with a 1024 × 1024 data matrix by using either 256 or 512 increments in the first dimension. An initial delay of 1 s was used. These data were processed by "pseudoecho" shaping prior to transformation. HETCOR spectra were acquired with sweep widths dictated by the appearance of the ^{13}C and ^{1}H spectra by using a 1024 × 512 data matrix and 128 increments in the first dimension. NOE-difference spectra were obtained with the decoupler gated off during acquisition time. A delay of 5 s was set between pulses. Spectra were obtained in an arrayed experiment with the decoupler set 10 000 Hz off-resonance and then with the decoupler cycled over the multiplet structure of the desired proton for irradiation; the procedure of Kinns and Saunders[10] was followed in this connection. The two resultant free induction decays (FIDs) were then subtracted and transformed.

Acknowledgment. Financial support of our study by the Air Force Office of Scientific Research, Air Force System Command (Grant AFOSR-84-0085, to A.P.M.), the Robert A. Welch Foundation (Grant P-093, to W.B.S., Grant B-963, to A.P.M.), and the North Texas State University Faculty Research Committee (to A.P.M.) is gratefully acknowledged.

Supplementary Material Available: The phase-sensitive, double quantum filtered COSY spectrum of **3** and the normal proton NMR spectrum of **3** with the NOE-difference spectra resulting from irradiation of the methyl group and irradiation of H-6 (4 pages). Ordering information is given on any current masthead page.

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[10] Kinns, M.; Saunders, J. K. M. *J. Magn. Reson.* **1984**, *56*, 518.

Isomerization and Thermolysis of Bis(9-borabicyclo[3.3.1]nonane)

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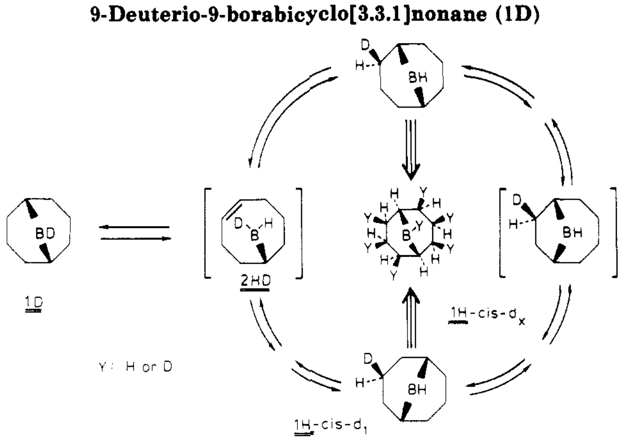
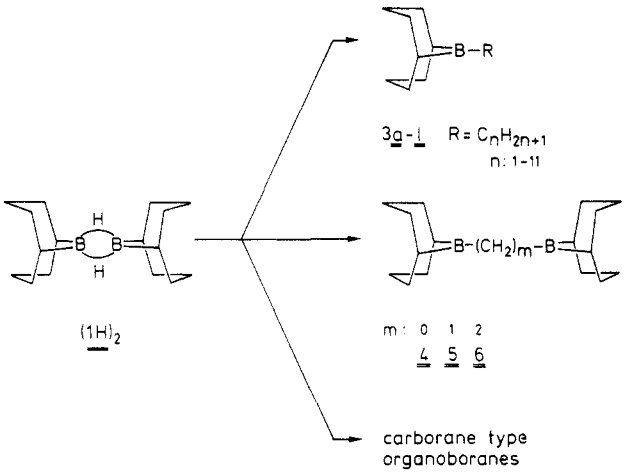
We recently reported that the spontaneous reaction of $Fe(CO)_5$ with bis(9-deuterio-9-borabicyclo[3.3.1]nonane) [(9-D-9-BBN)$_2$, $(\mathbf{1D})_2$][1] at temperatures above ≈140 °C leads to the formation of 9-alkyl-9-BBN derivatives **3** having only partially deuterated alkyl residues.[2] In contrast, at ≈100 °C $Co_2(CO)_8$ and $(\mathbf{1D})_2$ form the 9-alkyl-BBN derivatives with practically only perdeuterated alkyl substituents. The reduced number of deuterium atoms incorporated into the alkyl groups of the 9-alkyl-BBN's in the course of the reductive carbon monoxide oligomerizations at ≳140 °C was said to be the result of the fast reversible dehydroboration–deuteroborations of $(\mathbf{1D})_2$.[2]

