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BORON—NITROGEN COMPOUNDS

LXXVII *. THE REACTION OF (DIMETHYLAMINO)DIETHYLBORANE WITH 3,3'-DIAMINODIPROPYLAMINE

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Summary

The compounds $(C_2H_5)_2BN[(CH_2)_3NHB(C_2H_5)_2]_2$ (I) and $HN[(CH_2)_3NHB(C_2H_5)_2]_2$ (II) have been isolated from the reaction of (dimethylamino)diethylborane with 3,3'-diaminodipropylamine. The suggested structures are confirmed by spectroscopic data.

The chemistry of heterocyclic boron compounds derived from 3,3'-diaminodipropylamine, $HN[(CH_2)_3NH_2]_2$, has been studied in reasonable detail [2], whereas the first non-cyclic (but oligomeric) boron derivative of this amine was described only recently [3]. The reaction of (dimethylamino)diethylborane with 3,3'-diaminodipropylamine has now been found to yield the first monomeric noncyclic compounds containing two or three diethylboryl groups bonded to different nitrogen atoms of the amine.

The reaction of excess (diethylamino)diethylborane with 3,3'-diaminodipropylamine has previously been reported to yield $(C_2H_5)_2BN[(CH_2)_3NHB(C_2H_5)_2]_2$ (I); however, I decomposed on attempted distillation to yield $B(C_2H_5)_3$ and a heterocyclic species [4]. The use of (dimethylamino)diethylborane has now been found to yield distillable samples of I. Evidence that I contains two types of boron atoms is slightly different trigonal environment is provided by the ^{11}B NMR spectrum which exhibits a broad signal ($h_{1/2}$ approximately 280 Hz) with a chemical shift δ 47.3 ppm with a distinct shoulder, δ 53.0 ppm. The suggested structure of I is also supported by the IR and mass spectrum of the compound as well as by ^1H and ^{13}C NMR data (see Experimental section).

In addition to I, a lesser quantity of a second species (II) is obtained in the reaction as described above. Based on the data of the elemental analysis, II is a bis(diethylboryl) derivative of 3,3'-diaminodipropylamine. Subsequently, this

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* For part LXXVI, see ref. 1.

same compound was obtained in good yield by reacting (dimethylamino)diethylborane and the amine in a 2 : 1 molar ratio. Two structures are possible for II, viz. $(C_2H_5)_2BN[(CH_2)_3NH_2][(CH_2)_3NHB(C_2H_5)_2]$ or $HN[(CH_2)_3NHB(C_2H_5)_2]_2$. The proton-decoupled ^{13}C NMR spectrum (in C_6D_6) exhibits a broad singlet, δ 9.1 ppm, assigned to the carbon atoms of the boron-bonded ethyl groups, and three sharp singlets, δ 34.0, 41.3, and 48.2 ppm, respectively, assigned to the carbon atoms of the amine moiety. These data support the symmetrical structure $HN[(CH_2)_3NHB(C_2H_5)_2]_2$ for II, which is further substantiated by the observation of only one ^{11}B NMR signal, δ 41.1 ppm (neat liquid), and by the ^1H NMR data (see Experimental section).

Employing a 1 : 1 molar ratio of (dimethylamino)diethylborane and 3,3'-diaminodipropylamine, it was not possible to obtain a monoborylated species; rather, exclusive formation of II occurred and the excess of the amine was recovered.

Experimental

All reactions and transfers were carried out under an argon atmosphere. 3,3'-Diaminodipropylamine was supplied by the Ames Laboratory, Inc., Milford, CT; it was stored over KOH pellets and freshly distilled before use. (Dimethylamino)diethylborane was prepared by the literature procedure [6] by ligand exchange between tris(dimethylamino)borane and triethylborane. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY.

IR spectra were recorded on the neat liquids using a Perkin—Elmer Model 621 spectrometer under standard operating conditions. Mass spectral data were obtained on a Perkin—Elmer—Hitachi RMU-7 instrument. Proton NMR spectra were recorded on a Varian T-60 spectrometer using tetramethylsilane as internal reference. Boron-11 NMR spectra were recorded on a Bruker HX8 instrument using external $B(OCH_3)_3$ as standard; chemical shift data were then recalculated and are given with $(C_2H_5)_2O \cdot BF_3$ as reference. All ^{13}C NMR spectra were obtained on a Varian CFT-20 spectrometer and chemical shift data are reported versus tetramethylsilane as reference. All chemical shift values are reported with positive values indicating downfield from the given reference. All spectroscopic data are the averages of several recordings.

Reaction of excess (dimethylamino)diethylborane with 3,3'-diaminodipropylamine

A 50 ml flask equipped with reflux condenser and dropping funnel is charged with 23.0 g (204 mmol) of (dimethylamino)diethylborane and 8.70 g (66 mmol) of 3,3'-diaminodipropylamine is added dropwise with vigorous stirring. Evolution of gas is observed and the mixture is stored at ambient temperature overnight. Subsequently, it is heated slowly to 130°C (bath temperature) until gas evolution ceases (approximately 4 h). Unreacted (dimethylamino)diethylborane and traces of dimethylamine are removed under reduced pressure and the residue is distilled under vacuum to give 5.9 g of II, b.p. 95—99°C/0.05 Torr (after redistillation) and 9.5 g of I, b.p. 123°C/0.05 Torr (after redistillation).

Analyses: I: Found: C, 64.31; H, 13.06; N, 12.57; B, 9.72. $C_{18}H_{43}N_3B_3$ calcd.:

C, 64.54; H, 13.24; N, 12.54; B, 9.66%. II: Found: C, 62.67; H, 13.04; N, 15.45; B, 7.97. $C_{14}H_{34}N_3B_2$ calcd.: C, 62.96; H, 13.21; N, 15.73; B, 8.10%.

