ligand in the single oyxgen bridge mode VI.

The Al-O lengths, 1.852(9) and 1.868(9) Å, are normal,[7] and the overall geometry of the anion conforms closely to that found in related complexes such as $K[Al_2(CH_3)_6N_3]$[8] [i.e., Al-O-Al = 128.3 (7)° vs. Al-N-Al = 128.0 (3)°].

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Supplementary Material Available: Tables of bond distances, angles, final fractional coordinates, themal parameters, and observed and calculated structure factors are available (14 pages). Ordering information is given on any current masthead page.

(7) Atwood, J. L.; Hunter, W. E.; Crissinger, K. D. *J. Organomet. Chem.* **1977**, *127*, 403.
(8) Atwood, J. L.; Newberry, W. R. *J. Organomet. Chem.* **1974**, *65*, 145.

Enantioselective Aldol Reactions with High Threo or Erythro Selectivity Using Boron Azaenolates

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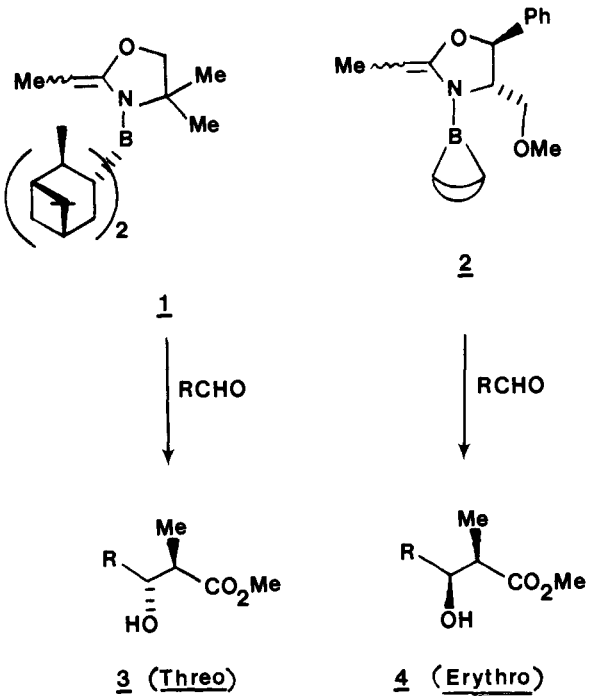
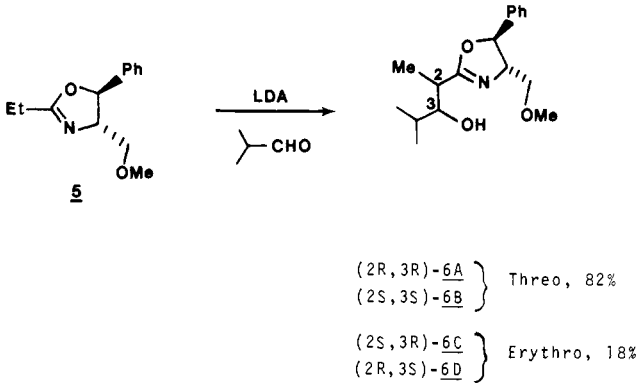
The extensive activity in recent years to control acyclic stereochemistry has resulted in a number of reports dealing with diastereoselection and/or enantioselection. A few of these have reached very impressive levels of success by using boron enolates.[1] We wish to report that our studies using the boron azaenolates, **1** and **2**, derived from achiral[2] and chiral oxazolines[3] has led to some useful and surprising results in the area of acyclic stereochemistry, particularly for the rarely reached threo isomers. Thus, by exchanging the chiral auxiliary from boron (**1**) to the heterocycle (**2**), we have been successful in altering the stereochemical course of the aldol process from threo to erythro products with enantioselectivities of ~90% (77-85% ee) in the former and ~70-80% (40-60% ee) in the latter. Table I depicts the results obtained by using boron azaenolate **1**[4-6] with several representative aldehydes. The reactions were carried out by adding 1.0 equiv of the aldehyde to preformed boron azaenolate **1** in ether at -78 °C, stirring for 2 h, and then warming to -20 °C for 1 h. Phosphate buffer (pH 7) was added along with methanol and 30% hydrogen peroxide at 0 °C. Usual extraction and drying procedures gave the alkylated oxazoline which was hydrolyzed to the



