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THE PRODUCTION OF TETRAMER FLUORINE-CONTAINING BORAZINE

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Cyclic dimer [1], trimer [2], and tetramer [3] polyborazines with the general formula $(RNBX)_X$ are known. Borazines with B-F bonds are known only in the form of trimers (borazoles) [4]. Earlier we suggested a convenient method for the production of fluorine-containing borazoles by the elimination of hydrogen fluoride from N-alkylsubstituted fluoroborates or borazanes (adducts of boron trifluoride with primary amines) [5]

$$BF_4NH_3R + AI \rightarrow \frac{1}{3} (RNBF)_3 + AIF_3 + \frac{3}{2}H_2$$
(1)

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$$BF_3NH_2R + \frac{2}{3}AI \rightarrow \frac{1}{3} (RNBF)_3 + \frac{2}{3} AIF_3 + H_2$$
 (2)

Reactions proceeding at 270-300° in the presence of Al dust permit the production of borazoles with $R = CH_3$, C_2H_5 , $n-C_3H_7$, $n-C_4H_9$, etc. When $R = CH_3$, together with crystalline B-trifluoro-N-trimethyl-borazole [(CH_3NBF)_3] with mp 90.5°, a previously uninvestigated liquid product with mp 20-24°, with composition (CH_3NBF)_x distills off from the reaction mixture.

It is known that in the decomposition of bis(dimethylamino)fluoroborane $[(CH_3)_2N]_2BF$, a polymer with composition $(CH_3NBF)_X$ is also formed; it was not a trimer [6], which was established according to the lower melting point than in the product of Wieberg and Horeld, and its lower volatility. The decomposition of methylsilylaminoborane difluoride evidently gives E-fluoroborazole [7], although the physical constants are not similar to the constants indicated in [8]. Thus, it can be assumed that there is one or several oligomer forms of E-fluoroborazine, differing from the cyclic trimer.

We have found that in the case of profound chemical dehydrofluorination of methylammonium fluoroborate or the corresponding borazane according to reactions (1) and (2), a borazine is formed, the molecular weight of which corresponds to a tetramer according to the cryoscopic data. An intermediate unstable compound is evidently the monomer borazine, which then polymerizes:

$$BF_4NH_3CH_3 \xrightarrow{-HF} BF_3NH_2CH_3 \xrightarrow{-2HF} [CH_3NBF] \rightarrow (CH_3NBF)_4$$
(3)

The tetramer borazine, in contrast to the trimer, is readily soluble in most organic solvents, and is readily hydrolyzed (the reaction with water and lower alcohols proceeds almost with explosion). When it is heated to 140°, a mixture of the trimer and polymer is formed, the ratio between which depends on the rate and the conditions of heating.

In the case of heating in an atmosphere of argon or under vacuum at a rate of 10 deg/min, the degree of tetramer--trimer conversion is 83-90%; trimer borazine sublimes in the form of colorless crystals with mp 90-91°. If the rate of heating is less than 10 deg/min, the yield of the subliming borazole is significantly reduced. Heating the tetramer borazine in a sealed tube to 280° leads to the formation of a yellowish polymer mass, insoluble in benzene, CCl_4 , and cyclohexane. In the case of treatment with hot water, there is a slow hydrolysis of the surface layers.

On a thermogram of the investigated substance, obtained at a rate of 20 deg/min, there is an exothermic effect at 163°, evidently corresponding to the tetramer-trimer transition.

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EXPERIMENTAL METHOD

The thermogram was taken on a pyrometer of the NTR-64 type. The cryoscopic measurements were performed in an instrument with a glass vibratory mill in an atmosphere of dry argon. The solvents were thoroughly rendered absolute. The IR absorption spectra were taken on a UR-10 spectrometer.

<u>Methods of Analysis</u>. In all the compounds with the exception of $(CH_3NBF)_4$, the boron content was determined by titration with alkali in the presence of mannitol after decomposition of a weighed sample by boiling with a solution of $CaCl_2[9]$. Fluorine was determined by the zirconium-alizarin method [10], nitrogen according to Kjeldahl [11]. The analysis of tetramer B-fluoro-N-methylborazine presented substantial difficulties on account of the extreme hydrolyzability and oxidizability of the product. All the operations were performed in an atmosphere of dry argon in the apparatus described in [12]. Carbon and hydrogen were determined by pyrolytic combustion at 900° in quartz apparatus in a layer of conditioned magnesium oxide [13], nitrogen according to the Dumas method [14]. The weighed samples for microdetermination of C, H, and N were collected in quartz capillaries with a diameter of the outlet opening 0.2-0.3 mm [15]. Boron was determined spectrophotometrically in the form of a complex with azomethine-H, after decomposition of the sample by fusion with KOH at 850° in a nickel microbomb [16]. To determine fluorine by the zirconium-alizarin method [10], a weighed sample of the substance was preliminarily cautiously hydrolyzed with a 0.1 N solution of alkali.