Results and Discussion

Scheme I. Thermal Isomerization of 9-Deuterio-9-borabicyclo[3.3.1]nonane (1D)



Scheme II. Thermolysis of Bis(9-borabicyclo[3.3.1]nonane) (1H)$_2$



We have now found, that $(\mathbf{1D})_2$ reacts regio- and stereospecifically both in solution (>140 °C, 1 h) and in the molten state (≈160 °C, 5 min.). Reversible >BD/>CH and >BH/>CD at the C_8 ring gives mixtures of $(\mathbf{1H}\text{-}d_x)_2$ and $(\mathbf{1D}\text{-}d_{x-1})_2$, which on protolysis of the >BH and >BD functions gives a gas consisting of 85.8% of H_2 and to 14.2% of HD. This HD/H_2 ratio remains unchanged on prolonged heating of the solutions (>5 h) or of the melt (≈0.5 h). Therefore it can be concluded that only 6 of the 14 ring H atoms of the C_8 ring are exchangeable.

$(\mathbf{1H}\text{-}d_x)_2$ or $(\mathbf{1D}\text{-}d_{x-1})_2$ with one to three D atoms per monomer molecule (x = 1–3) are formed if $(\mathbf{1D})_2$ is held for a short time in the molten state. Repetitions of the melting procedure, preceded by a >BH/>BD exchange with an appropriate deuterium-donating reagent [e.g., alkyldeuterodiborane(6)], lead to the sixfold deuteration of both eight-membered rings in $(\mathbf{1D})_2$ (mass spectra). The ^{13}C NMR spectra reveal that each of the methylene carbons (C atoms 2–4 and 6–8) are exclusively monodeuterated. A topotactical walk mechanism of the boron atom around the C_8 ring (cf. Scheme I) ensures the stereoselective formation of the all-cis configuration (cis-$\mathbf{1D}$-$d_6)_2$. The formation of monomeric $\mathbf{1H}$-d_x or $\mathbf{1D}$-d_{x-1} (x > 1) with more than one deuterium atom after only a very short time in the molten state shows that intermolecular deuterium transfer between the two 9-BBN parts by way of the diborane(6) bridged species $(\mathbf{2HD})_2$ or **2HD–1D** is also involved (cf. Scheme I).

The facile transformation of $(\mathbf{1D})_2$ to (cis-$\mathbf{1D}$-$d_6)_2$ enables the preparation of defined cis deuterated cyclooctane derivatives by way of known oxidative transformations to *cis*-cyclooctane-1,5-diol-*2,3,4,6,7,8*-d_6.

Furthermore, in contrast to some reports in the literature,[3] the thermal stability of $(\mathbf{1H})_2$ and $(\mathbf{1D})_2$ has been

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[1] Köster, R. *Methoden der Organischen Chemie* (*Houben-Weyl-Müller*), 4th ed.; Köster, R., Ed.; Thieme: Stuttgart, 1982; Vol. XIII/3a, pp 339f.

[2] Köster, R.; Yalpani, M. *Angew. Chem.* **1985**, *90*, 600; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 572.

[3] (a) Knights, E. F.; Brown, H. C. *J. Am. Chem. Soc.* **1968**, *90*, 5280. "9-Borabicyclo[3.3.1]nonane possesses the most remarkable thermal stability. Samples have been distilled at 195 °C (12 mm) or heated for 24 h to 200 °C under nitrogen without loss of hydride activity or any noticeable change". (b) "Reagenzien Merck, 9-Borabicyclo[3,3,1]-nonan"; Technisches Merkblatt 1979; p 1.

