Preparation and Properties of Some Mixed Amino-hydrazino-boranes

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Mixed Amino-hydrazino-boranes, 2-Hydrazino-1,3,2-diazaboracyclopentanes, Boron-hydrazine Derivatives, Boron-nitrogen-carbon Heterocycles

The three compounds N₂-(1,3-dimethyl-1,3,2-diazaboracyclopentyl)-N,N'-dimethyl-hydrazine, N₂-(1,3-dimethyl-1,3,2-diazaboracyclopentyl)-N,N'-dimethylhydrazine, and N₂-bis-(1,3-dimethyl-1,3,2-diazaboracyclopentyl)hydrazine, have been synthesized and characterized. The compounds can be viewed as mixed amino-hydrazino-boranes; they exhibit relatively high chemical and thermal stability which appears to be due to the incorporation of the boron into the heterocyclic system.

Hydrazinoboranes of the type R₂B-NH-NR' and R₂B-NH-NH-BR₂ where R is a substituent other than an organic group have hardly been explored. In particular, only two compounds which may be viewed as mixed amino-hydrazino-boranes have been postulated on the basis of some analytical data and infrared spectroscopic evidence and the species (CH₃)₃N-BCH₂-NH-NHC₆H₅ has been prepared in low yield only and is described as a fairly unstable material. On the other hand, mixed amino-hydrazino-boranes should be interesting materials inasmuch as the free electron pair of the amino as well as that of the hydrazino nitrogen adjacent to boron could compete for the latter's vacant p₂-orbital.

In an initial study on mixed amino-hydrazinoboranes, several methods have been explored for their preparation; the best presently available method for synthesizing each of the following three compounds 1 to 3 is described in the present accounting:

1. (-CH₂-NCH₃-)₂B-NH-N(CH₃)₂,
2. [(CH₂-NCH₃-)₂B]₂N-N(CH₃)₂,
3. (-CH₂-NCH₃-)₂B-NH-NH-B(-NCH₂-CH₂-)₂.

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Results and Discussion

Compound 1 was prepared by the reaction of N₂-bis-(1,3-dimethyl-1,3,2-diazaboracyclopentane with N,N'-dimethylhydrazine (equation 1) and – in equally good yield of about 70% – by direct hydrazinolysis of 1,3-dimethyl-2-chloro-1,3,2-diazaboracyclopentanes containing the structural unit 1 are known and are thus available for correlative interpretation of data.

H₂C-N CH₃

(1)

Equation 1

\[
(-\text{CH}_2-\text{NCH}_3-)_{2}\text{BCl} + (\text{CH}_3)_2\text{Si}-\text{NH}-\text{N}(\text{CH}_3)_2 \rightarrow
(\text{CH}_3)_2\text{SiCl} + (-(-\text{CH}_2-\text{NCH}_3-)_{2}\text{B}-\text{NH}-\text{N}(\text{CH}_3)_2
\]

(1)

Equation 2

\[
(-\text{CH}_2-\text{NCH}_3-)_{2}\text{BCl} + 2 \text{H}_2\text{N}-\text{N}(\text{CH}_3)_2 \rightarrow
(\text{CH}_3)_2\text{N}-\text{NHCl} + (-(-\text{CH}_2-\text{NCH}_3-)_{2}\text{B}-\text{NH}-\text{N}(\text{CH}_3)_2
\]

(2)
Combination of the two procedures utilizing appropriate quantities of reactants as well as employing triethylamine as a hydrogen chloride acceptor gave compound 2 in 55% yield (equation (3)).

$$2(-\text{CH}_2-\text{NCH}_2)-_2\text{BCl} + (\text{CH}_3)_3\text{Si}-\text{NH}-\text{N}(\text{CH}_3)_2 + \text{N}(\text{C}_2\text{H}_6)_3 \rightarrow (\text{C}_2\text{H}_6)_3\text{NHCl} + (\text{CH}_3)_3\text{SiCl} + [(-\text{CH}_2-\text{NCH}_2)-_2\text{B}]_2\text{N}-\text{N}(\text{CH}_3)_2 \quad (3)$$

Compound 3 was prepared in essentially quantitative yield by a condensation reaction of 2-methylthio-1,3-dimethyl-1,3,2-diazaboracyclopentane with anhydrous hydrazine (equation (4)).

$$2(-\text{CH}_2-\text{NCH}_2)-_2\text{BSCH} + \text{H}_3\text{N}-\text{NH}_2 \rightarrow 2\text{CH}_3\text{SH} + (-\text{CH}_2-\text{NCH}_2)-_2\text{B}-\text{NH}-\text{NH}-\text{B}(-\text{NCH}_3-\text{CH}_2-)_-2 \quad (4)$$

The three compounds 1 to 3 exhibit reasonable thermal stability and can be distilled under reduced pressure without noticeable decomposition.

