Synthesis, Stereochemistry, and Thermolysis of β-Aminoalkylboranes

Takayuki Kawashima,* Naoko Yamashita, and Renji Okazaki*
Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113

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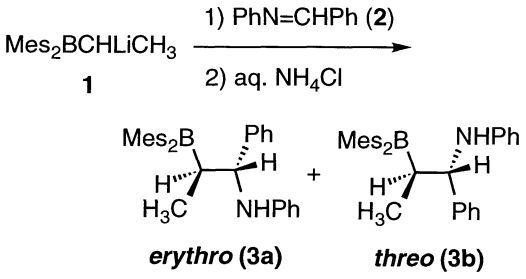
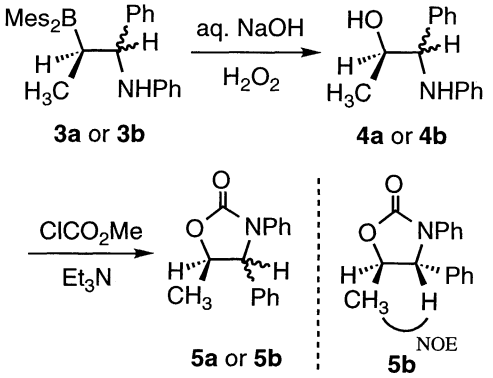
erythro- and *threo*-β-Amino boranes $Mes_2BCHMeCHPh$-NHPh were synthesized by the reaction of $Mes_2BCHMeLi$ with *N*-benzylideneaniline. The stereochemistry was determined by chemical derivation into the corresponding cyclic carbamates via β-amino alcohols. Their thermolysis gave a mixture of the corresponding (*E*)-enamine and its tautomer, (*E*)-imine, in sharp contrast to that of β-hydroxy boranes giving the olefins.

The boron-Wittig reaction is the only group 13 element analog of the Wittig reaction, and there have been several reports using dimesitylboranes.[1] Recently we achieved the synthesis of a tetracoordinate 1,2-oxaboretanide, an intermediate of the boron-Wittig reaction under basic conditions.[2] We also disclosed that on heating β-hydroxy boranes undergo *syn*-elimination of a hydroxyborane to give stereospecifically the corresponding olefins under neutral conditions.[2] The driving force of this reaction seems to be the large gain of a bond energy between boron and oxygen atoms. Although it was expected that β-aminoboranes also undergo *syn*-elimination of aminoboranes to give the corresponding olefins on heating, those prepared by hydroboration of enamines were reported to undergo *anti*-elimination under acidic conditions[3] or sometimes under neutral conditions.[4] We now wish to report the synthesis, stereochemistry, and thermolysis of β-aminoalkyldimesitylboranes.

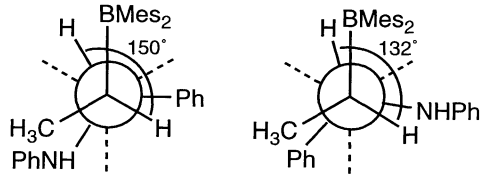
Sequential treatment of $Mes_2BCHMeLi$ (**1**)[1a,b,d,e] with PhCH=NPh (**2**), and with aqueous NH_4Cl in THF gave a diastereomeric mixture of $Mes_2BCHMeCHPhNHPh$ (**3a** (21%) and **3b** (31%)), providing a novel synthetic route to β-aminoalkylboranes.[5]

