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BORON–NITROGEN COMPOUNDS

XCVIII *. PREPARATION AND REACTIONS OF 2-(AZOL-1′-YL)-1,3,2-DIAZABORACYCLOALKANES

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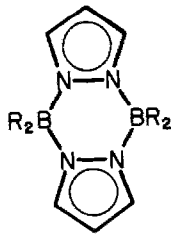
Summary

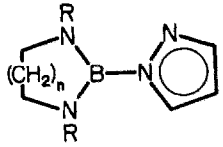
The preparation of several 1,3-dimethyl-2-(azol-1′-yl)-1,3,2-diazaboracyclohexanes is described and their NMR spectra are interpreted. The reaction of 2-(pyrazol-1′-yl)-1,3,2-diazaboracyclohexanes with pyrazoles was found to lead to 1/1 molar adducts which exist in equilibrium with the uncomplexed species, whereas *B*-tetraalkylpyrazaboles are obtained on reaction with (dimethylamino)dialkylboranes. Similar reactions of 2-(pyrazol-1′-yl)-1,3,2-diazaboracyclopentanes with several other nitrogen donor molecules were examined. The chemistry of the various species was found to be greatly affected by the N–B–N bond angle of the 1,3,2-diazaboracycloalkane ring. The reaction of pyrazabole with monoamines requires very high temperatures which, however, promote extensive ligand redistribution; no monomeric pyrazol-1-ylboranes could be obtained from the process.

Introduction

For many years studies of the chemistry of boron derivatives of pyrazole have been limited to investigations of pyrazol-1-ylborates, $[R_{4-n}Bpz_n]^-$ (pz = pyrazol-1-



(I)



(II, n = 2, 3; R = CH_3)

* For Part XCVII, see ref. 1.

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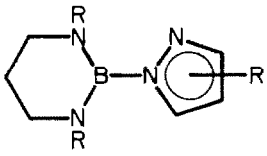
yl = $N_2C_3H_3$; $n = 1$ to 4), and pyrazaboles (= dimeric pyrazol-1-ylboranes) (I) [2]. Only most recently have monomeric pyrazol-1-ylboranes become known [3 to 6]. However, all of the isolated species contain 1,3,2-diazaboracycloalk-2-yl groups as shown in II, and there is as yet little known about the chemistry of such species.

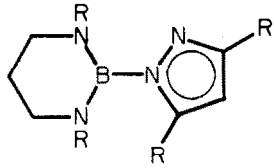
The two compounds II have been found to be fluxional [4], and the interaction of II with $n = 2$ and (pyrazole-)C-substituted derivatives thereof with pyrazoles and monoaminoboranes has recently been described [6]. The present study is concerned primarily with compounds of type II with $n = 3$.

Preparation of 2-(pyrazol-1′-yl)-1,3,2-diazaboracyclohexanes

Previously reported procedures for the preparation of monomeric 2-(pyrazol-1′-yl)-1,3,2-diazaboracycloalkanes of type II involve a condensation reaction of 2-hydro-1,3,2-diazaboracycloalkanes with pyrazole [3,4] or of α,ω-diamines with pyrazaboles of type I with R = H [5]. The former condensation has now been used to prepare the two new species III and IV by employing C-substituted pyrazoles in the reaction.



(III)



(IV)

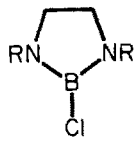
At ambient temperature, compound III (which was obtained from 3-methylpyrazole) is stereochemically nonrigid, and the boryl group migrates between the two nitrogen sites of the pyrazole moiety. This is in contrast to the corresponding 1,3,2-diazaboracyclopentane derivative (which is static with the methyl group being bonded to C(3′) of the pyrazole ring [6]) but is clearly evident from the NMR spectral data (see Experimental), which document the simultaneous presence of both possible isomers of III, i.e., with the CH_3 group located at either C(3′) (isomer a) or C(5′) (isomer b) of the pyrazole ring. This dependency of behavior on the ring size is rather surprising. It appears to be a consequence of the different N–B–N bond angles in the 1,3,2-diazaboracycloalkane rings which may lead to steric interference of the (N)CH_3 and (C)CH_3 groups in one case but not the other.

The chemical shifts of the various pyrazole nuclei of the three species IIIa, IIIb and IV are assigned using the same arguments as presented for the analogous 1,3,2-diazaboracyclopentane derivatives [6]. The individual chemical shift data (in ppm) are as follows:

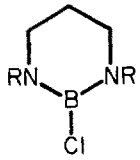
Nucleus	IIIa	IIIb	IV
C(3′)	140.8	140.8	148.9
C(4′)	104.6	104.6	103.8
C(5′)	133.2	140.3	141.2
(C)C(H_3)	12.9	10.5	13.0/10.4
H(3′)	–	7.36	–
H(4′)	6.00	6.05	5.79
H(5′)	7.51	–	–

As an alternate synthetic route, the transamination of 1,3-dimethyl-2-dimethylamino-1,3,2-diazaboracyclopentane with pyrazoles has been studied but was found to be of no preparative value [6]. The yields of the desired products were exceedingly low and substantial amounts of by-products containing four-coordinate boron were obtained. Surprisingly, it was now found that 1,3-dimethyl-2-ammino-1,3,2-diazaboracyclohexane as well as the corresponding 2-dimethylamino derivative react with pyrazole to yield 70% or more of the desired pyrazol-1-yl-borane II with $n = 3$; the process requires only a relatively short time and low reaction temperatures.

