3.07 and 3.15 (AB, J = 14.8 Hz, 2 H, N-CH_2-aryl), 3.36 (t, J = 6.7 Hz, 2 H, CH_2Cl), 3.58 (t, J = 6.6 Hz, 2 H, DPM-OCH_2CH_2), 3.7–3.9 (m, 4 H, Bp-OCH_2CH_2), 6.73 (dd, J = 7.7 and 1.3 Hz, 1 H, Bp-3 or 3′-H), 6.78 (m, 1 H, Bp-3 or 3′-H), 6.85 (s, 2 H, aryl-H_{DPM}), 6.87 (s, 2 H, aryl-H_{DPM}), 7.15–7.25 (m, 4 H, Bp-4,4′,5,5′-H); MS, m/z (relative intensity) 882 (62, M^+), 809 (100). Anal. Calcd for $C_{55}H_{80}N_3O_4Cl$ (882.8): C, 74.84; H, 9.14; N, 4.76; Cl, 4.02. Found: C, 74.68; H, 9.33; N, 4.53; Cl, 4.13.

A mixture of 663 mg (0.75 mmol) of **25** and 975 mg (3 mmol) of cesium carbonate in 30 mL of dry dimethylformamide was stirred under N_2 for 16 h at 80 °C. The cesium salts were removed by filtration and the solution was evaporated to dryness. Chromatography on silica gel from ethyl acetate/n-hexane/triethylamine (25:70:5) afforded 299 mg (47%) of **20**, which was shown by TLC, IR, NMR, and mp to be identical with **20** obtained from the diborane reduction as described above.

Acknowledgment. We thank the administration of the University of California, Los Angeles, for providing set-up funds to support this research. The 500-MHz NMR spectrometer was purchased from grants provided by NIH (BRSG-S10-RR01970-01) and by NSF (CHE 84-06829). We thank Professor H. A. Staab for the support of the early part of the work done at the Max-Planck-Institute in Heidelberg.

Addition Compounds of Alkali Metal Hydrides. 29. Preparation and Properties of Chiral Dialkylmonoalkoxyborohydrides. A New Class of Asymmetric Reducing Agents

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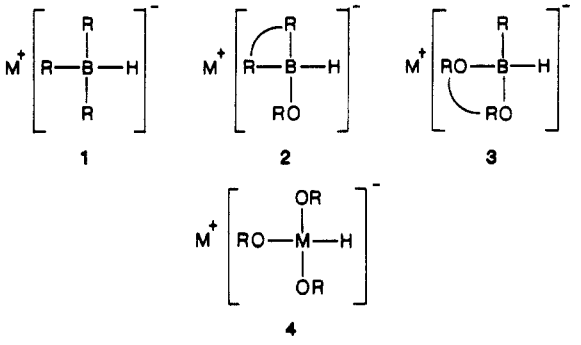
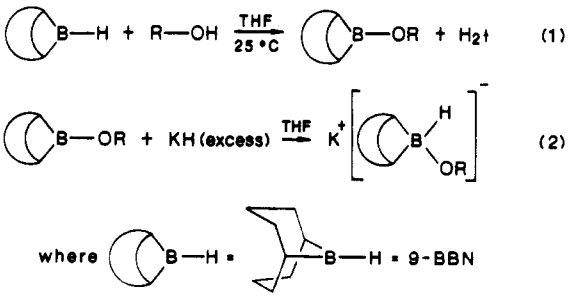
A series of chiral 9-alkoxy-9-borabicyclo[3.3.1]nonane derivatives were synthesized by the reaction of 9-borabicyclo[3.3.1]nonane (9-BBN) with several readily available chiral alcohols, such as (−)-isopinocampheol, (+)-menthol, (−)-4-isocaranol, (+)-*trans*-2-methylcyclopentanol, and (−)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose. A chiral borinic ester possessing a cyclic chiral dialkylboryl moiety, (+)-2-(cyclohexyloxy)-4,8-dimethyl-2-borabicyclo[3.3.1]nonane, was also synthesized. With one exception, all of these chiral borinic esters were readily converted into the corresponding chiral dialkylmonoalkoxyborohydrides by treatment with excess potassium hydride in THF at 25 °C. The addition of potassium hydride to (+)-9-(menthyloxy)-9-borabicyclo[3.3.1]nonane (9-*O*-Men-9-BBN) was very slow, requiring 15 days at 65 °C (refluxing THF). The chiral dialkylmonoalkoxyborohydrides thus formed are all stable at 25 °C and can be stored for several months. They were tested against acetophenone and 3-methyl-2-butanone as representative prochiral ketones. These reagents reduce acetophenone with up to 78% ee and 3-methyl-2-butanone with up to 61% ee at −78 °C.

