NEW DERIVATIVES OF CYCLOTRIBORAZANE—TRIMERIC B-ALKOXY-B-FLUORO-N-(β-FLUOROETHYL)BORAZENES

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The reaction of B-difluoro-N-(β-fluoroethyl)borazene with aliphatic alcohols leads to the formation of the previously unknown trimeric B-alkoxy-B-fluoro-N-(β-fluoroethyl)borazenes, the corresponding trialkyl borates, and β-fluoroethylamine tetrafluoroborate. Four compounds of this type have been synthesized and described, and their IR spectra have been studied. In the presence of anhydrous calcium chloride, the alcoholysis of B-difluoro-N-(β-fluoroethyl)borazene leads to the complete decomposition of the molecule with the quantitative formation of calcium fluoride, β-chloroethylamine hydrochloride, hydrogen chloride, and a trialkyl borate. The B-alkoxy-B-fluoro-N-(β-fluoroethyl)borazenes react with an alcoholic solution of $CaCl_2$ similarly with the quantitative formation of the corresponding trialkyl borates.

The action of alcohols on alkylboron and arylboron dihalides, preferably in the presence of hydrogen acceptors, forms the corresponding dialkoxy derivatives [1,2].

$$RBCl_2 + 2R'OH +$$
$$+ 2C_5H_5N \rightarrow RB(OR')_2 + 2C_5H_5N \cdot HCl.$$

Under certain conditions, it is also possible to obtain the monoalkoxy derivatives RB(OR')Cl [3]. It appeared to us to be of interest to use an analogous reaction for the synthesis of the previously unknown B-dialkoxy-N-(β-fluoroethyl)borazenes of the type $RNH \rightarrow B(OR')_2$, where R is FCH_2CH_2 and R' is an organic radical, all the more since the alcoholysis of B-dihaloborazenes has not previously been studied.

It was found that when B-difluoro-N-(β-fluoroethyl) borazene (I) [4] was heated with an aliphatic alcohol, only one of the fluorine atoms attached to boron was replaced by an alkoxy group, with the formation of a B-alkoxy-N-(β-fluoroethyl)borazene (II). Simultaneously, the cleavage of the B—N bond took place with the formation of the corresponding trialkyl borate and β-fluoroethylamine tetrafluoroborate (III). The reaction takes place by the general scheme:

$$\underset{\text{I}}{3FCH_2CH_2NHBF_2} + 4ROH \rightarrow \underset{\text{II}}{2FCH_2CH_2NHB(OR)F} +$$
$$+ \underset{\text{III}}{FCH_2CH_2NH_2 \cdot HBF_4} + B(OR)_3.$$

Until now, only one compound analogous to II has been known—B-n-butoxy-B-chloro-N-diethylborazene, obtained in the following way [5]:

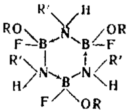
$$C_4H_9OBCl_2 + 2(C_2H_5)_2NH \rightarrow$$
$$\rightarrow (C_2H_5)_2NB(OC_4H_9)Cl + (C_2H_5)_2NH \cdot HCl$$
$$[(C_2H_5)_2N]_2BCl +$$
$$+ (C_4H_9O)_2BCl \rightarrow 2(C_2H_5)_2NB(OC_4H_9)Cl.$$

It has also been reported [6] that, on heating, B-trifluoroborazane reacts with ethanol as follows:

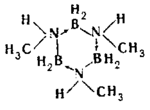
$$3NH_3BF_3 + 2C_2H_5OH \rightarrow (C_2H_5O)_2BF +$$
$$+ 2NH_4BF_4 + NH_3,$$

and under the action of ethanol the complexes of BF_3 with ethylenediamine and hexamethylenediamine form $BF_4NH_3(CH_2)_xNH_3BF_4$ and $BF_4NH_3(CH_2)_xNH_3F$, where x = 2 and 6. The reaction of $C_6H_5NH_2BF_3$ with methanol formed $C_6H_5NH_2 \cdot HBF_4$ and $B(OH)_3$ [12].

The compounds II that we have synthesized formed viscous readily-hydrolyzable liquids distilling without appreciable decomposition above 200° C in a vacuum of 3–4 mm. Such high boiling points give grounds for assuming a dimeric or trimeric structure for these compounds. A cryoscopic determination of the molecular weight of II in dioxane showed that it was trimeric. This gives grounds for ascribing to it the structure IV based on the cyclotriborazane heterocycle $(H_2NBH_2)_3$:



IV



IVa

Derivatives of cyclotriborazane of the type $(R_2NBR_2)_3$ with R = H, CH_3 (IVa) having a similar heterocyclic structure have been described previously [7].