This dependence of the transamination reaction on the ring size of the starting 1,3,2-diazaboracycloalkane is rather significant. The observed formation of substantial quantities of by-products containing four-coordinate boron in the synthesis of II with $n = 2$ suggests that the Lewis acidity of the boron in II may be a governing factor for the overall success of the transamination procedure. Indeed, the N–B–N bond angle of V is only 110.8° [7] but is 120.8° in VI [8].



(V, R = CH_3)



(VI, R = CH_3)

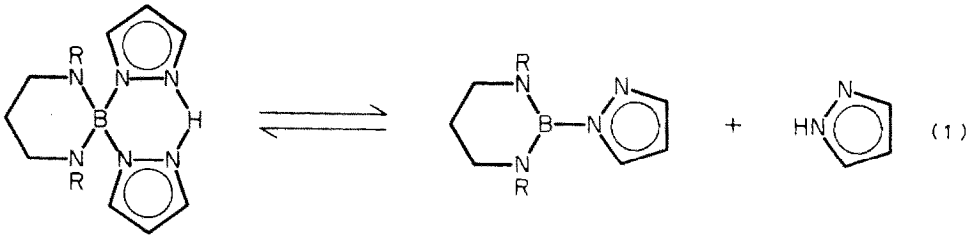
In other words, the cited bond angle in V is almost that for a tetrahedral environment of boron and thus may promote a greater Lewis acidity of the boron atom in a five-membered BN_2C_2 ring as compared to that in a six-membered BN_2C_3 ring, e.g., VI. This conclusion is in direct agreement with the above experimental data. It would also suggest that compounds of type II with $n = 3$ should be less prone to form adducts than those with $n = 2$. A number of such latter 1/1 molar adducts of II ($n = 2$) with pyrazoles have recently been described [6], and we have now also studied the interaction of compounds of type II with $n = 3$ and pyrazoles.

Interaction of pyrazoles with 1,3-dimethyl-2-(pyrazol-1′-yl)-1,3,2-diazaboracyclohexanes

When the pyrazol-1-ylborane II with $n = 3$ is combined with an equimolar quantity of pyrazole an exothermic reaction yields a colorless solid which can be recrystallized from hexane. A ^{11}B NMR spectrum of this material (solution in $CDCl_3$) exhibits two resonance signals, $\delta(^{11}B)$ 24.6 ($h_{1/2}$ 110 Hz) and 1.2 ppm ($h_{1/2}$ 25 Hz) *, respectively. The integration ratio of the two peaks changes with the concentration, i.e., on dilution the concentration of the trigonal boron increases. On addition of excess free pyrazole, however, the concentration of four-coordinate boron increases. Based on this observation (and supporting ^1H and ^{13}C NMR spectral data), the desired adduct VII seems to be in equilibrium with the starting materials as shown in eq. 1.

An estimate of the equilibrium constant for the dissociation of VII was obtained

* $h_{1/2}$ = half-maximum bandwidth.



(VII)

by ^{11}B NMR spectral data (see Experimental Section), and a value of approximately 0.09 mol/l was obtained. Additional NMR data on VII are readily explained on the basis of this equilibrium (see Experimental Section).

The adduct formation of the 1,3,2-diazaboracyclohexane derivatives was also studied by treating equimolar quantities of II ($n = 3$), III and IV with pyrazole and/or methylpyrazoles. In view of the anticipated dissociation according to eq. 1 no simple NMR spectra were to be expected. Additional complications arise from the simultaneous presence of two isomers of III (see above) and, if two different pyrazoles are contained in a given adduct of type VII, these latter can dissociate in different manner. For example, equilibration of the pyrazole adduct of III is expected to yield a total of eleven species in solution: six different adducts, three monomeric pyrazol-1-ylboranes and two different pyrazoles. Indeed, the ^{1}H and ^{13}C NMR spectra of the various mixtures of III and IV, respectively, with pyrazoles frequently exhibit broad almost featureless signals (see Experimental Section). The ^{11}B NMR spectra are characterized in all cases by the expected two signals near $\delta(^{11}B)$ 24 and 1 ppm, respectively, indicating the presence of both three- and four-coordinate boron, with the latter usually predominating by a factor of about 3. In contrast to the corresponding 1,3,2-diazaboracyclopentane species, this is even the case when IV is treated with 3,5-dimethylpyrazole. This latter observation indicates that a considerable steric influence is exerted by the (pyrazole-)methyl groups. With the annular N–B–N bond angle of IV presumably being wider than in the corresponding 1,3,2-diazaboracyclopentane derivative, there appears to be sufficient room available for the (pyrazole-)methyl groups being accomodated above and below the N–B–N plane; and, despite the weaker acceptor property of boron in IV, adduct formation predominates in this case.