The syntheses of trisubstituted borohydrides containing a single substituent, such as trialkylborohydrides[2] **1** and trialkoxyborohydrides[3] **4**, were well established some time ago. However, the general syntheses of "mixed" trisubstituted borohydrides became possible only recently by using cyclic moieties, such as 9-BBN in dialkylmonoalkoxyborohydrides[4,5] **2** and glycols in dialkoxymonoalkylborohydrides[6] **3**, to stabilize the products toward disproportionation.



1 **2** **3** **4**

Among these mixed trisubstituted borohydrides, the potassium 9-alkoxy-9-boratabicyclo[3.3.1]nonane (K 9-OR-9-BBNH) derivatives have achieved the most favorable stereoselectivities,[4,5] approaching those obtained by the trialkylborohydrides **1**. The syntheses of these dialkylmonoalkoxyborohydrides involve the reaction of 9-BBN with alcohols (eq 1), followed by conversion of the resulting borinic esters into the corresponding potassium dialkylmonoalkoxyborohydrides by treatment with excess potassium hydride (eq 2).



(1) (a) Postdoctoral research associate on Grant ARO DAAG-29-85-K-0062. (b) Postdoctoral research associate on a fellowship from the Korean Science and Engineering Foundation, Republic of Korea.

(2) (a) Krishnamurthy, S. *Aldrichimica Acta* **1974**, *7*, 55. (b) Brown, H. C.; Dickason, W. C. *J. Am. Chem. Soc.* **1970**, *92*, 709. (c) Krishnamurthy, S.; Brown, H. C. *Ibid.* **1976**, *98*, 3383; (d) *J. Org. Chem.* **1976**, *41*, 3064. (e) Brown, H. C.; Kim, S. C. *Synthesis* **1977**, 635. (f) Krishnamurthy, S.; Vogel, F.; Brown, H. C. *J. Org. Chem.* **1977**, *42*, 2534.

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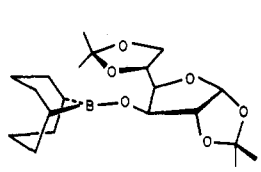
Table I. ^{11}B NMR Spectra and Physical Properties of Chiral Borinic Esters

chiral borinic esters	^{11}B NMR[a] (THF), δ	bp, °C (torr)	n^{20}_D	$[\alpha]^{22}_D$ (c, THF)
(−)-**5A**	56.3	198–201 (0.5)	*b*	−10.31 (5.3)
(−)-**6A**	55.5	165–166 (0.6)	1.5001	−37.24 (5.3)
(+)-**7A**	55.8	139–140 (0.3)	1.4882	+65.4 (4.96)
(−)-**8A**	55.1	158–160 (0.35)	1.4973	−63.9 (4.62)
(+)-**9A**	55.7	118–119 (0.15)	1.4890	+26.14 (3.93)
(+)-**10A**	55.0	128–131 (0.5)	1.4923	+5.52 (3.3)

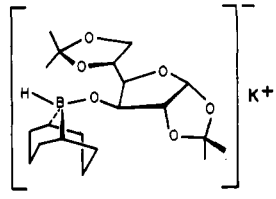
[a] The ^1H NMR spectra are complex and do not provide any useful information. [b] Compound is very viscous, too viscous to measure.

On the other hand, no work had been done on exploring the possible utility of these dialkylmonoalkoxyborohydrides as enantioselective reducing agents.

Accordingly, we undertook to synthesize several chiral borinic esters and to study the formation of the corresponding chiral potassium dialkylmonoalkoxyborohydrides and their asymmetric reducing characteristics toward selected prochiral ketones. In the course of this study, we discovered a highly promising asymmetric reducing agent, potassium 9-*O*-(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranosyl-9-boratabicyclo[3.3.1]nonane (K 9-*O*-DIPGF-9-BBNH) (**5B**).[7] This reagent was synthesized from the



