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Synthesis and Separation of the Isomeric Compounds Dimeric Dimethyl(2-pyridyl)borane and Dimethylboronium Bis(2-pyridyl)dimethylborate

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Introduction

Since the first examples of the pyrazabole ring system were reported by Trofimenko in 1966,[1] these compounds have been the subject of substantial research.[2] The two most important types of resonance structures for a pyrazabole are shown in Figure 1a. If the pyrazolyl moieties in a pyrazabole are replaced by 2-pyridyl groups, two possible isomers are produced, as shown in Figure 1b. The dimeric (2-pyridyl)boranes and the boronium bis(2-pyridyl)borates are analogous to the type A and type B structures for a pyrazabole, respectively. Isomeric pairs of the 2-pyridyl analogs of a pyrazabole have been unknown until now, with one possible exception. In 1984, Ishikura et al. reported the preparation of what may be a mixture of these kinds of isomers (Figure 1b, R = ethyl).[3] The present work describes the synthesis of the title compounds (Figure 1b, I and II) and the separation of these isomers.

Results and Discussion

The title compounds form when a solution of bromodimethylborane is added to a solution of 2-lithiopyridine[4] at −78 °C, according to eq 1. Four solid fractions were recovered by the

$$2(2\text{-LiC}_5H_4N) + 2(CH_3)_2BBr \rightarrow \{\text{I and II}\} + 2LiBr \quad (1)$$

stepwise reduction of the volume of the reaction mixture. The first two were mixtures of lithium bromide and polymeric materials. The third and fourth fractions (after recrystallization of the latter) were nearly identical mixtures of I and II in a ratio of 15:85, respectively, as determined by preparative thin-layer chromatography (TLC) and ^{1}H NMR data. The yield of mixtures containing only I and II was ca. 50%. Separation of these isomers was achieved using TLC on plates coated with basic alumina and an eluting solvent such as hexane, cyclohexane, 2,2-dimethylbutane, or pentane. On the basis of their mass and NMR spectra, the material recovered from the top band (the band nearest the solvent front) was assigned the structure I, dimeric dimethyl (2-pyridyl)borane, and that from the bottom band (the band nearest the origin) was assigned the structure II, dimethylboronium bis(2-pyridyl)dimethylborate.

The ^{11}B NMR signal arising from the boronium atom in II should be broadened by the quadrupolar nitrogen atoms; therefore, the broad singlet at +3.0 ppm is assigned to this atom, and the sharp singlet at +3.0 ppm is assigned to this atom, and the sharp singlet at −17.6 ppm is assigned to the borate atom. The partially resolved quartet at 0.06 ppm in the ^{1}H NMR spectrum of II was shown to be associated with the signal at $\delta(^{11}B) = -17.6$ ppm by a decoupling experiment, and so was assigned to the dimethylborate group. The shape of this signal may be explained on theoretical grounds[5,6] and is very similar to that in the ^{1}H NMR spectrum of $LiB(CH_3)_4$ at −2 °C.[7] The singlet at 0.36 ppm must therefore be assigned to the dimethylboronium group. These assignments are supported by a comparison between the $\delta(^1H)$ and $\delta(^{11}B)$ values of the $B(CH_3)_2$ moieties for compound II and several compounds containing structural similarities to II (see Table I).

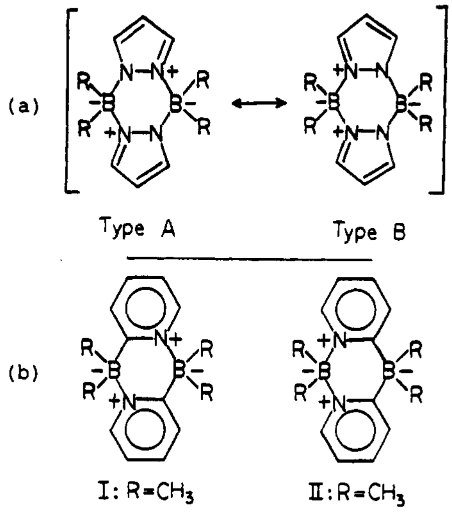

Figure 1. (a) Important resonance structures of a pyrazabole and (b) the 2-pyridyl analogs of a pyrazabole.

Table I. Selected ^{1}H and ^{11}B NMR Chemical Shifts for I, II, and Related Compounds in Aprotic Solvents

compound	$\delta(^1H)$ for BCH_3	$\delta(^{11}B)$	solvent
I	0.22	−5.2	$CDCl_3$
II	0.36, 0.06	+3.0, −17.6	$CDCl_3$
$[(CH_3)_2B(py)_2]^+Cl^-$ [a]	0.56[8]	+6.9[8]	CH_2Cl_2
$[(CH_3)_2B(py)_2]^+Br^-$ [a]	0.58[9]		CH_2Cl_2
$[(CH_3)_2B(bpy)]^+Br^-$ [b]		+7.8[10]	CH_3CN
$LiB(CH_3)_4$	−0.5[7]	−21.1[11]	ether
$NaB(C_6H_5)_4$		−6.3[11]	CH_3CN
$(CH_3)_2B(\mu\text{-pz})_2B(CH_3)_2$ [c]	0.26[12]	+1.2[12]	$CDCl_3$

[a] py = pyridine. [b] bpy = 2,2′-bipyridyl. [c] pz = pyrazolyl.