Interaction of 1,3-dimethyl-2-(pyrazol-1′-yl)-1,3,2-diazaboracyclopentane with nitrogen bases

In view of the documented adduct formation of monomeric pyrazol-1-ylboranes of type II and (pyrazole)C-substituted derivatives thereof with pyrazoles, such adduct formation with other nitrogen bases has also been examined. However, since the boron atom of II with $n = 2$ exhibited the stronger Lewis acid character as compared to II with $n = 3$, these studies were limited to derivatives of the five-membered BN_2C_2 ring system (i.e., II with $n = 2$). In general, specific species were not isolated but rather the two reactants were combined in 1/1 molar ratio and ^{11}B NMR data recorded on the resultant materials.

Pyridine does not form an adduct with II ($n = 2$). Rather, on mixing the reagents

(in $CDCl_3$) and recording a ^{11}B NMR spectrum of this mixture, only the signal of II ($n = 2$) is observed, and the pyridine is readily recovered from the mixture by simple distillation. A mixture of 2,6-dimethylpyridine (in slight molar excess) and II ($n = 2$) in $CDCl_3$ exhibits two signals, $\delta(^{11}B)$ 24.6 and 3.9 ppm, indicating partial adduct formation. The same observation (with $\delta(^{11}B)$ 26.0 and 4.0 ppm, respectively) is made on mixing II ($n = 2$) with a slight molar excess of pyrrole (in $CDCl_3$).

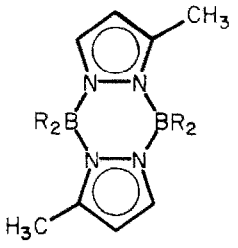
On mixing II ($n = 2$) with imidazole, only one ^{11}B NMR signal, $\delta(^{11}B)$ 3.9 ppm ($h_{1/2}$ 20 Hz) is observed. The relatively sharp resonance line suggests a BN_4 environment at boron. However, ^1H and ^{13}C NMR spectra are inconclusive and are characterized by extremely broad and featureless lines suggesting extensive exchange processes. The latter also holds true for a 1/1 molar mixture of 1,3-dimethyl-2-(pyrrol-1′-yl)-1,3,2-diazaboracyclopentane with pyrazole, exhibiting $\delta(^{11}B)$ 4.2 ppm ($h_{1/2}$ 80 Hz). Since in these cases the N-bonded proton cannot complete a six-membered heterocycle as in VII, one may assume that it migrates extensively between the various nitrogen sites of the formed adduct probably including the $N(CH_3)$ atoms. This feature is likely to account for the observed ^1H and ^{13}C NMR spectra.

1,2,4-Triazole and II ($n = 2$) interact and, after prolonged standing, a crystalline product is obtained exhibiting $\delta(^{11}B)$ 3.8 ppm ($h_{1/2}$ 110 Hz) as well as a minor peak at $\delta(^{11}B)$ 24.2 ppm. This observation illustrates that adduct formation is the major process. The small amount of three-coordinate boron may be due to partial dissociation of the adduct or due to an auto-rearrangement analogous to that observed for other compounds of type II with $n = 2$ [3,6]. Neither the ^1H nor the ^{13}C NMR spectrum is that expected for a pure compound similar to VII (see Experimental Section for details).

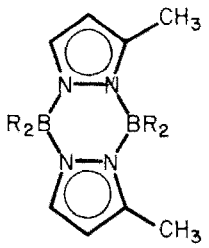
Triethylamine and II ($n = 2$) do not interact, and the former is readily removed from a mixture of the two compounds (under vacuum at ambient temperature). A mixture of II ($n = 2$) with diethylamine exhibits two ^{11}B NMR signals, $\delta(^{11}B)$ 26.1 and 3.6 ppm. On prolonged standing of the (liquid) mixture, some crystalline material is obtained and is identified (by NMR data) as the pyrazole adduct of II ($n = 2$). In addition, 1,3-dimethyl-2-diethylamino-1,3,2-diazaboracyclopentane is formed. Hence, complexation of the initial reactants may be the first process to occur. Subsequently, transamination generates free pyrazole and the 2-diethylamino-1,3,2-diazaboracyclopentane, and the former interacts with II ($n = 2$) to give the cited adduct. This overall process is well in line with the observations made on reaction of 2-amino-1,3,2-diazaboracyclopentanes with pyrazoles [6].

