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HETEROATOM DERIVATIVES OF AZIRIDINE

IV. Reaction of Ethylenimine with Boron Trifluoride*

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Reaction of ethylenimine with boron trifluoride at – 78° C gives N-β-fluoroethyl-B-difluoroborazene $FCH_2CH_2NHBF_2$. Acetylation of the latter with acetic anhydride gives N-acetyl-N-β-fluoroethyl-B-difluoroborazene $FCH_2CH_2N(COMe)BF_2$. The IR spectra of these two compounds are investigated. N-β-fluoroethyl-B-difluoroborazene can react further with ethylenimine to give ultimately a polymeric product with the composition $[(FCH_2CH_2NH)_2BF]_n$ which is also obtained by reacting BF_3 with excess ethylenimine. Reaction of N-B-fluoroethyl-B-trifluoroborane with triethylamine gives N-triethyl-B-trifluoroborane Et_3NBF_3.

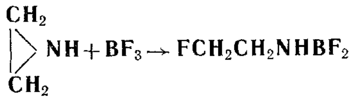
Research on coordination compounds of boron trimethyl with heterocyclic amines showed that ethylenimine (I) forms the complex $(CH_2)_2NH \cdot BMe_3$ with it. This complex is less stable than the corresponding adducts of BMe_3 with azetidine, pyrrolidine, and piperidine [2]. Subsequently a relatively stable complex of I with borane, $(CH_2)_2NH \cdot BH_3$, was obtained.

However, it did not prove possible to obtain the dimer $(C_2H_4NBH_2)_2$ or ethyleniminodiborane $C_2H_4NB_2H_5$ where the ethylenimine ring is even more strained. Depending on the conditions, reaction gave either polymeric products with an opened ring, or ethylaminodiborane $EtNHB_2H_5$ [3].

In a previous paper [1] we described complexes of I with trimethyl- and triphenylborate having a 1:1 composition.

Hitherto the reaction of I with such a powerful complexing agent as boron trifluoride has not been investigated. There exist only statements that BF_3 and its etherate cause polymerization of ethylenimine [4, 5], and that, in acetic acid, polymerization is explosive [6].

We find [7] that I reacts with boron trifluoride etherate at –78° C in an inert solvent with opening of the aziridine ring to give an over 70% yield of the hitherto unknown N-β-fluoroethyl-B-difluoroborazene (II).



I II

Compound II is accompanied by some liquid polymer (octamer) III of the same elementary composition. When a mixture of II and III in ether is kept at 0° for 24 hr, a solid material IV is formed, with the same elementary composition as II, and with a melting point close to its melting point, but which is insoluble in dioxane, so that it can readily be separated from II.

Hitherto, compounds with the general formula $RNHBX_2$ with X = F have not been known, although borazenes where X = Cl, Br could be prepared by reacting primary amines with BCl_3 or BBr_3, followed by splitting off of, respectively HCl or HBr ($t\text{-}C_4H_9NHBCl_2$, $C_6H_{11}NHBCl_2$, $C_6H_5NHBCl_2$, $EtNHBBr_2$) [8–11]. Complexes of secondary amines with boron halides readily lose a molecule of hydrogen halide with conversion to compounds of the type R_2NBX_2 [11, 12]. Dimethyldifluoroborazene Me_2NBF_2 is briefly described in the literature [13–16].

So II is the first example of N-mono-substituted B-difluoroborazenes of the type $RNHBF_2$.

Heating II above its melting point converts it into a polymer of composition corresponding to $[EtBF_3N]_n$. Even after prolonged boiling an aqueous solution of II is still neutral. It is not possible to recover II after evaporating an aqueous solution of it under reduced pressure (a transparent solid with the same elementary composition and melting point about 93° C is formed). II is hydrolyzed by aqueous solutions of NaOH, Na_2CO_3, and $Ca(OH)_2$. However, it was not possible to isolate β-fluoroethylamine (IV) from the hydrolysis products by steam distillation, since, under the conditions of hydrolysis, it is cyclized to ethylenimine. Action of a saturated sodium hydroxide solution on II leads to

