REACTIONS OF TRIALKYLSILOXYCHLOROSILANES

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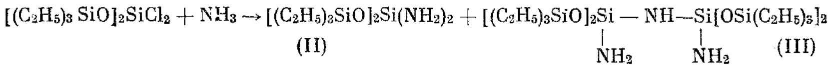
The ammonolysis of bis(trimethylsiloxy)dichlorosilane at room temperature in benzene proceeds with replacement of the halogen by the amino group, without cleaving the trimethylsiloxy group [1]. It was interesting to trace the effect of the radical in the siloxy group on the character and properties of the compounds. In the present paper we obtained bis(triethylsiloxy)dichlorosilane (I) in 57% yield by the reaction:

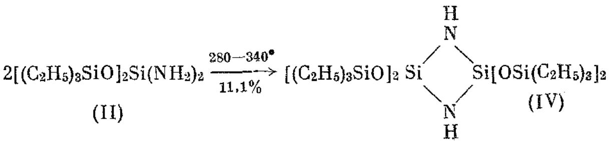
$$2(C_2H_5)_3SiOSi(C_2H_5)_3 + SiCl_4 \rightarrow \underset{(I)}{[(C_2H_5)_3SiO]_2SiCl_2} + 2(C_2H_5)_3SiCl$$

The reaction of (I) with ammonia at 45°C gave bis(triethylsiloxy)diaminosilane (II) (72%) and 1,3-bis(triethylsiloxy)-1,3-aminodisilazane (III) (11%)

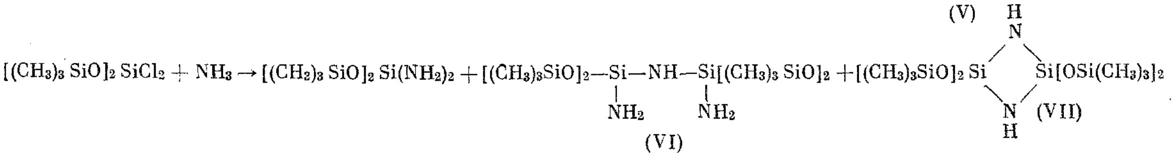


$$[(C_2H_5)_3SiO]_2SiCl_2 + NH_3 \rightarrow \underset{(II)}{[(C_2H_5)_3SiO]_2Si(NH_2)_2} + [(C_2H_5)_3SiO]_2\underset{NH_2}{Si} - NH - \underset{NH_2}{Si}[OSi(C_2H_5)_3]_2 \quad (III)$$

Apparently, the presence of a branched triethylsilyl grouping on the silicon atom blocks the condensation reaction and the yield of bis(triethylsiloxy)diaminosilane is considerably higher than that of bis(trimethylsiloxy)diaminosilane (53%) [1]. The ammonolysis of (I) at 75° for 18 h gives, together with (II) and (III), also 1,3-bis(triethylsiloxy)cyclodisilazane (IV) in 26% yield. In order to prove the structure of (IV) we ran the counter synthesis, where (II) was heated at 280-340° for 32 h



On the basis of the physicochemical analysis data, the cyclodisilazane (IV) obtained in this manner was identical with the compound obtained by the ammonolysis of (I). The ammonolysis of bis(trimethylsiloxy)dichlorosilane at 55° for 2 h gives a number of products. Here



the yields of bis(trimethylsiloxy)diaminosilane (V), 1,3-bis(trimethylsiloxy)-1,3-aminodisilazane (VI) and 1,3-bis(trimethylsiloxy)cyclodisilazane (VII) were respectively 7.8, 22.4 and 42.3%. An increase in the reaction time up to 4 h reduced the yield of (V) and (VI), and increased the yield of (VII) (50%). Compound (VII) proved to be identical with the compound obtained by us previously [1] by the high-temperature condensation of bis(trimethylsiloxy)diaminosilane.

The performed studies disclosed that an increase in the temperature and time of ammonolysis of the bis(trialkylsiloxy)dichlorosilanes both favor the formation of cyclic products.

The following absorption bands (ν, cm^{-1}) were observed in the IR spectra of the obtained cyclodisilazanes (IV) and (VII): 750, 840-860, 1240-1260 (Si–Alk), 1060-1080 (SiOSi), 1200 (γ_{H-N}), 3400 (NH), 2970 (C–H), and an absorption band at 970. We assign this band to the ($\nu_{Si-N-Si}$) vibrations in four-membered cyclosilazanes containing trialkylsiloxy groups on the silicon atoms.

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In the aminolysis of the bis(trialkylsiloxy)dichlorosilanes with aniline we observed that the bis(trimethylsiloxy)dichlorosilane reacts at 60° to give bis(trimethylsiloxy)diphenylaminosilane (VIII). A temperature of 75-80° is necessary in order to obtain bis(triethylsiloxy)diphenylaminosilane (IX).

The reaction proceeds according to the scheme:

$$(R_3SiO)_2SiCl_2 + 4C_6H_5NH_2 \rightarrow (R_3SiO)_2Si(NHC_6H_5)_2 + 2C_6H_5NH_2HCl$$
$$R = CH_3,\ C_2H_5$$

The hydrolysis of the bis(trialkylsiloxy)dichlorosilanes at –10° proceeds with the formation of the corresponding diols in high yields (73-82%) according to the scheme:

$$(R_3SiO)_2SiCl_2 + H_2O + 2KOH \rightarrow (R_3SiO)_2Si(OH)_2 + 2KCl$$
$$R = CH_3,\ C_2H_5$$

The high yield of the bis(trialkylsiloxy)dihydroxysilanes testifies to the fact that intermolecular condensation is practically absent under the given reaction conditions. Bis(trimethylsiloxy)dihydroxysilane, previously obtained by one of us [2], is a crystalline product, while bis(triethylsiloxy)dihydroxysilane (X) is a mobile liquid.

