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Boron Derivatives of 3-Methylpyrazole

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The reaction of KBH₄ with Hpzme (= 3-methylpyrazole) can be directed to yield K[H₂B(pzme)₂], K[HB(pzme)]₃, or K[B(pzme)]₄, respectively, depending on the experimental conditions. All three salts are stereochemically pure with the methyl group being located exclusively in the 3-position of the pyrazole ring.
In contrast, reaction of $(\text{CH}_3)_3\text{NBH}_3$ with Hpzme yields a mixture of 1,5- and 1,7-dimethylpyrazabole. Similarly, reaction of $\text{K[H}_2\text{B(pzme)}_2]$ with $(\text{CH}_3)_3\text{NBH}_2\text{I}$ produces a mixture of 1,5- and 1,7-dimethylpyrazabole, suggesting at least two different pathways for the latter process. In addition, the compounds 4,4,8,8-tetrabromo- and 4,4,8,8-tetrakis(3-methylpyrazole-1-yl)-1,5(7)-dimethylpyrazabole were also prepared. All compounds were characterized by $^1\text{H}$ and $^{11}\text{B}$ NMR data.
Boron Derivatives of 3-Methylpyrazole

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The knowledge of boron derivatives of 3-methylpyrazole, Hpzme, is extremely limited. This lack is likely due to the mobility of the N-bonded proton in 3-methylpyrazole, the replacement of which may yield isomeric products, i.e., derivatives of either 3- or 5-methylpyrazole. Indeed, when trimethylborane was reacted with 3-methylpyrazole, the resultant pyrazabole was found to be a mixture of 1 and 2 (R = CH₃) in approximately 4:3 molar ratio (based on $^1$H NMR data) which could not be separated. Stereochemically pure 1 with R = C₂H₅ was obtained from the interaction of (dimethylamino)diethylborane with 1,3-dimethyl-2-(methylpyrazol-1-yl)-1,3,2-diazaboracyclohexane.
The only other known boron derivative of 3-methylpyrazole, i.e., the salt $K[H_2B(pzme)_2]$, was obtained by condensation of $KBH_4$ with Hpzme. Based on high-resolution $^1H$ NMR data, the product of this latter reaction consisted of only one isomer, $3$, with the methyl group being exclusively in the 3-position of the pyrazole ring.$^4$

We have now found that the salts $K[HB(pzme)_3]$ and $K[B(pzme)_4]$, which are also readily obtained from the interaction of $KBH_4$ with Hpzme, analogously exist in only one isomeric form corresponding to $3$.

As expected, reaction according to eq 1 yielded the two isomers 1 and 2 ($R = H$), which were obtained in approximately 3:2 molar ratio.

$$2 \text{Hpzme} + 2 \text{(CH}_3\text{)}_3\text{NBH}_3 \rightarrow 2 \text{(CH}_3\text{)}_3\text{N} + 2 \text{H}_2 + \text{H}_2\text{B}(<\text{pzme})_2\text{BH}_2$$  \hspace{1cm} (1)

It seems that base displacement is the first step of the reaction. For steric reasons, this should result in the formation of 5-methylpyrazol-2-ylborane, which then loses $\text{H}_2$. 

\[
\begin{align*}
\text{K}^+ & \quad \text{CH}_3 \\
\text{H} & \quad \text{N-N} \\
\text{B} & \quad \text{H} \\
\text{H} & \quad \text{N-N} \\
\text{3} & \quad \text{CH}_3
\end{align*}
\]
to yield the 3-methylpyrazol-1-ylborane $4$ as illustrated in eq 2.

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{H} \\
\text{H} & \quad \text{BH}_3 \\
\end{align*}
\]

\[
\rightarrow
\begin{align*}
\text{H}_3\text{C} & \quad \text{H} \\
\text{H} & \quad \text{BH}_2 \\
\end{align*}
\]

Subsequently, the dimerization of $4$ to yield the pyrazabole $1$ ($R = H$) could compete with a sigmatropic boryl group shift and following dimerization of the thus rearranged material to yield $2$ ($R = H$). Based on the observed isomer distribution in the reaction product, the former process seems to be slightly preferred.

