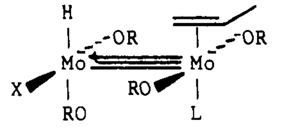
We have found that Lewis base association to $Mo_2(OR)_6$ compounds which give $Mo_2(OR)_6L_2$ compounds is very sensitive to the steric properties of L and the alkoxy group and, furthermore, the binding of L is cooperative: the coordination of one ligand is followed by a more rapid coordination of the second. It is thus possible to rationalize the aforementioned reactions by invoking a common cooperative β-hydrogen elimination/alkene insertion mechanism in which a key intermediate is depicted by I.



I

Elimination of alkane occurs during alcoholysis when L = $HNMe_2$ and X = alkyl. For electronic reasons, the preferred alignment of the alkene should be along the M–M bond, and for steric reasons, the methyl group would be favored distal to the M–M bond. Thus, insertion to give the isopropyl ligand can occur when X = OR. Providing the olefin can gain access to a position in which the methyl substituent is over the Mo–Mo bond, ultimately the presence of L will allow for isomerization of the alkyl ligand, *i*-Pr → *n*-Pr.

Further studies are in progress.[10]

Supplementary Material Available: Listing of fractional coordinates and isotropic thermal parameters (2 pages). Ordering information is given on any current masthead page.

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[10] We thank the Deparment of Energy, Office of Basic Research, Chemical Sciences Division, for financial support and the National Science Foundation for Instrument Grant CHE 81-05004.

Boronic Ester Homologation with 99% Chiral Selectivity and Its Use in Syntheses of the Insect Pheromones (3*S*,4*S*)-4-Methyl-3-heptanol and *exo*-Brevicomin

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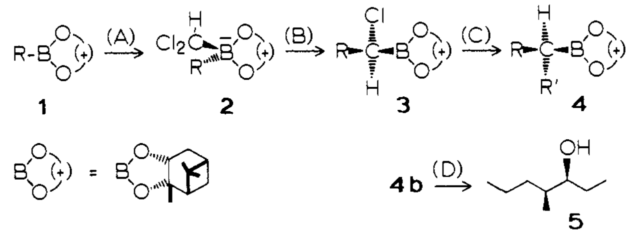
Our directed chiral synthesis of α-chloro boronic esters (**3**) from pinanediol boronic esters (**1**; Scheme I)[1-3] has been dramatically improved by zinc chloride catalysis of the rearrangement of the intermediate borate complexes (**2**). Diastereoselectivities are 98.5–99.5% (except R = CH_3), yields 82–99% (Table I). The utility is demonstrated by efficient syntheses of two insect pheromone components, (3*S*,4*S*)-4-methyl-3-heptanol (**5**) and *exo*-brevicomin (**10**). This chemistry is compatible with a wide variety of structural types and may allow the controlled sequential construction of an unlimited number of adjacent chiral centers.

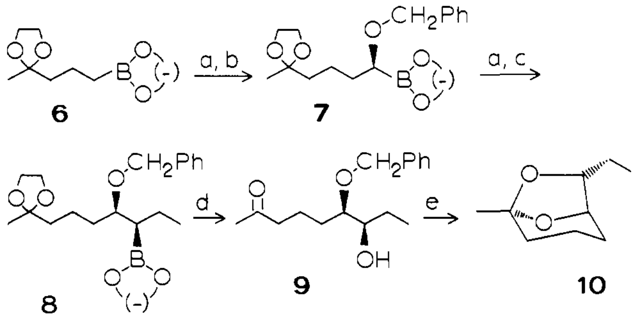
Failure of the original procedure[1] to give satisfactory yields from pinanediol 2-methylpropane-1-boronate (**1e**)[4] prompted a search for better conditions. Noting that lithium chloride catalyzes[1,5] and mercuric chloride inhibits[5] epimerization of **3**, we tested the effects of several metal salts capable of complexing chloride ion in the preparation of **3**. Zinc chloride,[6] 0.5–0.65 equiv, was added to **2** at −100 °C and the mixture kept for 6–8 h at 20–25 °C to yield the results summarized in Table I.