The mass spectra of compounds 1 and 2 show the molecular ions P as the parent peaks of the spectra. For compound 3, the ion P minus 15 is the parent peak of the mass spectrum. Such a ready loss of methyl groups (= 15 mass units) from 1,3-dimethyl-1,3,2-diazaboracyclopentanes under electron impact is well documented; a more detailed accounting of the mass spectral fragmentations will be presented in another context.

The $^1\text{H}$ NMR spectrum of 1 exhibits three sharp singlets of relative intensities 2.0:3.1:3.0 with the individual chemical shifts $\delta = 2.97, 2.60$ and 2.33 ppm, respectively, in addition to a broad singlet at $\delta = 3.83$ ppm (relative intensity approximately 0.5). The latter resonance signal is indicative of N-bonded hydrogen. Based on the intensity data, the methylene protons are readily assigned at $\delta = 2.97$ ppm. The two types of methyl protons can be assigned in conjunction with the $^1\text{H}$ NMR spectrum of 3. The latter consists of three singlets with chemical shifts $\delta = 3.87, 2.96$ and 2.57 ppm, respectively, and relative intensities 1.0:4.1:5.7 (calculated: 1:4:6.6). In this spectrum, the intensity data clearly suggest the assignment of the N-bonded protons at $\delta = 3.87$ ppm and of the N-$\text{CH}_3$ protons at $\delta = 2.57$ ppm. Hence, in the spectrum of 1 the protons of the methyl groups bonded to the anular nitrogen must be assigned at $\delta = 2.60$, whereas those of the methyl groups bonded to the hydrazine nitrogen are assigned at $\delta = 2.33$ ppm. This latter value is identical to that of the methyl protons in N,N-dimethylhydrazine, and in the spectrum of (CH$_3$)$_3$Si–NH–N(CH$_3$)$_2$ the corresponding resonance signal is found at $\delta = 2.30$ ppm. This observation seems to suggest that the chemical shift of the methyl protons of (CH$_3$)$_3$N–NH$_2$ is reasonably insensitive to monosubstitution at the second nitrogen of the hydrazine moiety. However, disubstitution of the latter causes a noticeable shift of this $\delta$ value: The $^1\text{H}$ NMR spectrum of 2 shows three sharp singlets with $\delta = 3.12, 2.62$ and 2.47 ppm, respectively, and relative intensities of 7.4:11.8:6.0 (calculated: 4:6:3), assigned to the methylene protons, the protons of the methyl groups bonded to the annular nitrogen atoms, and those of the methyl groups bonded to the hydrazine nitrogen, in that order.

The infrared spectrum of 1 shows an absorption of weak to medium intensity at 3295 cm$^{-1}$, which is assigned to the N–H stretching mode. This same absorption is observed at 3287 cm$^{-1}$ in the spectrum of (CH$_3$)$_3$Si–NH–N(CH$_3$)$_2$ and compares favorably with a broad absorption at 3303 cm$^{-1}$ observed in the spectrum of (CH$_3$)$_2$N–NH$_2$. In the spectrum of 3, N–H stretching is observed at 3380 cm$^{-1}$ as a strong and broad band. Antisymmetric B–N stretching modes are tentatively assigned at 1525 cm$^{-1}$ (1), 1500 cm$^{-1}$ (2), and 1515 cm$^{-1}$ (3), respectively. These are all very strong absorptions with a shoulder on the high frequency side indicative of the boron-10 isotope; they are located in a range where the antisymmetric B–N stretch of 1,3,2-diazaboracycloalkanes is normally observed. A more detailed analysis of the vibrational data on compounds 1 to 3 is not yet feasible.

