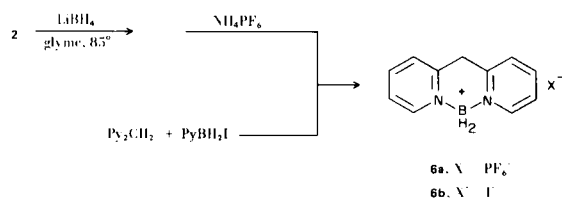




tions observed near  $2500\text{ cm}^{-1}$  in the infrared spectrum and a singlet at  $\delta$  4.92 in the nmr spectrum which integrates for two hydrogens. Furthermore, lack of ultraviolet absorption above 300 nm demonstrates lack of conjugation between the two pyridine rings.



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  $\text{BF}_2$  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.  $172\text{--}173^\circ$ ; nmr (deuterium oxide, TSS):  $\delta$  5.12 (s, 2,  $\text{CH}_2$ ), 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  $\text{C}_{11}\text{H}_{12}\text{B}_2\text{F}_8\text{N}_2$ : 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

$190\text{--}200^\circ$  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.  $130^\circ$ ;  $^1\text{H}$  nmr (deuteriochloroform, TMS):  $\delta$  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);  $^{19}\text{F}$  nmr (deuteriochloroform, trifluoroacetic acid):  $\delta$  22.3 ppm (1:1:1:1 quartet,  $J_{\text{FB}} = 32$  Hz); uv max (chloroform): 286 (log  $\epsilon$  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.  $172\text{--}173^\circ$ ; nmr (deuterium oxide, TSS):  $\delta$  4.88 (s, 2,  $\text{CH}_2$ ), 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  $\text{C}_{11}\text{H}_{10}\text{B}_2\text{F}_6\text{N}_2$ : 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-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.  $60^\circ$ ) 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.  $220\text{--}222^\circ$  dec.; ir (potassium bromide): 2510, 2440 ( $\text{BH}_2$ ), and  $845\text{ cm}^{-1}$  ( $\text{PF}_6^-$ ); nmr ( $\text{DMSO-d}_6$ , TSS):  $\delta$  4.92 (s, 2,  $\text{CH}_2$ ), 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  $\text{C}_{11}\text{H}_{12}\text{BF}_6\text{N}_2\text{P}$ : 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  $\text{cm}^{-1}$  ( $\text{BH}_2$ ); nmr (deuterium oxide, TSS)  $\delta$  5.12 (s, 2,  $\text{CH}_2$ ), 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  $\text{C}_{11}\text{H}_{12}\text{BIN}_2$ : 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.

Support for this work by grants GP-7835 and GP-14793 from the National Science Foundation is gratefully acknowledged.

#### REFERENCES

- (1) For previous papers see (a) J. E. Douglass, H. M. Shih, R. E. Fraas, and D. E. Craig, Jr., *J. Heterocyclic Chem.*, **7**, 1185 (1970); and (b) J. E. Douglass, J. D. Fellman, R. Carpenter, H. M. Shih, and Y. F. Chiang, *J. Org. Chem.*, **34**, 3666 (1969).
- (2) H. J. Friedrich, W. Gückel, and G. Scheibe, *Chem. Ber.*, **95**, 1378 (1962).
- (3) V. R. Miller and G. E. Ryschkewitsch, *J. Am. Chem. Soc.*, **92**, 1558 (1970).
- (4) R. W. Alder, P. S. Bowman, W. R. S. Steele, and D. R. Winterman, *Chem. Commun.*, 723 (1968).
- (5) E. Leete and L. Marion, *Can. J. Chem.*, **30**, 563 (1952).