This paper describes the intermolecular condensation of some alkyltriaminosilanes and their N-substituted derivatives, which proceeds with evolution of ammonia or amine and the first stage of which would be according to the general equation



This reaction has been performed for $\text{R} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5$ and *n*- C_3H_7 and $\text{R}' = \text{H}, \text{CH}_3$ and C_2H_5 .

When methyl-, ethyl-, or *n*-propyltrichlorosilane reacted with ammonia, the monomeric alkyltriaminosilanes, $\text{RSi}(\text{NH}_2)_3$, were not obtained even if the reactions were performed in liquid ammonia. Presumably these compounds were first formed according to the equation

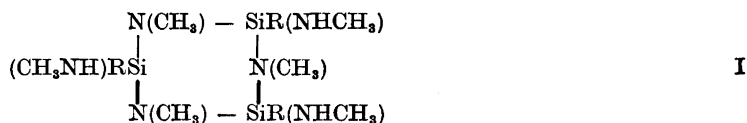


but they very easily condensed intermolecularly, as mentioned above, with the formation of ether-soluble polymeric silazanes with Si—NH—Si linkages, which, after evaporation of the solvent gave viscous oils. Upon heating of these, more ammonia was split out and high polymers with a three dimensional

network resulted. This is analogous to the ammonolysis of trichlorosilane¹ which gave a polymer, $\text{HSi}(\text{NH})_{1.5}$, with a cross-linked structure and a very high degree of polymerization. Nor did Larsson² observe any low-molecular products from the ammonolysis of *n*-butoxitrchlorosilane. Chugunov³, however, obtained a compound which appeared to be $\alpha\text{-C}_{10}\text{H}_7\text{Si}(\text{NH}_2)_3$, by bubbling dry gaseous ammonia into an ether solution of α -naphthyltrifluorosilane, but no analyses or further studies of the compound were given to authorize the formula. It was mentioned only that the compound rapidly hydrolyzed in contact with moist air with evolution of ammonia. The bulky α -naphthyl-group can certainly be expected to exert a greater retarding influence on the intermolecular condensation than the R-groups investigated in this paper, but it seems not unlikely that what was interpreted as a hydrolysis may have been the first stages of a condensation of the type mentioned above.

It was reported in a previous paper⁴ that *n*-propyltri-(methylamino)-silane and *n*-propyltri-(ethylamino)-silane are stable at their normal boiling points and it was now found that the corresponding methyl- and ethyl-compounds could be isolated without difficulty. This shows that organic groups on the nitrogen atoms effectively impede the tendency toward intermolecular condensation of the compounds compared with that of the unsubstituted alkyl-triaminosilanes. Tri-(ethylamino)-silane, with the silicon bearing only a hydrogen atom beside the ethylamino groups, could also be isolated, but no uncondensed products were obtained from the reaction mixture of trichlorosilane and methylamine.

The accelerating effect of hydrogen ion on the reaction of N-substituted *n*-propyltriaminosilanes with primary and secondary amines was demonstrated in part II of this work⁵. As can be expected the intermolecular condensation, which is apparently of the same nature as the exchange reactions studied in the previous paper, is also catalyzed by the hydrogen ion. Thus, methyl-, ethyl- and *n*-propyltri-(methylamino)-silane all gave a vigorous evolution of methylamine far beneath their ordinary reflux temperatures when heated with a small amount of ammonium sulfate. The reaction mixtures, which were soluble in organic solvents, crystallized on cooling and gave good yields of compounds the analyses of which corresponded to the cyclic structure I.



The building up of high-molecular-weight cross-linked structures from these by further condensation seems to be effectively sterically hindered for they could all be heated with ammonium sulfate present to 200°C for several hours without any noteworthy liberation of methylamine. However, when the mixture of low-molecular condensation products which was obtained from the reaction of trichlorosilane and methylamine was heated with a small amount of ammonium sulfate to the same temperature, a considerable evolution of methylamine occurred, and after a few hours there remained an insoluble hard and glassy mass, typical of cross-linked structures.