Interaction of 1,3-dimethyl-2-(pyrazol-1′-yl)-1,3,2-diazaboracyclohexane with (dimethylamino)dialkylboranes

(Dimethylamino)dialkylboranes have been found to react with 2-(pyrazol-1′-yl)-1,3,2-diazaboracyclopentanes by an exchange of the dimethylamino versus the pyrazolyl group to yield 2-dimethylamino-1,3,2-diazaboracyclopentanes and *B*-tetraalkylpyrazaboles [6]. An analogous reaction has now been found to occur also with 2-(pyrazol-1′-yl)-1,3,2-diazaboracyclohexanes. This observation lends credence to the previously postulated pathway of this ligand exchange for which the formation of the *B*-tetraalkylpyrazaboles is viewed as the driving force. However, since III is really a mixture of the isomers IIIa and IIIb, its reaction with (dimethylamino)diethylborane could potentially lead to two isomeric pyrazaboles, i.e., VIIIa and VIIIb.

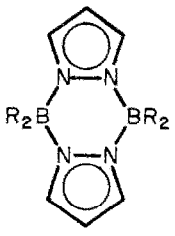


(VIIIa)

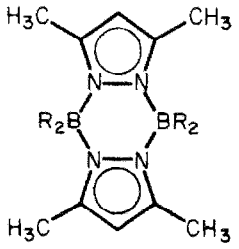


(VIIIb)

(R = C_2H_5)



(VIIIc)



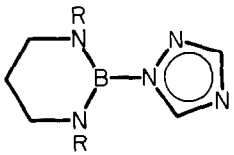
(VIIId)

The *trans* species VIIIa should be favored for steric reasons and appears to be the exclusive product. This conclusion is derived from the proton-decoupled ^{13}C NMR spectrum of the reaction product in which only one (sharp) signal is observed for the $(CH_2)CH_3$ carbon atoms with $\delta(^{13}C)$ 8.9 ppm. Furthermore, 200-MHz ^1H NMR data on the above product were compared with those of VIIIc and VIIId. The ^1H NMR spectrum of VIIIc exhibits the expected triplet-quartet pattern for the protons of the four equivalent (boron-bonded) ethyl groups: a triplet with $\delta(^1H)$ 0.48 ppm and a quartet with $\delta(^1H)$ 0.68 ppm. In the ^1H NMR spectrum of VIIId, the corresponding signals are observed with $\delta(^1H)$ 0.38 (t) and 0.76 (q), respectively. If isomer VIIIb were formed in the reaction cited above, its ^1H NMR spectrum in the same region would be expected to be a superposition of both VIIIc and VIIId since one half of VIIIb is identical with VIIIc and the other one with VIIId. However, this is not observed. Rather, the spectrum consists of a triplet with $\delta(^1H)$ 0.43 ppm (exactly intermediate between the triplets observed for VIIIc and VIIId) and a complex multiplet centered at $\delta(^1H)$ 0.73 for all eight $(B)CH_2$ protons. These data are then consistent with structure VIIIa. The complex multiplet for the $(B)CH_2$ protons reduces to a quartet (rather than a singlet) on decoupling the triplet for the ethyl-CH_3 protons. This observation indicates restricted rotation of the boron-bonded CH_2 groups in VIIIa.

1,3-Dimethyl-2-(1′,2′,4′-triazol-1′-yl)-1,3,2-diazaboracyclohexane

In conjunction with the present work it seemed desirable to synthesize and characterize at least one related triazol-1-ylborane. A 1,3,2-diazaboracyclohexane derivative was chosen in order to avoid an auto-rearrangement of the material as was observed for 1,3,2-diazaboracyclopentane derivatives [3,6] and thus to have available

a compound for later variable-temperature NMR spectroscopic studies. Hence, compound VIII was prepared by refluxing 1,3-dimethyl-1,3,2-diazaboracyclohexane with an equimolar quantity of 1,2,4-triazole.



(VIII)

The freshly distilled compound exhibits only one signal in the ^{11}B NMR spectrum (solution in $CDCl_3$) with $\delta(^{11}B)$ 23.3 ppm ($h_{1/2}$ 150 Hz) confirming the trigonal environment of the boron. The ^1H NMR spectrum exhibits two overlapping singlets $\delta(^1H)$ 8.09/8.03 ppm (2H, C(3′)- and C(5′)-bonded), a triplet $\delta(^1H)$ 2.97 ppm (4H, NCH_2), a singlet with $\delta(^1H)$ 2.39 ppm (6H, NCH_3), and an unresolved multiplet with $\delta(^1H)$ 1.94 ppm (2H, CCH_2C). The two signals $\delta(^{13}C)$ 151.8 and 146.2 ppm observed in the ^{13}C NMR spectrum are readily assigned to C(3′) and C(5′), i.e., the triazole moiety. Their broadness suggests borotropism to occur among the various nitrogen sites of the triazole. It remains to be seen if this involves only a 1,2-shift or a 1,3-shift or both in an intra- or inter-molecular process. The remaining signals in the ^{13}C NMR spectrum are readily assigned in consonance with the spectra of other 1,3,2-diazaboracyclohexane derivatives.

