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BORON—NITROGEN COMPOUNDS

LXX *. BORON DERIVATIVES OF 3,3'-DIAMINODIPROPYLAMINE

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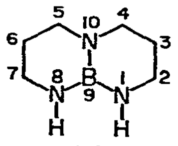
Summary

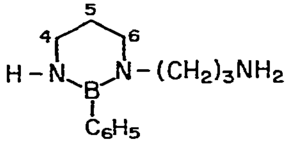
The reaction of borane(3) with 3,3'-diaminodipropylamine yields BH_2B-bridge associated [3,3'-bis(dihydroborylamino)dipropylamino]dihydroborane, 1-aminopropyl-1,3,2-diazaboracyclohexane, or 1,8,10,9-triazaboradecalin (I), depending on the reaction conditions and the stoichiometry of the reactants. If tris(dimethylamino)borane is treated with 3,3'-diaminodipropylamine, only I or 1-bis(dimethylamino)boryl-1,8,10,9-triazaboradecalin are obtained.

Introduction

The reaction of tris(dimethylamino)borane, $B[N(CH_3)_2]_3$, with an equimolar amount of 3,3'-diaminodipropylamine, $HN[(CH_2)_3NH_2]_2$, readily yields the heterocycle 1,8,10,9-triazaboradecalin (I) [2].



(I)



(II)

The chemistry of I has already been studied in considerable detail and has led to the synthesis of various types of novel boron derivatives [3]. In contrast, very few additional reactions of 3,3'-diaminodipropylamine with boron compounds have been studied. Bis(dimethylamino)phenylborane, $C_6H_5B[N(CH_3)_2]_2$, was found to react with the cited amine in a 1 : 1 molar ratio to yield II, and

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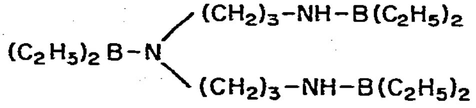
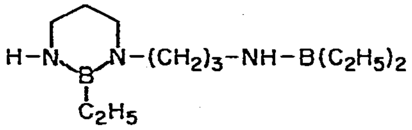
excess (diethylamino)diethylborane, $(C_2H_5)_2N{-}B(C_2H_5)_2$, reacted with the amine with the formation of III [4].



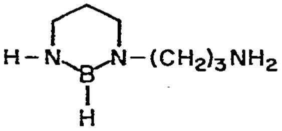
(III)

However, III could not be isolated in pure form. Rather, on attempts to purify the material by distillation, intramolecular condensation occurred with the formation of IV [4].



(IV)

Also, the 1 : 1 molar interaction of BH_3 (generated in situ from $NaBH_4$) with 3,3'-diaminodipropylamine has been studied [5]. It was possible to isolate the intermediate V which, on heating to 150°C, eliminated hydrogen to yield I.



(V)

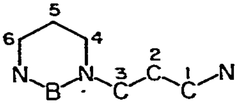
The assignment of the structures of II—V was based primarily on the results of the elemental analyses and infrared spectroscopic evidence. It was not established whether or not the boron in II, IV, and V is truly in trigonal environment or is tetracoordinated by either intra- or intermolecular coordination. Furthermore, no attempt has been reported to obtain additional species which might be formed either as precursors to the heterocycles or from interaction of the latter with any of the starting materials.

The present work is concerned with the interaction of 3,3'-diaminodipropylamine with BH_3 and $B[N(CH_3)_2]_3$ in various molar ratios and a study of the physical and chemical properties of the resultant products.

The reaction of borane(3) with 3,3'-diaminodipropylamine

Trimethylamine-borane, $(CH_3)_3NBH_3$, is a ready and convenient source for the generation of borane(3), BH_3. On refluxing of a 1 : 1 molar mixture of trimethylamine-borane with 3,3'-diaminodipropylamine, compound V is formed in approximately 72% yield. No intermediate of the amine-borane type resulting from a simple base displacement could be obtained under these conditions. As expected, pyrolysis of V at 150°C under atmospheric pressure results in essentially quantitative conversion to I.