9-*O*-DIPGF-9-BBN, 5A



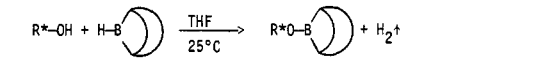
K 9-*O*-DIPGF-9-BBNH, 5B

corresponding chiral borinic ester, 9-*O*-(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranosyl-9-borabicyclo[3.3.1]nonane (9-*O*-DIPGF-9-BBN) (**5A**) by additon of potassium hydride in THF. The new reagent is proving highly effective in the reduction of several types of prochiral ketones, such as alkyl phenyl ketones,[7] relatively hindered aliphatic ketones,[7] acetylenic ketones,[8] and α-keto esters.[8]

Results and Discussion

Representative readily available chiral alcohols, such as (−)-isopinocampheol (**6**), (+)-menthol (**7**), (−)-4-isocaranol (**8**), and (+)-*trans*-2-methylcyclopentanol (**9**), were selected for the synthesis of the corresponding 9-alkoxy-9-BBN borinic ester derivatives possessing chirality on the alkoxy moiety. A borinic ester possessing chirality on the cyclic dialkylboryl moiety, (+)-2-(cyclohexyloxy)-4,8-dimethyl-2-borabicyclo[3.3.1]nonane (LimBOChx) (**10A**) was also synthesized. These chiral borinic esters were then converted into the corresponding chiral potassium dialkylmonoalkoxyborohydrides by treatment with excess potassium hydride. The stability of the resulting borohydrides was examined by ^{11}B NMR spectra and by measuring the number of moles of H_2 evolved by hydrolysis of aliquots of the supernatant solution at appropriate time intervals. The stable chiral dialkylmonoalkoxyborohydrides were characterized by ^{11}B NMR and IR spectroscopy and their enantioselectivities as asymmetric reducing agents examined with acetophenone and 3-methyl-2-butanone.

Synthesis of Chiral Borinic Esters. Chiral *B*-alkoxy-9-BBN borinic ester derivatives possessing chirality on the alkoxy moiety were synthesized according to the previously mentioned procedure (eq 1) by treatment of 9-BBN with selected chiral alcohols, (−)-**6**, (+)-**7**, (−)-**8**, and (+)-**9** (eq 3). The reactions proceeded smoothly in THF



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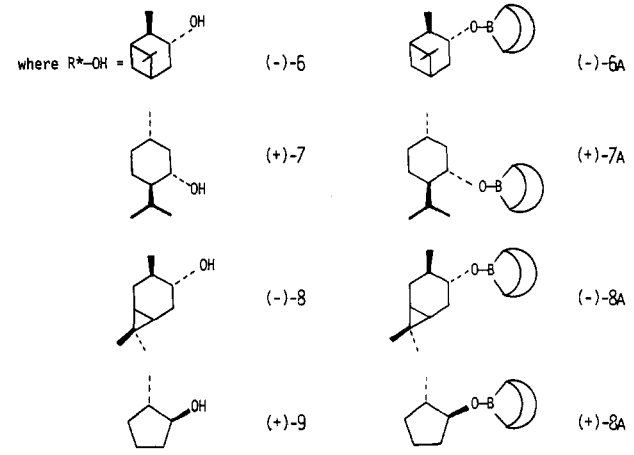
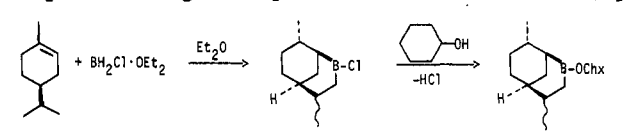


at 25 °C with the evolution of 1 equiv of H_2 within 2 h. The ^{11}B NMR spectra of the resulting solution revealed complete disappearance of 9-BBN (δ 28.0) with the appearance of only the desired borinic ester (δ 55.1–55.8). These borinic esters, (−)-**6A**, (+)-**7A**, (−)-**8A**, and (+)-**9A** were produced in high yields (90–95%). Chiral alcohols (−)-**6** and (+)-**7** were commercially available (Aldrich), whereas (−)-**8** and (+)-**9** were synthesized in essentially 100% ee according to the published procedures[9,10] developed in this laboratory recently.

(+)-9-(Cyclohexyloxy)-4,8-dimethyl-2-borabicyclo[3.3.1]nonane (LimBOChx) (**10A**), an example of a chiral borinic ester possessing a chiral group on the dialkylboryl moiety, was synthesized by treatment of *B*-chloro-4,8-dimethyl-2-borabicyclo[3.3.1]nonane (LimBCl) with cyclohexanol with concurrent removal of a byproduct, HCl, followed by distillation under reduced pressure. Synthesis of LimBCl, in turn, was performed by hydroborating (−)-limonene with monochloroborane etherate[11] ($BH_2Cl\cdot Et_2O$) according to the procedure in the literature[12] (eq 4).



