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BORON—NITROGEN COMPOUNDS

LXXXVII *. 1,3-DIMETHYL-2-(PYRAZOL-1′-YL)-1,3,2-DIAZABORACYCLOHEXANE, A MONOMERIC PYRAZOL-1-YLBORANE CONTAINING TRIGONAL BORON

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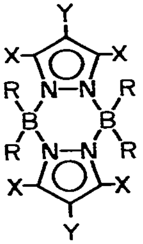
Summary

1,3-Dimethyl-2-(pyrazol-1′-yl)-1,3,2-diazaboracyclohexane has been prepared by thermolysis of a mixture of 1,3-dimethyl-1,3,2-diazaboracyclohexane with pyrazole. Spectroscopic data confirm the monomeric nature of the compound, which is the first known example of a pyrazol-1-ylborane containing a trigonal boron atom.

Introduction

Although a wide variety of boron derivatives of pyrazoles are known [2], only one example of a monomeric pyrazol-1-ylborane has been described in the literature [3]. However, in this latter case the 3,5-bis(trifluoromethyl)-pyrazol-1-ylborane is coordinated with trimethylamine to provide for four-coordination about the boron atom. All other pyrazol-1-ylboranes are reported to exist in the dimeric "pyrazabole" structure I.



(I)

Very few studies on pyrazaboles other than their syntheses have been

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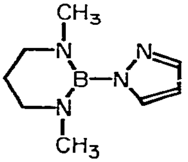
* For part LXXVI, see ref. 1.

reported. Two spectroscopic investigations on such species [4,5] are primarily concerned with their mass spectral fragmentation and some additional spectroscopic data are scattered throughout the literature [2]. Within a study of the chemistry and electronic nature of pyrazaboles, the synthesis of various B-amino derivatives and similar species containing electron-donating exocyclic boron substituents was of particular interest.

Most of the known pyrazaboles of type I feature, as boron substituents, either hydrogen, halogen, alkyl or aryl groups. In addition, two B-organyloxy derivatives have been described and the few known B-amino species feature exocyclic pyrazol-1-yl groups exclusively [2].

Results and discussion

When the parent pyrazabole (I, R = X = Y = H) is heated with *o*-phenylenediamine, the B_2N_4 ring system is cleaved and a borazine derivative is obtained [6]. This observation suggests that the preparation of B-amino-substituted pyrazaboles by replacement of boron-bonded hydrogen by an amino group is difficult to achieve. However, when a mixture of 1,3-dimethyl-1,3,2-diazaboracyclohexane and pyrazole is heated, hydrogen is slowly evolved and monomeric 1,3-dimethyl-2-(pyrazol-1′-yl)-1,3,2-diazaboracyclohexane (II) is formed.

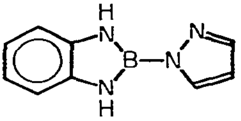


(II)

The monomeric nature of the species is clearly demonstrated by the spectroscopic data. The 80 MHz ^1H NMR spectrum (solution in CD_2Cl_2) consists of a not completely resolved doublet with $\delta(^1H)$ 7.69 ppm (1 H), a doublet with $\delta(^1H)$ 7.55 ppm (1 H), and a triplet with $\delta(^1H)$ 6.35 ppm (1 H) for the hydrogen atoms of the pyrazole ring; a sharp singlet with $\delta(^1H)$ 2.44 ppm (6 H) for those of the methyl groups; and a triplet ($\delta(^1H)$ 3.03 ppm, 4 H) and a quintuplet ($\delta(^1H)$ 1.99 ppm, 2 H) for those of the anular CH_2 groups. The nonequivalence of C(3) and C(5) of the pyrazole ring, which also disputes a dimeric pyrazabole structure for the species, is evident from the ^{13}C NMR spectrum of the compound (solution in $CDCl_3$); signals with $\delta(^{13}C)$ 141.1, 132.8 and 105.2 ppm are readily assigned to the carbon atoms of the pyrazole ring. The signal $\delta(^{13}C)$ 37.1 ppm is assigned to the carbon atoms of the two methyl groups, while those of the anular methylene groups of the 1,3,2-diazaboracyclohexane ring are observed at $\delta(^{13}C)$ 48.4 (C(4,6)) and 26.1 (C(5)) ppm, respectively. The ^{11}B NMR spectrum of the (neat) compound exhibits only one signal, $\delta(^{11}B)$ 24.6 ppm, which again confirms the presence of three-coordinate boron and, thus the monomeric nature of the compound. The low quality ^{14}N NMR spectrum (neat compound) shows a broad signal with $\delta(^{14}N)$ near —372 ppm which is assigned to the two nitrogen atoms of the boron-containing heterocycle, and a reasonably sharp signal with $\delta(^{14}N)$ near —156 ppm for the boron-bonded atom of the pyrazole ring with a shoulder on the lowfield side, indicating the N(2) pyrazole nitrogen.