EXPERIMENTAL METHOD

Bis(triethylsiloxy)dichlorosilane (I). A mixture of 246 g of hexaethyldisiloxane, 77 g of $SiCl_4$ and 1 g of bromine was heated in an autoclave at 260° for 3 h. From the reaction products were isolated: 126.7 g (84.1%) of triethylchlorosilane, bp 46–148°; n_D^{20} 1.4319 and 103.0 g (57.2%) of bis(triethylsiloxy)dichlorosilane, bp 91-92° (2 mm); n_D^{20} 1.4372, d_4^{20} 0.9995. Found: C 40.36; H 8.45; Si 23.22; Cl 19.21%; MR 94.65. $C_{12}H_{30}Si_3O_2Cl_2$. Calculated: C 39.88; H 8.31; Si 23.40; Cl 19.66%; MR 94.59.

Bis(triethylsiloxy)diaminosilane (II) and 1,3-Bis(triethylsiloxy)-1,3-aminodisilazane (III). To 200 ml of absolute benzene at 45°, in an ammonia stream, with constant stirring, was added 22 g of (I) in 30 ml of absolute benzene. A white precipitate of NH_4Cl was obtained. Ammonia was passed through for another 1.5 h. The NH_4Cl precipitate was filtered, the benzene was distilled off, and two products were isolated from the residue by fractional distillation in vacuo: 1) 14.2 g (72.3%) of (II), bp 116-117° (2 mm); n_D^{20} 1.4412; d_4^{20} 0.9257. Found: C 45.22; H 10.17; Si 25.42; N 7.83%; mol. wt. 320; MR 92.04. $C_{12}H_{34}Si_3O_2N_2$. Calculated: C 44.66; H 10.62; Si 26.11; N 8.68%; mol. wt. 322.8; MR 91.91; 2) 2.1 g (11.0%) of (III), bp 165-166° (1 mm); n_D^{20} 1.4477; d_4^{20} 0.9452; MR found 117.84, Calculated 117.39. Found: C 59.48; H 8.73; Si 17.93; N 5.46%. $C_{24}H_{65}Si_6N_3O_4$. Calculated: C 60.69; H 8.91; Si 17.74; N 5.89%.

1,3-Bis(triethylsiloxy)cyclodisilazane (IV). Compound (II) (6.6 g) was heated at 280-340° for 32 h. Here a deposit of 1.2 g (11.1%) of transparent crystals with mp 186° was obtained. Found: C 47.24; H 9.93; Si 27.74; N 4.59%; mol. wt. 598.6. $C_{24}H_{62}O_4N_2Si_6$. Calculated: C 47.19; H 10.23; Si 27.50; N 4.58%; mol. wt. 610.75.

1,3-Bis(trimethylsiloxy)cyclodisilazane (VII). To 260 ml of benzene in a constant stream of ammonia, at 35°, was added 40 g of bis(trimethylsiloxy)dichlorosilane in drops. The mixture was heated at 55° for 2 h. From the reaction mixture was isolated by distillation 13.5 g (43.3%) of (VII) with bp 148-149° (2 mm), and mp 99-100°. Found: C 32.77; H 8.05; Si 37.25; N 6.31%; mol. wt. 438.51. $C_{12}H_{38}O_4Si_6N_2$. Calculated: C 32.61; H 8.58; Si 38.01; N 6.33%; mol. wt. 442.

Bis(trimethylsiloxy)diphenylaminosilane (VIII). For this reaction we took 10 g of bis(trimethylsiloxy)dichlorosilane and 13.4 g of aniline in 100 ml of absolute benzene. After heating at 60-65° for 9 h, followed by removal of the aniline hydrochloride precipitate, the benzene was distilled from the reaction mass. The residue in the flask crystallized to give 6.2 g (44% yield) of (VIII) with mp 60°. Found: C 53.20; H 7.81; Si 21.95; N 6.95%; mol. wt. 387. $C_{18}Si_3O_2N_2H_{30}$. Calculated: C 55.38; H 7.69; Si 21.53; N 7.17%; mol. wt. 390.

Bis(triethylsiloxy)diphenylaminosilane (IX). To a mixture of 45.4 g of aniline in 400 ml of absolute benzene at 75° was added 32.8 g of (I). We obtained 35.1 g (81.3%) of (IX) with bp 173-174° (1 mm); n_D^{20} 1.5094; d_4^{20} 1.0028. Found: C 59.48; H 8.73; Si 17.93; N 5.46%; mol. wt. 483.1; MR 140.51. $C_{24}Si_3O_2N_2H_{42}$. Calculated: C 60.69; H 8.91; Si 17.74; N 5.89%, mol. wt. 474.8; MR 140.89.

Bis(triethylsiloxy)dihydroxysilane (X). To a solution of 8 g of NaOH in 80 ml of water at −10° was added 25 g of (I). From the ether layer after removal of the solvent we isolated 14.5 g (82.8%) of (X) with bp 113° (1 mm). Found: C 44.70; H 9.83; Si 26.08; OH 9.81%. $C_{12}H_{32}Si_3O_4$. Calculated: C 44.44; H 9.87; Si 25.92; OH 10.49%.

CONCLUSIONS

The ammonolysis of bis(trialkylsiloxy)dichlorosilanes in benzene proceeds with the formation of 1,3-bis(trialkylsiloxy)cyclodisilazanes.

LITERATURE CITED

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2. K. A. Andrianov and V. V. Severnyi, Zh. Obshch. Khim., 32, 1633 (1962).