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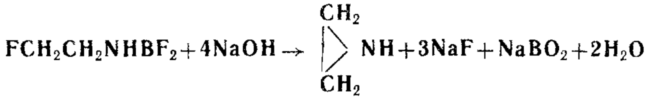
[*] For Part III see [1].

quantitative isolation of sodium fluoride and ethylenimine.



$$\mathrm{FCH_2CH_2NHBF_2+4NaOH \rightarrow \begin{array}{l}CH_2\\ |\!\!> NH+3NaF+NaBO_2+2H_2O\\ CH_2\end{array}}$$

Compound II reacts with solid alkali with great evolution of heat, and sometimes explosively, forming ethylenimine, a small quantity of piperazine, and a substance of composition $C_4H_{10}B_2N_2O_3$ (V).

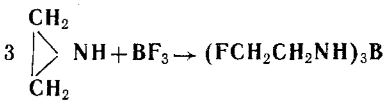
When a solution of calcium chloride is added to an aqueous solution of II (neutral to methyl orange), it becomes acid, and more so on heating, and this is due to formation of free HCl. Further heating of the solution leads to formation of a precipitate of CaF_2.

Compound II forms an addition product with triethylamine (1:1), and heating of this gives N-triethyl-B-trifluoroborazane (VI) and triethylamine, the equation evidently being [17]

$$\mathrm{3FCH_2CH_2NHBF_2 \cdot N(C_2H_5)_3 \xrightarrow{t^\circ} (C_2H_5)_3N+2\underset{VI}{(C_2H_5)_3N \cdot BF_3}+(FCH_2CH_2NH)_3B}$$

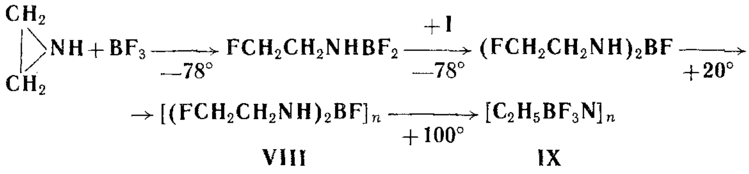
However, it was not possible to isolate the second reaction product $(FCH_2CH_2NH)_3B$.

An attempt to synthesize tris (β-fluoroethylamino) boron by the following reaction



$$\mathrm{3\begin{array}{l}CH_2\\ |\!\!> NH+BF_3 \rightarrow (FCH_2CH_2NH)_3B\\ CH_2\end{array}}$$

was unsuccessful. Reaction of boron trifluoride etherate with a two or three fold excess of I gives one and the same compound VII, liquid at −70° C, and insoluble in ether. When rapidly heated to room temperature it decomposes with a large evolution of heat, separation of volatile basic products, and formation of a solid of composition corresponding to $(EtBF_3N)n$. When, however, the reaction products are slowly brought to room temperature, (in 48 hr), there is gradually formed a solid which is insoluble in organic solvents, and which readily hydrolyzes (VIII). It decomposes with gas evolution at 90° C, and on further heating forms compound IX. The equations for these reactions are



$$\mathrm{\begin{array}{l}CH_2\\ |\!\!> NH+BF_3\\ CH_2\end{array} \xrightarrow[-78^\circ]{} FCH_2CH_2NHBF_2 \xrightarrow[-78^\circ]{+I} (FCH_2CH_2NH)_2BF \xrightarrow[+20^\circ]{}}$$
$$\mathrm{\rightarrow \underset{VIII}{[(FCH_2CH_2NH)_2BF]_n} \xrightarrow[+100^\circ]{} \underset{IX}{[C_2H_5BF_3N]_n}}$$

The same product VIII is formed when II reacts with ethylenimine in ether at 0° and the temperature is slowly raised to room temperature.

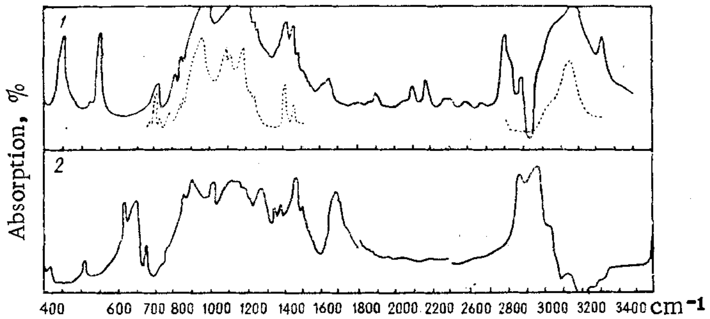
With a I : BF_3 ratio of 3:1, in accordance with the above equation, still only two molecules of I undergo reaction.

