6.85–8.05 (m, 11 H). Anal. Calcd for $C_{18}H_{17}IS_2O_3$: C, 45.76; H, 3.63; I, 26.86. Found: C, 45.93; H, 3.79; I, 27.08.

p-Tolyl(2-thienyl)iodonium tosylate: isolated by evaporation of the reaction solvent and trituration of the residual brown crystals with Et_2O; white crystals; mp 110–113 °C dec; ^1H NMR (CD_3OD) δ 2.33 (s, 5.5 H), 6.85–8.35 (m, 11.5 H), peaks of minor impurities apparent. Anal. Calcd for $C_{18}H_{17}IS_2O_3$: C, 45.76; H, 3.63; I, 26.86. Found: C, 45.94; H, 3.68; I, 26.60.

(o-Fluorophenyl)(2-thienyl)iodonium tosylate: precipitated from reaction solvent with Et_2O, white crystals; mp 137–139 °C dec; ^1H NMR (CD_3OD) δ 2.34 (s, 3 H), 6.9–8.5 (m, 11 H, includes 1 H br "t" at δ 8.30). Anal. Calcd for $C_{17}H_{14}IFS_2O_3$: C, 42.86; H, 2.97; I, 26.64. Found: C, 42.68; H, 3.07; I, 26.44.

(o-Fluorophenyl)(5-methyl-2-thienyl)iodonium tosylate: precipitated from reaction solvent with Et_2O, white crystals; mp 135–137 °C dec; ^1H NMR (CD_3OD) δ 2.30 (s, 3 H), 2.51 (s, 3 H), 6.6–8.4 (m, 10 H, includes 1 H br "t" at δ 8.18 and 1 H d at 6.72). Anal. Calcd for $C_{18}H_{16}IFS_2O_3$: C, 44.08; H, 3.29; I, 25.88. Found: C, 44.10; H, 3.29; I, 25.83.

(p-Chlorophenyl)(2-thienyl)iodonium tosylate: product crystallized from reaction solvent, white crystals; mp 146–147 °C dec; ^1H NMR (Me_2SO-d_6) δ 2.29 (s, 3 H), 6.9–8.5 (m, 11 H); peaks of minor impurities apparent. Anal. Calcd for $C_{17}H_{14}IClS_2O_3$: C, 41.43; H, 2.87; I. 25.75. Found: C, 41.60; H, 2.99; I. 25.59.

(p-Chlorophenyl)(5-methyl-2-thienyl)iodonium tosylate: precipitated from reaction solvent with Et_2O, white crystals; mp 131–134 °C dec; ^1H NMR (CD_3OD) δ 2.28 (s, 3 H), 2.50 (s, 3 H), 6.57–8.20 (m, 10 H). Anal. Calcd for $C_{18}H_{16}IClS_2O_3$: C, 42.66; H, 3.19; I, 25.04. Found: C, 42.77; H, 3.24; I, 25.14.

(p-Chlorophenyl)(5-ethyl-2-thienyl)iodonium tosylate: precipitated from reaction solvent with Et_2O, white crystals; mp (after reprecipitation from MeOH with Et_2O) 124–131 °C dec; ^1H NMR (Me_2SO-d_6) δ 1.21 (t, 3 H), 2.30 (s, 3 H), 2.92 (q, 2 H), 6.75–8.45 (m, 10 H, includes 1 H d at δ 7.93); weak s of an impurity at δ 3.36. Anal. Calcd for $C_{19}H_{18}IClS_2O_3$: C, 43.81; H, 3.49; I, 24.36. Found: C, 43.89; H, 3.65; I, 24.57.

(p-Chlorophenyl)(3-methyl-2-thienyl)iodonium tosylate: precipitated from reaction solvent with Et_2O, white crystals; mp 139–142 °C dec; ^1H NMR (CD_3OD) δ 2.33 (s, 3 H), 2.50 (s, 3 H), 6.85–8.2 (m, 10 H). Anal. Calcd for $C_{18}H_{16}IClS_2O_3$: C, 42.66; H, 3.19; I, 25.04. Found: C, 42.43; H, 3.32; I, 24.86.

(p-Bromophenyl)(5-methyl-2-thienyl)iodonium tosylate: precipitated from reaction solvent with Et_2O, white crystals; mp 133–135 °C dec; ^1H NMR (Me_2SO-d_6) δ 2.29 (s, 3 H), 2.53 (s, 3 H), 6.7–8.35 (m, 10 H, includes 1 H d (hint of fine structure) at δ 6.87. Anal. Calcd for $C_{18}H_{16}IBrS_2O_3$: C, 39.21; H, 2.93; I, 23.02. Found: C, 39.53; H, 3.04; I, 23.35.