By fractional crystallization and sublimation it was possible to enrich mixtures of $1$ and $2$ ($R = H$) to approximately 85% of an individual species. It was found that $1$ is slightly less volatile and less soluble and has the higher melting point (near 90-100 °C). $^1$H NMR signals for $1$ ($R = H$) are observed at $\delta(^1\text{H}) = 7.49, 6.07, 3.5^*$ and 2.34 ppm; $\delta(^{11}\text{B}) = -10.5$ ppm. The fraction enriched with $2$ ($R = H$) has a melting point of 72-78 °C; NMR data for $2$ ($R = H$): $\delta(^1\text{H}) = 7.48, 6.07, 3.5^*$ and 2.36 ppm; $\delta(^{11}\text{B}) = -9.0$ and -12.2 ppm. Based on the $^{11}\text{B}$ NMR spectral data for $(\text{C}_2\text{H}_5)_2\text{B}(\text{pzme}_2)_2\text{BH}_2$ (Hpzme$_2$ = 3,5-dimethylpyrazole), the signal $\delta(^{11}\text{B}) = -12.2$ ppm is assigned to $B8$ of $2$, i. e., the boron atom closest to the (C)CH$_3$ groups.
Based on the structure of $\mathcal{J}$, it was hoped that the reaction according to eq 3 would proceed with the formation of only one isomer of the resultant pyrazabole, i.e., $2 \ (R = H)$.

$$3 + (\text{CH}_3)_3\text{NBH}_2\text{I} \rightarrow (\text{CH}_3)_3\text{N} + \text{KI} + 2 \ (R = H) \quad (3)$$

However, this was not the case and only a mixture of $1$ and $2 \ (R = H)$ in approximately 2:1 molar ratio was obtained. This result suggests at least two different pathways for the cited process. It is reasonable to assume that the first step of the overall reaction involves the formation of KI, thus providing for the neutral molecule $\mathcal{S}$.

$$\begin{array}{c}
\text{CH}_3 \\
\text{N-N} \\
\text{H}_2\text{B} \\
\text{N} \text{N} \\
\text{CH}_3
\end{array}$$

There are four donor-acceptor bonds in $\mathcal{S}$ that can be broken in the transformation process to yield a pyrazabole and free trimethylamine. Cleavage of $b$ would give the initial anion $[\text{H}_2\text{B(pzme)_2}]^-$ and the (supposedly unstable) cation $(\text{CH}_3)_3\text{NBH}_2^+$ containing trigonal boron and, thus, seems not very likely to occur; and cleavage of $d$ would yield the pzme-anion and the cation $(\text{CH}_3)_3\text{N(H}_2\text{)B(μ-pzme)BH}_2^+$, the latter also containing trigonal boron. Simple displacement of $(\text{CH}_3)_3\text{N}$ from $\mathcal{S}$ by the two-coordinate nitrogen of the terminal methylpyrazolyl group, i.e., cleavage of $a$ (the anticipated
The formation of an isomer mixture in the reaction according to eq 3 accounts for some earlier observations: The reaction of poly(pyrazol-1-yl)borates with $R_2BX$ species (where X is a ready leaving moiety) has previously been used for the preparation of 4,8-unsymmetrically substituted pyrazaboles. However, the yields were generally not very satisfying due to the simultaneous formation of symmetrically substituted species as byproducts. Since these reactions should also involve intermediates similar to $\mathbf{5}$, and since the present study illustrates that there are at least two reasonable pathways for the conversion of such intermediates to pyrazaboles, the
unsatisfactory yields of the desired products are readily explained. Moreover, the present data suggest the transient existence of monomeric pyrazol-1-ylboranes containing trigonal boron, even for reactions carried out at a relatively low temperature. This occurrence had previously been established for high-temperature processes.

