Diazaboracyclic Cations. III. A Homomorph of 9,10-Dihydroanthracene (1)

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Several years ago we reported (1b) a rather general method for preparing diazaboracyclic cations by means of the fusion of a mixture of a 1,2- or 1,3-diamine salt and sodium borohydride. For example, the difluoborate salt of 1,3-bis(dimethylamino)propane yields compound 1, the diazaboracyclic cation of which is homomorphic with 1,1,3,3-tetramethylcyclohexane.

$$Me_{2}N(CH_{2})_{3}NMe_{3}\cdot 2HBF_{4} \xrightarrow{NaBH_{4}} Me_{2}N \xrightarrow{B}_{H_{2}} NMe_{2}BF_{4}^{-} + NaBF_{4} + H_{2}$$

We now wish to report that this procedure gives a dramatically different result when carried out with the difluoborate salt of 2,2'-dipyridylmethane (2). The product of its fusion with sodium borohydride is an orange, covalent compound whose structure proved to be 6,6-difluoro-6,6-dihydrodipyrido[1,2-c:2',1'-f][1,3,2]diazaborine (3).

Its spectral data, combined with satisfactory elemental analyses, permit an unambiguous assignment of structure: (1) lack of infrared absorption in the 2500-2300 cm⁻¹ region rules out the possibility of a bridging BH₂ group; (2) only one fluorine-19 nuclear magnetic resonance peak (split into a 1:1:1:1 pattern by boron-11) is consistent with a bridging BF₂ group; (3) a proton nmr singlet at δ 5.45 of unit intensity calls for a vinyl hydrogen on the bridging carbon atom; and (4) strong electronic absorption at 468 nm is compatible only with a structure in which the two pyridine rings are conjugated (2).

Compound 3 possesses several quite unexpected features. In addition to being a neutral diazaboracyclic compound rather than a cationic one, the boron atom which is incorporated carries fluorine, rather than hydrogen atoms. In our earlier work (1b), a redistribution reaction between fluoborate and borohydride ions was recognized as a

distinct possibility at the high temperatures (180° and above) required for fusion with diamine salts. However, no such scrambling of ligands on boron was observed, and the use of fluoborate salts was continued in subsequent studies, primarily because of their relatively low melting points. We can find no reasonable explanation for the anomalous behavior of the dipyridylmethane salt. Finally, it is important to note that deprotonation has occurred at the bridging methylene group in some precursor of 3. That this precursor is quite probably the diazaboracyclic cation of salt 4 follows from the experimental observations that 3, upon treatment with one mole of fluoboric acid, is converted into salt 4, and that conversely 4 can be readily deprotonated (e.g., with triethylamine) to regenerate 3. In the case of the fusion reaction, borohydride ion must serve as the base to bring about the latter transformation.

Compound 2 is stable in air indefinitely (no detectable decomposition upon standing for over a year), and is also quite resistant to hydrolysis in a pH range near 7. Not surprisingly, it is susceptible to acid and base catalyzed hydrolysis, particularly the latter, which leads to the regeneration of diamine. The intriguing possibility that 3 would react with boron trifluoride to yield salt 5, the cation of which is homomorphic with anthracene, was not realized in several attempts.

In view of the unexpected results with the fusion reaction, alternative schemes for achieving the original goal, i.e., the synthesis of the unsubstituted salt 4, were considered. Two satisfactory procedures were discovered, one of which is closely related to the fusion reaction. Lithium borohydride in boiling glyme reacts with 2 to give the expected product in fair yield. It proved to be desirable to metathesize the initially formed fluoborate salt to the more readily crystallizable hexafluorophosphate salt (6a). The salient structural features of the compound are revealed by the characteristic BH₂ stretching vibra-

tions observed near 2500 cm $^{-1}$ in the infrared spectrum and a singlet at δ 4.92 in the nmr spectrum which integrates for two hydrogens. Furthermore, lack of ultraviolet absorption above 300 nm demonstrates lack of conjugation between the two pyridine rings.

