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Abstract

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SYNTHESIS AND STUDY OF DISPROPORTIONATION REACTIONS OF CERTAIN TRIFLUOROBORAZANE DERIVATIVES

Compounds containing the B—N bond are promising for obtaining heat-resistant inorganic materials. Organic derivatives of trifluoroborazane are of particular interest. However, the methods described in the literature for their synthesis are very complicated ($^{1-10}$), and in a number of cases do not provide good reproducibility (^{4}).

Having studied the thermal stability of methyl and ethyl derivatives of trifluoroborazane BF_3NH_3, we developed a simpler and more convenient method for obtaining and purifying the indicated compounds. It turned out that the use of low temperatures (down to −35°), as had been recommended (^{3,4}), is not necessary.

As an example, below is a description of the synthesis of N-diethyl-B-trifluoroborazane $BF_3NH(C_2H_5)_2$ from boron trifluoride etherate and diethylamine. Into a three-necked flask equipped with a stirrer, reflux condenser, dropping funnel, or a tube for introducing gaseous amines, 350 ml of absolute ether and 42.8 g of boron fluoride etherate are placed. With cooling in an ice bath and stirring, 31.0 g of diethylamine is added from the dropping funnel over 40 min. The temperature of the reaction mixture is maintained within 5-10°. After the reaction is complete, the ether is distilled off, and the residue is fractionated in vacuo. In this way a product with a boiling point of 98-99° (1 mm) is obtained. Its yield is 38.1 g, 90% of that required by the equation

$$BF_3O(C_2H_5)_2 + NH(C_2H_5)_2 = BF_3NH(C_2H_5)_2 + O(C_2H_5)_2.$$

The conditions for the synthesis of other compounds, as well as the results of analyses of the products obtained, are given in Tables 1 and 2.

From the data of Table 1 it is seen that the yields of borazanes in all cases are high, of the order of 82-97%. It turned out that the compounds obtained are readily distilled in vacuo without noticeable decomposition, and some even at atmospheric pressure. For example, *N*-triethyl-*B*-trifluoroborazane boils at 237-238° (760 mm). Such resistance to heating provides a convenient method for purifying trifluoroborazane derivatives from impurities. Most of the boiling points given in Table 1 were determined for the first time.

Certain difficulties were encountered in determining the melting point of trifluoroborazane itself, since the substance readily decomposes. The literature (1,3) gives values of 180 and 163°. The first figure was obtained by the usual method with rapid heating of a sealed capillary containing the substance; the second, with the aid of a special apparatus in which melting occurred in air. Neither method could exclude decomposition of the sample upon melting. Our determinations, carried out in a thermostated bath with Wood' s alloy, gave a value of 152-153°. A series of capillaries filled with BF_3NH_3 and sealed at both ends were immersed in the bath for 30-40 sec at various temperatures, approaching the melting point—

···as from the side of higher, and from the side of lower temperatures. Comparing the entire series of capillaries, the true melting point was determined.

One of the interesting properties of trifluoroborazane and its derivatives is the ability to disproportionate upon heating. For example—

Table 1

Synthesis of trifluoroborazane and its derivatives

Nos.	Amine	Ratio amine : BF_3 etherate, mol	Composition of the compounds obtained	Yield, %	M.p., °C	B.p., °C/mm
1	NH_3	3 : 1	BF_3NH_3	97	152—153	sublim. 180/1
2	$NH_2(CH_3)$	3 : 1	$BF_3NH_2(CH_3)$	83	61—61.5	158—160/1
3	$NH(CH_3)_2$	2.5 : 1	$BF_3NH(CH_3)_2$	86	50—50.5	102—103/1.5
4	$N(CH_3)_3$	2 : 1	$BF_3N(CH_3)_3$	94	142—143	82—83/3
5	$NH_2(C_2H_5)$	2 : 1	$BF_3NH_2(C_2H_5)$	86	75—76	147—148/1
6	$NH(C_2H_5)_2$	1.5 : 1	$BF_3NH(C_2H_5)_2$	90	−25, −26	98—99/1

Nos.	Amine	Ratio amine : BF_3 etherate, mol	Composition of the compounds obtained	Yield, %	M.p., °C	B.p., °C/mm
7	$N(C_2H_5)_3$	1.5 : 1	$BF_3N(C_2H_5)_3$	82	28—29	79—80/2.5; 237—238/760

Note. In all experiments the same amount of boron trifluoride etherate was used (42.8 g, or 0.28 g-mol).

Table 2

Analysis of borazanes (in percent)

Nos.	Formula	Found F	Found B	Found N	Calculated F	Calculated B	Calculated N
1	BF_3NH_3	66.4	12.4	15.7	67.20	12.76	16.50
2	$BF_3NH_2(CH_3)$	56.9	11.0	14.0	57.68	10.95	14.17
3	$BF_3NH(CH_3)_2$	49.7	9.5	12.3	50.52	9.59	12.41
4	$BF_3N(CH_3)_3$	44.1	8.4	11.0	44.94	8.53	11.04
5	$BF_3NH_2(C_2H_5)$	49.3	9.4	12.5	50.52	9.59	12.41
6	$BF_3NH(C_2H_5)_2$	40.3	7.8	9.7	40.48	7.68	9.94
7	$BF_3N(C_2H_5)_3$	33.5	6.4	8.3	33.76	6.41	8.29

for example, BF_3NH_3 decomposes into ammonium fluoroborate and boron nitride (^{1}), according to the equation $4BF_3NH_3 = 3BF_4NH_4 + BN$. It may be assumed that this reaction proceeds in several stages:

$$
\begin{aligned}
&1)\quad 6n\,BF_3NH_3 = 3n\,BF_4NH_4 + 3n\,BF_2NH_2;\\
&2)\quad 4n\,BF_2NH_2 = 2n\,BF_3NH_3 + 2(BFNH)_n;\\
&3)\quad 2(BFNH)_n = n\,BF_2NH_2 + n\,BN.
\end{aligned}
$$