(4)

(+)-10A

The ^{11}B NMR spectra and physical properties, including optical rotation values, of all the chiral borinic esters synthesized, are summarized in Table I.

All of the borinic esters exhibited ^{11}B chemical shifts in the range of δ 55.0–56.3 downfield relative to $BF_3\cdot OEt_2$ as the reference, consistent with the results observed for achiral borinic esters in the literature.[5] Signs of optical

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Table II. Formation and Physical Properties of Chiral Dialkylmonoalkoxyborohydrides[a]

chiral borohydrides	formation temp, °C	formation time, h	^{11}B NMR (THF[b]), δ	IR, ν_{B-H} cm^{-1}	stability
5B	25	2.0	+1.3 (br s)	2038	stable
6B	25	2.0	−1.51 (d, J_{B-H} = 75.6 Hz)	2003	stable
7B	65	15 days[c]	−1.5 (d, J_{B-H} = 85.3 Hz)	2004	*d*
8B	25	2.0	−1.7 (d, J_{B-H} = 85.0 Hz)	2006	stable
9B	25	2.0	−1.1 (d, J_{B-H} = 82.5 Hz)	2005	stable
10B	25	2.0	+0.7 (br s)	2021	stable

[a] By the reaction of potassium hydride (excess) with the chiral borinic esters in THF. [b] At ca. 0.1 M in THF. [c] For ca. 90% conversion. [d] Relatively unstable at 65 °C but stable at 25 °C.

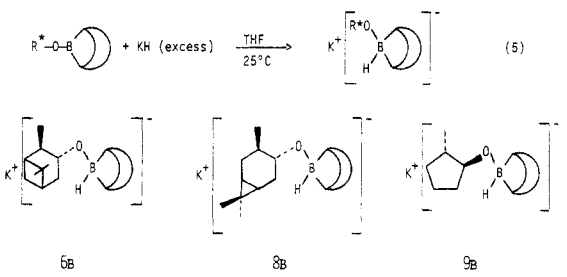
Table III. Asymmetric Reduction of Representative Ketones with Chiral Dialkylmonoalkoxyborohydrides[a]

chiral dialkylmonoalkoxyborohydrides	acetophenone time, h	acetophenone yield,[b] %	acetophenone % ee[c] (config)	3-methyl-2-butanone time, h	3-methyl-2-butanone yield,[b] %	3-methyl-2-butanone % ee[c] (config)
5B	24	98	78 (*R*)	6	96	39 (*R*)
6B	24	95	47 (*S*)	6	98	61 (*S*)
7B	24	90	12 (*S*)	6	98	40 (*R*)
8B	24	97	34 (*R*)	6	93	28 (*S*)
9B	24	98	26 (*R*)	6	91	37 (*R*)
10B	24	96	3 (*R*)	6	98	14 (*R*)

[a] In THF at −78 °C, [H$^-$]:[ketone] = 1.1:1.0, [ketone] = 0.3 M. [b] By GC analysis. [c] By capillary GC analysis of MTPA esters.

rotation observed for the 9-alkoxy-9-BBN derivatives were always the same as those of the corresponding chiral alcohols.

Formation and Stability of Chiral Dialkylmonoalkoxyborohydrides. When chiral *B*-alkoxy-9-BBN derivatives (−)-**6A**, (−)-**8A**, and (+)-**9A** were allowed to react with a vigorously stirred suspension of a modest exesss of potassium hydride in THF at 25 °C, slightly exothermic reactions were observed, following a short induction period of 10–30 min, with completion of the reaction taking place within 2 h (eq 5). The course of the reaction was monitored by withdrawing aliquots of the mixture at appropriate time intervals and observing their ^{11}B NMR spectra. The borinic esters exhibited signals between δ 55.0 and 56.3 in ^{11}B NMR, whereas the corresponding borohydrides exhibit signals of δ −1.7 to −1.1. Consequently, the reactions could be easily followed by the disappearance of the borinic ester signal with the concurrent appearance of the borohydride signal.