(p-Iodophenyl)(5-methyl-2-thienyl)iodonium tosylate: product precipitated from reaction solution with Et_2O after unreacted p-$IC_6H_4I(OH)OTs$ removed (0.39 g) and after volume reduction to 5 mL, yellow crystals; mp 125–128 °C dec; ^1H NMR (CD_3OD) δ 2.35 (s, 3 H), 2.57 (s, 3 H), 6.65–8.0 (m, 10 H, includes intense s at δ 7.79 and 1 H d (with fine structure) at δ 6.81). Anal. Calcd for $C_{18}H_{16}I_2S_2O_3$: C, 36.13; H, 2.70; I, 42.42. Found: C, 36.30; H, 2.96; I, 42.09.

Registry No. 1 (R = H), 27126-76-7; 1 (R = 2-Me), 73177-97-6; 1 (R = 3-Me), 84383-97-1; 1 (R = 4-Me), 73177-96-5; 1 (R = 2-F), 84383-95-9; 1 (R = 4-Cl), 73178-07-1; 1 (R = 4-Br), 73178-08-2; 1 (R = 4-I), 73178-09-3; 2 (R′ = H), 110-02-1; 2 (R′ = 2-Me), 554-14-3; 2 (R′ = 2-Et), 872-55-9; 2 (R′ = 3-Me), 616-44-4; 2 (R′ = 2-Br), 1003-09-4; 2 (R′ = 2-CH_2OH), 636-72-6; 2 (R′ = 2-CHO), 98-03-3; 3 (R = H, R′ = 3′-Me), 91228-41-0; 3 (R = 2-Me, R′ = H), 91228-43-2; 3 (R = H, R′ = H), 91228-44-3; 3 (R = H, R′ = 5′-Me), 91228-46-5; 3 (R = H, R′ = 5′-Et), 91228-48-7; 3 (R = H, R′ = 5′-Br), 91228-50-1; 3 (R = H, R′ = 5′-CH_2OH), 91228-52-3; 3 (R = H, R′ = 5′-CHO), 91228-54-5; 3 (R = 2-Me, R′ = 5′-Me), 91228-56-7; 3 (R = 2-Me, R′ = 5′-Et), 91228-58-9; 3 (R = 2-Me, R′ = 3′-Me), 91228-60-3; 3 (R = 3-Me, R′ = H), 91228-61-4; 3 (R = 4-Me, R′ = H), 91228-62-5; 3 (R = 2-F, R′ = H), 91228-64-7; 3 (R = 2-F, R′ = 5′-Me), 91228-66-9; 3 (R = 4-Cl, R′ = H), 58506-46-0; 3 (R = 4-Cl, R′ = 5′-Me), 91228-68-1; 3 (R = 4-Cl, R′ = 5′-Et), 91228-70-5; 3 (R = 4-Cl, R′ = 3′-Me), 91228-72-7; 3 (R = 4-Br, R′ = 5′-Me), 91228-74-9; 3 (R = 4-I, R′ = 5′-Me), 91228-76-1; 4 (R = H, R′ = 3′-Me), 91228-77-2; 4 (R = 2-Me, R′ = 3′-Me), 91228-78-3; 4 (R = H, R′ = 5′-Me), 91228-79-4; 4 (R = H, R′ = 5′-Br), 91228-80-7; 4 (R = 3-Me, R′ = H), 38070-40-5; 4 (R = 2-Me, R′ = 5′-Me), 91228-81-8; 4 (R = 2-Me, R′ = H), 91228-82-9; ArI (R = H), 591-50-4; ArI (R = 2-Me), 615-37-2; ArI (R = 3-Me), 625-95-6; ThI (R′ = 3-Me), 16494-40-9; ThI (R′ = 5-Me), 16494-36-3; ThI (R′ = 5-Br), 29504-81-2; ThI (R′ = H), 3437-95-4.