The physicochemical properties of V are essentially identical to the literature data [5], minor deviations probably being due to the inherent instability of the compound. Although the material does not readily decompose at temperatures up to 100°C, a slow decomposition occurs even at room temperature and leads to the formation of I. The observed boiling point of 54—55°C/1 Torr is lower than the literature value of 66—68°C/0.5 Torr and the NH stretching mode could not be resolved but appeared as a relatively broad absorption centered at 3418 cm^{-1}. However, the BH stretching mode assigned at 2486 cm^{-1} corresponds closely with the literature value. The ^1H NMR spectrum of V consists of two overlapping quintuplets centered at δ 1.80 ppm and two triplets at δ 2.98 and 2.68 ppm, respectively. The ^{11}B NMR spectrum of the compound shows a single resonance line with a chemical shift δ 23.7 ppm which is close to that of other 1,3,2-diazaboracyclohexanes [8]. Based on the data available for the 1,3,2-diazaboracyclohexane system [6], an interpretation of the proton-decoupled ^{13}C NMR spectrum of V, containing a total of twelve lines, can be attempted despite the fact that some decomposition (as evidenced by gas evolution) occurs during the recording procedure.



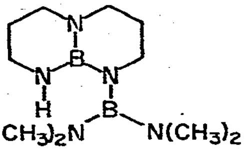
The signal with δ 51.3 ppm is assigned to C(4), δ 28.6 ppm to C(5) and δ 38.8 ppm to C(6) of the compound. The C(1) atom has a chemical shift of 41.4 ppm, C(2) one of 34.5 ppm, and C(3) has δ 45.1 ppm. Three signals with chemical shifts of 27.6, 40.0, and 48.5 ppm, respectively, are likely to be due to partial formation of I (see below). The remaining three signals with δ 40.2, 33.8, and 48.2 ppm, respectively, may be due to signals of some unreacted 3,3′-diaminopropylamine (see below).

Reaction of a 3 : 1 molar ratio of trimethylamine-borane and 3,3′-diaminodipropylamine in benzene at reflux temperature of the mixture results in the formation of a species analysing as $H_2B—N[(CH_2)_3—NH—BH_2]_2$ (VI).

No mass spectrum of VI could be obtained since, under the available operating conditions, the compound decomposes with the formation of I. However, the elemental analysis is in good agreement with the values calculated for VI. The infrared spectrum of the material exhibits two broad absorptions in the NH stretching region centered near 3410 and 3250 cm^{-1}, respectively. An unresolved, broad and intense absorption ranging from 2260 to 2440 cm^{-1} with maxima near 2360 and 2295 cm^{-1} is indicative of BH stretching. However, both values are at quite low frequency and, hence, seem to suggest terminal BH modes rather than terminal BH_2 modes (the latter are normally observed near 2600 cm^{-1}). Consequently, a relatively broad absorption at 1575 cm^{-1} is readily explained as evidence for BH_2B-bridge bonding. Indeed, neither of the starting materials of the synthesis of VI nor the ultimate product of the reaction, i.e., I, show absorbances in this particular frequency region. Cryoscopic molecular weight determinations (in benzene) suggest the existence of dimeric and trimeric species in extremely dilute solution and thus indicate that intermolecular bridging exists. Hence, it is not surprising that VI is a solid and additional evidence for the tetracoordinate nature of boron in VI is obtained by ^{11}B NMR data. Two relatively broad resonance signals are observed in the ^{11}B spectrum of the compound (solution in benzene) with δ —5.1 and —15.5 ppm, respectively, indicative of tetracoordinate boron. The latter signal is of lower relative intensity and thus should be assigned to the boron atom that is bonded to the secondary amino group of the molecule.

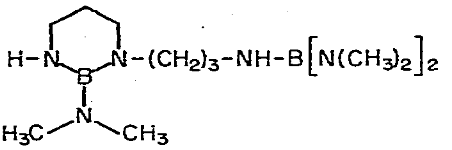
The reaction of tris(dimethylamino)borane with 3,3'-diaminodipropylamine

In previous studies [2,4] only equimolar amounts of tris(dimethylamino)borane and 3,3'-diaminodipropylamine were reacted to yield I. However, utilizing an excess of tris(dimethylamino)borane, compound VII is obtained in essentially quantitative yield (calculated for the 3,3'-diaminodipropylamine).



(VII)

VII is a liquid material that can be distilled under reduced pressure without noticeable decomposition. Although the product obtained in this fashion is analytically pure, mass spectral data suggest contamination of the material with traces of a second compound, most likely VIII.