To date, the intermediate products BF_2NH_2 and $(BFNH)_n$ have not been isolated, while the borazane BF_2NH_2 was obtained from dimethylborazane $(CH_3)_2BNH_2$ and boron trifluoride BF_3 (^{10}). It is described as a polymeric product soluble in water. Our experiments did not lead to the production of these compounds as intermediate products of the disproportionation reaction of trifluoroborazane. However, indirect confirmation of such a mechanism is provided by the behavior upon heating of trifluoroborazane derivatives containing ethyl radicals at the nitrogen atom. In this case disproportionation proceeds more smoothly and can be easily stopped at the stage of borazene formation. For example, the disproportionation reaction of N-diethyl-B-trifluoroborazane $BF_3NH(C_2H_5)_2$ to N-diethylammonium fluoroborate $BF_4NH_2(C_2H_5)_2$ and N-diethyl-B-difluoroborazene $BF_2N(C_2H_5)_2$ proceeds rather readily at 250–300°.

$$2BF_3NH(C_2H_5)_2 = BF_4NH_2(C_2H_5)_2 + BF_2N(C_2H_5)_2.$$

The shift of the equilibrium toward borazene formation occurs owing to the volatility of $BF_2N(C_2H_5)_2$, which has b.p. 92–92.5°.

We have carried out a more detailed study of the disproportionation reaction of $BF_3NH(C_2H_5)_2$ and of the conditions for its conversion into borazene in the presence of various metals (Table 3). A description of one of the typical experiments is given below.

Table 3

Conversion of N-diethyl-B-trifluoroborazane into N-diethyl-B-difluoroborazene

No. of experiment	Added metal	Ratio $BF_3NH(C_2H_5)_2$: metal, mol	Yield of reaction products, % $BF_2N(C_2H_5)_2$	Yield of reaction products, % H_2	Yield of reaction products, % $BF_4NH_2(C_2H_5)_2$	Degree of conversion of $BF_3NH(C_2H_5)_2$ to $BF_2N(C_2H_5)_2$, %
1	–	1 : 0	51	–	35	25,5
2	–	1 : 0	54	–	34	27
3	Al powder	1 : 2	52	–	29	26
4	Al powder	1 : 2	35	37	–	35
5	Mg powder	1 : 1	31	10	30	31
6	Zn dust	1 : 2	29	12	41	29
7	Al dust	1 : 1,5	86	97	–	86
8	Na metal	1 : 1,5	–	–	Reduction occurs	Reduction occurs

Note. All experiments, except Nos. 1 and 3, were carried out in a medium of dry vaseline oil.

Into a flask equipped with a stirrer are placed 11.4 g (0.08 g-mol) of $BF_3NH(C_2H_5)_2$. Heating is carried out in a bath with Wood' s alloy. At about 240—250° an energetic reaction begins, accompanied by distillation of borazene $BF_2N(C_2H_5)_2$, b.p. 91—93°, which is collected in a receiver. The reaction is completed within 20–30 min. The limiting heating temperature is 320°. Yield of $BF_2N(C_2H_5)_2$: 2.5 g, 51%; $BF_4NH_2(C_2H_5)_2$: 3.9 g, 60%.

Found, %: B 8,85; N 11,35; F 31,30
$BF_2N(C_2H_5)_2$. Calculated, %: B 8,96; N 11,59; F 31,45

Found, %: B 6,60; N 8,75; F 36,15
$BF_4NH_2(C_2H_5)_2$. Calculated, %: B 6,73; N 8,70; F 35,44

From the data of Table 3 it is evident that the process of borazene formation also occurs in the absence of metals. In experiments 1 and 2 the disproportionation reaction appears in pure form. Vaseline oil does not substantially change the course of the reaction; the yield of borazene increases only insignificantly. In the presence of aluminum, another process is superimposed on the disproportionation reaction (experiment 3), with formation of aluminum fluoride and liberation of hydrogen:
$6BF_3NH(C_2H_5)_2 + 2Al = 2AlF_3 + 6BF_2N(C_2H_5)_2 + 3H_2$.

In a medium of vaseline oil this process becomes predominant (experiments 4 and 7). Zn dust and Mg powder are less active under these conditions; both reactions–disproportionation and formation of AlF_3 and hydrogen–proceed simultaneously. The yield of hydrogen in this case is 10–12% (experiments 5 and 6). With metallic sodium (experiment 8), a process of deeper reduction takes place, accompanied by rupture of the B–N bond, since evolution of diborane is observed, as a result of which, in individual cases, spontaneous ignition of the reaction mixture in air occurred.

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