The product obtained by acetylating II with acetic anhydride in benzene is crystalline N-acetyl-N-(β-fluoroethyl)-B-difluoroborazene (X):

$$\mathrm{FCH_2CH_2NHBF_2+(CH_3CO)_2O \rightarrow \underset{X}{FCH_2CH_2N(COCH_3)BF_2}+CH_3COOH}$$

Acetylation of II without a solvent cuts the yield of X from 71% to 60%. Acetylation of II with a mixture of acetic anhydride and pyridine gives the tetrafluoroboropyridinium salt $C_5H_5N \cdot HBF_4$ (XI), whose structure is confirmed by retrosynthesis [18]. Acetic anhydride acetylation (no solvent) of the second product of reaction of ethylenimine with boron trifluoride (III) gives a small amount of X, which serves to confirm the similarity between II and III.

The figure shows the IR spectrum of II and of its acetyl derivative X. The spectrum of II has very strong absorption bands at 1085 cm^{-1}, due to C–F bond valence vibrations, and also at 709 cm^{-1}, the latter corresponding to vibrations of the BF_2 group [19]. Vibrations of N–H, C–N, C–H bonds and of the CH_2 group, are respectively characterized by frequencies 3328, 1251, 1465 and 2800–3000 cm^{-1} [22]. The IR spectrum of X lacks the N–H bond frequency at 3328 cm^{-1}, indicating replacement of the hydrogen atom of the amino group by acetyl. At the same time, the spectrum exhibits a new intense band at 1680 cm^{-1}, characteristic of the carbonyl group.



IR spectra: 1) N-β-fluoroethyl-B-difluoroborazene: —— in nujol; .... in hexachlorobutadiene; 2) N-acetyl-N-β-fluoroethyl-B-difluoroborazene in nujol.

Finally, it should be mentioned that cellulosic materials (textile cloths, paper, etc.) after treating with II and many of the above-mentioned compounds no longer ignite in contact with an open flame.

Experimental*

Starting materials. Commercial 97–98% ethylenimine was dried over sodium and distilled, bp 56–57°, n_D^{20} 1.4120. Boron trifluoride etherate was prepared by saturating dry ether with boron trifluoride made by the action of H_2SO_4 on $Na_2O \cdot (BF_4)_4$ [21]; it was purified by distillation (bp 127° C).

Analyses. All the analyzable products were readily soluble in water. To determine the boron and hydrolyzable fluorine in them, a weighed amount was boiled with aqueous $CaCl_2$ solution, then titrated with 0.2–0.5 N NaOH in the presence of mannitol (naphtholphthalein indicator) [22]. Alternatively, a weighed amount was boiled with a solution of anhydrous $CaCl_2$ in dry MeOH, followed by distilling off the azeotrope of trimethylborate and alcohol. The distillate was then diluted with water, and titrated in the presence of mannitol, using naphtholphthalein. Hydrolyzable fluorine was determined gravimetrically (as CaF_2) [23], as well as by transforming the fluorine to SiF_4 by boiling with sulfuric acid, silica gel, and finely powdered glass, followed by distilling off and hydrolyzing the SiF_4, and determining the fluoro ion by titrating with thorium nitrate solution in the presence of alizarin S indicator [24].

To determine total fluorine, the organic matter in a weighed portion was destroyed by fusing with sodium in a Parr bomb, and the F then determined as described above. The total F in II was also determined by weighing the precipitate of NaF obtained by heating a weighed quantity of the compound with a saturated NaOH solution.

For all the compounds N was determined by the micro-Dumas method.

The molecular weight of II was determined cryoscopically in benzene. The other compounds were insoluble in the usual cryoscopic solvents.

The IR spectra were measured with a double beam UR-10 IR spectrophotometer (solutions in hexachlorobutadiene, and suspensions in liquid paraffin).