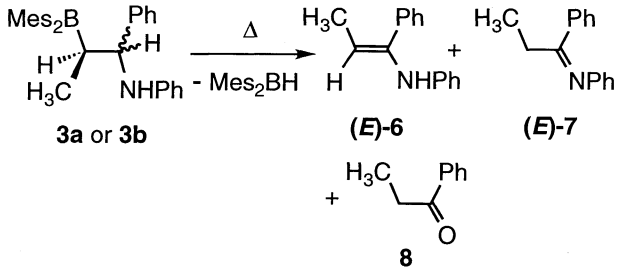


In order to determine the stereochemistry of **3a** and **3b** they were oxidized with aqueous NaOH and H_2O_2[1b,e] to give amino alcohols **4a** (47%) and **4b** (54%),[6] which were allowed to react with methyl chloroformate in the presence of triethylamine[7] to afford cyclic carbamates **5a** and **5b** in high conversion yields, respectively.[8] Although their stereochemistry could not be unambiguously determined from the vicinal coupling constants (J= 7.9 Hz for **5a**, J= 6.6 Hz for **5b**) between two methine protons of the alkyl chain, it was found by a differential NOE experiment that $OCHC\underline{H}_3$ and $PhNC\underline{H}Ph$ are *cis* to each other in **5b**, indicating that **3a** and **3b** are *erythro*- and *threo*-isomers, respectively. It is very interesting that the reaction of **1** with **2** gave mainly the *threo*-isomer, while that of **1** with benzaldehyde afforded the *erythro*-isomer as a main product.[1a,1e,2]



The vicinal coupling constants between two methine protons were observed to be 8.5 Hz and 6.4 Hz for **3a** and **3b**, respectively. Therefore, weight averaged conformers **A** and **B** can be estimated to have the dihedral angles of ca. 150° and 132° from Karplus equation, respectively. All signals due to two methine protons and α-methyl protons of **3b** were observed at higher field than those of **3a**, because the shielding by the anisotropy effect of aromatic rings is stronger in **B** than in **A**.





erythro-β-Amino borane (**3a**) was heated (102 °C, 5 h, C_6D_6) to give (*E*)-enamine **6**[9] (31%) and (*E*)-imine **7**[9] (60%) with 9% recovery of **3a**, by ^1H NMR spectroscopy. On the other hand, *threo*-β-amino borane (**3b**) needed more drastic conditions (150 °C, 7 h, toluene-d_8) than **3a**, and afforded mainly (*E*)-**7** (84%) along with a small amount of (*E*)-**6** (7%) and propiophenone (**8**) (9%). Imine **7** is considered to be formed by thermal isomerization of the first formed enamine **6**.[10] Under the conditions all products would be converted to thermodynamically more stable (*E*)-isomers.

It is interesting that the thermolysis of **3a** and **3b** gave the corresponding enamine **6** with an elimination of dimesitylborane instead of the expected β-methylstyrene, demonstrating a novel reactivity of β-aminoalkylboranes. The results can be explained as follows: (1) Since *anti*-elimination of aminoborane under neutral conditions is proposed to proceed via a bimolecular process,[4] such a reaction was prohibited by the bulky dimesityl groups. (2) The expected olefin formation with *syn*-elimination of aminoborane is also sterically unfavorable, because of difficult interaction between amino nitrogen and boron. (3) The transition state of the elimination of dimesitylborane is readily accessible as shown in the thermolysis of bulky silyl ethers of β-hydroxyalkylborane.[11]

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5 **3a**: ^{1}H NMR ($CDCl_3$, 500.1 MHz) δ 1.23 (d, ^3J = 7.8 Hz, 3H), 2.11 (s, 12H), 2.26 (s, 6H), 2.88 (dq, ^3J = 7.8, 8.5 Hz, 1H, C<u>H</u>CH$_3$), 4.24 (br s, 1H), 4.73 (d, ^3J = 8.5 Hz, 1H, C<u>H</u>Ph), 6.38 (d, ^3J = 8 Hz, 2H), 6.55 (t, ^3J = 8.5 Hz, 1H), 6.72 (s, 4H), and 6.87-7.05 (m, 7H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 12.56 (q), 20.97 (q), 23.30 (q), 42.67 (d), 59.54 (d), 113.23 (d), 116.94 (d), 126.23 (d), 127.31 (d), 127.81 (d), 128.55 (d), 128.94 (d), 137.99 (s), 138.74 (s), 141.97 (brs), 144.40 (s), and 147.53 (s). ^{11}B NMR ($CDCl_3$, 86 MHz) δ 83.2. HRMS (70 eV) *m/z* Found: 459.3077. Calcd for $C_{33}H_{38}N^{11}B$, M^+: 459.3097. **3b**: ^{1}H NMR ($CDCl_3$, 500.1 MHz) δ 0.93 (d, ^3J = 7.1 Hz, 3H), 2.18 (br s, 12H), 2.27 (s, 6H), 2.69 (dq, ^3J = 6.4, 7.1 Hz, 1H, C<u>H</u>CH$_3$), 4.39 (brs, 1H, N<u>H</u>), 4.64 (d, ^3J = 6.4 Hz, 1H, C<u>H</u>Ph), 6.18 (d, ^3J = 8 Hz, 2H), 6.53 (t, ^3J = 8 Hz, 1H), 6.79 (s, 4H), 6.94 (t, ^3J = 8 Hz, 2H), and 7.15-7.24 (m, 5H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 13.20 (q), 21.01 (q), 23.15 (q), 43.62 (d), 62.36 (d), 113.75 (d), 117.05 (d), 126.77 (d), 127.14 (d), 128.23 (d), 128.72 (d), 128.76 (d), 138.32 (s), 138.87 (s), 141.29 (brs), 144.06 (s), and 146.75 (s). ^{11}B NMR ($CDCl_3$, 86 MHz) δ 83.1. HRMS (70 eV) *m/z* Found: 459.3098. Calcd for $C_{33}H_{38}N^{11}B$, M^+: 459.3097.

