of the Co(III)/(II) reduction at +0.27 V and the simultaneous appearance of a new couple at +0.01 V. The addition of the same relative amount of 1-methylimidazole to $RuCl_2nic_4CoTPP$ causes the peak at +0.90 V to disappear and a new peak at +0.29 V to appear (i.e., a ~600-mV change compared to a ~300-mV change for CoTPP).

The addition of moderate excesses (×5) of either Cl^- or 1-methylimidazole to DMF solutions of $RuCl_2nic_4CoTPP$ produces no detectable changes in the visible spectra. This result indicates that there is no significant binding of either ligand in the Co^{2+} oxidation state. By assumption of a one-to-one stoichiometry, the binding constants for the Co^{3+} species calculated from potential shifts are $K_f = 2.8 \times 10^7$ for Cl^- and $K_f = 2.2 \times 10^{10}$ for 1-methylimidazole.

Given the spectral similarities between CoTPP and $RuCl_2nic_4CoTPP$ and the similarity of the Ru(II)/(III) potential to those of the other species in Table I, it is unlikely that the unusual coordination chemistry of the Co^{3+} species can be reasonably attributed to an electronic metal–metal interaction. We feel that the binding difference between the two cobalt complexes are instead primarily steric in nature. The Co in $RuCl_2nic_4CoTPP$ is confronted with a fixed "ligand", i.e., the $RuCl_2$ moiety, which sterically prevents other ligands from binding to one side of the porphyrin and enforces an otherwise unencountered (for CoTPP) "trans effect". Again, a large electronic interaction would be expected to effect the potential of the Ru(II)/(III) couple, which is not observed.

While no effects as large as those evident for the cobalt complex have been observed for other species in Table I, small differences in reduction potentials (relative to MTPP) are evident for Mn^{3+} and Fe^{3+}. Further study is underway to determine the extent of this phenomenon with respect to other complexes of **1**.

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Registry No. 1, 68000-73-7; **2**, 82248-51-9; **3**, 82265-56-3; **4**, 82248-52-0; **5**, 82265-57-4; **6**, 82281-48-9; **7**, 82265-58-5; **8**, 82265-59-6; **9**, 82265-60-9; **10**, 82265-61-0.

Direct Chiral Synthesis of Boronic Acids and Esters of High Optical Purity via Asymmetric Hydroboration Displacement

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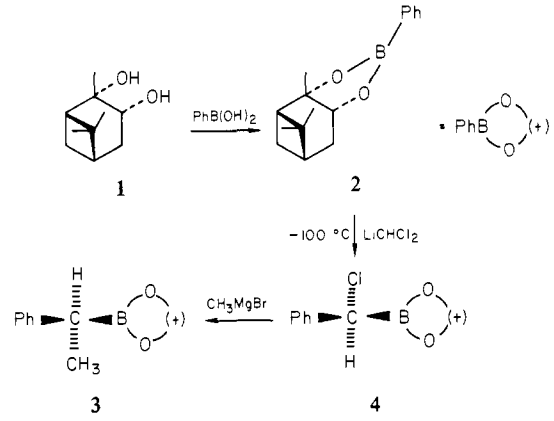
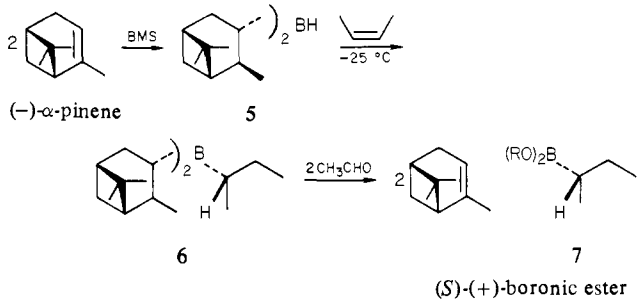
Chiral hydroboration of appropriate alkenes by diisopinocampheylborane (Ipc_2BH)[2] or isopinocampheylborane ($IpcBH_2$)[3] produces intermediates that readily eliminate α-pinene on treatment with acetaldehyde. This procedure makes readily available optically active boronic acids and esters of high optical purities.