β-hydroxy acid by heating (12 h) in 3 N sulfuric acid. The crude acids were transformed into the methyl esters **3** by treatment with diazomethane. The five-step sequence from 2-ethyloxazoline to the hydroxy ester was carried out without any isolation and purification of intermediates. None of these steps have been as yet optimized. The threo configuration was assigned on the basis of ^1H NMR data which showed the α proton as a quintet at δ 2.6-2.7 with $J = 7$ Hz.[7] In order to assign absolute stereochemistry to threo-**3**, the chiral oxazoline **5** was metalated and treated with isobutyraldehyde to give four diastereoisomers as previously reported;[7b] **6a** and **6b** were correlated to (-)-and (+)-*threo*-**3**,



(1) (a) Fenzl, W.; Köster, R.; Zimmerman, H. J. *Liebigs Ann. Chem.* **1975**, 2201. (b) Masamune, S.; Mori, D.; Horn, D. V.; Brooks, D. W. *Tetrahedron Lett.* **1979**, 1665. (c) Hirama, M.; Masamune, S. *Ibid.* **1979**, 2225. (d) van Horn, D.; Masamune, S. *Ibid.* **1979**, 2229. (e) Hirama, M.; Garvey, D. S.; Lu, L. D.; Masamune, S. *Ibid.* **1979**, 3937. (f) Evans, D. A.; Vogel, E.; Nelson, J. V. *J. Am. Chem. Soc.* **1979**, *101*, 6120. (g) Herold, T.; Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 768. (h) Hoffmann, R. W., Zeiss, H. J. *Ibid.* **1980**, *19*, 218. (i) Hoffmann, R. W. Ladner, W. *Tetrahedron Lett.* **1979**, 4653. (j) Sugasawa, T.; Toyada, T. *Ibid.* **1979**, 1423. (k) Evans, D. A.; Nelson, J. V.; Vogel, E.; Taber, T. R. *J. Am. Chem. Soc.*, in press. Undoubtedly, the most impressive example of diastereo- and enantioselective erythro aldols arises from the recent work of Evans (private communication) involving the boron enolates of chiral oxazolidinones.
(2) Meyers, A. I.; Temple, D. L.; Nolen, R. L.; Mihelich, E. D. *J. Org. Chm.* **1974**, *39*, 2778.
(3) Meyers, A. I.; Knaus, G.; Kamata, K.; Ford, M. E. *J. Am. Chem. Soc.* **1976**, *98*, 567.

(4) The boron azaenolates **1** and **2** were prepared from the oxazolines by using boryl triflates as reported by Mukaiyama.[5] Preparation of **1**: Borane in THF (1 M, 57 mL), (+)-α-pinene (17.8 g, $[\alpha]_D$ 41.1°) was added together under nitrogen and stored at 0 °C for 3 days upon which a precipitate appeared. After cooling the solution to -30 °C, the precipitate was collected, giving diisopinocampheylborane of 99.8% optical purity as described by Brown.[6] After drying in vacuo (13.5 g, 83%), the borane was dissolved in hexane (250 mL) and trifluoromethanesulfonic acid (7.1 g) was added at 0 °C (hydrogen evolution!). After stirring overnight, the solution was filtered and evaporated and the residue (diisopinocampheylboryl triflate) was used without further purification. Addition of 2-ethyl-4,4-dimethyloxazoline (0.72 g) to 2.5 g of the boryl triflate in 42 mL of ether and addition of 0.73 g diisopropylethylamine at -78 °C gave a mixture which was stirred for 1 h (amine triflate precipitated). The solution and precipitate were used as such for the aldol reactions. Preparation of **2**: this was accomplished by using 0.88 g of (4*S*,5*S*)-2-ethyl-4-(methoxymethyl)-5-phenyloxazoline, 1.08 g of 9-borabicyclononane triflate,[5] and 0.52 g of diisopropylethylamine in the manner described above.
(5) Inoue, T.; Uchimaru, T.; Mukaiyama, T. *Chem. Lett.* **1977**, 153.
(6) Brown, H. C.; Yoon, N. M.*Israel j. Chem.* **1976**, *15*, 12.

