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Cyclic Boron Derivatives of Carbohydrazide[1]

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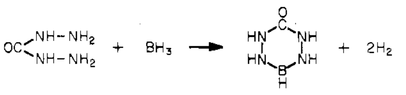
No boron derivatives of carbohydrazide, $OC(NH{-}NH_2)_2$, have been described in the literature. This lack is not really surprising since carbohydrazide is soluble only in protic media which are normally not employed in synthetic boron chemistry. For a study of reactions of carbohydrazide and similar carbonyl derivatives with boranes, some two-phase processes have recently been investigated. The present work reports the cyclization of carbohydrazide via a boryl group in such a procedure.

Results and Discussion

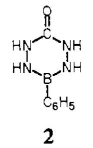
A solution of trimethylamine–borane in toluene or of tetrahydrofuran–borane in tetrahydrofuran reacts slowly with a vigorously stirred slurry of carbohydrazide in toluene or tetrahydrofuran, respectively, at elevated temperatures to yield 1,2,4,5-tetraaza-3-boracyclohexan-6-one, **1**, as is illustrated in the equation



1

A confirmation of the structure of **1** rests primarily on the data of the elemental analysis. The compound is insoluble in common organic solvents, and no NMR could be recorded. The low-quality infrared spectrum of the material (KBr pellet) exhibits a strong and broad BH absorption centered at 2395 cm^{-1}. Strong absorptions in the NH stretching region are also broad and overlapping, but a maximum at 3190 cm^{-1} is evident.

Additional support for the structure of **1** is obtained by the preparation of the B-phenylated derivative: slurry of carbohydrazide was found to react with bis(dimethylamino)phenylborane, $C_6H_5B[N(CH_3)_2]_2$, to yield **2**.



2

The mass spectrum of **2** features a parent ion peak at *m/e* 276. The compound is only very slightly soluble in anhydrous organic solvents, and a low-quality ^{1}H NMR spectrum was recorded on a saturated solution of **2** in $(CD_3)_2CO$; an aromatic multiplet with $\delta(^1H)$ centered at 8.4 and an NH signal (CO bonded) at $\delta(^1H)$ 9.67 were observed. The infrared spectrum of the compound (KBr pellet) exhibits a very broad absorption in the NH stretching region.

Noteworthy seems to be the formation of *B*-triphenylboroxine, $(-BC_6H_5-O-)_3$, during the preparation of **2**. Since atmospheric oxygen was carefully excluded, the boroxine is likely to have originated from a breakage of the C=O bond. On this basis one must assume that whenever a carbonyl compound such as carbohydrazide is reacted with a trigonal borane species, the formation of boroxines can be expected. This event may considerably impair the synthesis of boron derivatives of carbonyl species (or their purification).

Experimental Section

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 recored under standard operating conditions by using a Perkin-Elmer Model 621 spectrometer (frequencies are listed in cm^{-1}; abbreviations are s = strong, m = medium, w = weak, v = very, b = broad, sh = shoulder). Mass spectral data were obtained with a Hitachi Perkin-Elmer RMU-7 double-focusing instrument, and proton NMR spectra were recorded on a Varian Model T-60 spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Carbohydrazide, trimethylamine–borane, and tetrahydrofuran–borane were commercial products. Bis(dimethylamino)phenylborane was prepared by the literature procedure.[2]

1,2,4,5-Tetraaza-3-boracyclohexan-6-one, 1. A mixture of 9.0 g (100 mmol) or carbohydrazide, 7.66 g (105 mmol) of trimethylamine–borane, and 200 mL of toluene is refluxed for 16 h with vigorous stirring. Solids are filtered off the hot solution and washed with hot toluene and then with hot hexane. The residue is dried under vacuum for 13 h at 80 °C to give 9.44 g of product (94.5%) which does not melt up to 400 °C. Anal. Calcd for CH_5ON_4B (mol wt 99.91): C, 12.02; H, 5.05; N, 56.09; B, 10.82. Found: C, 12.08; H, 5.33; N, 56.01; B, 10.80. Infrared spectrum (cm^{-1}): 3310/3190/3075 s (b), 2450 sh, 2395 s (b), 1660 vs (b), 1637 sh, 1525 w, 1460 sh, 1435 m, 1400 m, 1330 w (b), 1220 m, 1167 w, 1020 w (b), 925 w, 800 vw, 763 w (b), 580 mw (b). Alternately, the material is obtained by refluxing a mixture of 9.0 g of carbohydrazide and 100 mL of a 1 M solution of tetrahydrofuran–borane in tetrahydrofuran for 7 h, collecting insolubles, and washing them with hot hexane.

3-Phenyl-1,2,4,5-tetraaza-3-boracyclohexan-6-one, 2. A mixture of 9.62 g (54.6 mmol) of bis(dimethylamino)phenylborane, 4.92 g (54.6 mmol) of carbohydrazide, and 80 mL of tetrahydrofuran is refluxed with stirring for 7 h. Approximately half of the solvent is stripped off, and 9.37 g (97.5%) of colorless crystals, melting from 126 to 132 °C (with some apparent decomposition), is collected. They are recrystallized from tetrahydrofuran to yield three fractions of 2.02, 0.80, and 4.85 g, respectively. The first two fractions are significantly contaminated with *B*-triphenylboroxine (as evidenced by mass spectral data) and are discarded. The third fraction is washed with hot benzene (to remove traces of *B*-triphenylboroxine) and hot hexane (to remove adhering tetrahydrofuran) to yield (after drying under vacuum) the final product, decomposing at 132 to 135 °C. Anal. Calcd for $C_7H_9ON_4B$ (mol wt 176.01): C, 47.76; H, 5.16; N, 31.84; B, 6.14. Found: C, 47.16; H, 5.58; N, 31.22; B, 6.29. Mass spectrum (70 eV; relative abundances (in parentheses) of greater than 5% only): *m/e* 176 (75.4), 175 (5.6), 130 (5.7), 104 (11.1), 103 (10.8), 91 (6.1), 78 (100), 77 (14.0), 53 (10.3), 51 (10.4), 50 (8.1). Infrared spectrum (cm^{-1}): 3415/3305/3245/3195/3075 s (vb), 1663 s (b), 1603 sh, 1440 sh, 1432 m, 1403 ms, 1332 w (b), 1260 mw, 1210 m, 1090 vw, 1067 mw, 1020 mw, 746 m, 700 m.

Registry No. **1**, 72765-25-4; **2**, 72778-71-3; carbohydrazide, 497-18-7; trimethylamine–borane, 75-22-9; tetrahydrofuran–borane, 14044-65-6; bis(dimethylamino)phenylborane, 1201-45-2.

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[1] Boron–Nitrogen Compounds. 84. For part 83 of this series see D. P. Emerick, L. Komorowski, J. Lipinski, F. C. Nahm, and K. Niedenzu, *Z. Anorg. Allg. Chem.*, in press.

[2] K. Niedenzu, H. Beyer, and J. W. Dawson, *Inorg. Chem.*, **1**, 738 (1962).