It is noteworthy that compound 2 may also be viewed as a diborylamine. Such species are quite rare and have been found susceptible to rearrangement reactions, particularly in the presence of ammonium ions. Hence, the thermal stability of 2 is surprising, especially since it is obtained in the presence of triethylammonium ion and at elevated temperatures. However, the present data suggest that the incorporation of the boron into the heterocyclic 1,3,2-diazaboracycloalkane system has a stabilizing effect and that the exocyclic 2-substituent does not noticeably affect intraannular interactions. This is in complete agreement with recent observations on the chemical stability of a variety of novel diborylamines, that also contain boron in an annular environment.
Experimental

All experiments were conducted in an atmosphere free of moisture and oxygen under inert gas cover (argon or nitrogen). Melting points (uncorrected) were determined in sealed capillaries. Infrared spectra were recorded under standard operating conditions on the neat liquids at ambient temperature using a Perkin-Elmer Model 621 spectrophotometer and cesium iodide windows. Mass spectral data were obtained with a Hitachi-Perkin-Elmer Model RMU-8 double focusing instrument at the University of Kentucky Mass Spectrometry Center; all compounds were analyzed at an inlet temperature of 180 °C and at 70 eV. Low voltage spectra were recorded for mol. wt. determinations. Proton NMR spectra were recorded on the neat liquids at instrument temperature (approximately 35 °C) using a Varian Model T-60 spectrometer and TMS as internal standard. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, New York.

\[ N,\text{-}N\text{-}2\text{-(1,3-dimethyl-1,3,2-diazaboracyclopentyl)}N',N'\text{-dimethylhydrazine} \]

**Method 1:** A solution of 31.5 g (0.238 mole) of 1,3-dimethyl-2-chloro-1,3,2-diazaboracyclopentane in 100 ml of dry n-pentane was cooled in an ice-bath and 32.5 g (0.246 mole) of N-trimethylsilyl-N',N'-dimethylhydrazine was added slowly with vigorous stirring. The mixture was stirred at ambient temperature for approximately three hours, was filtered, and solvent and trimethylchlorosilane were evaporated. The residue was distilled under reduced pressure to yield 25.7 g (69.2%) of 1, b.p. 40-42 °C/2 Torr.

C_{10}H_{17}BN_4 (156.0)

Calcd C 46.18 H 10.98 B 6.93 N 35.91,

Found C 46.34 H 11.00 B 6.70 N 35.83.

Molecular weight (by mass spectrometry): 156.

**Method 2:** A solution of 48 g (0.363 mole) of 1,3-dimethyl-2-chloro-1,3,2-diazaboracyclopentane in 100 ml of dry n-hexane was cooled in an ice-bath and 48.1 g (0.800 mole) of anhydrous N,N-dimethyl-hydrazine was added dropwise with stirring. The mixture was stirred for four hours at ambient temperature, was filtered, and solvent and excess N,N-dimethylhydrazine were evaporated. Distillation of the residue under reduced pressure gave 44.5 g (78%) of the desired compound 1, identical with the product obtained by Method 1 (above).

**N,N-Bis-2-(1,3-dimethyl-1,3,2-diazaboracyclo-pentyl)-N',N'-dimethylhydrazine** (2)

A mixture of 41.6 g (0.314 mole) of 1,3-dimethyl-2-chloro-1,3,2-diazaboracyclopentane, 175 ml of dry benzene, and 16.0 g (0.158 mole) of anhydrous triethylamine was cooled in an ice-bath and 20.8 g (0.157 mole) of N-trimethylsilyl-N',N'-dimethylhydrazine was added dropwise. The mixture was stirred at ambient temperature for three hours and was then refluxed for an additional four hours. After filtration, the solvent and trimethylchlorosilane were evaporated and the residue was distilled under reduced pressure to yield 23 g (58%) of the desired compound 2, b.p. 81-82 °C/1 Torr.

C_{15}H_{26}B_2N_6 (252.0)

Calcd C 47.67 H 10.40 B 8.58 N 33.10,

Found C 47.67 H 10.70 B 8.24 N 33.10.

Molecular weight (by mass spectrometry): 252.

**N,N'-Bis-2-(1,3-dimethyl-1,3,2-diazaboracyclo-pentyl) hydrazine** (3)

A solution of 49.8 g (0.398 mole) of 1,3-dimethyl-2-methylthio-1,3,2-diazaboracyclopentane in 100 ml of dry n-pentane was cooled in an ice-bath and 6.5 g (0.203 mole) of anhydrous hydrazine was added dropwise with vigorous stirring. The mixture was then refluxed for two hours and volatiles were removed at ambient temperature under vacuum whereupon colorless pure crystals of 3, m.p. 36-41 °C, formed in essentially quantitative yield; the b.p. of the compound is 80-83 °C/10^-1 Torr.

C_{16}H_{28}B_2N_6 (223.9)

Calcd C 42.91 H 9.90 B 9.66 N 37.53,

Found C 42.79 H 9.69 B 9.58 N 37.25.

Molecular weight (by mass spectrometry): 224.


7 K. Niedenzu and coworkers, unpublished data.

8 Ref. 2, p. 282.