(VIII)

The mass spectrum of VII shows the parent peak *P* (disregarding a minor impurity at *m/e* 281) at *m/e* 237, which corresponds to the molecular ion. The base peak of the spectrum is observed at *m/e* 193; it is readily interpreted by the loss of a dimethylamino group from the parent species. It is worth noting that the low-voltage mass spectrum (12 eV) shows only four peaks: The molecular ion (which is also the base peak) and peaks at *m/e* 193, 139, and 45, respectively. The cited impurity with *m/e* 281 would be in consonance with the presence of a minute amount of VIII, that could not be detected in the elemental analysis.

The infrared spectrum of VII shows a single sharp absorption at 3460 cm^{-1} assigned to a NH stretching mode. A BN stretching mode may tentatively be assigned to an intense absorption near 1498 cm^{-1}, exhibiting a shoulder on the high frequency side. Any further interpretation of the multi-line spectrum cannot be attempted. The ^{1}H NMR spectrum of VII exhibits a singlet with a chemical shift δ 2.37 ppm attributable to the N-methyl protons. The anular methylene group protons are evidenced by a triplet with δ 2.68 ppm and a quintuplet with δ 1.62 ppm in the calculated intensity ratio. As expected, two resonance signals are observed in the ^{11}B NMR spectrum of the compound with chemical shifts δ 23.5 ± 0.4 and 27.2 ± 0.1 ppm, respectively. Since $\delta(^{11}B)$ of tris(dimethylamino)borane has been reported to occur in the 27.1 to 27.5 ppm region [6] and that of I to be at δ 22.0 to 22.1 ppm [7], the chemical shift of the anular boron atom of VII is assigned to the signal at 23.5 ppm.

The ^{13}C NMR spectrum of VII is readily interpreted in conjunction with the spectra of I and of 3,3'-diaminodipropylamine. The proton-decoupled ^{13}C NMR spectrum of the latter compound shows only three resonance signals with chemical shifts δ 33.9, 40.5, and 48.0 ppm, respectively (tetramethylsilane as internal standard). (It should be noted that the spectrum was recorded in $CDCl_3$; some H/D exchange occurred and, consequently, a signal line of small intensity corresponding to $CHCl_3$ is also observed.) Based on previous studies [6] $\delta(^{13}C)$ 33.9 ppm ($^1J(CH)$ 122 Hz) is assigned to the two central methylene carbon atoms of the amine, the signal with δ 40.5 ppm (J 132 Hz) to the carbon atoms bonded to the NH_2 groups, and the one with δ 48.0 ppm (J 132 Hz) to the remaining carbon atoms that are bonded to the secondary nitrogen atom. The proton-decoupled spectrum of I also shows only three resonance signals. The resonance signal of C(3) and C(6) is assigned at δ 27.4 ppm (J 128 Hz). The second singlet with δ 39.2 ppm (J 134 Hz) is assigned to C(2) and C(7), since the ^{13}C NMR signal for C(4) and C(6) of 1,3,2-diazaboracyclohexane, $HB(-NH-CH_2-)_2CH_2$, is observed with a chemical shift δ 39.7 ppm [6]. The remaining singlet observed in the spectrum of I must therefore be assigned to C(4) and C(5) with δ 47.0 ppm (J 133 Hz). Based on the assignment of the spectrum of I and previous data reported for 1,3,2-diazaboracyclohexane systems [6], the spectrum of VII can tentatively be assigned as follows (numbering of anular atoms according to the numbering of I; C(1) atoms are the exocyclic dimethyl groups of the $B[N(CH_3)_2]_2$ moiety bonded to the N(1) atom of I): C(1) δ 39.1 ppm (J 133 Hz); C(2) δ 43.1 ppm (J 134 Hz); C(3) δ 28.3 ppm (J 125 Hz); C(4) δ 48.1 ppm (J 132 Hz); C(5) δ 47.7 ppm (J 132 Hz); C(6) δ 27.7 ppm (J 126 Hz); C(7) δ 39.6 ppm (J 134 Hz). No additional resonance signals are observed in the spectrum of VII.

Even when a large excess of tris(dimethylamino)borane is utilized in the above reaction, the desired 1,8-di[bis(dimethylamino)boryl]-1,8,10,9-triazaboradecalin could not be obtained. This observation tends to suggest that steric factors prevent the displacement of the second N-bonded hydrogen of 1,8,10,9-triazaboradecalin by a bis(dimethylamino)boryl group.

