

SYNTHESIS OF ORGANOSILAZANES

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Earlier we investigated the reaction of joint ammonolysis of various triorganochlorosilanes, leading to the formation of hexaorganodisilazanes according to the following scheme [1, 2]:

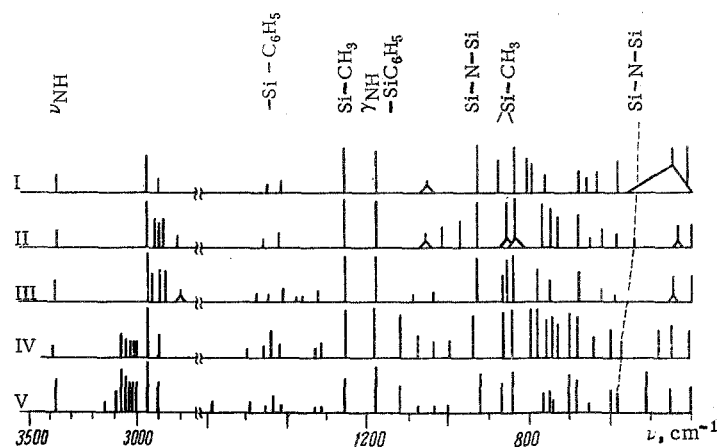


Fig. 1. Infrared spectra of organotrisilazanes. The serial numbers of the compounds correspond to Table 1.

TABLE 1.

No.	Compound	Excess (CH ₃) ₃ Si- Cl, mole	Yield, %	Bp, °C (P, mm)	d ₄ ²⁰	n _D ²⁰	MR	
							found	theo- retical
I	[(CH ₃) ₃ SiNH] ₂ Si(CH ₃) ₂	10	60	194—196	0,8316	1,4275	72,26	72,16
II	[(CH ₃) ₃ SiNH] ₂ Si(C ₂ H ₅) ₂	4	81	224—225	0,8462	1,4400	81,67	81,94
III	[(CH ₃) ₃ SiNH] ₂ SiCH ₃ (<i>i</i> -C ₄ H ₉)	5	61	231—233	0,8421	1,4370	85,85	86,6
IV	[(CH ₃) ₃ SiNH] ₂ SiCH ₃ (C ₆ H ₅)	7*	60*	131—135 (1—2)	0,9180	1,4815	92,06	92,79
V	[(CH ₃) ₃ SiNH] ₂ Si(C ₆ H ₅) ₂	2	79	140—145 (1—2)	0,9900	1,5300	111,7	112,9

No.	Found, %				Molecular formula	Theoretical, %			
	C	H	Si	N		C	H	Si	N
I	41,29 41,03	11,23 11,42	34,91 35,08	12,20 12,01	C ₈ H ₂₆ Si ₃ N ₂	41,00	11,10	36,00	11,90
II	45,64 45,66	11,83 11,85	31,44 31,70	11,42 11,52	C ₁₀ H ₃₀ Si ₃ N ₂	45,80	11,50	32,00	10,70
III	48,07 48,87	12,01 11,81	30,29 30,31	10,44 10,27	C ₁₁ H ₃₂ Si ₃ N ₂	48,00	11,60	30,40	10,00
IV	52,21 52,30	9,38 9,32	28,05 28,38	9,36 9,17	C ₁₃ H ₂₈ Si ₃ N ₂	52,70	9,45	28,40	9,45
V	57,9	8,45	22,52	7,65 7,53	C ₁₈ H ₃₀ Si ₃ N ₂	60,40	8,40	23,40	7,80

* The product yield amounted to 50% with a 5-fold excess of (CH₃)₃SiCl and 74% with a 9-fold excess.

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where R and R' are various aliphatic or aromatic radicals. Investigation of the reaction of ammonia with alkyl(aryl)dichlorosilanes and trimethylchlorosilane showed that the reaction occurs predominantly with the formation of mixed organotrisilazanes according to the following scheme:



where R_2Si is $Si(CH_3)_2$, $Si(C_2H_5)_2$, $Si(CH_3)(i-C_4H_9)$, $SiCH_3(C_6H_5)$, or $Si(C_6H_5)_2$.

As the excess trimethylchlorosilane increases, the product yield of the joint ammonolysis increases. The properties of the new compounds obtained are shown in Table 1. The infrared spectra of the organotrisilazanes in respect of their absorption bands are given in Fig. 1.

EXPERIMENTAL

Ammonia was passed into a solution containing the mixture of the initial organochlorosilanes in an inert solvent (benzene or saturated hydrocarbons with boiling points up to 100°C). The ammonia was bubbled through the liquid or passed over the surface of the solution. In the latter case the ammonolysis product yield was 10-15% greater. At the end of the reaction the ammonium chloride precipitate was filtered off and washed with solvent, the solvent was distilled, and the residue was subjected to fractional distillation, selecting the respective organotrisilazanes in the temperature ranges shown in Table 1.

CONCLUSIONS

Organotrisilazanes have been prepared by ammonolysis from mixtures of various diorganodichlorosilanes with excess trimethylchlorosilane.

LITERATURE CITED

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2. K. A. Andrianov, A. M. Kononov, A. K. Klimov, and G. N. Tikhonova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 617 (1969).