Trimeric Alkoxy-B-fluoro-N-(β-fluoroethyl)borazenes—$[FCH_2CH_2NHBF(OR)]_3$ (IV)

Compound	R	Bp, °C (pressure, mm)	n_D^{20}	Empirical formula	Found, %			Calculated, %			Mol. wt. cryoscopically in dioxane			Yield, %
												calculated		
					B	F	N	B	F	N	found	II	IV	
V	CH_3	225 (11)	1.394	$(C_3H_8BF_2NO)_3$	8.85	31.05	9.99	8.80	30.94	11.40	359	122.8	368.4	62.0
VI	C_2H_5	218 (4)	1.389	$(C_4H_{10}BF_2NO)_3$	7.95	27.82	8.89	7.90	27.77	10.23	440	136.8	410.4	31.6
VII	n-C_3H_7	240 (14)	1.399	$(C_5H_{12}BF_2NO)_3$	7.25	25.2	9.60	7.15	25.21	9.28	505	150.8	452.4	34.0
VIII	n-C_4H_9	234 (12)	1.396	$(C_6H_{14}BF_2NO)_3$	5.56	23.0	7.90	6.55	23.06	8.49	463	164.8	494.4	27.4

The dimerization and trimerization of nitrogen compounds of boron take place through a donor-acceptor interaction between the boron and nitrogen atoms with the appearance of a negative charge on the boron atoms and a positive charge on the nitrogen atoms. From a study of the capacity for dimerization of various amino derivatives of boron, certain characteristic features were found such as that the tendency to dimerization rises in the sequence $R_2NBCl_2 <$ $< R_2NBHCl < R_2NBH_2$ [7].

All the compounds II (IV) are readily soluble in water (with a weakly acidic reaction due to hydrolysis, which is enhanced by the addition of $CaCl_2$ solution) and in ethanol and are sparingly soluble in dioxane and nitrobenzene. They are insoluble in ether, hexane, and chloroform. The physical constants, analytical data, and yields of compounds IV are given in the table.

The IR spectra of compounds IV (see figure) show the similarity of their structures. All the spectra have bands characteristic for CH_2 groups (1465, 2830, 2960 cm^{-1}), and for N—H (3270 cm^{-1}), B—O (1330 cm^{-1}), B—N (1560, 1610 cm^{-1}), and B—F bonds (460, 1400 cm^{-1}) [8].

The yields of the trialkyl borates formed together with the compounds IV amounted to 46–100% of theoretical.

Heating I with an ethanolic solution of calcium chloride led to its complete decomposition in accordance with the following equation:

$$2FCH_2CH_2NHBF_2 +$$
$$+ 3CaCl_2 + 6ROH \rightarrow 2B(OR)_3 +$$
$$+ 2ClCH_2CH_2NH_2 \cdot HCl + 3CaF_2 + 2HCl.$$

In this reaction, calcium fluoride and β-chloroethylamine hydrochloride are formed quantitatively.

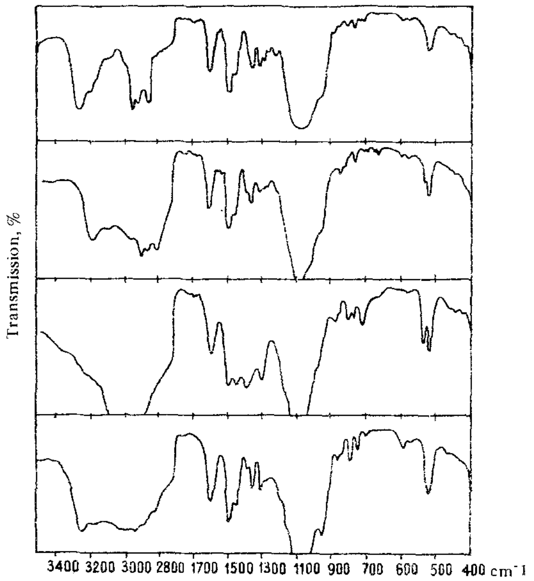
On being boiled with an ethanolic solution of $CaCl_2$, compoonds II (IV) are likewise converted quantitatively into trialkyl borates*:

$$FCH_2CH_2NHBF(OR) +$$
$$+ 2ROH + CaCl_2 \rightarrow B(OR)_3 +$$
$$+ ClCH_2CH_2NH_2 \cdot HCl + CaF_2.$$

EXPERIMENTAL

Initial compounds. B-Difluoro-N-(β-fluoroethyl)borazene, with mp 55–56° C, was obtained by the reaction of ethyleneimine with boron trifluoride etherate [4]. The initial alcohols were made absolute by boiling with metallic calcium, after which they were redistilled.