6 **4a**: ^{1}H NMR ($CDCl_3$, 500.1 MHz) δ 1.13 (d, ^3J = 6.4 Hz, 3H), 1.55 (br s, 1H), 4.18 (dq, ^3J = 6.4, 4.1 Hz, 1H, C<u>H</u>CH$_3$), 4.36 (d, ^3J = 4.1 Hz, 1H, C<u>H</u>Ph), 4.60 (br s, 1H), 6.54 (d, ^3J = 7 Hz, 2H), 6.64 (t, ^3J = 7 Hz, 1H), 7.06-7.10 (m, 2H), 7.25-7.30 (m, 1H), 7.30-7.40 (m, 4H). HRMS (70 eV) *m/z* Found: 227.1302. Calcd for $C_{15}H_{17}ON$, M^+: 227.1310. **4b**: ^{1}H NMR ($CDCl_3$, 500.1 MHz) δ 1.26 (d, ^3J = 6.3 Hz, 3H), 1.55 (br s, 1H), 4.01 (dq, ^3J = 6.3, 5.3 Hz, 1H, C<u>H</u>CH$_3$), 4.22 (d, ^3J = 5.3 Hz, 1H, C<u>H</u>Ph), 4.55 (br s, 1H), 6.57 (d, ^3J = 7 Hz, 2H), 6.66 (t, ^3J = 7 Hz, 1H), 7.09 (t, ^3J = 7 Hz, 2H), 7.24-7.27 (m, 1H), 7.32-7.34 (m, 4H). HRMS (70 eV) *m/z* Found: 227.1307. Calcd for $C_{15}H_{17}ON$, M^+: 227.1310.

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8 **5a**: ^{1}H NMR ($CDCl_3$, 500.1 MHz) δ 1.00 (d, ^3J = 6.5 Hz, 3H), 5.03 (dq, ^3J = 6.5, 7.9 Hz, 1H, C<u>H</u>CH$_3$), 5.29 (d, ^3J = 7.9 Hz, 1H, C<u>H</u>Ph), and 7.10-7.20 (m, 9H). HRMS (70 eV) *m/z* Found: 253.1089. Calcd for $C_{16}H_{15}O_2N$, M^+: 253.1102. **5b**: ^{1}H NMR ($CDCl_3$, 500.1 MHz) δ 1.58 (d, ^3J = 6.2 Hz, 3H), 4.44 (dq, ^3J = 6.2, 6.6 Hz, 1H, C<u>H</u>CH$_3$), 4.90 (d, ^3J = 6.6 Hz, 1H, C<u>H</u>Ph), and 7.15-7.25 (m, 9H). HRMS (70 eV) *m/z* Found: 253.1116. Calcd for $C_{16}H_{15}O_2N$, M^+: 253.1102.

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10 As the referees pointed out, the stereochemistry of elimination of Mes_2BH can be clarified by use of *N*-silyl or *N*-methyl derivatives of **3a,b**, which do not undergo such an isomerization. Unfortunately, attempted syntheses of these compounds were unsuccessful, probably because of steric hindrance. Further investigations are in progress.

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