Scheme I[a]



[a] (A) $LiCHCl_2$, −100 °C; (B) $ZnCl_2$; (C) R'MgBr; (D) H_2O_2/NaOH.

Scheme II[a]



[a] (a) A + B of Scheme I; (b) $LiOCH_2Ph$;[3] (c) EtMgBr, −78 °C; 36 h at 20 °C; (d) H_2O_2/NaOH, H^+/SiO_2; (78%); (e) H_2/Pd.[12b]

Table I. Homologation of Boronic Esters (1) to α-Chloroboronic Esters (3)

$RBO_2C_{10}H_{16}$ (1)	yield, %[a]		diastereoselectivity, %		anal. method[b]
	no $ZnCl_2$	with $ZnCl_2$	no $ZnCl_2$	with $ZnCl_2$	
1a		87		99	A
1c	57[c]	83	74[c]	95.7	B
1d	61[c]	92[d]	90[c]	98.5	A
1e	30[e]	89	88[e]	99.5	B
1f	75	99	92.5	99.5	B
6		93		99.5[f]	B
7		82		99.5	B

[a] Isolated 3 or 4. [b] (A) Rotation of derived alcohol;[1] (B) 200-MHz NMR analysis of 3 or NHAc derivative[2,4] compared with epimeric mixture. [c] Reference 1. [d] Data by Mark Peterson. [e] Reference 4. [f] Derived 7, 98%.

The improved procedure was immediately applicable to the synthesis of (3*S*,4*S*)-4-methyl-3-heptanol (**5**; European elm bark beetle, *Scolytus multistriatus*;[7] Scheme I). (+)-Pinanediol propane-1-boronate (**1a**)[8,9] was homologated to **4a** ≡ **1b** and then to **4b**, which was oxidized to **5**: overall yield 58–63%; $[\alpha]^{24}{}_D$ −19.8° (*c* 4.4, hexane) [lit.[7c] $[\alpha]^{22}{}_D$ −21.7° (*c* 0.57, hexane)]; proton NMR and IR spectra in accord with reported data.[7] The diastereomeric impurity in **5** was not detectable by 200-MHz NMR, even of the

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[5] Matteson, D. S.; Erdik, E., manuscript in preparation.

[6] Zinc chloride was dried to a fine powder at 0.01–0.02 torr at up to 100 °C with magnetic stirring. Other experimental procedures resembled those already described,[1-3] except that 3 were isolated by concentration below 30 °C, workup with saturated aqueous ammonium chloride and hexane, and concentration to crude 3 satisfactory for preparation of 4. Products 3–9 were chromatographed on silica.

[7] (a) Pearce, G. T.; Grove, W. E.; Silverstein, R. M.; Peacock, J. W.; Cuthbert, R. A.; Lanier, G. N.; Simeone, J. B. *J. Chem. Ecol.* **1975**, *1*, 115. (b) Mori, K. *Tetrahedron* **1977**, *33*, 289–294. (c) Mori, K.; Iwasawa, H. *Ibid.* **1980**, *36*, 2209–2213.

[8] Boronic acids are readily prepared from Grignard reagents: Washburn, R. M.; Levens, E.; Albright, C. F.; Billig, F. A. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, pp 68–72. Esterification: ref 1 and 2. Hydroboration routes to boronic acids are of potential interest: Brown, H. C.; Jadhav, P. K.; Desai, M. C. *J. Am. Chem. Soc.* **1982**, *104*, 4303–4304.

[9] Pinanediol: Ray, R.; Matteson, D. S. *J. Indian Chem. Soc.* **1982**, *52*, 119–123. Enantiomeric purification: ref 2.

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MTPA ester[7c,10] with Eu-fod shift reagent, but may be ~1%. The double homologation should reduce the enantiomer of **5** to the 0.01% level.