Asymmetric Reduction of Representative Ketones with *tert*-Butoxyisopinocampheylborane, a New Chiral Reducing Agent

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Monoisopinocampheylborane ($IpcBH_2$), a less hindered, optically active borane reagent, is highly effective for the asymmetric hydroboration of hindered olefins.[1,2]

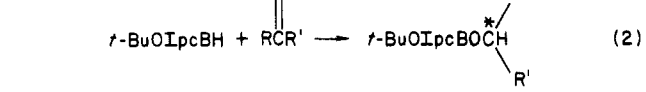
However, in the reduction of prochiral ketones, it achieves only moderate asymmetric induction.[3] As part of a recent investigation of the reaction of representative monoalkylboranes with alcohols,[4] we observed that $IpcBH_2$ reacts at 0 °C with only 1 mol of *tert*-butyl alcohol (eq 1).

$$IpcBH_2 + t\text{-BuOH} \rightarrow \underset{\mathbf{1}}{t\text{-BuOIpcBH}} \qquad (1)$$

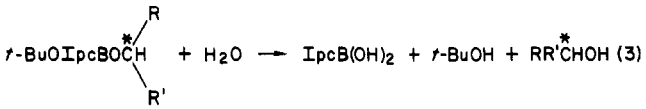
There is no significant reaction with a second mole of *tert*-butyl alcohol at 0 °C. (2,6-Dimethylphenol also reacts with $IpcBH_2$ similarly at 25 °C.)

The IR spectrum of $IpcBH_2$ in THF exhibits a strong absorption at 1549 cm^{-1}, characteristic of typical boron–hydrogen bridges. However, this bridge absorption disappears completely in 1. Consequently, the product must be the monomeric species. Many years ago, Burg established that dimethoxyborane, $(CH_3O)_2BH$ is monomeric.[5] Apparently, the present derivative also shows the same decreased tendency to dimerize.

The ready synthesis of this new derivative 1 encouraged us to explore its utility for the asymmetric reduction of representative ketones.[6] Accordingly, several such ketones were treated with the reagent in THF at 0 °C. The reductions proceeded readily (eq 2). Hydrolysis produced



(2)



(3)

the desired alcohol (eq 3). Distillation provided the product. It was purified by GC and the rotation measured. The results are summarized in Table I.

(1) Brown, H. C.; Yoon, N. M. *J. Am. Chem. Soc.* **1977**, *99*, 5514.
(2) Brown, H. C.; Jadhav, P. K.; Mandal, A. K. *J. Org. Chem.* **1982**, *47*, 5074.
(3) Brown, H. C.; Jadhav, P. K.; Mandal, A. K. *Tetrahedron* **1981**, *37*, 3547.
(4) Research in progress with Kim, G. P.; Kim, K. W.
(5) Burg, A. B.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1933**, *55*, 4020.
(6) Hydroboration with 1 proceeds relatively slowly with 1-octene requiring 3 h for completion at 0 °C. The reaction with more hindered olefins, such as 2-methyl-2-butene, is much slower. Consequently, asymmetric reduction of ketones in the presence of many types of double bonds is practical. The utility of chiral hydroboration of representative alkenes by this new reagent is under exploration.

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Table I. Asymmetric Reduction of Representative Ketones by *tert*-Butoxyisopinocampheylborane in THF at 0 °C

	tert-butoxyisopinocampheylborane[a]						$IpcBH_2$[b]	
$RCOCH_3$, R =	time, h	H^-/compd	yield,[c] %	$[\alpha]_D$ neat	ee, %	config[h]	ee, %	config
ethyl	3.0	1.5	86	-0.656	4.9[d]	*R*	22	*S*
isopropyl	3.0	1.5	82	-0.978	18.3[e]	*R*	46	*S*
tert-butyl	6.0	2.0	74	-1.850	22.8[f]	*R*	21	*S*
phenyl	3.0	1.5	71	+9.843	23.0[g]	*R*	15	*S*

[a] (+)-α-Pinene of 92% ee was used. [b] Reference 3, the results obtained by using $IpcBH_2$ of 100% ee, which was prepared from (+)-α-pinene of 94% ee. [c] Isolated yield. [d] Based on maximum rotation $[\alpha]_D$ -13.5° (neat): Leroux, P. J.; Lucas, H. J. *J. Am. Chem. Soc.* **1951**, *73*, 41. [e] Based on maximum rotation $[\alpha]_D$ +5.34° (neat): Pickard, R. H.; Kenyon, J. *J. Chem. Soc.* **1913**, *103*, 1957. [f] Based on maximum rotation $[\alpha]_D$ +8.1° (neat): Newman, P.; Lutkin, P.; Mislow, K. *J. Am. Chem. Soc.* **1958**, *80*, 465. [g] Based on maximum rotation $[\alpha]_D$ +42.85° (neat): Pickard, R. H.; Kenyon, J. *J. Chem. Soc.* **1911**, *99*, 45. [h] Absolute configurations from Klyne, W.; Buckingham, J. "Atlas of Stereochemistry"; Oxford University Press: New York, 1974.