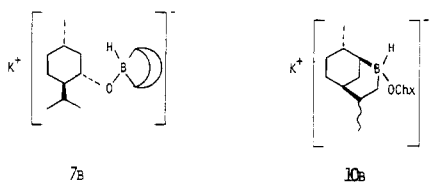


IR spectra of solutions of the chiral borohydrides in THF thus formed displayed characteristic strong absorptions around 2000 cm^{-1} attributed to the B–H stretching vibrations. The ^{11}B NMR spectra of the solutions (ca. 0.1 M) of these chiral borohydrides exhibit doublets in the region slightly upfield from the standard BF_3·OEt_2 (δ −1.7 to −1.1). However, when the concentration of the compound is relatively high (≥0.5 M), the solutions exhibit a broad singlet, probably due to the relatively high viscosity of these solutions. This phenomenon is similar to that previously observed for K 9-(3-ethyl-3-pentoxy)-9-BBNH[5] containing a bulky alkoxy group.

The stabilities of the resulting borohydrides were examined utilizing the ^{11}B NMR spectra and measuring the number of moles of H_2 evolved by hydrolysis of clear aliquots of the supernatant solution (the solutions were stored under a positive pressure of nitrogen in the presence of excess potassium hydride, but the suspended potassium hydride was removed prior to analysis). Over a period of several months the chiral borohydrides **6B**, **8B**, and **9B** were all stable at 25 °C in THF. Apparently, the presence of the cyclic dialkylboryl group of 9-BBN induces major stabilization of these chiral dialkylmonoalkoxyborohydrides.

The borinic ester derived from (+)-7 and 9-BBN, (+)-*O*-Men-9-BBN (**7A**), proved to be relatively resistant to the addition of potassium hydride, probably a result of the steric bulkiness of the isopropyl group adjacent to the C–O bond in the (+)-menthol structure. Thus, it required ca. 15 days to achieve ca. 90% conversion of the borinic ester in refluxing THF (65 °C) with partial decomposition of the resulting borohydride **7B**. However, the reagent appeared to be stable at 25 °C since the concentration of the hydride and ^{11}B NMR spectra [δ −1.5 (d, J_{B-H} = 85.3 Hz)] of the reagent remained constant over an extended period of time. The IR spectrum (ν_{B-H} = 2004 cm^{-1}) also indicated the presence of the corresponding borohydride **7B**.

The reaction of a chiral borinic ester possessing a chiral dialkylboryl group, (+)-LimBOChx (**10A**), with excess potassium hydride also took place smoothly in THF at 25 °C. The resulting borohydride, **10B**, in THF exhibited characteristic ^{11}B NMR spectrum [δ +0.7 (br s), even at ca. 0.1 M in THF] and IR spectrum (ν_{B-H} = 2021 cm^{-1}).

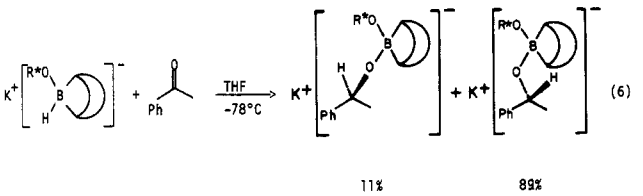


The reagent is stable at 25 °C. The reagent is an example of another class of a stable dialkylmonoalkoxyborohydride that is not a 9-BBN derivative. All of these results on the formation and stability of chiral dialkylmonoalkoxyborohydrides, including those of K 9-*O*-DIPGF-9-BBNH[7] (**5B**), are summarized in Table II.

Asymmetric Reduction of Representative Ketones. Two representative prochiral ketones, acetophenone, an

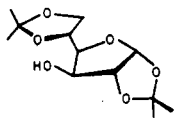
aralkyl ketone, and 3-methyl-2-butanone, an aliphatic ketone, were selected to observe the reactivities and the effectiveness of the asymmetric reduction by these new chiral dialkylmonoalkoxyborohydrides.

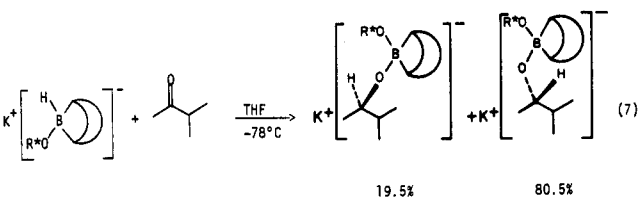
All of these chiral borohydride reagents, **6B, 7B, 8B, 9B, 10B, and 5B**, reduce acetophenone and 3-methyl-2-butanone smoothly in THF at −78 °C with >90% yields, within 24 and 6 h, respectively. The chiral borohydrides reduced acetophenone with 3–78% ee and 3-methyl-2-butanone with 14–61% ee. Among these new chiral borohydride reagents, K 9-*O*-DIPGF-9-BBNH (**5B**) provided the highest optical purity of the product alcohol (78% ee) in the reduction of acetophenone (eq 6), whereas K 9-*O*-Ipc-9-BBNH (**6B**) provided the highest optical yield (61% ee) in the reduction of 3-methyl-2-butanone (eq 7).