The functional group compatibility of the new procedure was tested in the simple synthesis of *exo*-brevicomin (**10**; western pine beetle, *Dendroctonus brevicomis*)[11,12] outlined in Scheme II. (−)-Pinanediol[1,9] as chiral directing group led to the natural enantiomer of **10**, $[\alpha]^{23}_{D}$ +81.1° (*c* 1.4, ether) [lit. $[\alpha]^{25}_{D}$ +84.1°,[12a] +81.5°[12b]], which contained 2% *endo*-brevicomin by GC,[11a] 3% by 200-MHz NMR (t at δ 0.97[11a]). Most of the loss in stereoselectivity occurred during the displacement of chloride by benzyl oxide. The intermediate **9**, reported as an oil,[12b] matched the reported IR, mass spectral, and NMR data[13] but crystallized and could thus be freed from its diastereomer, from ether/pentane, mp 30-31 °C, $[\alpha]^{23}_{D}$ −13.4° (*c* 3.4, $CHCl_3$).

Acknowledgment. We thank the National Science Foundation for a grant (CHE-8025229) and the Boeing Corp. for a gift in support of the Nicolet 200-MHz NMR instrument.

Supplementary Material Available: Preparation and characterization of new cmpounds (**3**–**9**) and NMR curves showing diastereomeric purity of **3c**, **3f**, and **6** (7 pages). Ordering information is given on any current masthead page.

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(11) Racemic examples: (a) Bellas, T. E.; Brownlee, R. G.; Silverstein, R. M. *Tetrahedron* **1969**, *25*, 5149-5153. (b) Wasserman, H. H.; Barber, E. H. *J. Am. Chem. Soc.* **1969**, *91*, 3674-3675. (c) Hoffmann, R. W.; Kemper, B. *Tetrahedron Lett.* **1982**, *23*, 845-848. (d) Yamamoto, Y.; Saito, Y.; Maruyama, K. *Ibid.* **1982**, *23*, 4959-4962. (e) Wuts, P. G. M.; Bigelow, S. S. *Synth. Commun.* **1982**, *12*, 779-785.

(12) Chiral syntheses: (a) Mori, K. *Tetrahedron* **1974**, *30*, 4223-4227. (b) Sherk, A. E.; Fraser-Reid, B. *J. Org. Chem.* **1982**, *47*, 932-935. (c) Johnston, B. D.; Oehlschlager, A. C. *Ibid.* **1982**, *47*, 5384-5386. (d) Masaki, Y.; Nagata, K.; Serizawa, Y.; Kaji, K. *Tetrahedron Lett.* **1982**, *23*, 5553-5554 and references cited therein.

(13) We thank Professor Fraser-Reid for a copy of the 60-MHz NMR spectrum of **9**.

Light-Induced Reversible pH Change

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Although a stopped-flow pH jump is a suitable technique for kinetic studies in aqueous solution,[1] its use is limited to relatively slow processes ($\tau > 10^{-3}$ s), and it can not be applied to reactions in complex systems such as vesicles or membranes. In contrast to this technique, a laser-induced pH jump,[2] using an appropriate proton or hydroxide ion emitter, is a more convenient method for perturbing chemical and biochemical reactions by a proton or hydroxide ion pulse. It is applicable to closed systems such as reactions inside vesicles, and the time necessary for pH change can be reduced to less than 10^{-9} s with a short laser pulse. The light-induced pH jump is of particular interest in connection with the function of bacteriorhodopsin. Bacteriorhodopsin uses light energy to translocate protons across the membrane. The cell uses the energy stored in the electrochemical gradient for ATP synthesis.[3]

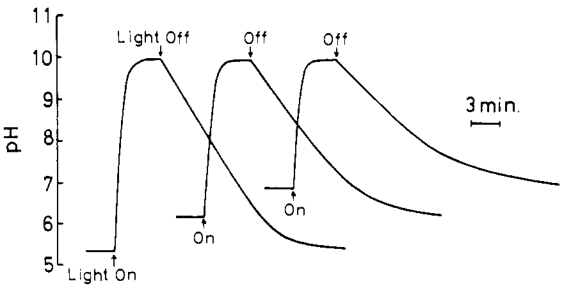
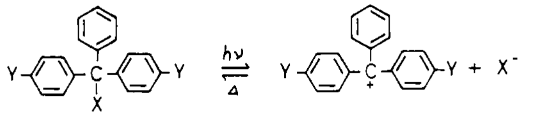