Discussion

The reaction of an excess of tris(dimethylamino)borane with 3,3'-diaminodipropylamine leads to the ready formation of VII. Although mass spectral data suggest the existence of VIII, no open-chain diborylated derivative of 3,3'-diaminodipropylamine is observed. The same holds true for the interaction of trimethylamine-borane with 3,3'-diaminodipropylamine. However, in this latter case, it was possible to isolate and characterize a triborylated open-chain derivative, VI.

Since all isolable materials with two boron atoms in the molecule contain at least one heterocyclic moiety, some speculation about the interaction of boron derivatives with 3,3'-diaminodipropylamine seems feasible. Apparently, the free rotation in open-chained derivatives permits close proximity of boron moieties σ bonded to one nitrogen of the 3,3'-diaminodipropylamine to another nitrogen atom of the species. This event is likely to be promoted by the desire of boron to attain the fourcoordinate state, as is evidenced by BH_2B bridge bonding in VI. Hence, if a diborylated open-chain intermediate is formed, back-coordination of one boron atom to the third, non-borylated nitrogen atom of the species seems most likely. However, under the prevailing experimental conditions, intramolecular condensation occurs readily and then results in the formation of IV, V, or VII, respectively. The lack of isolating a hydroborylated analog of IV can be explained by the BH_2B bridge bonding observed in VI. This feature may promote the elimination of B_2H_6 rather than BH_3, and V appears to be the most reasonable product from such a process.

Somewhat surprising is the lack of formation of I in which both H atoms bonded to N are displaced by $B[N(CH_3)_2]_2$ groups, particularly since both NH groups of I can be lithiated and even bulky substituents can subsequently be bonded to the N(1) and N(8) atoms of I [10].

The observation of a sharp infrared absorption band for the NH stretching mode of VII at 3460 cm^{-1} disputes any intramolecular hydrogen bonding (which could render the NH site of the molecule inert). Hence, one must assume that the bis(dimethylamino)boryl substituent at N(1) and VII is indeed protecting the N(8) site from further attack by steric factors only.

Experimental

All reactions and transfers were carried out in inert atmosphere (usually an argon cover). Solvents were dried by conventional methods and freshly distilled before use; 3,3-diaminodipropylamine (Ames Laboratories, Milford, CT) was stored over KOH pellets and freshly distilled before use. Melting points (uncorrected) were determined using a Mel—Temp block. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Infrared spectra were recorded using a Perkin—Elmer Model 621 spectrometer employing standard operating conditions. Proton NMR spectra were recorded on a Varian T-60 spectrometer using tetramethylsilane as reference. Boron-11 NMR spectra were recorded on a Varian HA-100 spectrometer at 32.1 MHz using external $B(OCH_3)_3$ as reference; the observed chemical shifts were recalculated and are given versus $(C_2H_5)_2O \cdot BF_3$ as reference. All carbon-13 NMR spectra were obtained on a Varian CFT-20 spectrometer. Lock signals were provided from a deuterated solvent or a sealed capillary tube filled with acetone-d_6; tetramethylsilane is used as reference. All chemical shift values are reported in ppm with positive values indicating downfield from the reference. Mass spectral data were obtained on a Perkin—Elmer—Hitachi RMU-7 instrument.

The reaction of trimethylamine-borane with 3,3'-diaminodipropylamine

Reaction in 1 : 1 molar ratio; preparation of 1-(ω-aminopropyl)-1,3,2-diazaboracyclohexane (V). A solution of 22.50 g (0.308 mol) of trimethylamine-borane in 150 ml of benzene is warmed to approximately 75°C and 40.7 g (0.310 mol) of 3,3'-diaminodipropylamine are added very slowly with stirring and continued heating. After heating for another hour, benzene is distilled of and the residue is distilled under reduced pressure over a 20-cm silver-mantle column to yield approximately 33 g of V as a colorless liquid, b.p. 54—55°C/1 Torr.

Analysis: Found: C, 51.28; H, 11.68; N, 29.67; B, 7.74. $C_6H_{16}N_3B$ calcd.: C, 51.11; H, 11.44; N, 29.81; B, 7.67%.

The material does not readily decompose on heating to 100°C; however, on prolonged storing at room temperature, slow gas evolution is observed. Ready decomposition occurs within several hours at 170°C and under atmospheric pressure and leads to the quantitative formation of I. The nature of the latter was verified by comparison with an authentic sample of the compound [2].