(6)

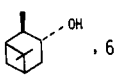
where R*OH =





(7)

where R*OH =



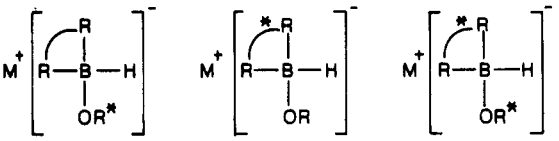
, 6

It is unexpected, but highly interesting, that the enantiomeric selectivity achieved in the reduction of 3-methyl-2-butanone with K 9-*O*-Ipc-9-BBNH, 61% ee, is considerably better than with the corresponding trialkylborohydride Li 9-Ipc-9-BBNH, 36% ee,[13] and is almost as good as the 68% ee achieved with the improved reagent, NB-Enantride.[14]

All results of asymmetric reduction are summarized in Table III.

Conclusion

Chiral borinic esters derived from relatively easily available chiral precursors could be readily converted into the corresponding chiral potassium dialkylmonoalkoxyborohydrides by treatment with excess potassium hydride in THF at 25 °C. In one case, that of the chiral borinic ester derived from (+)-menthol and 9-BBN, it was necessary to raise the temperature to 65 °C (refluxing THF). These new chiral dialkylmonoalkoxyborohydrides are stable at 25 °C in THF and reduce representative prochiral ketones smoothly in THF at −78 °C. These reagents reduce acetophenone with 3–78% ee and 3-methyl-2-butanone with 14–61% ee. Thus, the present study provides a convenient synthesis of stable chiral dialkylmonoalkoxyborohydrides with the general structures **11** and **12**.



11 **12** **13**

The present study suggests that it should be possible to design highly effective chiral dialkylmonoalkoxyborohydrides **13**, possessing two chiral groups so selected that the effect of the two chiral centers work in the same direction to achieve high asymmetric reduction. Such a possibility is now being studied.

Experimental Section

Materials and General Procedures. All operations were carried out under nitrogen atmosphere with oven-dried glassware. The experimental techniques used in handling air-sensitive materials are described elsewhere.[15] Tetrahydrofuran was dried over 4-Å molecular sieves and distilled from sodium benzophenone ketyl just prior to use. Potassium hydride was used as received from Aldrich and was freed from mineral oil according to the published procedure.[16] (−)-Isopinocampheol, (+)-menthol, and 9-BBN were purchased from the Aldrich Co. and used without further purification. (+)-3-Carene, (−)-limonene, and 2-methylcyclopentene were obtained from commercial sources and distilled over small excess of lithium aluminum hydride. (−)-4-Isocaranol[9] (**8**) and (+)-2-methylcyclopentanol[10] (**9**) were prepared according to the published procedures. Cyclic hydroboration of the limonene is described in detail in a later section. ^{11}B NMR spectra were recorded on a Varian FT-80 spectrometer and all ^{11}B chemical shifts were reported in δ (ppm) relative to BF_3·OEt_2. ^{1}H NMR spectra were recorded on a Varian T-60A spectrometer with Me_4Si as an internal standard, and all of the chemical shifts were reported in δ (ppm) relative to Me_4Si. IR spectra were recorded on a Perkin-Elmer 700 spectrophotometer equipped with a Perkin-Elmer 3600 IR data station. GC analyses were carried out with a Hewlett-Packard 5750 chromatograph equipped with a Hewlett-Packard 3390 A integrator/plotter using a capillary column (15 M Supelcowax). Rotations were measured on a Rudolph Polarimeter Autopol III.