A mixture of 1 and 2 (R = H) was reacted with excess Hpzme to yield the B-pyrazolylpyrazabole (pzme)_2B(μ-pzme)_2B(pzme). The reaction proceeded smoothly and, as based on ^1H NMR data, the terminal pzme groups of the product are exclusively boron-bonded at the same nitrogen site, i.e., most likely forming the 3-methylpyrazol-1-yl derivative. Isomers could not be detected in the ^11B NMR spectrum, where only one signal at δ(^11B) = -0.6 ppm (h = 42 Hz) was observed. Based on the digital resolution, the ^11B chemical shifts of the possible isomers cannot differ by more than 0.1-0.2 ppm. (Note: δ(^11B) of the structurally related (pzme)_2B(μ-pzme)_2B(pzme)_2 is observed at -0.7 ppm.) In contrast to the starting material, the ^1H NMR signal for the CH₃ groups of the bridging pzme moieties at lower field was found to be the more intensive in the product. Unless the effect of boron substitution would cause a cross-over of signals, one must assume that the isomer distribution with respect to the location of the cited groups was changed during the course of the reaction. This can be explained only by an opening of the central B₂N₄ ring during the (high-temperature) process, most likely a complete symmetrical cleavage of the pyrazabole molecule.
Reaction of a mixture of 1 and 2 (R = H) with elemental bromine gave the B-tetrabromo species. Surprisingly, the $^1H$ and $^{11}B$ NMR data suggest the presence of only one isomer in the product. On the other hand, this observation is disputed by the $8^\circ$ melting range of the material. Presumably, the latter contains a planar $B_2N_4$ ring; $^9$-$^{11}$ this event would seem to be more likely to cause an accidental overlap of the NMR signals of isomers than in species containing the $B_2N_4$ ring in the (more usual) boat conformation. This interpretation is supported by the fact that the $^1H$ NMR signals of the brominated pyrazabole $Br_2B(\mu-pzme)_2BBr_2$ are distinctly broader than those normally observed for stereochemically pure pyrazaboles.

**Experimental Section**

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY; all compounds gave satisfactory results. Melting points (uncorr.) were determined on a Mel-Temp block. NMR spectra were recorded on a Varian XL-200 spectrometer. Chemical shift data are given in ppm with positive values indicating downfield from the reference (internal $Me_4Si$ for $^1H$, external $Et_2OBF_3$ for $^{11}B$); an asterisk denotes a broad signal. Coupling constants $J$ are given in Hz. Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrometer under standard operating conditions (frequencies in cm$^{-1}$).
Potassium dihydrobis(3-methylpyrazol-1-yl)borate. The salt was prepared by basically following the earlier procedure. When a mixture of 50 g (609 mmole) of 3-methylpyrazole and 10 g (185 mmole) of potassium tetrahydroborate had been heated to 110-120 °C for 3.5 h, an almost clear melt was obtained and hydrogen evolution had essentially ceased. A few solid particles were mechanically removed and the clear melt was poured with stirring into 150 mL of benzene. The insoluble material was collected, washed with benzene and twice with petroleum ether. After drying under vacuum, the product, 39 g (96 % yield), had a mp 217 °C (lit.: 204-206 °C).

NMR data (solution in CD_{3}CN): \( \delta(1H) = 7.29 \) (1 H, d), 5.75 (1 H, d), 2.16 (3 H, s); \( \delta(11B) = -6.9 \) (t, J = 100). Additional \( ^1H \) NMR data recorded in various solvents have been reported elsewhere. IR spectrum: \( \nu(\text{B}-\text{H}) = 2400-2300 \) (s, br).

Potassium hydrotris(3-methylpyrazol-1-yl)borate. A mixture of 10 g (185 mmole) potassium tetrahydroborate and 50 g (609 mmole) 3-methylpyrazole was slowly heated to 180-190 °C and was kept at the latter temperature for approximately 4.5 h. After that time, the essentially clear melt started to solidify. The temperature was maintained for another 45 min and the reaction was then stopped. After cooling to room temperature, the material was crushed and washed with copious amounts of benzene, then with
50 mL of petroleum ether, and was dried under vacuum to give 51 g (93%) of a product mp 244-246 °C.

NMR data (solution in CD$_3$CN): $\delta$(H) = 7.41 (1 H, d, $J = 1.9$), 5.81 (1 H, d, $J = 1.7$), 2.19 (3 H, s); $\delta$(B) = -1.3 (d, $J = 105$). The boron-bonded H was not observed.

**Potassium tetrakis(3-methylpyrazol-1-yl)borate.** A mixture of 2.7 g (50 mmole) of potassium tetrahydroborate and 20 g (250 mmole) of 3-methylpyrazole was heated to maintain gentle reflux of the excess 3-methylpyrazole for 12 h. After that period of time, the mixture began to turn yellow and the reaction was stopped. The solid but moist material was crushed under benzene cover and washed with copious amounts of benzene. The colorless insoluble product was collected and dried under vacuum to give 16.9 g (90%) of product. An analytical sample was prepared by dissolving the crude material in methanol and precipitation with dichloromethane to give an asbestos-like material, mp near 340 °C (with decomposition).

NMR data (solution in CD$_3$OD): $\delta$(H) = 7.21 (1 H, d, $J = 1.8$), 5.93 (1 H, d, $J = 2.1$), 2.23 (3 H, s); $\delta$(B) = +0.9 (s, $H_{1/2} = 20$ Hz).