Interaction of pyrazabole with monoamines

Since α,ω-diamines condense with pyrazabole (I, R = H) to yield species of type II via symmetrical cleavage of I [5], the preparation of additional monomeric pyrazol-1-ylboranes by reaction of pyrazabole with secondary monoamines was also attempted. However, when a neat 1/4 molar mixture of pyrazabole and diisopropylamine (b.p. 84°C) is refluxed for a prolonged period of time, no reaction whatsoever occurs and the starting materials are recovered unchanged. When a 4/1 molar mixture of diisobutylamine (b.p. 138°C) and pyrazabole is refluxed, some hydrogen is released quickly but then the reaction turns very sluggish. Hydrogen evolution ceases completely after about two weeks of reflux; even at that time less than 50% of the calculated quantity of hydrogen gas has evolved. After distillative removal of unreacted diisobutylamine, the ^{11}B NMR spectrum of the remaining raw product exhibited three signals, $\delta(^{11}B)$ 24.1, 0.1, and −5.5 ppm, respectively. A small amount of crystalline material separated after prolonged standing. This material shows signals for $\delta(^{11}B)$ 0.2 and −4.9 ppm and the mass spectrum suggests it to be a mixture (which could not be separated) of the pyrazabole $H_2BpzBH(NR_2)$ with $R = i\text{-}C_4H_9$ and a species of the composition $H_4B_2pz(NR_2)$ ($R = i\text{-}C_4H_9$) but of uncertain structure. The mass spectrum of the remaining liquid (which could not be separated by fractional distillation) indicates the presence of unreacted diisobutylamine as well as some high molecular weight boron-containing species, perhaps tris(diisobutylamino)borane. In view of the fact that both *N,N′*-dimethylethylenediamine (b.p. 119°C) and *N,N′*-dimethylpropylenediamine (b.p. 123°C) react readily and quantitatively with pyrazabole, the above reaction was not further pursued. On

the other hand, when a 4/1 molar mixture of *N*-methylaniline (b.p. 196°C) and pyrazabole is refluxed for a few hours, four molar equivalents of hydrogen evolve quite readily. The resultant product proved to be a mixture of tris(methylphenylamino) borane, $B[N(CH_3)(C_6H_5)]_3$, $\delta(^{11}B)$ 31.3, and (primarily) 4,4,8,8-tetrakis(pyrazol-1-yl)pyrazabole (I, R = pz). It is possible that the initial product is indeed the expected bis(methylphenylamino)pyrazol-1-ylborane which, under the reaction conditions undergoes ligand redistribution to afford the cited products.

Conclusions

Significant differences in the chemical behavior exist between monomeric pyrazol-1-yl derivatives of boron depending on the ring size of the heterocycle in which the boron is incorporated. The boron atom in 1,3,2-diazaboracyclopentane derivatives is considerably more acidic than that in a 1,3,2-diazaboracyclohexane system. Hence, the former species coordinate quite readily with free pyrazoles and several other nitrogen bases whereas pyrazole adducts of 1,3-dimethyl-2-(pyrazol-1′-yl)-1,3,2-diazaboracyclohexane were found to exist only in equilibrium with the free Lewis acid and base. The difference in Lewis acidity of the boron in 1,3,2-diazaboracycloalkanes seems to be a function of the annular N–B–N bond angle. Its significance can be seen by the different results obtained on transamination of 2-amino-1,3,2-diazaboracycloalkanes with pyrazole. In contrast, the interaction of 2-(pyrazol-1′-yl)-1,3,2-diazaboracycloalkanes with (dimethylamino)dialkylboranes is not influenced by the ring size since the overall driving force in the formation of *B*-tetraalkylpyrazaboles. On the other hand, the wider N–B–N bond angle of the 1,3,2-diazaboracyclohexanes permits adduct formation even in those cases where the corresponding five-membered ring derivative was found to be unreactive. Hence, in addition to the Lewis acidity of the boron, steric effects also seem to play a distinct role in the adduct formation of 2-(pyrazol-1′-yl)-1,3,2-diazaboracycloalkanes.

Studies on the interaction of pyrazabole with monoamines document the stabilizing factor of boron being incorporated into a heterocyclic system with respect to the formation of monomeric pyrazol-1-ylboranes.

Experimental

All reactions and transfers were carried out under a dry argon cover. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined in sealed capillaries on a Mel-Temp block. Proton NMR spectra were recorded on a Varian T-60, EM-390 or XL-200 spectrometer and are referenced to TMS; ^{11}B (reference: $(C_2H_5)_2OBF_3$) NMR spectra were recorded on a Varian FT-80A instrument. All chemical shift data are reported in ppm with positive values indicating downfield from the cited (unless otherwise noted: external) references. The spectra were normally obtained at ambient temperature. An asterisk denotes a relatively broad unresolved signal; abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet. Infrared spectra were recorded on a Perkin–Elmer Model 621 instrument under standard operating procedures. Wavenumbers are given in cm^{-1}, abbreviations of intensities are: s = strong, m = medium, w = weak, v = very, (sh) = shoulder, (br) = broad. Mass spectral data were obtained on a Hitachi–Perkin–Elmer RMU-7

instrument at 70 eV. Data are listed only for ions with a relative abundance (in parentheses) of 5% or greater.