found to be low at ≥170 °C. Molten **(1H)**$_2$ at ≥175 °C or in solution (e.g., in mesitylene) at ≈165 °C reacts slowly but irreversibly by way of various C–C hydroboration and other reactions. During the heating (≈20 h) the >BH borane bonds of **(1H)**$_2$ disappear completely.[4] Gas is not evolved. The ^{11}B NMR spectrum of the dark yellow viscous product shows new narrow signals at 90, 87, and 84 ppm and broad resonance signals in the region of +15 to −17 ppm. The obtained mixture consists of a volatile fraction (≈50%), containing (gas chromatography/mass spectra) the 9-alkyl-9-BBN derivatives [C_1–C_8; **3a–3h**; C_9–C_{11}; **3j–3l**) with homologous unbranched alkyl groups, the 9-cyclooctyl-9-BBN (**3i**), as well as the three compounds **4–6** with the presumed structures depicted in Scheme II. [**4**; *m/e* 242 (B_2); **5**; *m/e* 256 (B_2); **6**; *m/e* 270 (B_2); $\delta_{^{11}B}$ 90, 87, and 84 pm, respectively]. The resinous residue of the high-vacuum distillation ($\delta_{^{11}B}$ +15 to −17 ppm) probably consists of organoboron derivatives with carborane structures.

Similar results were obtained when dimeric 1- and 2-methyl-9-H-9-BBN derivatives (Me-**1H**)$_2$[5] were heated to >170 °C. Me-**3a–l** are formed as the main products (gas chromatography/mass spectra).

The thermal transformation of the diorganohydroboranes **(1H)**$_2$ or (Me-**1H**)$_2$ to the triorganoboranes **3a–l** or Me-**3a–l** are probably the result of a series of irreversible hydroborations of various C–C single bonds, as well as carboborations of C=C double bonds. In the formation of **4–6**, hydroborations of intermediates having B_3C groupings may also be assumed.[6]

Experimental Section

Gas chromatograms were obtained with a Siemens Sinchromat 1 instrument with a 30m OV 101 capillary column, injection port at 120 °C, oven at 60–330 °C, programmed at 6 deg/min; mass spectra were obtained on a Varian Mat CH 7A; ^{11}B NMR spectra were obtained on a Brucker WH 400 and ^{13}C NMR on a Brucker WM 300 spectrometer. All operations were performed under an argon atmosphere.

Thermal Isomerization of (1D)$_2$. (a) Formation of (1H-d_x)$_2$/(1D-d_x)$_2$; x ≤ 3. **(1D)**$_2$ (1 g) was kept in molten state at ≈160 °C for ≈5 min, then cooled to ≈20 °C; mass spectrum (70 eV; *m/e*, relative intensity): **1H** (M^+, 122, 33), **1D** or **1H**-d_1 (M^+, 123, 39), **1D**-d_1 or **1H**-d_2 (M^+, 124, 22), **1D**-d_2 or **1H**-d_3 (M^+, 125, 6). The products were analyzed after conversion to 9-ethyl-9-BBN mixtures by the reaction of a THF solution of (**1H**-d_x)$_2$/(**1D**-d_{x-1})$_2$ at 60–70 °C with ethylene; ^{13}C NMR (75.5 MHz, [D_8]toluene) δ 33.23 (s) [C2(2 H) attached to C3(2 H)], 33.14 (s) [C2(2 H) attached to C3(HD)], 32.85 (t) [C2(HD) attached to C3(2 H)], 32.75 (t) [C2(HD) attached to C3(HD)], 30.9 (br) [C1], 23.40 (s), [C3(2 H) attached to C2(2 H) and C4(2 H)], 23.31 (s) [C3(2 H) attached to C2(HD) and C4(2 H)], 23.21 (s) [C3(2 H) attached to C2(HD) and C4(HD)], 22.97 (t) [C3(HD) attached to C2(2 H) and C4(2 H)], 22.88 (t) [C3(HD) attached to C2(HD) and C4(HD)], 22.79 (t) [C3(HD) attached to C2(HD) and C4(HD)], 19.9 (br) [C9], 8.06 (s) [C9′(3 H)], and 7.77 (t) [C9″(2 H, D)].

(b) Preparation of (1D-d_6)$_2$. To a sample of 0.2 g of **(1D)**$_2$, which had been melted at ≈160 °C and then cooled, was added 0.4 ml of deuteroalkyldiborane(6). After the mixture was heated (≈5 min) to 80–100 °C, the volatiles were removed in vacuo. This procedure was repeated ten times. A (**1H**-d_x)$_2$/(**1D**-d_{x-1})$_2$ mixture with 75% (**1D**-d_6)$_2$ [refluxing **(1H)**$_2$ or **(1D)**$_2$ with an excess of the deuterium donor led to perdeuteration of the C_8 ring, i.e., (**1D**-d_{6+x}), $x < 8$] was obtained.