Recently Matteson and Ray reported[4] an elegant directed chiral synthesis of boronic acids and esters based on (+)- and (−)-pinanediol. In a typical procedure they converted (+)-pinanediol (**1**) (Scheme I) to the phenylboronate (**2**). Treatment with (dichloromethyl)lithium at −100 °C, followed by methylmagnesium bromide at 20 °C gave (*S*)-1-phenylethaneboronate (**4**) of high optical purity, as estimated by oxidation to (*S*)-1-phenylethanol and its acetate (93.7% ee).

Scheme I



Scheme II



Alkylboronic esters, containing only one alkyl group attached to boron, are esthetically appealing intermediates for carbon–carbon bond-forming reactions.[5] These reactions are especially promising for chiral synthesis proceeding through boron intermediates. Accordingly, we undertook to see whether hydroboration might provide an alternative convenient route to these derivatives.

Both (+)- and (−)-diisopinocampheylborane (**5**) (Scheme II) with optical purities approaching 100% are now readily synthesized from commercially available α-pinene of lower optical purities (92–95% ee).[2b,c,6c] Hydroboration of *cis*-2-butene with Ipc_2BH gives organoborane **6** containing the chiral 2-butyl group with >98% ee.[2b,c]

Treatment of organoborane **6** with acetaldehyde[6] (25 °C) liberated α-pinene quantitatively and provided optically active diethyl 2-butylboronate (**7**, R = Et). This intermediate is readily separated from α-pinene by extraction with aqueous sodium hydroxide and converted by reesterification to (*S*)-(+)-dimethyl 2-butylboronate (**7**, R = Me, 71%): bp 38 °C (30 mmHg); $[\alpha]^{23}_D$ +9.1° (*c* 11.7, THF). Oxidation of the boronate with alkaline hydrogen peroxide gave (*S*)-(+)-2-butanol, $[\alpha]^{23}_D$ +13.1° (neat), suggesting an ee of ≥97%[7] for **7**.

Isopinocampheylborane (**8**) (Scheme III) of high optical purity is now also readily available from commercially available (92–95%

(1) Postdoctoral research associates on Grant 2R01 GM 10937-19 from the National Institutes of Health.

(2) (a) Brown, H. C.; Ayyangar, N. R.; Zweifel, G. *J. Am. Chem. Soc.* **1964**, *86*, 397. (b) Brown, H. C.; Yoon, N. M. *Isr. J. Chem.* **1977**, *15*, 12. (c) Brown, H. C.; Desai, M. C.; Jadhav, P. K., submitted for publication.

(3) (a) Brown, H. C.; Yoon, N. M. *J. Am. Chem. Soc.* **1977**, *99*, 5514. (b) Mandal, A. K.; Jadhav, P. K.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 3543. (c) Brown, H. C.; Jadhav, P. K. *Ibid.* **1981**, *46*, 5047. (d) Brown, H. C.; Jadhav, P. K.; Mandal, A. K., submitted for publication.

(4) Matteson, D. S.; Ray, R. *J. Am. Chem. Soc.* **1980**, *102*, 7590.

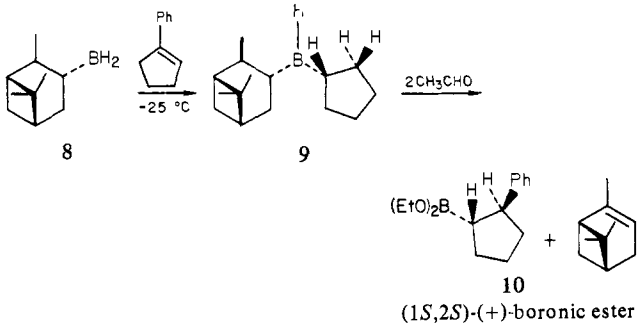
(5) (a) Matteson, D. S.; Majumdar, D. S. *J. Am. Chem. Soc.* **1980**, *102*, 7588. (b) Brown, H. C.; Imai, T., to be submitted for publication.