Azoles were commercial products. They were dried over a small amount of metallic sodium and then distilled or sublimed. 1,3-Dimethyl-1,3,2-diazaboracyclohexane [9], 1,3-dimethyl-2-ammino- [10] as well as 1,3-dimethyl-2-dimethylamino-1,3,2-diazaboracyclohexane [11], 1,3-dimethyl-2-(pyrazol-1'-yl)-1,3,2-diazaboracyclopentane [4], 1,3-dimethyl-2-(pyrrol-1'-yl)-1,3,2-diazaboracyclopentane [12], pyrazabole [13], (dimethylamino)diethylborane [14] and (dimethylamino)di-n-propylborane [15] were prepared by the indicated literature procedures.

1,3-Dimethyl-2-(methylpyrazol-1'-yl)-1,3,2-diazaboracyclohexane (III)

A mixture of 29.1 g (260 mmol) of 1,3-dimethyl-1,3,2-diazaboracyclohexane and 23.0 g (260 mmol) of 3-methylpyrazole was refluxed for 25 h. Subsequent distillation over a 30-cm silver-mantle column yielded 49 g (98%) of III, b.p. 78°C/1 Torr. Analysis: Found: C, 56.06; H, 9.16; N, 29.01; B, 5.66. $C_9H_{17}N_4B$ calcd.: C, 56.30; H, 8.92; N, 29.17; B, 5.62%.

NMR data: $\delta(^1H)$ (neat) 7.41*/7.32* (1H), 6.97* (1H), 2.92 (t, 4H), 2.33/2.29/2.26 (three overlapping s, 9H), 1.88 (p, 2H); (solution in CCl_4) 7.31*/7.24 (1H), 5.98* (s, 1H), 2.96 (t, 4H), 2.38/2.31/2.22 (three overlapping s, 9H), 1.94 (p, 2H); (solution in $CDCl_3$) 7.53* + 7.36(d) (1H), 6.04* (two overlapping d, 1H), 2.97 (t, 4H), 2.44(s) + 2.32/2.31(two overlapping s) + 2.23(s) (9H), 1.97 (p, 2H). $\delta(^{11}B)$ (neat) 25.9 ($h_{1/2}$ 560 Hz); (solution in $CDCl_3$) 24.5 ($h_{1/2}$ 130 Hz). $\delta(^{13}C)$ (neat) 148.6* (s), 140.8 (d, J 181 Hz), 140.3 (s), 133.2 (d, J 182 Hz), 104.6 (d, J 171 Hz), 48.1 (t, J 134 Hz), 36.7 (q, J 134 Hz), 25.9 (t, J 126 Hz), 12.9 (q, J 126 Hz), 10.5 (q, J 126 Hz).

1,3-Dimethyl-2-(3',5'-dimethylpyrazol-1'-yl)-1,3,2-diazaboracyclohexane (IV)

A mixture of 15.4 g (160 mmol) of 3,5-dimethylpyrazole and 19.6 g (175 mmol) of 1,3-dimethyl-1,3,2-diazaboracyclohexane was refluxed for 35 h. Subsequent distillation over a 30-cm silver-mantle column yielded 31.2 g (93%) of IV, b.p. 101–104°C/1 Torr. Analysis: Found: C, 58.41; H, 9.41; N, 27.06; B, 4.93. $C_{10}H_{19}N_4B$ calcd.: C, 58.28; H, 9.29; N, 27.19; B, 5.25%.

NMR data: $\delta(^1H)$ (solution in $CDCl_3$) 5.79 (s, 1H), 2.97 (m, 4H), 2.35 (s, 6H), 2.27 (s, 3H), 2.17 (s, 3H), 1.96 (p, 2H). $\delta(^{11}B)$ (neat) 26.7 ($h_{1/2}$ 400 Hz). $\delta(^{13}C)$ (neat) 148.9 (s), 141.2 (s), 103.8 (d, J 170 Hz), 47.7 (t, J 133 Hz), 36.0 (q, J 134 Hz), 25.9 (t, J 126 Hz), 13.0 (q, J 126 Hz), 10.4 (q, J 126 Hz).

Mass spectrum: Parent ion m/z 206.

Preparation of 1,3-dimethyl-2-(pyrazol-1'-yl)-1,3,2-diazaboracyclohexane (II, n = 3) by transamination

(a) From 1,3-dimethyl-2-ammino-1,3,2-diazaboracyclohexane. A mixture of 2.7 g (40 mmol) of pyrazole and 5.0 g (40 mmol) of 1,3-dimethyl-2-ammino-1,3,2-diazaboracyclohexane was refluxed for 5 h. Distillation over a 30-cm silver-mantle column yielded 5.1 g (71%) of II ($n = 3$) characterized by spectral data [3].