**1,5(7)-Dimethylpyrazabole.** A mixture of 18.25 g (0.25 mole) of trimethylamine-borane, 20.44 g (0.25 mole) of 3-methylpyrazole, and 250 mL toluene was heated to gentle reflux for 6 h. After cooling to room temperature, a small amount of gelatinous material
was filtered off and toluene was removed from the clear filtrate under reduced pressure. The remaining crude material was recrystallized from ethanol to give 16.64 g (71% yield) of a product, melting from 68-88 °C.

NMR data (solution in CDCl₃): $\delta^{(1}H) = 7.29$ (1 H, two overlapping unresolved d), 6.07 (1 H, two overlapping unresolved d), ca. 3.5** (2 H), 2.36 (s) + 2.34 (s) (3 H; ratio approximately 2:3); $\delta^{(11}B) = -9.0$ (t, $J = 105$) + $-12.2$ (t, $J = 105$) (ca. 2 B), $-10.5$ (t, $J = 105$, ca. 3 B).

Alternate Procedure. A mixture of 7.0 g (32.7 mmole) of potassium dihydrobis(3-methylpyrazol-1-yl)borate, 6.5 g (32.7 mmole) of trimethylamine-monoiodoborane,¹² and 150 mL of toluene was heated with stirring first for 12 h at 70 °C, another 12 h at 85 °C, and finally 4 h to gentle reflux. After cooling to room temperature, the mixture was filtered and toluene was evaporated from the clear filtrate. The residue was recrystallized from ethanol to give 4.7 g (61%) of material, mp 74-84 °C.

NMR data (solution in CDCl₃): $\delta^{(1}H) = 7.28$ (1 H, two overlapping unresolved d), 6.07 (1 H, two overlapping unresolved d), ca. 3.5** (2 H), 2.36 (s) + 2.34 (s) (3 H, ratio approximately 1:2); $\delta^{(11}B) = -9.0 + -12.2$ (ca 1 B), $-10.5$ (ca. 2 B). IR: $\nu(BH) = 2448$ (ms), 2395-2340 (s, br).

1,5(5)-Dimethyl-4,4,8,8-tetrabromopyrazabole. A solution of 3.0 mL (59 mmole) of Br₂ in 15 mL of CH₂Br₂ was added dropwise to a saturated solution of 1,5(7)-dimethylpyrazabole in (ca. 15 mL) CH₂Br₂. Subsequently, the mixture was refluxed
for 30 min. On cooling to room temperature, colorless crystals of the desired compound precipitated, were collected and washed with a small amount of CH$_2$Br$_2$ and then petroleum ether, and dried under vacuum. Yield: 5.42 g (67%), mp 249-257 °C.

NMR data (solution in CDCl$_3$): $\delta$(H) = 8.51* (1 H, unresolved d), 6.60* (1 H, unresolved d), 2.88* (3 H, s); 

$\delta$(11B) = -7.4 (s, $h_2$ = 25 Hz).

1,5(7)-Dimethyl-4,4,8,8-tetrakis(methylpyrazol-1-yl)pyrazabole. A mixture of 9.4 g (50 mmole) of 1,5(7)-dimethylpyrazabole and 20 g (244 mmole) of 3-dimethylpyrazole was slowly heated in an oil bath. Hydrogen evolution began at a bath temperature near 130 °C. After 6 h, the temperature was slowly increased to reflux (of the excess methylpyrazole), which was maintained for 12 h. After cooling to room temperature, 50 mL of petroleum ether was added to the viscous oil and the mixture was stirred for several h to give a solid precipitate of the desired crude product. The latter was collected, dried and recrystallized from cyclohexane to give 16.2 g (64%) of material, mp 240-242 °C.

NMR data (solution in CDCl$_3$): $\delta$(1H) of terminal pyrazolyl groups = 6.49 (1 H, d, J = 2.4), 5.72 (1 H, d, J = 2.5), 2.19 (3 H, s); of bridging pyrazolyl groups: isomer A = 7.29 (d, J = 2.4), 6.27 (d, J = 2.5), 1.79 (s); isomer B = 7.42 (d, J = 2.5), 6.55 (unresolved d), 1.72 (s), with ratio A : B ca. 2 : 1; $\delta$(11B) = -0.6 (s, $h_2$ = 40 Hz).
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References


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