β-Fluoroethyl-B-difluoroborazene (II). A solution of 141.8 g (1 mole) BF_3 etherate in 50 ml dry ether was cooled to –78° C and stirred, then a solution of 43.0 g (1 mole) ethylenimine in 50 ml ether added in 1 hr. The white precipitate formed was filtered off and carefully washed with 100–150 ml ether. This solid reaction product (92–101 g) was dissolved in 70–100 ml dioxane, and warmed to 40–50°C. When the solution cooled, coarse colorless crystals separated; they were filtered off with suction, and washed with cold dioxane. Vacuum-evaporation of the mother liquor (no heating) gave a further quantity of crystals. Total yield of II (mp about 50°C), 85–56 g (77.7–50.4%). After further recrystallization from dioxane it had mp 55–56° C. Found: N 12.51; B 9.85; F 51.40; F_{hydrol} 34.6%; M 107.3, 106.6. Calculated for $C_2H_5BF_3N$: N 12.63; B 9.75; F 51.30; F_{hydrol} 34.45%; M 110.8. II formed colorless crystals readily

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soluble in water, EtOH, and acetone, less soluble in dioxane, and insoluble in ether, hexane, benzene, and $CHCl_3$.

Heating II above its melting point converts it into a hygroscopic friable polymer mp 88–90° C, insoluble in organic solvents.

Vacuum-evaporation (no heating) of the bulked dioxane solutions from the washing and recrystallizing of II gave 25–40 g (22–36%) pale yellow viscous polymer (III), whose composition was the same as that of II. Its cryoscopic molecular weight in dioxane corresponded to an octamer. Found: N 12.40; B 9.95; F_{hydrol} 35.10%; M.844.7. Calculated for $(C_2H_5BF_3N)_8$: N 12.63; B 9.75; F_{hydrol} 34.45%.

Compound III was soluble in water EtOH, dioxane, acetone, but insoluble in ether, benzene, hexane, and $CHCl_3$.

When the reaction products obtained from I and BF_3 at −78° C were allowed to stand at 0° for 24 hr, a third reaction product (IV) was formed, as a white, dioxane-insoluble precipitate, mp 55—58° C, hydrolyzed in air and on solution in water. Its solubility in EtOH was low, and it was insoluble in other organic solvents. Sometimes the yield amounted to 30%. Found: N 12.17; B 9.80; F_{hydrol} 34.21%. Calculated for $C_2H_5BF_3N$: N 12.63; B 9.75; F_{hydrol} 34.45%.

Preparation of polymer VIII. a) A solution of 14.1 g (0.1 mole) BF_3 etherate in 20 ml ether was stirred, and a solution of 8.6 g (0.2 mole) ethylenimine in 20 ml ether added dropwise with the temperature kept at −78° C. At the end of the reaction, the reaction products separated into 2 layers, (upper ether, lower reaction product). The latter, a transparent liquid, did not contain ethylenimine rings. On slow warming up to room temperature (2–3 days), the lower layer gradually thickened, became turbid, and solidified to a very coarse mass (VIII) mp about 90° C (decomp and gas evolution). Yield 15.3 (100%). The material was readily hydrolyzed in water. It was insoluble in organic solvents, except EtOH. Found: N17.27; B 7.10; F 38.11%. Calculated for $C_4H_{10}BF_3N_2$: N 18.30; B 7.07; F 37.22%.

b) In a similar experiment where the reaction products were quickly warmed up to room temperature (by pouring into another vessel), there was a spontaneous exothermic reaction accompanied by gas evolution (amine) and formation of a porous solid mass mp 60° C. Yield 11.3 g. Sometimes the strong heating of the mixture was accompanied by autoignition of the ether. Found: N 12.90; B 9.85; F_{hydrol} 28.60%. Calculated for $C_2H_5BF_3N$: N 12.63; B 9.75; F_{hydrol} 34.45%. On prolonged storage (6 months). VIII melted to a viscous transparent mass.

c) When a solution of 0.86 g (0.02 mole) I in 5 ml ether was added to a solution of 2.2 g (0.02 mole) II in 15 ml ether at 0° C, a liquid reaction product formed at the bottom of the flask, and solidified next day. This coarse white material melted at 70–80° C with decomposition and gas evolution. Yield 2.62 g (87%). The material was analogous in composition and properties to VIII, obtained in the preceding experiment a. Found: N 17.95; B 7.31; F 35.71%. Calculated for $C_4H_{10}BF_3N_2$: N 18.30; B 7.07; F 37.22%.