An alternative synthesis of 6 was achieved using a method similar to that reported by Miller and Ryschkewitsch (3). 2,2'-Dipyridylmethane was found to react with pyridine-iodoborane in benzene to afford the iodide salt (6b) in good yield.

Considering the ease with which cation 4 can be deprotonated, it is somewhat surprising that cation 6 does not suffer the same fate in the above two reactions (by borohydride ion and pyridine, respectively). This cation, however, proves to be quite resistant to deprotonation; triethylamine fails, as does the quite basic diamine, 1,8-bis(dimethylamino)naphthalene (4). When 6 is treated with aqueous sodium hydroxide, a fleeting red color is observed, but the only isolable product is 2,2'-dipyridylmethane. The greater acidity of 4 with respect to 6 may be due to the strongly electron-withdrawing effect of the BF₂ group in the former.

EXPERIMENTAL

Melting points were determined on a calibrated Mel-Temp apparatus. Infrared spectra were recorded on a Perkin-Elmer 237 spectrophotometer, nmr spectra on a Varian A-60A spectrometer. The fluorine-19 nmr spectrum was kindly provided by the Union Carbide Technical Center, South Charleston, West Virginia. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

2,2'-Dipyridylmethane·2(Fluoroboric Acid) (2).

A solution of 35.1 g. (0.40 mole) of 48% fluoboric acid in 50 ml. of 95% ethanol was added slowly to a stirred solution of 34 g. (0.20 mole) of 2,2'-dipyridylmethane (5) in 100 ml. of ether. The precipitate was recrystallized twice from 95% ethanol to yield 65 g. of white needles: m.p. 172-173°; nmr (deuterium oxide, TSS): δ 5.12 (s, 2, CH₂), 8.2 (m, 4, H-3,3',5,5'), 8.7 (m, 2, H-4,4'), and 9.0 ppm (m, 2, H-6,6').

Anal. Calcd. for $C_{11}H_{12}B_2F_8N_2\colon C,38.20;\ H,3.50;\ N,8.12.$ Found: $C,38.18;\ H,3.44;\ N,8.03.$

6,6-Difluoro-6,6-dihydrodipyrido [1,2-c:2',1'-f][1,3,2] diazaborine (3).

A mixture of 10.0 g. (29.0 mmoles) of finely powdered 2 and 1.09 g. (29.0 mmoles) of 99% sodium borohydride was placed in a 100-ml. Fischer-Porter pressure tube and heated in a sand bath at

190-200° for 4 hours. After cooling to room temperature, 20 ml. of water was added and when gas evolution ceased, the undissolved material was filtered off and washed with 5 ml. of water. Two recrystallizations from 80% aqueous ethanol gave 2.37 g. of orange fibrous crystals: m.p. 130° ; ¹H nmr (deuteriochloroform, TMS): δ 5.45 (s, 1, H-12), 6.8 (m, 4, H-1,3,9,11), 7.4 (m, 2, H-2,10), and 8.1 ppm (m, 2, H-4,8); ¹⁹F nmr (deuteriochloroform, trifluoroacetic acid): δ 22.3 ppm (1:1:1:1 quartet, JFB = 32 Hz); uv max (chloroform): 286 (log ϵ 3.92), 344 (3.66), and 468 nm (4.25).

Fluoborate Salt of 3(4).

A solution of 0.42 g. (2.3 mmoles) of 48% fluoboric acid in 10 ml. of ethanol was added slowly to a stirred solution of 0.50 g. (2.3 mmoles) of compound 3 dissolved in 50 ml. of ethanol. The solvents were removed on a rotary evaporator and the residue was recrystallized from 95% ethanol to give 0.54 g. of white needles: m.p. 172-173°; nmr (deuterium oxide, TSS): δ 4.88 (s, 2, CH₂), 8.0 (m, 4, H-1,3,9,11), 8.5 (m, 2, H-2,10), and 8.9 ppm (m, 2, H-4,8).