Spectroscopic data

I: Mass spectrum (70 eV, relative intensities (in parentheses) of greater than 5% of the base peak): *M/e* = 307 (6.4), 306 (36.0), 305 (23.9), 304 (6.1), 238 (35.2), 237 (16.7), 208 (7.9), 207 (5.5), 153 (14.6), 139 (17.0), 138 (6.4), 127 (6.1), 126 (10.0), 125 (100), 124 (30.9), 123 (6.1), 113 (8.8), 112 (30.0), 111 (11.8), 110 (7.6), 98 (22.4), 97 (23.9), 96 (35.2) 95 (10.0), 84 (33.5), 83 (8.5), 82 (7.9), 70 (51.7), 69 (41.2), 68 (32.6), 67 (8.8), 66 (5.8), 58 (10.9), 57 (12.7), 56 (23.9), 55 (9.1), 54 (7.3), 43 (38.6), 42 (23.3), 41 (40.3), 40 (13.0), 39 (5.2). IR spectrum (NaCl region, neat liquid; w = weak, m = medium, s = strong, sh = shoulder, b = broad, v = very): 3407w, 2957s, 2942(sh), 2919s, 2878vs, 1508(sh), 1494vs, 1461s, 1432(sh), 1407m, 1369(sh), 1358(sh), 1336m, 1295(sh), 1288m, 1240m, 1223(sh), 1193m, 1166m, 1122wb, 1083wb, 1061w, 1018m, 921w, 862vw, 855(sh), 770m, 757(sh). ^1H NMR spectrum (in $CDCl_3$): δ 0.78 ppm (broad singlet, $C_2\underline{H}_5$), 1.43 (quintet) and 2.72 (slightly unsymmetrical quartet). ^{13}C NMR spectrum (in $CDCl_3$, proton-decoupled): δ 8.3 ppm (singlet, $R_2NBCH_2\underline{C}H_3$), 9.0 and 9.2 ppm (singlets, $NHBCH_2\underline{C}H_3$), 10.3 and 11.9 ppm (broad singlets, $B\underline{C}H_2CH_3$), 34.5 ppm (singlet, $CH_2\underline{C}H_2CH_2$), 40.3 ppm (singlet, $BNH\underline{C}H_2$), 46.0 ppm (singlet, $\underline{C}H_2N\underline{C}H_2$).

II: Mass spectrum (70 eV, relative intensities (in parentheses) of greater than 5% of the base peak): *M/e* = 239 (14.4), 238 (86.7), 237 (43.3), 236 (6.7), 211 (5.6), 208 (17.8), 207 (10.0), 197 (6.7), 183 (7.8) 181 (11.1), 180 (6.7), 170 (10.0), 152 (6.7), 143 (8.9), 139 (48.9), 138 (42.2), 137 (8.9), 127 (7.8), 126 (13.3), 125 (100), 124 (43.3), 123 (7.8), 113 (11.1), 112 (12.2), 111 (8.9), 110 (6.7), 98 (10.0), 97 (12.2), 96 (18.9), 96 (5.6), 94 (7.8), 85 (8.9), 84 (11.1), 60 (10.0), 57 (20.0), 56 (5.6). IR spectrum (NaCl region, neat liquid; abbreviations see above): 3408w, 3340wb, 2960vs, 2945(sh), 2922s, 2881s, 2840(sh), 1565(sh), 1510(sh), 1496s, 1460m, 1438(sh), 1407w, 1355(sh), 1338m, 1296m, 1245w, 1233(sh), 1185(sh), 1130m, 1019w, 940(sh), 919w, 818(sh), 771w, 755(sh). ^1H NMR spectrum (in $CDCl_3$): δ 0.83 ppm (broad, $BC_2\underline{H}_5$), 2.63 and 3.07 ppm (triplets, $NC\underline{H}_2$), 1.57 ppm (quintet, $CH_2C\underline{H}_2CH_2$).

Reaction of (dimethylamino)diethylborane with 3,3'-diaminodipropylamine in 2 : 1 molar ratio

A mixture of 5.94 g (45 mmol) of 3,3'-diaminodipropylamine and 9.03 g (80 mmol) of (dimethylamino)diethylborane is prepared by adding the borane to the amine and is stored overnight. Subsequently, the mixture is heated in an oil bath at 100°C for 3 h after which period the ^1H NMR spectrum of the crude mixture is essentially identical to that of II.

In working up the reaction mixture it is best not to use a column but to first collect a rather wide fraction boiling from 93 to 102°C/0.02 Torr, which is subsequently redistilled to give a pure product, b.p. 94—95°C/0.02 Torr in approximately 70% yield. Employing a column in a single-distillation work up leads to substantial symmetrization of II with the formation of I.

Reaction of (dimethylamino)diethylborane with 3,3'-diaminodipropylamine in 1 : 1 molar ratio

A mixture of 10.16 g (77.6 mmol) of 3,3'-diaminodipropylamine and 8.83 g (78.1 mmol) of (dimethylamino)dimethylborane was reacted in identical manner as described in the preceding experiment. Distillation of the crude product gave an initial fraction of the free amine (b.p. 63—65° C/0.02 Torr, approximately 3.8 g) and approximately 9.6 g of II, b.p. 94—95° C/0.02 Torr (after redistillation). The lack of any rearrangement during the distillation was ascertained by recording a ^{1}H NMR spectrum of the crude product, which essentially reflected a spectrum of the amine superimposed on that of II.

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