Polymer VIII was insoluble in organic solvents, making it impossible to determine its molecular weight cryoscopically. It dissolved readily in water, to give a solution acid to methyl orange. VIII was completely hydrolyzed by boiling with an aqueous solution of $CaCl_2$. When VIII was heated it decomposed evolving ethylenimine and then piperazine, identified as their picrates, mp 152° C, and 275° C, respectively, mixed mps with authentic picrates undepressed.

N-Acetyl-N-(β-fluorethyl)-B -difluoroborazene (X). A mixture of 11 g (0.1 mole) II, 30 ml benzene, and 20 ml Ac_2O was refluxed for 5 hr on a water bath. The solvent was distilled off, then the AcOH and excess Ac_2O vacuum-distilled off. The residue was vacuum-distilled and a cut bp 150–152° C (4 mm) taken. The distillate solidified in the receiver to colorless needles, which were washed with a small quantity of cold EtOH. Yield 11.0 g or 71.7%. Mp 69–71° C. X dissolved readily in water, acetone, and dioxane, was less soluble in cold EtOH, and was insoluble in ether and hexane. Found: N 9.11; B 6.92; F_{hydrol} 24.55%. Calculated for $C_4H_7BF_3NO$: N 9.16; B 7.08; F_{hydrol} 24.92%. On prolonged storage in a sealed tube, it changed into a transparent viscous mass. X gave a picrate, yellow needles mp 154° C (ex EtOH). Found: N 16.68%. Calculated for $C_{10}H_{10}BF_3N_4O_8$: N 16.47%.

Acetylation of II in the presence of pyridine. A mixture of 5.5 g (0.05 mole) II, 6 ml Ac_2O, and 44 ml pyridine was refluxed for 30 min. The solvent was vacuum-distilled off under a water pump, and the residue thus obtained, distilled at 4 mm. The distillate bp 163–165° C even crystallized in the distilling flask outlet tube. It was washed with cold EtOH, yield of XI 1.1 g. The white crystals obtained had mp 206° C, and 217° C after recrystallizing from EtOH. Mixed mp with authentic tetrafluoroboropyridinium compound, prepared as in [20], undepressed. Found: N 8.15; B 6.77; F 45.31%. Calculated for $C_6H_6BF_4N$: N 8.39; B 6.48; F 45.57%.

Acetylation of polymer III. A mixture of 10.0 g II and 30 ml Ac_2O was refluxed for 5 hr, then vacuum-distilled. An oily liquid distilled over at 150–155° C, which, on standing, gave crystals of a compound mp 70° C (yield 4.0 g). It gave a picrate mp 154° C, undepressed mixed mp with the picrate of X prepared as in the previous experiments.

Reaction of II with triethylamine. 1.04 g Et_3N (0.01 mole) was added to a suspension of 2.2 g (0.02 mole) II in 20 ml petrol ether, A liquid product, insoluble in petrol ether, was formed. Solvent and excess amine were distilled off, and the residue vacuum-distilled. 0.6 g N-triethyl-B-trifluoroborazane (VI) passed over at 101-105° C (5-6 mm). The literature gives [25] bp 80° C (3 mm). Found: N 8.34; B 6.46%. Calculated for $C_6H_{15}BF_3N$: N 8.29; B 6.40%. On cooling, the undistilled residue solidified to a pale yellow transparent glass, which was rapidly hydrolyzed in air.

Reaction of III with alkali. 30 ml 50% NaOH solution was added to 10.8 g (0.1 mole) II in 25 ml water, and the amine formed steam-distilled off. In addition to ethylenimine picrate mp 132° C, fractional precipitation and crystallization gave, from the distillate, a small quantity of picrate mp 276° C (decomp), undepressed mixed mp with authentic piperazine picrate. 12.0 g NaF (0.3 mole) i.e., 97% calculated on the weight of the fluorine in II, crystallized out when the distillation residue cooled.

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