(6) Benzaldehyde has been used previously for such displacements. (a) Mikhailov, B. M.; Bubnov, Yu, N.; Kiselev, V. G. *J. Gen. Chem. USSR* **1966**, *36*, 65. (b) Midland, M. M.; Tramontano, A.; Zderic, S. A. *J. Organomet. Chem.* **1978**, *156*, 203. (c) Brown, H. C.; Jadhav, P. K.; Desai, M. C. submitted for publication. However, acetaldehyde is more reactive. Its greater volatility also offers advantages.

(7) Leroux, P. J.; Lucas, M. J. *J. Am. Chem. Soc.* **1951**, *73*, 41. These authors report $[\alpha]^{25}_D$ −13.5° (neat) for 2-butanol.

0002-7863/82/1504-4303$01.25/0

Scheme III



ee) (+)- and (−)-α-pinene.[8] This reagent possesses significant advantage for the hydroboration of more hindered alkenes.[3] Accordingly, it was used to hydroborate 1-phenylcyclopentene.[3b] The intermediate **9** was readily converted into the desired chiral boronic ester by displacement of α-pinene with acetaldehyde.[6] In this case the excess acetaldehyde, THF solvent, and the displaced α-pinene were readily removed by distillation under vacuum from the boronic ester. Distillation of the product gave (1*S*,2*S*)-(+)-diethyl *trans*-(2-phenylcyclopentyl)boronate (**10**, 66%): bp 92 °C (0.02 mmHg); $[\alpha]^{23}_D$ +25.4° (*c* 9.65, THF). Oxidation of **10** with alkaline hydrogen peroxide gave (1*S*,2*S*)-(+)-*trans*-2-phenylcyclopentanol (bp 129–131 °C (6 mmHg), $[\alpha]^{23}_D$ +71.2° (*c* 11.9, C_2H_5OH)) suggesting 100% ee for **10**.

The following procedures are representative.

A. Preparation of (*S*)-(+)-Dimethyl 2-Butylboronate (7, R = Me). All operations were carried out under nitrogen.[9] To a stirred solution of BMS (9.89 M, 5 mL, 50 mmol) in THF (15 mL) at 0 °C was added slowly (−)-α-pinene (15.9 mL, 100 mmol, 95% ee), and the reaction mixture was further stirred for 2.5 h. Dimethyl sulfide and THF were pumped off (20 mmHg, 15 min, 25 °C) and collected in a cold trap (−78 °C). More THF (18 mL) and (−)-α-pinene (2.4 mL, 15 mmol) were added, and the reaction flask was kept at 0 °C for 3 days. At the end of this period, the reaction mixture was cooled to -25 °C, and *cis*-2-butene (4.5 mL, 50 mmol) was added and stirred for 6 h. Then it was brought to 25 °C, and acetaldehyde (11 mL, 200 mmol) was added and stirred at 25 °C for 36 h. Excess acetaldehyde was pumped off (25 °C, 30 mmHg, 1 h), and pentane (50 mL) was added. The resulting mixture of α-pinene and boronate ester (**7**, R = Et) was stirred with 3 M NaOH (3 × 50 mL; each portion stirred for 1 h). The combined aqueous phase was acidified with aqueous hydrochloric acid and extracted with ether (3 × 50 mL) and dried (anhydrous $MgSO_4$). Ether was removed to give 2-butylboronic acid (**7**, R = H), which was dried under vacuum (0.5 mmHg, 10 h). It was then converted into methyl ether[10] (**7**, R = Me) by refluxing it with a 1:2.4 mixture of methanol/chloroform (200 mL) using a Soxhlet apparatus filled with 4-Å-type molecular sieves for 20 h. At the end of this period, after the removal of chloroform and methanol, (*S*)-(+)-dimethyl 2-butylboronate (**7**, R = Me) was isolated by distillation (4.6 g, 71%); bp 38 °C (30 mmHg); $[\alpha]^{23}_D$ +9.1° (*c* 11.7, THF). It showed satisfactory ^1H NMR, ^{11}B NMR, and ^{13}C NMR.