It is best to employ at least a 10% excess of 1,3-dimethyl-1,3,2-diazaboracyclohexane in the above reaction. Otherwise, a 1/1 molar complex of II with pyrazole is obtained as a by-product, lowering the yield of the desired material and complicating the purification of II. Furthermore, rigorous exclusion of moisture is mandated to prevent the formation of small amounts of bis(1,3-dimethyl-1,3,2-diazaboracyclohex-2-yl) oxide; contamination of II with the former species [7] is readily seen in the mass spectrum of the material.

The successful synthesis of II provides an explanation for the observation that a B-amino-substituted pyrazabole cannot be isolated when *o*-phenylenediamine is allowed to react with the parent pyrazabole. It is likely that III is the initial product of this reaction but, under the prevailing conditions, it eliminates pyrazole with the formation of a borazine derivative.



(III)

In conjunction with the illustrated existence of II, this interpretation may suggest that B-amino-substituted pyrazaboles do not exist, provided the amino group can donate the free electron pair of the nitrogen readily to boron. This latter situation saturates the boron atom electronically and thus prevents the formation of a pyrazabole structure.

Experimental

All reactions and transfers were carried out under an argon cover. Commercial pyrazole was dried over metallic sodium and was freshly distilled before use. 1,3-Dimethyl-1,3,2-diazaboracyclohexane was prepared by the literature procedure [8]. Elemental analyses were furnished by the Schwarzkopf Microanalytical Laboratory, Woodside, NY.

IR spectra were recorded on the neat liquid using a Perkin—Elmer Model 621 spectrometer under standard operating conditions. Mass spectral data were obtained on a Perkin—Elmer—Hitachi RMU-7 instrument. Carbon-13 and proton NMR spectra were recorded on a Varian Model CFT-20 spectrometer, ^{11}B and ^{14}N spectra on a Bruker Model WP200 instrument, courtesy of Professor H. Nöth, Universität München, Germany. The chemical shift data (external references: $(CH_3)_4Si$ for ^1H and ^{13}C, $(C_2H_5)_2OBF_3$ for ^{11}B, aqueous NH_4NO_3 for ^{14}N) are given with positive values indicating downfield from the reference.

1,3-Dimethyl-2-(pyrazol-1'-yl)-1,3,2-diazaboracyclohexane (II)

A mixture of 59.6 g (0.53 mol) of 1,3-dimethyl-1,3,2-diazaboracyclohexane and 21.2 g (0.31 mol) of dry pyrazole is heated to reflux (with stirring). Within 40 h the calculated quantity of hydrogen is evolved and excess of 1,3-dimethyl-1,3,2-diazaboracyclohexane is stripped off under vacuum. Vacuum distillation of the residue through a 20 cm silver-mantle column yields 47.7 g (86% of theory) of the colorless liquid compound, boiling point 90°C/2 Torr.

Analysis: Found: C, 54.18; H, 8.54; N, 31.44; B, 6.34. $C_8H_{15}N_4B$ calcd.: C, 53.95; H, 8.50; N, 31.48; B, 6.07%.

Mass spectral data (70 eV, inlet temperature 180°C, relative abundances (in parentheses) of greater than 5% only): *M/z* 179 (10), 178 (100), 177 (48), 176 (6.0), 163 (17), 150 (22), 149 (22), 148 (8.5), 136 (11), 135 (9.2), 134 (14), 122 (20), 121 (9.2), 120 (5.2), 119 (5.6), 110 (6.0), 109 (18), 108 (35), 107 (13), 106 (5.5), 95 (11), 94 (9.8), 81 (22), 80 (12), 79 (8.8), 68 (10), 67 (5.6), 52 (6.4), 42 (6.8). Infrared spectral data (wavenumbers in cm^{-1}; s, strong; m, medium; w, weak; v, very; (sh), shoulder; (br), broad; 4000 to 600 cm^{-1} region, neat liquid): 3010(sh), 3096w, 2990(sh), 2913(sh), 2865s, 2838(sh), 2794w, 1704w, 1552(sh), 1530vs, 1509w, 1493w, 1445m, 1414ms, 1400wm, 1388wm, 1357ms, 1327m, 1294wm, 1279w, 1226s, 1203wm, 1189w, 1174(sh), 1137w, 1104ms, 1069m, 1040m, 1014wm, 938ms, 919w, 908vw, 879w, 850vw, 813w(br), 752s, 674(sh), 650(sh), 637m, 623wm. NMR data see text.

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