0002-7863/81/1503-4278$01.25/0

Table I. Chiral *threo*-β-Hydroxy Esters **3** via Boron Azaenolate **1**

RCHO	threo:erythro,[a] %	*threo*-**3**,[d,e] % ee	$[\alpha]_D^{CHCl_3}$ [f] (*c*)	**3**, overall[g] yield, %
EtCHO	92:8	77	−9.9 (1.3)	26
PrCHO	91:9	77	−2.5 (1.0)	22
n-PentCHO[h]	90:10[b]	77	−3.1 (1.2)	25
Me_2CHCHO	91:9	85	−12.5 (1.0)	36
c-HexCHO[h]	95:5	84	−8.1 (1.0)	31
t-BuCHO	94:6[c]	79	−21.2 (1.0)	29

[a] Determined by GLC with base line separation of both peaks (35% DEGS; 1-m column; 140–200 °C; He flow, 40 mL/min. [b] Separation of peaks was >85%, prohibiting exact ratio determination. [c] Complete peak separations were accomplished by using 10% SE-30 at 110 °C. [d] Determined by chiral shift reagent tris[3-[(heptafluoropropyl)hydroxymethylene]-*d*-camphorato]europium III using 10 mg of LISR and 10 mg of GLC purified methyl ester **3** in 0.4 mL of $CDCl_3$ on a Varian T-60 instrument. The OCH_3 signal was completely separated and integrated at ~δ 4.08 (major) and ~4.13 (minor). Slight variations in chemical shifts were noted for each compound. [e] Absolute configurations are 2*R*,3*R* except for last entry which is 2*R*,3*S* due to priority change. [f] Rotations for pure threo products after purification by VPC. [g] Yields based on diisopinocampheylborane and the subsequent five steps to **3**. Due to the instability of the borane triflate[4] and the boron enolate **1**, it is not currently possible to assess the yields of each individual step, only the overall yield of 3. Improvements toward this end are in progress. [h] Pent, pentyl; c-Hex, cyclohexyl.

Table II. Chiral *Erythro*-β-Hydroxy Esters **4** from Boron Azaenolate **2**

RCHO	erythro: threo,[a] %	*erythro*-**4**, % ee[b]	config[c]	$[\alpha]_D^{CHCl_3}$ [f] (*c*)	overall yield, %
EtCHO	98:2	40	2*S*,3*R*	1.4 (2.7)	44
Me_2CHCHO	98:2	41	2*S*,3*R*[d]	−2.3 (2.4)	42
t-BuCHO	97:3	60	2*S*,3*S*[e]	−6.6 (2.1)	50

[a] Determined by GLC as described in Table I. [b] These were determined by using the chiral shift reagents (Table I) without exclusion of the threo product. [c] Configuration assigned by similarity in shifts using chiral shift reagent. The CCH_3 doublet of the major enantiomer always appeared at lower field than the minor one. [d] Based on reported configuration of (+)-(2*R*,3*S*).[1] [e] Assigned with the same sense of configuration as other cases; however, a priority change results in *S* for the β carbon. [f] Rotations include the 2–3% of threo product.

whereas **6c** and **6d** were (−) and (+)-*erythro*-**4**, confirmed by comparison with (+)-(2*R*,3*S*)-**4** prepared by Evans.[1k] The threo pair **6a** and **6b** were identified with regard to their absolute configuration by epimerization at C-2. Thus, **6a** was treated with 2.0 equiv of *tert*-butyllithium (−78 °C, THF) and then quenched with acetic acid. HPLC analysis (silica gel) showed a mixture of **6a** and **6c**, indicating they now differed only at C-2. Similarly, **6b** was epimerized to a mixture of **6b** and **6d**. These studies confirm the relationship between **6a–d**, and their absolute configurations are indicated.