In the ^{13}C NMR spectrum of I, the position of the signal at 14.9 ppm is consistent with those from other compounds containing boron-bonded methyl groups.[13] The annular carbon atoms that are directly bonded to boron most likely give rise to the signals at 182 and 187.0 ppm in the ^{13}C NMR spectra of I and II, respectively. The methyl region of the ^{13}C NMR spectrum of II unexpectedly exhibits only one signal (at 14.7 ppm) whose position closely coincides with the methyl signal of I. An integrated spectrum of II revealed that this signal probably represents both kinds of methyl carbon atoms present in this molecule.

The similarities between I and II in their physical and chemical properties are striking. Both are soluble in a variety of organic solvents but not in water. Both are air-stable solids with similar melting points (I, 187–188 °C; II, 178–179 °C). Interestingly, the melting points of these two compounds more closely resemble that of the all-carbon analog 9,9,10,10-tetramethyl-9,10-dihydroanthracene (III, 166–167 °C)[14] than that of 4,4,8,8-tetramethylpyrazabole (IV (Figure 1a, R = CH_3), 59–60 °C).[12] In fact, a preliminary X-ray crystal study of II indicates that this

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compound contains a planar central ring,[15] as does III.[16] Both I and II are unusually stable toward oxidation, as evidenced by the necessity, during the elemental analyses for boron, to heat the samples with concentrated nitric acid in sealed ampules to 275 °C for 24 h, instead of the usual 4 h, to ensure complete decomposition.

The mass spectra of I and II are also very similar. In both cases, the parent ion at m/z 238 is not observed, but prominent peaks appear at m/z 223 (loss of CH_3), m/z 208 (loss of $2CH_3$), m/z 207 (loss of $2CH_3$ and H), and m/z 104 (symmetrical cleavage of the m/z 208 ion). The mass spectrum of IV is similar in these respects.[12]

The formation of II as the major product of the reaction of bromodimethylborane with 2-lithiopyridine may be explained by the formation of the bis(2-pyridyl)dimethylborate anion as an intermediate. In order to test this hypothesis, a derivative of this anion was recently synthesized under reaction conditions similar (except for the stoichiometry of the reactants) to those described here for the synthesis of I and II. A report on the synthesis and chemistry of this anion will be published soon.

Experimental Section

Bromodimethylborane, 2-bromopyridine, anhydrous diethyl ether, and a solution of 1.6 M *n*-butyllithium in hexane were purchased from Aldrich and used as received. NMR spectra were recorded on solutions in $CDCl_3$ on a Bruker 500-MHz NMR spectrometer. Chemical shift data are given in ppm with positive values indicating downfield shifts from the reference (internal $(CH_3)_4Si$ for ^1H and ^{13}C NMR, external $(C_2H_5)_2O{\cdot}BF_3$ for ^{11}B NMR); $h_{1/2}$ = peak width at half-height. Mass spectral data were obtained on a Kratos MS-80 spectrometer operating in the electron impact mode; data are listed to m/z 50 for 5% of more relative abundances (in parentheses) only. Melting points (uncorrected) were determined on a Mel-Temp block. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Inc., Woodside, NY.

Synthesis of Mixtures of I and II. A solution of 2-bromopyridine (5.05 g, 32.0 mmol) in 25 mL of diethyl ether was added over a 5-min period to a stirred solution of 1.6 M *n*-butyllithium in hexane (20.0 mL, 32 mmol) and 75 mL of diethyl ether at −78 °C (dry ice–acetone bath) under a nitrogen cover. The solution became red-brown. After 10 min, a solution of bromodimethylborane (3.87 g, 32.0 mmol) in 50 mL of hexane was added over a 30-min period, and the solution became noticeably lighter in color. Stirring was continued while the reaction mixture warmed to room temperature overnight.

Subsequently, a mixture of dark tarry materials and a light-colored solid was removed by filtration and dried under vacuum (1.24 g). About half the solvent was removed from the filtrate by distillation, and a rust-colored precipitate appeared, which was dried in vacuo (2.20 g). Most of a sample of this material darkened but remained solid when heated to 310 °C.

The volume of the filtrate was reduced further, and a third precipitate was removed by filtration and dried in vacuo (0.53 g, mp 176–179 °C). The filtrate was evaporated to dryness, leaving a dark brown solid (2.49 g). A sample of this residue (1.21 g) was dissolved in diethyl ether, and a tarry material (0.08 g) was removed by filtration. Hexane was added, the solution was treated with activated charcoal, and two crops of crystals were obtained by reducing the volume of the solution. The first weighed 0.42 g (mp 175–178 °C); the second weighed 0.21 g (mp 160–173 °C). Preparative TLC later established that these two crops had nearly the same composition. An ^1H NMR spectrum of this first crop was identical to that of the third precipitate mentioned above and showed that two compounds containing 2-pyridyl rings were present in a ratio of 15:85. Proton NMR spectra established that separation of these two compounds by sublimation or recrystallization from hexane was not feasible.