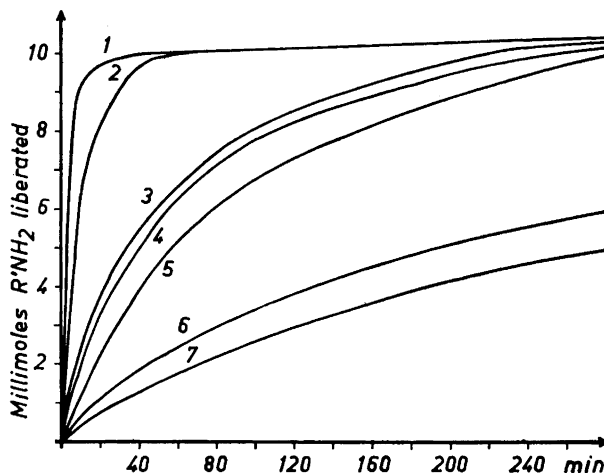


Fig. 1. Intermolecular condensation of $\text{RSi}(\text{NHR}')_3$. 1. $\text{HSi}(\text{NHC}_2\text{H}_5)_3$; 2. $\text{CH}_3\text{Si}(\text{NHCH}_3)_3$; 3. $\text{C}_2\text{H}_5\text{Si}(\text{NHCH}_3)_3$; 4. $n\text{-C}_3\text{H}_7\text{Si}(\text{NHCH}_3)_3$; 5. $\text{CH}_3\text{SiNHC}_2\text{H}_5)_3$; 6. $\text{C}_2\text{H}_5\text{Si}(\text{NHC}_2\text{H}_5)_3$; 7. $n\text{-C}_3\text{H}_7\text{Si}(\text{NHC}_2\text{H}_5)_3$.

In Fig. 1 are given the results of a series of experiments in which 0.01 mole of some substituted triaminosilanes, $\text{RSi}(\text{NHR}')_3$, were heated in the presence of a small amount of ammonium sulfate at 120°C and the liberated amine, $\text{R}'\text{NH}_2$, was titrated with standard acid. It appears that the rate of evolution of amine depends on the nature of R and R' , being increased in the order $\text{R} = n\text{-C}_3\text{H}_7, \text{C}_2\text{H}_5, \text{CH}_3, \text{H}$ and $\text{R}' = \text{C}_2\text{H}_5, \text{CH}_3$.

The physical constants and analyses of the following compounds are given in Table 1: I, $\text{CH}_3\text{Si}(\text{NHCH}_3)_3$; II, $\text{CH}_3\text{Si}(\text{NHC}_2\text{H}_5)_3$; III, $\text{C}_2\text{H}_5\text{Si}(\text{NHCH}_3)_3$; IV, $\text{C}_2\text{H}_5\text{Si}(\text{NHC}_2\text{H}_5)_3$.

EXPERIMENTAL

The method of the determination of the physical constants of the compounds and the analyses have been previously described⁴. The experiments, the results of which are given in Fig. 1, were performed in the following way. The triaminosilanes (0.01 mole) and 6 mg (5×10^{-5} mole) of ammonium sulfate were introduced into a 10 ml flask which was heated to $120 \pm 0.5^\circ\text{C}$ in a thermostat. The liberated amine was withdrawn by a weak, uniform stream of nitrogen, which had been carefully dried with conc. sulphuric acid and phos-

Table 1. Physical constants and analyses of $\text{RSi}(\text{NHR}')_3$

No.	M	B.p. $^\circ\text{C}$	Pressure mm Hg	n_D^{20}	d^{20}	MRD	% Si		Equiv. wt.	
							found	calc.	found	calc.
I	133.27	61	40	1.4339	0.8942	38.81	21.1	21.1	44.8	44.4
II	175.35	62–63	10	1.4300	0.8522	53.15	16.0	16.0	58.8	58.5
III	147.30	51–52	10	1.4410	0.8966	43.38	19.2	19.1	49.3	49.1
IV	189.38	78–79	10	1.4360	0.8581	57.70	14.9	14.8	63.4	63.1

phorus pentoxide, and had to pass a reflux condenser cooled with water before it was absorbed in a known volume of standard hydrochloric acid. The acid was added in small portions into the absorption vessel and the times of neutralization (methyl red as the indicator) were noted. All the investigated N-substituted alkyltriaminosilanes gave only a very slow evolution when heated without ammonium sulfate but tri-(ethylamino)-silane condensed rapidly even in the absence of the catalyst.