Figure 1. Light-induced pH increase of aqueous solutions containing 4,4′-bis(dimethylamino)triphenylmethane leucohydroxide (4.8×10^{-4} mol/L) and dodecyltrimethylammonium chloride (0.1 mol/L) at 35 °C. Initial pH was controlled by the addition of sodium hydroxide solution.

Clark et al. and Gutman et al. adopted 2-naphthol-6-sulfonate, 2-naphthol-3,6-disulfonate, and 8-hydroxypyrene-1,3,6-trisulfonate as proton emitters. These compounds, ArOH, release protons in the photoexcited state and the reprotonation of ArO^- takes place within 0.1-1 μs at $(H^+) = 10^{-4}$-10^{-5} M.[2] The rapid recombination limits the application to specific reactions.

We adopted triphenylmethane leucohydroxide as hydroxide ion emitters. Triphenylmethane leuco derivatives are well-known photochromic molecules, which dissociate into ion pairs under ultraviolet irradiation with production of intensely colored triphenylmethyl cations. The cations thermally recombine with counterions as in eq 1.[4] These compounds have long been employed advantageously for their color change on photoirradiation rather than for the chemical property change.[4,5] According to the reaction scheme 1, triphenylmethane leucohydroxide derivative (**1**, X = OH) functions as a light-induced hydroxide ion emitter. Investigations of the derivatives have indicated that the dissociation proceeds very rapidly (within 40 ns) in high quantum yield.[4,6]



(1)

(1)

Although triphenylmethane leucohydroxide has promise as a hydroxide ion emitter, one serious disadvantage is its very low solubility in water. To overcome this difficulty, the following two methods have been employed: (1) solubilization using surfactants; (2) chemical modification to water soluble form.

Figure 1 shows the light-induced pH increase from various initial pHs in aqueous solution containing 4,4′-bis(dimethylamino)triphenylmethane leucohydroxide (**1**, X = OH, Y = $N(CH_3)_2$)[7] and cationic surfactant, dodecyltrimethylammonium chloride. The initial pH was controlled by the addition of sodium hydroxide solution. A high-pressure mercury lamp (Ushio, 1 kW) was used as a light source, and the irradiation wavelength was limited to the ultraviolet region ($410 > \lambda > 280$ nm) using glass filters (Toshiba UV-D25 and UV-31). The pH was measured by a conventional pH meter (Horiba F-7ss).[8] In the most pronounced case, the pH was increased from 5.4 to 10.0 by irradiation.[9] After removal of the light, the pH returned to the initial value after 15 min in the dark. The cycle, an increase in pH by irradiation and a return in the dark, could be repeated several times without any noticeable fatigue. No change in pH was detected in the absence of 4,4′-bis(dimethylamino)triphenylmethane leucohydroxide. Photoirradiation of an aqueous solution of malachite

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(7) 4,4′-Bis(dimethylamino)triphenylmethane leucohydroxide was prepared by treating phenyllithium with Michler's ketone in ether. Anal. Calcd for $C_{23}H_{26}N_2O$: C, 79.73; H, 7.56; N, 8.09. Found: C, 80.02; H, 7.63; N, 7.85.

(8) To avoid any photoirradiation effect onto the electrode, light was focused to the solution below the electrode. The cell (15 × 15 × 45 mm) is made of quartz and the solution sample (6 mL) was stirred with a magnetic stirrer during the measurement.

(9) The pH change was also confimed by using a pH probe such as pyranine fluorescence probe (Kano, K.; Fendler, J. H. *Biochim. Biophys. Acta* **1978**, *509*, 289).

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