Methylammonium Fluoroborate. To 87.2 g of a 40% aqueous solution of HF in a polyethylene flask, 67 g boric acid was added in small portions while cooling with ice. After 2 h, the tetrafluoroboric acid obtained was neutralized according to methyl orange with a 33% aqueous solution of methylamine, also with cooling, and the water was distilled off under vacuum. After two recrystallizations from ethanol, a product with mp 198° was obtained: Found: B 9.02; N 11.6; F 63.1%. CH₆NBF₄. Calculated: B 9.09; N 11.76; F 63.87%.

<u>Adduct of Boron Trifluoride with Methylamine</u>. A 31 g portion of methylamine was passed with cooling for 6 h into a mixture containing 40 ml boron trifluoride etherate and 300 ml of ether. We obtained 24.4 g (83%) of a product with mp 65°. After redistillation at 160° (1 mm), mp 69°. According to the data of [17], mp 70-71°. Found: E 11.0; N 14.0; F 56.9%. CH_5NBF_3 . Calculated: B 10.45; N 14.17; F 57.68%.

Interaction of Methylammonium Fluoroborate with Aluminum Dust. A mixture of 9.2 g BF₄NH₃CH₃ and 2.7 g Al dust, washed with ether and dried, was placed in a flask and heated in an atmosphere of dry argon on a bath with Wood's metal (5 deg/min). Vigorous evolution of hydrogen began at a bath temperature of 280-290°; it was removed through a special outlet and collected under water. A colorless liquid, fuming in air, was accumulated in the receiver; needle-like crystals were collected on the packing. The liquid distillate was filtered off, yield 1.4 g (31.1%), mp 20-24° (not sharp). Further purification of the product was impossible, since the sample changes when it is heated. The substance could not be recrystallized as a result of its extremely high solubility in organic solvents; evaporation of the solution in benzene and CH₂Cl₂ leads to condensation of the substance. The reproducibility of the data of elementary analysis and IR spectroscopy permits us to consider the purity of this substance as satisfactory. Found: C 20.22; H 5.05; N 23.44; B 18.28; F 31.01%; mol. wt. 230 (cryoscopically in benzene) and 222 (in cyclohexane). (CH₃NBF)₄. Calculated: C 20.40; H 5.10; N 23.80; B 18.39; F 32.30%. Calculated mol. wt. 235.3. IR spectrum in a cuvette with layer thickness 0.04 mm (ν , cm⁻¹): 550, 650, 700-740, 875, 900, 920, 1040, 1110-1200, 1280, 1350-1575.

Sublimation of the crystalline product yielded 0.8 g (17.7%) B-trifluoro-N-trimethylborazole with mp 90°. According to the data of [8]: mp 85°; [4]: 90.5°. Found: N 23.8; B 18.5; F 31.8%. Calculated: N 23.80; B 18.39; F 32.30%.

IR spectrum of $(CH_3NBF)_3$ in liquid petrolatum (interval 1300-1500 cm⁻¹) in hexachlorobutadiene (ν , cm⁻¹): 725, 738, 875, 940, 1055, 1165, 1385, 1420, 1435, 1485-1495.

Interaction of Methylaminotrifluoroborane with Aluminum Dust. Analogously from 7.1 g $BF_3NH_2CH_3$ and 2.2 g Al dust we obtained 1.5 g (35.5%) tetramer B-fluoro-N-methylborazine and 0.7 g (16.5%) B-tri-fluoro-N-trimethylborazole.

Conversion of Tetramer B-Fluoro-N-methylborazine to B-Trifluoro-N-trimethylborazole. A 3.6 g portion of $(CH_3NBF)_4$ was heated (15 deg/min) in the instrument for sublimation. Colorless needle-like crystals (3.2 g; 88.8%) sublimed at the temperature 140°; mp 91°. According to the data of [4]: mp 90.5°.

The IR spectrum was similar to the spectrum of a sample of $(CH_3NBF)_3$ obtained by fluorination of B-trichloro-N-trimethylborazole [18]. The residue contained a polymer, which was not investigated (0.3 g; 8.3%).

CONCLUSIONS

1. As a result of the reaction of methylammonium fluoroborate with aluminum dust at 270°, B-fluoro-N-methylborazine was obtained in the form of a tetramer. The same product is obtained from a complex of BF_3 with methylamine.

2. The conditions of conversion of the tetramer borazine to B-trifluoro-N-trimethylborazole were studied.

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