Reaction in 3 : 1 molar ratio; preparation of [3,3'-bis(dihydroborylamino)-dipropylamino]dihydroborane (VI). A mixture of 12.40 g (0.170 mol) of trimethylamine-borane, 7.55 g (0.058 mol) of 3,3'-diaminodipropylamine, and 100 ml benzene is refluxed for approximately 15 h. (After approximately 3 h some inhomogeneity of the mixture is observed which disappears after a relatively short period of additional heating.) Benzene is stripped off at atmospheric pressure and remaining volatiles are removed at room temperature under vacuum to leave VI as a colorless glassy material.

Analysis: Found: C, 42.47; H, 12.18; N, 25.06; B, 19.63. $C_6H_{20}N_3B_3$ calcd.: C, 43.24; H, 12.09; N, 25.21; B, 19.46%.

The product has no sharp melting point. It begins to soften near 80°C but even at 120°C some solid remains and decomposition occurs as is evidenced by the evolution of gas.

The mass spectrum of the material does not show the expected parent peak at *m/e* 167. Rather, the highest peak is observed at *m/e* 139 (corresponding to I), thus indicating decomposition of VI under the operating conditions.

Reaction in 2 : 1 molar ratio; simultaneous formation of V and VI. A mixture of 3.99 g (0.055 mol) of trimethylamine-borane, 3.59 g (0.027) of 3,3'-diaminodipropylamine, and 75 ml benzene is heated to gentle reflux. After a period of about 3 h, the mixture separates into two layers; a small sample of the lower layer was removed (see below). The mixture is further heated and a homogeneous solution is quickly obtained. After a total heating time of 9 h benzene is removed and a liquid fraction is distilled off the residue under vacuum to yield a material, b.p. 55°C/1 Torr, identical to V (see above) as evidenced by the spectroscopic properties. The remaining solid is similarly identified as VI (see above).

The small sample taken from the preceding reaction was stored under vacuum for 15 h. Continuous gas evolution was observed and no consistent elemental analysis data could be obtained. However, the data as well as infrared spectral evidence would tend to suggest that this intermediate is impure 1-(ω-dihydroborylaminopropyl)-1,3,2-diazaboracyclohexane. However, no bis(dihydroboryl) derivative of 3,3'-diaminodipropylamine is formed. In order to confirm this assumption, the following experiment was performed:

A quantity, 3.34 g (0.020 mol) of VI is dissolved in a minimal amount of benzene and 1.34 g (0.010 mol) of 3,3'-diaminodipropylamine is added. The mixture is refluxed overnight, benzene is stripped off, and the residue is distilled over a 20-cm silver-mantle column to yield V and a very minor amount of I. Hence, this reaction can be described by the equation:

$$[H_2B{-}NH{-}(CH_2)_3]_2N{-}BH_2 + 2\ [H_2N{-}(CH_2)_3]_2NH \rightarrow 3\ V + 3\ H_2$$

1-Bis(dimethylamino)boryl-1,8,10,9-triazaboradecalin (VII)

A mixture of 6.0 g (0.045 mol) of 3,3′-diaminodipropylamine and 20.0 g (0.140 mol) of tris(dimethylamino)borane [9] is stirred vigorously and slowly warmed in a reflux system. At 40°C homogeneity of the mixture is achieved and slow evolution of gas is observed. (Note: Reaction at 50°C is quite vigorous!) The mixture is maintained at 45°C for a period of 8 h and then heated to 100°C for 2 h. Excess tris(dimethylamino)borane is distilled off under reduced pressure and the residue is distilled under high vacuum. Redistillation of the latter product using a 20-cm silver-mantle column yields 6.2 g (58.6%) of pure VII, b.p. 83—84°C/0.05 Torr.

Analysis: Found: C, 50.77; H, 10.52; N, 29.31; B, 9.12. $C_{10}H_{25}N_5B_2$ calcd.: C, 50.68; H, 10.63; N, 29.56; B, 9.12%.

Alternate procedure. A solution of 9.7 g (0.69 mol) of 1,8,10,9-triazaboradecalin (I) [2] in 50 ml of benzene is warmed to approximately 75°C and 20.0 g (0.140 mol) of tris(dimethylamino)borane is added dropwise. The mixture is refluxed overnight and benzene is stripped off. The excess tris(dimethylamino)borane is removed under vacuum and the residue is distilled. Redistillation of the product employing a 20-cm silver-mantle column yields 9.8 g (59%) of VII, identical to the material described above.

Acknowledgement

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