Ammonolysis of ethyltrichlorosilane. In a 500 ml three-necked flask immersed in a Dry Ice and acetone-bath were placed about 100 ml of liquid ammonia. From a dropping funnel, 16.4 g (0.1 mole) of ethyltrichlorosilane in 250 ml of ether was added dropwise during 2 h to the stirred ammonia. The temperature was slowly raised by the removal of the bath. After 2 h at room temperature most of the excess of ammonia had evaporated. Ether was distilled from the mixture until the distillation temperature reached 35°C and about 50 ml were removed at this temperature to take away most of the residual ammonia. Filtration left 16.0 g (calc. for the total exchange of chlorine 16.0 g) of ammonium chloride on the filter. No silicon was found in the precipitate so the reaction product was still quite ether soluble. The filtrate gave after the filtration only a weak odour of ammonia, but after standing for a few hours in a sealed bottle, an additional pressure, owing to free ammonia, had been formed. During the course of the distillation of ether ammonia continuously escaped, and after the last traces of ether had been removed at reduced pressure, there remained a viscous, colourless oil which could again be dissolved in ether and neutralized some acid when agitated with 0.1 N hydrochloric acid. Attempts to distil the oil at reduced pressure only caused more ammonia to evolve giving a residue of an amorphous plastic solid which on heating to about 200°C lost a little more ammonia and changed to a brittle, colourless resin. When treated with strong warm alcoholic potassium hydroxide, ammonia was set free in an amount corresponding to a nitrogen content of 26.0 %; calc. for $C_2H_5Si(NH)_{1.5}N$ 26.4. The silicon content was 34.2 against 35.3 for the formula above. The low silicon content points to incomplete condensation. Wagner *et al.*⁶ found that brittle polymers obtained by hydrolysis of vinyltrichlorosilane contained as much as 9.5 % silanol hydroxyl so it is apparent that complete condensation is not necessary to give silicon polymers with a high degree of polymerization. That there was not found a corresponding increase of the nitrogen content of the product is probably due to partial hydrolysis.

The ammonolysis of *methyltrichlorosilane* and *n-propyltrichlorosilane* was performed in the same way and proceeded analogously to give insoluble, high-molecular-weight products as above.

Tri-(methylamino)-silane. 27.1 g (0.2 mole) of trichlorosilane in 100 ml of ether were added dropwise to an ice-cooled, stirred solution of 50 g (1.6 mole) of methylamine in 300 ml of ether. The temperature was then slowly raised by the removal of the ice-bath. Filtration of the reaction mixture left 40.3 g (calc. 40.5 g) of methylamine hydrochloride on the filter. On distillation of the filtrate, no distillate was obtained beneath 100°C (9 mm Hg) where tri-(methylamino)-silane can be supposed to distil. Between 125–175°C/9 mm, however, 8.0 g of an ether soluble product were obtained (Found: Equiv. wt. 43.8; Si 30.6. Calc. for $[HSi(NHCH_3)(NCH_3)]_n$: Equiv. wt. 44.1; Si 31.8.) On further heating of the distillation flask a vigorous evolution of methylamine took place and 5.5 g of an insoluble, hard and glassy residue were obtained.

When the distillate was heated to 200°C with a small amount of ammonium sulfate, methylamine was set free and after 3 h a high-molecular-weight product had been formed as above.