Thermolysis of (1H)$_2$. Formation of 9-Alkyl-9-BBN Derivatives 3a–l and 4–6. **(1H)**$_2$ (8.5 g, 35 mmol) was heated at 170 °C for 72 h. From the dark yellow product that was viscous at room temperature 4.1 g of colorless liquid was obtained by distillation at 0.001 torr and up to 180 °C. The distillate was analyzed by gas chromatography; t_r (min, %): **3a** (5.0, 3.8), **3b** (7.2, 4.8), **3c** (9.2, 1.9), **3d** (11.4, 2.5), **3e** (3.7, 2.3), **3f** (16.0, 7.8), **3g** (18.1, 12.4), **3h** (20.3, 27.5), **4i** (22.6, 7.2), **3j** (22.2, 1.9), **3k** (24.0, 4.0), **3l** (25.8, 2.6), **4** (22.5, 7.2), **5** (24.5, 6.9), **6** (26.0, 4.6). MS (relative intensity): **4** *m/z* 242 (M^+, B_2, 90), 132 (B_2, 60), 120 (B_1, 95), 41 (100); **5** *m/z* 256 (M^+, B_2, 100), 145 (B_2, 80), 41 (75); **6** *m/z* 270 (M^+, B_2, 35), 148 (B_1, 100), 41 (53).

Acknowledgment. We are grateful to Dr. R. Benn and Dr. R. Mynott for ^{11}B and ^{13}C NMR spectra and to F. Sageb and W. Schmöller for the gas chromatographic and mass spectroscopic analyses.

Registry No. **(1D)**$_2$, 88644-67-1; **(1H)**$_2$, 21205-91-4.

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(4) From DSC analysis a half-life time of 0.7 h for **(1H)**$_2$ at 200 °C can be estimated.

(5) The mixture of (1-Me-**1H**)$_2$ and (2-Me-**1H**)$_2$ was prepared from 1-methylcycloocta-1,5-diene and ethyldiboranes(6) according to ref 1.

(6) Cf. ref 1, 4th ed., 1984, Vol. XIII/3c, p 162.

A Simple Method for Distinguishing Optical Isomers of Chiral Amines, Hydroxylamines, Amino Acids, and Peptides

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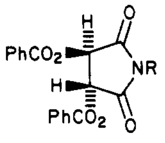
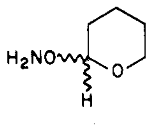
Distinguishing the optical isomers of amino acids, amines, and other functional chiral compounds is of considerable importance.[1] The demonstrated utility of dibenzoyltartarimide (DBT) derivatives **1** for the resolution of D,L-*O*-(tetrahydropyranyl)hydroxylamine (**2**)[2] and *O*-α-phenethylhydroxylamine (**3**)[4] suggested that related derivatives might be useful for the determination of the optical purity of other amines and amino acids. Herein we report on the general utility of DBT derivatives for differentiating the optical isomers of amino acids and other amines.



1



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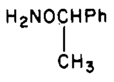
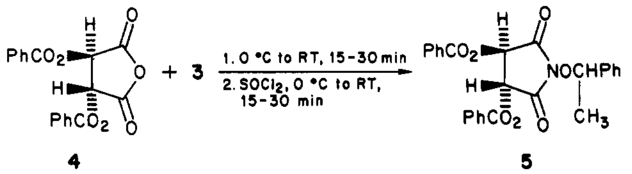


3

The simple reaction of dibenzoyl-L-(natural)tartaric anhydride (DBTA, **4**)[3] with DL-*O*-α-phenethylhydroxylamine (**3**) provided the diastereomeric dibenzoyl-DL-*N*-α-phenethoxytartarimides **5** (eq 1). Especially notable about the NMR spectrum of **5** were the two sharp singlets at 5.65 and 5.74 ppm corresponding to the two methine protons of the DBT residue (Table I, entry 31). Similarly, the ^{1}H NMR spectrum of dibenzoyl-*N*-DL-α-phenethyl-L-tartarimide (Table I, entry 1) displayed two singlets at 5.83 and 5.91 ppm. However, the NMR spectrum of the *N*-D-phenethyl derivative (Table I, entry 2) displayed only *a single sharp singlet at 5.83 ppm.*



(1)

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