The use of boron azaenolate **2**, wherein the oxazoline ring represents the chiral auxiliary and boron contains the achiral bicyclo system (9-borabicyclononane), gave mainly the *erythro*-β-hydroxy esters **4** upon reaction with several aldehydes. Although the diastereoselection was quite high, the enantioselection was only moderate (Table II). The complexities of this process are currently outside the realm of our complete understanding due partially to the fact that the geometry of the azaenolates **1** and **2** are not known. It is known, however, that at the conditions of their formation, kinetically generated from a dialkylboryl triflates, they produce only a single species. This was confirmed by ^{13}C NMR spectroscopy of the enriched methyl group[8] (~50% ^{13}C) on the olefin in **2** which showed only a single signal at temperatures from −78 to −25 °C. Equilibration was effected by prolonged stirring of **2** (3 h) at room temperature which showed a steady increase of a second methyl signal finally reaching a ratio of 2:1. Despite the single azaenolate **2** at temperatures where the aldol was normally run, the % ee of erythro product was only 40–60%. Thus, there appears at this time that there is little correlation between the population of the azaenolates and the enantioselectivity observed. The other factor contributing to our lack of understanding of this process is the nature of the transition states. The aldol transition states proposed by Zimmerman[9] and employed by others[10] do not seem to give a clear indication of the process, and it has been suggested[11] that "boatlike" rather than "chairlike" transition states should also be considered. We continue to probe this interesting yet mystifying process.[12]

Acknowledgment. We are grateful to the National Science Foundation for financial support of this work.

Supplementary Material Available: Methods of purification, $[\alpha]_D$ values, and IR and NMR data for the hydroxy esters (2 pages). Ordering information is given on any current masthead page.

(7) (a) House, H. O.; Crumrine, D. S.; Teranishi, A. Y.; Olmstead, H. D. *J. Am. Chem. Soc.* **1973**, *95*, 3310. (b) Meyers, A. I.; Reider, P. J. *Ibid.* **1979**, *101*, 2501. (c) Buse, C. T.; Heathcock, C. H. *Ibid.* **1977**, *99*, 8109.
(8) Meyers, A. I.; Synder, E. S.; Ackerman, J. J. H. *J. Am. Chem. Soc.* **1978**, *100*, 8186.
(9) Zimmerman, H. E.; Traxler, M. D. *J. Am. Chem. Soc.* **1957**, *79*, 1920.
(10) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868. Evans, D. A.; Taber, T. R. *Tetrahedron Lett.* **1980**, *21*, 4675.
(11) We thank Professor David Evans for discussion on this matter.
(12) Additional data pertaining to the β-hydroxy esters reported herein are given as supplementary material.

Polymerized Microemulsions

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Emulsion polymerization has been the focus of intensive investigative efforts since its discovery by Harkins.[1] Such polymerizations are characterized by rapid rates of polymerization that culminate in the production of high molecular weight polymer

(1) (a) H. D. Harkins, *J. Am. Chem. Soc.*, **69**, 1428 (1947); (b) W. V. Smith and R. H. Ewart, *J. Chem. Phys.*, **16**, 592 (1948); (c) D. C. Blackley, "Emulsion Polymerization", Applied Science, London, 1975; (d) S. W. Landowne, R. G. Gilbert, D. H. Napper, and D. F. Sangster, *J. Chem. Soc., Faraday Trans. 1*, **76**, 1344 (1980).

0002-7863/81/1503-4279$01.25/0