Tri-(ethylamino)-silane. 27.1 g (0.2 mole) of trichlorosilane in 100 ml of ether were added to 75 g (1.7 mole) of ethylamine in 400 ml of ether, cooled to 0°C. On filtration, 48.7 g (calc. 48.9 g) of ethylamine hydrochloride were left on the filter. On distillation of the filtrate, 8.0 g (25 %) of tri-(ethylamino)-silane were obtained, b.p. 62–63°/10 mm, (Found: Equiv. wt. 54.0; Si 17.5. Calc. for $HSi(NHC_2H_5)_3$: Equiv. wt. 53.8; Si 17.4.) On further heating a considerable amount of ethylamine escaped from the distillation flask. After the content had been heated for two hours at about 150°C the distillation was continued giving:

125–45°/0.5 mm: 2.0 g; equiv. wt. 57.5; Si 22.7;
 145–60°/0.5 mm: 7.2 g; equiv. wt. 57.5; Si 22.9;
 160–80°/0.5 mm: 4.2 g; equiv. wt. 58.1; Si 23.6.

Methyltri-(methylamino)-silane. To an ice-cooled, stirred solution of 30 g (1.0 mole) of methylamine in 300 ml of ether, a solution of 15.0 g (0.1 mole) of methyltrichlorosilane was added dropwise. The stirred mixture was heated to reflux temperature for 1 h and was then filtered giving 20.2 g (calc. 20.3 g) of methylamine hydrochloride on the filter. Distillation of the filtrate gave 9.5 g (71 %) of methyltri-(methylamino)-silane with the data given in Table 1.

5.8 g of the compound was heated for 5 h at 150°C with 10 mg of ammonium sulfate and gave a product which crystallized on cooling (m.p. 133–36°). Recrystallization from pentane at –20° gave 2.0 g, m.p. 136–38° (Found: Equiv. wt. 52.0, Si 27.9, *M* (in benzene) 320. Calc. for $[\text{CH}_3\text{Si}(\text{NHCH}_3)(\text{NCH}_3)_2]_3$ (I): Equiv. wt. 51.1, Si 27.5, *M* 307.)

Methyltri-(ethylamino)-silane. 11.1 g (0.074 mole) of methyltrichlorosilane in 50 ml of ether were added to 45 g (1.0 mole) of ethylamine in 300 ml of ether. The stirred mixture was refluxed for 1 h. Filtration left 18.0 g (calc. 18.1 g) of ethylamine hydrochloride on the filter. On distillation of the filtrate 10.1 g (78 %) of methyltri-(ethylamino)-silane were obtained.

Ethyltri-(methylamino)-silane (22.3 g; 76 %) was obtained in the same way as described for methyltri-(methylamino)-silane from 32.7 g (0.2 mole) of ethyltrichlorosilane and excess of methylamine. 6.0 g of it were heated for 5 h at 150°C with 10 mg of ammonium sulfate. The reaction mixture, which crystallized on cooling, was recrystallized from pentane at –20° and gave 2.2 g, m.p. 189–92° (Found: Equiv. wt. 59.0, Si 24.2, *M* 355. Calc. for $[\text{C}_2\text{H}_5\text{Si}(\text{NHCH}_3)(\text{NCH}_3)_2]_3$: Equiv. wt. 58.1, Si 24.2, *M* 349.)

Ethyltri-(ethylamino)-silane (33.5 g; 88 %) was obtained in the same way as was described for methyltri-(methylamino)-silane, from 32.7 g (0.2 mole) of ethyltrichlorosilane and excess of ethylamine.

The synthesis of *n*-propyltri-(methylamino)-silane and *n*-propyltri-(ethylamino)-silane was described in a previous paper⁴.

16.1 g of *n*-propyltri-(methylamino)-silane were heated for 5 h at 180°C in the presence of 20 mg of ammonium sulfate. On distillation of the reaction mixture, no *n*-propyltri-(methylamino)-silane was removed. Between 167–75°/1 mm 11.1 g of a product were obtained which crystallized on cooling (m.p. 67–70°). Recrystallization from pentane at –20° gave 7.5 g, m.p. 69–70° (Found: Equiv. wt. 65.9, Si 21.6, *M* 404. Calc. for $[n\text{-C}_3\text{H}_7\text{Si}(\text{NHCH}_3)(\text{NCH}_3)_2]_3$: Equiv. wt. 65.1, Si 21.6, *M* 391.)

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