B. Preparation of (1*S*,2*S*)-(+)-Diethyl *trans*-(2-Phenylcyclopentyl)boronate (10). $IpcBH_2$ (**8**) in THF was prepared by following the reported procedure.[8] Thus a solution of $IpcBH_2$ in THF (0.867 M, 40.3 mL, 35 mmol) was cooled to −25 °C. To it was added 1-phenyl-1-cyclopentene (5 mL, 35 mmol), and this was stirred at −25 °C for 48 h while dialkylborane precipitated out of the solution. Then acetaldehyde (7.8 mL, 140 mmol) was added, and the flask was allowed to warm to 25 °C and stirred for 6 h. The excess acetaldehyde and THF were pumped off (25 °C, 14 mmHg), and then α-pinene was removed (25 °C, 0.2 mmHg). The residue was distilled under high vacuum to afford (1*S*,2*S*)-(+)-diethyl *trans*-(2-phenylcyclopentyl)boronate (**10**, 5.8 g, 66%): bp 92 °C (0.02 mmHg); $[\alpha]^{23}_D$ +25.4° (*c* 9.65, THF). The compound showed satisfactory ^1H NMR, ^{11}B NMR, and ^{13}C NMR.

It is evident that chiral hydroboration of appropriate alkenes with either diisopinocampheylborane or isopinocampheylborane of high optical purity provides chiral organoboranes from which α-pinene can be readily displaced with acetaldehyde. The products thus formed are readily isolated as boronic acids or boronic esters of high optical purity for application in organic synthesis. Consequently, the present procedure, in conjunction with the chiral synthesis of Matteson and Ray,[4] makes these optically active boronic acids and esters readily available for the first time. In both procedures, the chiral intermediates, α-pinene and pinanediol, are readily recovered without loss of activity for recycle in the synthesis.

(8) Brown, H. C.; Schwier, J. R.; Singaram, B. *J. Org. Chem.* **1978**, *43*, 4395.

(9) For handling of air- and moisture-sensitive compounds, see: Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975; p 191.

(10) Torsell, K. *Acta Chem. Scand.* **1954**, *8*, 1779.

Registry No. 5, 21932-54-7; **6**, 26673-63-2; **7** (R = Et), 82248-41-7; **7** (R = Me), 82248-42-8; **7** (R = H), 82248-43-9; **8**, 64234-27-1; **9**, 82248-44-0; **10**, 82248-45-1; (−)-α-pinene, 7785-26-4; (*S*)-(+)-2-butanol, 4221-99-2; 1-phenylcyclopentene, 825-54-7; (+)-*trans*-2-phenylcyclopentanol, 38805-89-8; *cis*-2-butene, 590-18-1.

Book Reviews

Odor Quality and Chemical Structure: ACS Symposium Series. No. 148. Edited by Howard R. Moscowitz (Weston Group) and Craig B. Warren (International Flavors and Fragrances, Inc.). American Chemical Society, Washington, D.C. 1981. ix + 243 pp. $24.50.

This symposium consists of twelve papers, which certainly serve to confirm the editors' prefatory observation that "We still lack an understanding of why chemicals smell the way they do." A considerable portion of the work deals with the quantitation of odor characteristics and their correlation with other physical properties such as vapor pressure, molecular weight and geometry, type of functional groups, solubility, polarity, and infrared and Raman spectra. Studies in both humans and animals (e.g., insects, fish, salamanders, dogs) are cited. In the absence of a unified theory of olfaction, such information can still be used for practical purposes such as design of perfumes or insect pheromone analogues.

Three of the contributions consider the prediction of the odors of mixtures from those of their components. There are also chapters on the relation of olfaction to general chemical sensitivity and on the formation and activation of receptor sites. One chapter discusses the role of odorants as indicators of human disease and as chemical messengers in humans and other mammals.

This is not a book for the casual perfumer or flavorist, but should be useful to researchers with considerable technical resources at their hands. Although some of the contributors are clearly "beating their own drums", the total presentation achieves a reasonable balance because of the citation of close to 400 references. A subject index is included.

Keith T. Buck, *Fries & Fries Division, Mallinckrodt, Inc.*