(b) From 1,3-dimethyl-2-dimethylamino-1,3,2-diazaboracyclohexane. A mixture of 2.7 g (40 mmol) of pyrazole and 6.5 g (42 mmol) of 1,3-dimethyl-2-dimethylamino-1,3,2-diazaboracyclohexane was refluxed for 5 h; work-up as above gave II ($n = 3$) in 65% yield.

Interaction of pyrazoles with 1,3-dimethyl-2-(pyrazol-1′-yl)-1,2,3-diazaboracyclohexanes (general procedure)

Equimolar amounts of a (liquid) freshly distilled 1,3-dimethyl-2-(pyrazol-1′-yl)-1,3,2-diazaboracyclohexane and a pyrazole are combined with stirring. Slight warming of the mixture yields a viscous liquid product which, depending on the nature of the pyrazole moieties, may solidify on standing. The products are characterized by NMR spectroscopic data (without further purification).

(a) Pyrazole / 1,3-dimethyl-2-(pyrazol-1′-yl)-1,3,2-diazaboracyclohexane. The product solidified on standing, m.p. 73°C. NMR data (solution in $CDCl_3$): $\delta(^1H)$ 8.08* (s, 1H), 7.68*/7.57(d)/7.50*/7.19(d) (4H), 6.28*/6.17(t) (2H), 2.98(t)/2.63(m) (4H), 1.96(m)/1.54(m) (2H); $\delta(^{11}B)$ 24.6 ($h_{1/2}$ 110 Hz), 1.2 ($h_{1/2}$ 25 Hz) (ratio peak 1.2/24.6 = 3.2 for a 1.2 *M* solution, = 7.6 for a 0.6 *M* solution in a 0.6 *M* solution of free pyrazole); $\delta(^{13}C)$ (proton-decoupled) 141.3, 135.0, 134.0, 133.2, 104.9, 104.5, 49.6, 48.5, 37.2, 34.0, 26.1, 24.2.

(b) Pyrazole / 1,3-dimethyl-2-(methylpyrazole-1′-yl)-1,3,2-diazaboracyclohexane. Viscous oil. NMR data (solution in $CDCl_3$): $\delta(^1H)$ 9.07 (s, 1H), 7.75*/7.64*/7.36*/7.05(d) (3H), 6.28(t)/6.18(t) (1H), 6.03(d)/5.94(d) (1H), 2.97(t)/2.63(m) (4H), 2.43(s)/2.34(s)/2.30(s)/2.22(s) (9H), 1.95(m)/1.58(m) (2H); $\delta(^{11}B)$ 24.7 ($h_{1/2}$ 110 Hz), 0.8 ($h_{1/2}$ 20 Hz); $\delta(^{13}C)$ (proton-decoupled) 148.2*, 140.2 to 139.6 (overlapping broad lines), 135 to 133 (overlapping broad lines), 104.1*, 49.4 to 48.0 (overlapping broad lines), 36.7*, 35.1, 33.5, 25.7, 24.2*, 13.2 to 11.4 (overlapping broad lines).

(c) 3-Methylpyrazole / 1,3-dimethyl-2-(methylpyrazol-1′-yl)-1,3,2-diazaboracyclohexane. Viscous oil. $\delta(^{11}B)$ (solution in $CDCl_3$) 24.8 ($h_{1/2}$ 120 Hz), 0.4 ($h_{1/2}$ 20 Hz).

(d) 3,5-Dimethylpyrazole / 1,3-dimethyl-2-(methylpyrazol-1′-yl)-1,3,2-diazaboracyclohexane. Solidified on standing (no sharp melting point; melting with apparent decomposition). $\delta(^{11}B)$ (solution in $CDCl_3$) 24.7 ($h_{1/2}$ 160 Hz), 0.1 ($h_{1/2}$ 50 Hz).

(e) 3,5-Dimethylpyrazole / 1,3-dimethyl-2-(3′,5′-dimethylpyrazol-1′-yl)-1,3,2-diazaboracyclohexane. A slight excess of the free pyrazole was used. Product solidified on standing, melting point 116°C. NMR data (solution in $CDCl_3$): $\delta(^1H)$ 8.76*, 8.20(s), 5.87(s), 2.96* (m), 2.44 (s), 2.25 (s), 1.74 (m); $\delta(^{11}B)$ 24.7, 1.6, 0.4; $\delta(^{13}C)$ (proton-decoupled) 151.8, 148.3, 146.1, 143.8, 103.6, 49.5, 37.1, 24.1, 11.7.

Interaction of 1,3-dimethyl-2-(pyrazol-1′-yl)-1,3,2-diazaboracyclopentane (II, n = 2) with nitrogen bases (general procedure)

Equimolar amounts of freshly distilled 1,3-dimethyl-2-(pyrazol-1′-yl)-1,3,2-diazaboracyclopentane and the nitrogen bases are combined with stirring. Unless already liquid, the mixture is slightly warmed to liquefy all material. After cooling to room temperature, the resultant product is examined.