Preparation of Chiral Borinic Esters (−)-6A, (+)-7A, (−)-8A, and (+)-9A. The preparation of (−)-9-*O*-Ipc-9-BBN (**6A**) is representative. An oven-dried, 250-mL, round-bottom flask with a sidearm, a condenser, and an adaptor attached to a mercury bubbler was flushed with nitrogen and cooled to room temperature. In the flask were placed 12.2 g (100 mmol) of 9-BBN and 50 mL of THF. To the stirred slurry of 9-BBN in THF was added a total of 15.4 g (100 mmol) of (−)-isopinocampheol dissolved in 50 mL of THF slowly via a double-ended needle at 25 °C. Hydrogen evolved immediately. The reaction mixture was stirred for 2 h to complete hydrogen evolution. In a separate experiment in a small-scale reaction, the measurement of hydrogen evolution indicated the following profile: 62% (0.25 h); 80% (0.5 h); 91% (1.0 h); 97% (1.5 h); 99% (2.0 h). Evaporation of solvent, followed by distillation, yielded 26.0 g (95% yield) of (−)-**6A**: bp 165–166 °C (0.6 mm); n^{20}_D 1.5001; ^{11}B NMR δ 55.5 (THF); $[\alpha]^{22}_D$ −37.24° (*c* 5.3, THF); MS, *m/e*, M^+ 274. The results for other chiral 9-alkoxy-9-BBN, **7A**, **8A**, and **9A**, are summarized in Table I.

Preparation of *B*-(Cyclohexyloxy)-4,8-dimethyl-2-borabicyclo[3.3.1]nonane (LimBOChx; 10A). *B*-Chloro-4,8-dimethyl-2-borabicyclo[3.3.1]nonane (LimBCl) was prepared according to the literature procedure[12] by cyclic hydroboration of (−)-limonene with monochloroborane etherate[11] (BH_2Cl·Et_2O). LimBCl, thus synthesized (18.4 g, 100 mmol), was placed in a 100-mL round-bottom flask in a water bath at 25 °C. To this was added a total of 10.0 g of cycloehexanol (100 mmol) dropwise by using a syringe while the byproduct HCl gas was pumped off with a water aspirator. The mixture was stirred for 3 h, after which the ^{11}B NMR indicated complete disappearance of LimBCl (δ 78.9)

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and the presence of **10A** (δ 53.6). Distillation of the residue under reduced pressure yielded 21.8 g of **10A** (88 mmol, 88% yield): bp 128–131 °C (0.5 mm); ^{11}B NMR δ 53.6 (s, THF); MS, *m/e* M^+ 248; n^{20}_D 1.4923; $[\alpha]^{22}_D$ 5.52° (*c* 3.3, THF).

General Procedure for the Syntheses of Chiral Dialkylmonoalkoxyborohydrides. The procedure for the synthesis of K 9-*O*-Ipc-9-BBNH (**6B**) is representative. An oven-dried, 100-mL, round-bottom flask equipped with a Teflon stopclock on a sidearm was attached a condenser connected to a mercury bubbler. The flask was cooled to room temperature under a stream of nitrogen. To the flask was transferred potassium hydride as an oil suspension by using a double-ended needle. The potassium hydride was allowed to settle and most of the oil decanted with a double-ended needle. Then the potassium hydride was washed with pentane (3 × 50 mL). To this oil-free potassium hydride (2.4 g, 60 mmol), suspended in THF (40 mL), was added the THF solution (40 mL) of **6A** (10.96 g, 40 mmol) via a doulbe-ended needle with vigorous stirring. The reaction was monitored both by hydrolysis of centrifuged aliquots and ^{11}B NMR. The reaction became slightly exothermic after a 10–30-min induction period. It was complete within 2 h, producing the addition compound **6B**. After the reaction was complete, the condenser was replaced with a tapered ground-glass adaptor equipped with a stopclock, and the excess potassium hydride was allowed to settle for 48 h. An aliquot of the clear solution was hydrolyzed in a THF–glycerine–2 N HCl mixture (1:1:1) and the hydrogen evolved was measured, indicating the concentration of **6B** as 0.48 M (96% yield): ^{11}B NMR, δ −1.51 (d, THF, J_{B-H} = 75.6 Hz at ca. 0.1 M); IR, ν_{B-H} = 2003 cm^{-1}. The solution stored under a positive pressure of nitrogen revealed no change in hydride concentration and in ^{11}B NMR spectra over a period of several months. The concentration of boron was estimated as 1,5-cyclooctanediol following oxidation of an aliquot with alkaline hydrogen peroxide, indicating [B] = 0.50 M. The content of potassium was measured as KOH following hydrolysis of an aliquot. Titration with standard acid indicated [K^+] = 0.49 M. Therefore, a stoichiometry of K:B:H as 1:1:1 was established.