Analysis. The boron contents of the reaction products were determined by boiling weighed samples with an aqueous solution of $CaCl_2$ with subsequent titration with 0.2–0.5 N NaOH in the presence of mannitol (indicator—naphtholphthalein) [9]. The total amount of alkali consumed corresponds to three equivalents (1 mole of H_3BO_3 and 2 moles of HCl liberated). We also used a method involving the decomposition of the substances with a boiling solution of anhydrous calcium chloride in absolute methanol or ethanol, with subsequent azeotropic distillation of the trimethyl borate with the alcohol. The distillate was diluted with water and titrated to naphtholphthalein in the presence of mannitol. The second method gives more accurate results. The fluorine was determined in the form of the fluoride ion [10] and the nitrogen by the Dumas-Pregl micro method.



IR spectra of trimeric B-alkoxy-B-fluoro-N-(β-fluoroethyl)borazenes. R = 1) CH_3, 2) C_2H_5, 3) n-C_3H_7, 4) n-C_4H_9.

The molecular weights of the B-alkoxy-B-fluoro-N-(β-fluoroethyl)borazenes were determined cryoscopically in dioxane.

The IR spectra were recorded on a UR-10 double-beam spectrophotometer.

B-Methoxy-B-fluoro-N-(β-fluoroethyl)borazene (V). A solution of 5.5 g (0.05 mole) of I in 50 ml of absolute methanol was heated to the boil under reflux for 8 hr. The excess of methanol and the trimethyl borate formed were distilled off (the yield of V determined by titration was 1.7 g or 100%). The residual oily liquid was distilled in vacuum. At 200–225° C (11 mm), 2.5 g (62%) of V passed over. Colorless liquid hydrolyzing in the air. Sparingly soluble in organic solvents (apart from ethanol).

B-Ethoxy-B-fluoro-N-(β-fluoroethyl)borazene (VI). A solution of 5.5 g (0.05 mole) of I in 50 ml of absolute ethanol was heated to boiling for 8 hr. About 0.5 g of a viscous yellow substance deposited on the walls of the flask. The solution was decanted and the excess of ethanol and the triethyl borate formed were distilled off from it. The yield of the latter, determined by titration, was 1.7 g or 72%. The residue was distilled in vacuum. At 195–200° C (5 mm), 1.45 g (31.5%) of VI passed over with n_D^{20} 1.3839. After redistillation, the substance had the constants given in the table.

B-n-Propoxy-B-fluoro-N-(β-fluoroethyl)borazene (VII). This was obtained in a similar manner to VI. The excess of propanol and the tripropyl borate formed were distilled off under reduced pressure. After redistillation the yield of $(C_3H_7O)_3B$ with bp 45° C (3 mm), n_D^{20} 1.3940, was 1.3 g or 40.5% [literature data [11]: bp 177° C (760 mm), n_D^{20} 1.3945]. Further vacuum distillation gave 1.7 g (34%) of VII with bp 210° C (2–3 mm); n_D^{20} 1.3990.

B-n-Butoxy-B-fluoro-N-(β-fluoroethyl)borazene (VIII). A solution of 5.5 g (0.05 mole) of I in 50 ml of n-butanol was heated to boiling for 6 hr. On the walls of the flask 0.8 g of a viscous dark yellow substance deposited. The solution was decanted off and the excess of butanol was distilled off from it, whereupon the reaction mixture separated into two layers. The upper, colorless layer consisted mainly of tributyl borate and the lower of an oily yellow liquid—VIII. Distillation of the upper layer gave 1.8 g (46%) of tributyl borate with bp 98–100° C (10 mm); n_D^{20} 1.4082 [literature data [11]: bp 115° C (15 mm), n_D^{20} 1.4085]. Redistillation of the lower layer gave 1.5 g (27.4%) of VIII with bp 234° C (12 mm); n_D^{20} 1.3961.

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*We have successfully used the reaction of an alcoholic solution of $CaCl_2$ to determine the boron in many compounds simultaneously containing boron and fluorine.

Reaction of II with an ethanolic solution of $CaCl_2$. To a solution of 8.2 g (0.74 mole) of $CaCl_2$ in 50 ml of absolute methanol was added 4.8 g (0.043 mole) of **II**, and the mixture was heated to boiling over 30 min. The precipitate of CaF_2 (5.07 g, or 0.65 mole) was filtered off, and the solvent was distilled off from the filtrate. The contents of HCl and H_3BO_3 in the distillate, which contained HCl and triethyl borate were determined alkalimetrically. From the 6.15 g of undistillable residue was isolated β-chloroethylamine hydrochloride with mp 140° C and this was converted into the benzoyl derivative with mp 103° C. A mixture with β-chloroethylamine hydrochloride obtained by independent synthesis melted without depression of melting point. The balance of the hydrolysis products was as follows. Found, %: CaF_2 5.07; $(C_2H_5O)_3B$ 6.43; $ClCH_2CH_2NH_2 \cdot HCl$ 5.05; HCl 1.58 g. Calculated: CaF_2 5.07; $(C_2H_5O)_3B$ 6.31; $ClCH_2CH_2NH_2 \cdot HCl$ 5.05; HCl 097 g.

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