(a) With 1,2,4-triazole. Viscous product which crystallized after very long standing (several months). NMR data (solution in $CDCl_3$): $\delta(^1H)$ 8.40*/8.23*/8.10*/7.95* (2H), 7.59* (2H), 7.25* (1H), 6.26 (t, 1H), 3.14* (s, 4H), 2.25/2.23 (6H). $\delta(^{11}B)$ 24.7 (very small), 3.2 ($h_{1/2}$ 110 Hz). $\delta(^{13}C)$ (proton-decoupled) 153.5 to 151.5 and 149.2 to 147.3 (overlapping broad lines), 140.1*, 133.5*, 105.2, 50.8, 34.6.

(b) With imidazole. Viscous product. NMR data (solution in $CDCl_3$): $\delta(^{11}B)$ 3.9 ($h_{1/2}$ 70 Hz). $\delta(^{13}C)$ 140*, 136*, 126*, 122*, 119*, 109*, 103*, 53*, 50.9, 48*, 34*.

1/1 Molar adduct of pyrazole with 1,3-dimethyl-2-(pyrrol-1'-yl)-1,3,2-diazaboracyclopentane

A mixture of 5.21 g (32 mmol) of 1,3-dimethyl-2-(pyrrol-1'-yl)-1,3,2-diazaboracyclopentane and 2.17 g (32 mmol) of pyrazole was warmed sufficiently to melt all of the pyrazole. The product solidified on cooling to room temperature and was characterized by NMR spectroscopy (solution in $CDCl_3$): $\delta(^1H)$ 7.98 (d, 2H), 7.52* (1H), 7.24* (2H), 6.68 (unresolved m, 3H), 3.53 (s, 4H), 2.78(s)/2.76(s) (6H). $\delta(^{11}B)$ 4.2 ($h_{1/2}$ 80 Hz). $\delta(^{13}C)$ (proton-decoupled) 141*, 136*, 127*, 124*, 120*, 112*, 109*, 102*, 53*, 50.9, 49*, 35*.

Reaction of (dimethylamino)dialkylboranes with 1,3-dimethyl-2-(pyrazol-1'-yl)-1,3,2-diazaboracyclohexane (II, n = 3) (general procedure)

A flask equipped with dropping funnel, reflux condenser and magnetic stirrer is charged with the 1,3-dimethyl-2-(pyrazol-1'-yl)-1,3,2-diazaboracyclohexane and is cooled to 0°C. An equimolar amount of (dimethylamino)dialkylborane (alkyl = C_2H_5, n-C_3H_7) is added with stirring and the mixture is warmed to room temperature. Subsequently the mixture is heated to gentle reflux for several hours. The resultant 1,3-dimethyl-2-dimethylamino-1,3,2-diazaboracyclohexane is distilled off under reduced pressure and the residual 4,4,8,8-tetraalkylpyrazabole is purified by recrystallization; yields of the two major products range from 70 to 85%. Characterization by spectroscopic data: *B*-tetraethylpyrazabole [16]; *B*-tetra-n-propylpyrazabole [6].

1,3-Dimethyl-2-(1',2',4'-triazol-1'-yl)-1,3,2-diazaboracyclohexane (VIII)

A mixture of 6.9 g (100 mmol) of 1,2,4-triazole (recrystallized from $CHCl_3$) and 22.4 (200 mmol) of 1,3-dimethyl-1,3,2-diazaboracyclohexane was refluxed for 18 h. Subsequent distillation yielded 7 g (40%) of VIII, b.p. 195–200°C/3 Torr, m.p. approximately 74°C (with apparent decomposition or rearrangement). Analysis: Found: C, 45.71; H, 7.96; N, 38.87; B, 5.94. $C_7H_{14}N_5B$ calcd.: C, 46.96; H, 7.88; N, 39.12; B, 6.04%.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ 8.09(s)/8.03(s) (2H), 2.97 (t, 4H), 2.39 (s, 6H), 1.94 (m, 2H). $\delta(^{11}B)$ 23.3 ($h_{1/2}$ 150 Hz) (another peak near −4.1 is very small). $\delta(^{13}C)$ (proton-decoupled) 151.8*, 146.2*, 47.3, 35.9, 24.9 (very small peaks: 47.9, 34.5, 25.8).

Interaction of pyrazabole with N-methylaniline

A mixture of 22.4 g *N*-methylaniline and 8.36 g pyrazabole was refluxed for 28 h. On cooling to room temperature the material solidified. It was washed several times with toluene and 13.4 g of colorless solid, m.p. 211°C, remained and was identified (NMR, IR and mass spectral data) as tris(methylphenylamino)borane, $\delta(^{11}B)$ 31.3 ppm. The toluene washings were combined and solvent stripped off to leave a glassy residue. NMR data suggested this to be a mixture of pyrazol-1-ylpyrazaboles (primarily tetrakis(pyrazol-1-yl) pyrazabole) [17] which was not further characterized.

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