Anal. Calcd. for $C_{11}H_{10}B_2F_6N_2$: C, 43.21; H, 3.32; N, 9.16. Found: C, 43.06; H, 3.46; N, 9.02.

6,6,12-Trihydrodipyrido[1,2-c:2',1'f][1,3,2]diazaborinium Salts. A. Hexafluorophosphate (**6a**).

Compound 2 (10.4 g., 30.0 mmoles) and 200 ml. of glyme (freshly distilled from sodium) were added to a 1-\mathcal{L}. flask equipped with a reflux condenser, mechanical stirrer, and a dropping funnel with a heated jacket. After heating the mixture to the reflux temperature of the solvent, a hot (ca. 60°) solution of 0.68 g. (30 mmoles) of lithium borohydride dissolved in 200 ml. of dry glyme was added with stirring over a period of ca. 1 hour. All operations, including preparation of the borohydride solution, were performed under dry nitrogen. When the addition was complete, the mixture was stirred under reflux for an additional 18 hours.

The cooled mixture, including a small amount of white solid which had crystallized on the wall of the flask, was transferred to a rotary evaporator and the solvent was removed. After dissolving the semi-solid residue in 20 ml. of water, a 5% solution of aqueous ammonium hexafluorophosphate was added dropwise until no further precipitation occurred. The material was filtered off, washed with 10 ml. of cold water, and recrystallized from water to yield 4.52 g. (46%) of white powder: m.p. 220-222° dec.; ir (potassium bromide): 2510, 2440 (BH₂), and 845 cm⁻¹ (PF₆); nmr (DMSO-d₆, TSS): δ 4.92 (s, 2, CH₂), 8.0 (m, 4, H-1,3,9,11), 8.5 (m, 2, H-2,10), and 8.9 ppm (m, 2, H-4,8).

Anal. Calcd. for $C_{11}H_{12}BF_6N_2P$: C, 40.28; H, 3.69; N, 8.54. Found: C, 40.42; H, 3.68; N, 8.42.

B. Iodide Salt (6b).

A solution to pyridine-iodoborane, prepared by adding 5.08 g. (20.0 mmoles) of iodine to 3.90 g. (42.0 mmoles) of pyridine-borane dissolved in 50 ml. of benzene (3), was added over a period of 1 hour to a stirred solution of 6.81 g. (40.0 mmoles) of 2,2'-dipyridylmethane in 50 ml. of benzene at room temperature under nitrogen. The mixture was then heated under reflux for 6 hours, cooled to room temperature, and the supernatant liquid was decanted from the viscous reddish-brown residue. The residue was triturated with two 25-ml. portions of anhydrous ether; the ether extracts combined with the benzene supernatant gave 1.12 g. of unreacted diamine.

The residue was dissolved in 60 ml. of chloroform, and after allowing the resulting solution to evaporate to about one-half its original volume, 25 ml. of pentane was added with vigorous stirring. The slightly pasty, brick red solid which precipitated was filtered off, and after standing in a vacuum desiccator over concentrated sulfuric acid for two days solidified completely. The solid was recrystallized twice from absolute ethanol to afford 7.46 g. (72% conversion) of pale yellow needles: m.p. 79-81°; ir (potassium bromide) 2500 and 2440 cm⁻¹ (BH₂); nmr (deuterium oxide, TSS) δ 5.12 (s, 2, CH₂), 8.2 (m, 4, H-1,3,9,11), 8.6 (m, 2, H-2,10), and 9.0 ppm (m, 2, H-4,8).

Anal. Calcd. for $C_{11}H_{12}BIN_2$: C, 42.62; H, 3.90; N, 9.03; I, 40.94. Found: C, 42.80; H, 3.88; N, 8.91; I, 40.73. Acknowledgement.

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