General Procedure for Asymmetric Reduction of Prochiral Ketones. The following procedure for the asymmetric reduction of acetophenone with **6B** is representative. The THF solution of acetophenone (5 mL, 5 mmol) precooled to −78 °C was added to the solution of **6B** in THF (0.48 M, 11.5 mL, 5.5 mmol) at −78 °C via a double-ended needle. After a 24-h reaction, unreacted hydride was quenched by injecting anhydrous HCl in Et_2O precooled to −78 °C. Then the mixture was raised to 25 °C and the solvent evaporated. The reduction product was extracted with pentane after hydrolysis of the residue with dilute HCl, followed by conversion of the borinic acid moiety into the "ate" complex[4] using aqueous NaOH. The pentane layer was washed with brine, dried ($MgSO_4$), and filtered and the solvent evaporated. Bulb-to-bulb distillation of the residue yielded a mixture of product 1-phenylethanol and (−)-isopinocampheol. The distilled mixture was directly utilized for derivatization with MTPA-Cl. The corresponding MTPA esters of the product alcohols were prepared according to the procedure in the literature.[17] Capillary GC analysis (Supelcowax, 15M) of MTPA esters revealed a composition of 73.5% *S* and 26.5% *R* (i.e., 47% ee). GC analysis of the product mixture obtained by alkaline H_2O_2 oxidation in a separate small-scale experiment indicated 95% yield of product 1-phenylethanol. For a reduction of 3-methyl-2-butanone, a slightly modified procedure was used. After carrying out the reduction in 10-mmol scale for 6 h at −78 °C, unreacted hydride was destroyed by injecting ca. 1 equiv of precooled MeOH and stirring for 1 h at −78 °C. After raising the temperature to 25 °C, it was important to evaporate all the solvent and volatiles before hydrolyzing the product ate complex with dilute HCl. The residue was extracted with pentane following the same procedure as before. The product alcohol was separated from the solvent pentane by distillation using a Widmer column. Capillary GC analysis of MTPA esters of the product alcohols indicated a composition of 19.5% *R* and 80.5% *S* (i.e., 61% ee). GC analysis of a separate experiment indicated 98% yield of 3-methyl-2-butanol after alkaline H_2O_2 oxidation.

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Registry No. **5B**, 101696-41-7; (−)-**6**, 1196-00-5; (−)-**6A**, 103068-09-3; **6B**, 103190-48-3; (+)-**7**, 15356-60-2; (+)-**7A**, 103068-10-6; **7B**, 103148-25-0; (−)-**8**, 4017-88-3; (−)-**8A**, 103148-24-9; **8B**, 103190-49-4; (+)-**9**, 39947-48-3; (+)-**9A**, 103068-11-7; **9B**, 103148-26-1; (+)-**10A**, 103068-12-8; **10B**, 103148-27-2; 9-BBN, 280-64-8; $BH_2Cl{\cdot}Et_2O$, 36594-41-9; LimBCl, 81805-73-4; (−)-limonene, 5989-54-8; cyclohexanol, 108-93-0; acetophenone, 98-86-2; 3-methyl-2-butanone, 563-80-4; (*R*)-1-phenylethanol, 1517-69-7; (*S*)-1-phenylethanol, 1445-91-6; (*R*)-3-methyl-2-butanol, 1572-93-6; (*S*)-3-methyl-2-butanol, 1517-66-4.

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Chemistry of 1,1-Dioxothiopyrans. 1. Syntheses and Reactions of 2,6-Diphenyl-4*H*-thiopyran-4-one 1,1-Dioxide and 4*H*-Thioflaven-4-one, 1,1-Dioxide

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Improved syntheses and certain reactions of 2,6-diphenyl-4*H*-thiopyan-4-one 1,1-dioxide and 4*H*-thioflaven-4-one 1,1-dioxide are reported. Many of these derivatives, which display *reversible*, one-electron reduction waves in their cyclic voltammograms between $E^\circ_{1/2}$ = −0.10 and −0.40 V (vs. SCE), are of interest as a potential new class of organic acceptors. Single-crystal X-ray analysis of 4-(dicyanomethylene)-2,6-diphenyl-4*H*-thiopyran 1,1-dioxide (DCTD) showing its molecular dimensions and packing order is described.

2,6-Diphenyl-4*H*-thiopyran-4-one (**1**)[1] has been the key building block for the syntheses of a variety of donors,[2] sensitizers,[3] and dyes[4] of interest in research on organic conductors and photoconductors. The properties of many

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