Isolation of I and II by Preparative Thin-Layer Chromatography. The 1 mm thick coating on the 20 cm × 20 cm glass plates was cast from an aqueous slurry made from anhydrous $CaSO_4$ (5–10%) and basic alumina containing a fluorescent indicator (Fluka). Each plate was activated by heating it to 145 °C for 2 h immediately before use. (Care was taken to minimize contact of the activated plates with humid air.)

Several chromatographic separations were performed in order to obtain enough of each isomer for analysis. In a typical separation, a benzene solution of a sample from the third precipitate (40.2 mg/0.5 mL) was placed on a plate in a 1 cm wide band. The plate was developed in *n*-hexane, and then dried, four times; the solvent front was allowed to travel 4–5 cm farther from the origin each successive time. When the solvent front was located 17.3 cm from the origin, two bands were visible when viewed under ultraviolet light (λ = 254 nm) and were located 8.3–10.7 and 10.7–11.6 cm from the origin. The material from each band was recovered by repeated elution with CH_2Cl_2 to give a colorless solid in each case: 5.3 mg from the top band and 29.6 mg from the bottom band.

Using fresh plates, the separation outlined above was repeated on the material recovered from each band until ^1H NMR spectra showed each to be isomerically pure. Final purification was achieved by sublimation in an evacuated ampule at bath temperatures of 55–65 °C over a period of several weeks. The sublimate from the top band, consisting of thin diamond-shaped platelets, melted at 187–188 °C; that from the bottom band, which also consisted of diamond-shaped platelets, melted at 178–179 °C.

Elemental Analyses. Anal. Calcd for $C_{14}H_{20}B_2N_2$ (M_r = 237.95): C, 70.67; H, 8.47; B, 9.09; N, 11.77. Found for I: C, 70.43; H, 8.65; B, 9.07; N, 11.84. Found for II: C, 70.59; H, 8.56; B, 9.16; N, 11.53.

Spectral Data for I. ^1H NMR, δ: 8.45 (1H, d, J = 6.0 Hz), 7.71 (1H, d, J = 6.7 Hz), 7.64 (1H, td, J = 7.6, ca. 1 Hz), 7.19 (1H, td, J = 6.7, 1.5 Hz), 0.22 (6H, s). ^{11}B NMR, δ: −5.2 (s, $h_{1/2}$ = 65 Hz). $^{13}C\{^1H\}$ NMR, δ: 182 (broad), 142.1, 135.6, 129.9, 120.2, 14.9 (broad apparent d, J = ca. 60 Hz). Mass spectrum, m/z (relative intensity): 224 (22), 223 (100), 222 (58), 221 (12), 209 (5), 208 (33), 207 (40), 206 (12), 193 (5), 192 (5), 191 (6), 190 (5), 181 (17), 180 (13), 168 (6), 167 (5), 144 (6), 129 (6), 128 (8), 127 (6), 104 (48), 103 (6), 102 (5), 69 (13), 57 (13), 55 (13).

Spectral Data for II. ^1H NMR, δ: 8.36 (1H, d, J = 6.3 Hz), 7.82 (1H, d, J = 8.1 Hz), 7.63 (1H, td, J = 7.6, 1.5 Hz), 7.16 (1H, td, J = 6.8, 1.5 Hz), 0.36 (3H, s), 0.06 (3H, partially resolved q, J = 4.7 Hz, which became a singlet when the peak at $\delta(^{11}B)$ = −17.6 ppm was irradiated). ^{11}B NMR, δ: +3.0 (1B, s, $h_{1/2}$ = 89 Hz), −17.6 (1B, s, $h_{1/2}$ = 18 Hz). $^{13}C\{^1H\}$ NMR, δ: 187.0 (q, J = 48.5 Hz), 141.4, 135.7, 130.1, 119.5, 14.7 (q, J = 41.0 Hz); no other signals were observed from +200 to −100 ppm; integration gave a peak area ratio of ca. 1.5:3.0:2.8:3.0:3.0:6.5, respectively. Mass spectrum, m/z (relative intensity): 224 (31), 223 (100), 222 (72), 221 (8), 209 (8), 208 (56), 207 (32), 206 (10), 193 (9), 191 (5), 190 (6), 182 (6), 181 (21), 180 (9), 168 (5), 167 (5), 144 (8), 129 (5), 128 (12), 104 (27), 103 (5), 102 (6).

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(15) The X-ray crystal study of II was performed on a Siemens P4 X-ray diffractometer. The crystal used was disordered, but only to the extent that molecules of II appeared to possess a center of symmetry. This is not consistent with the ^1H and ^{11}B NMR data for this compound and indicates that the $(CH_3)_2BC_2$ moiety has nearly the same shape as the $(CH_3)_2BN_2$ moiety.

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