As shown in Table I, 2-butanone is reduced to (*R*)-(-)-2-butanol in only 4.9% ee. However, the introduction of alkyl substituents in the α-position increases the asymmetric induction significantly. Thus, 3-methyl-2-butanone is reduced to (*R*)-(-)-3-methyl-2-butanol in 18.3% ee and 3,3-dimethyl-2-butanone is reduced to (*R*)-(-)-3,3-dimethyl-2-butanol in 22.8% ee. Acetophenone also yields the corresponding *R* alcohol in 23% ee. Thus, the *tert*-butoxyisopinocamphenylborane [from (+)-α-pinene] yields the product alcohols consistently enriched in the *R* enantiomer.

This is in sharp constrast to the earlier results[3] with $IpcBH_2$ [from (+)-α-pinene] in which the configuration of the reduced alcohols were consistently *S*. It is interesting that the introduction of the *tert*-butoxy group into the $IpcBH_2$ moiety has reversed the direction of reduction, presumably by reversing the orientation of the ketones in the transition states for these reductions.

A new chiral alkylalkoxyborane, *tert*-butoxyisopinocampheylborane, is prepared conveniently by merely adding 1 molar equiv of *tert*-butyl alcohol to $IpcBH_2$ in THF at 0 °C. In the reduction of four representative ketones, its asymmetric induction is consistently opposite to that realized in the reduction with $IpcBH_2$. Other applications of this reagent in asymmetric synthesis are under investigation.

Experimental Section

All operations were carried out under nitrogen, using oven-dried glassware. GC analyses were carried out on a Varian 3600 gas chromatograph using a 10% Carbowax 20M on Chromosorb W-HP 80/100 mesh size. The optical rotations were measured on a Rudolph Polarimeter Autopol III.

Materials. THF was treated with lithium aluminum hydride and distilled under nitrogen and stored over molecular sieves (Linde 5A, Ventron) under a slight positive nitrogen pressure. The borane-THF solution was standardized by hydrolyzing an aliquot of the solution with glycerine-water-THF mixture and measuring the hydrogen evolved.[7] The commercial ketones were purified by distillation and maintained under nitrogen. (+)-α-Pinene (Aldrich, 98%) was used without purification; it had an optical rotation of $[\alpha]^{22}_D$ +47.1°, indicating an optical purity of 92.0%.

Reduction of 3-Methyl-2-butanone. The following procedure for the asymmetric reduction of 3-methyl-2-butanone is representative. An oven-dried, 500-mL flask with a septum inlet, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler was cooled in an ice bath under a dry stream of nitrogen. The flask was charged with 126 mL of 1.19 M BH_3·THF solution (150 mmol) and then 24.3 mL of (+)-α-pinene (98%, 150 mmol) was introduced slowly with stirring. After the addition was completed, the reaction mixture was warmed up to room temperature and stirring was continued for 96 h.[8] The $IpcBH_2$ solution was cooled to 0 °C and 14.2 mL of *tert*-butyl alcohol (150 mmol) was slowly added. When the evolution of hydrogen gas had been completed, 10.7 mL of 3-methyl-2-butanone (100 mmol) was added to the reaction flask and the mixtrue was stirred for 3 h at 0 °C. Then 6 mL of water was added to destroy residual hydride. The oxidation of the boronic acid was effected by successive additions of 52.5 mL of 3 M NaOH and 17 mL of 30% aqueous H_2O_2 (1 h, 40 °C). The reaction mixture was then saturated with potassium carbonate, and the organic layer was separated and dried over anhydrous potassium carbonate. After the solvent was removed by distillation, the residue was fractionally distilled to provide 7.2 g (82%) of 3-methyl-2-butanol, bp 112-113 °C, 95% purity by GC. It was further purified by preparative GC, using a 20% DC-200 column: n^{25}_D 1.4056, $[\alpha]^{25}_D$ -0.978° (neat), an optical purity of 18.3% in *R* configuration.

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Registry No. 1, 91425-14-8; *t*-BuOH, 75-65-0; $IpcBH_2$, 83730-00-1; BH_3, 13283-31-3; $RCOCH_3$ (R = ethyl), 78-93-3; $RCOCH_3$ (R = isopropyl), 563-80-4; $RCOCH_3$ (R = *tert*-butyl), 75-97-8; $RCOCH_3$ (R = phenyl), 98-86-2; (*R*)-$RCH(OH)CH_3$ (R = ethyl), 14898-79-4; (*R*)-$RCH(OH)CH_3$ (R = isopropyl), 1572-93-6; (*R*)-$RCH(OH)CH_3$ (R = *tert*-butyl), 1572-96-9; (*R*)-$RCH(OH)CH_3$ (R = phenyl), 1517-69-7; 2,6-dimethylphenol, 576-26-1; (+)-α-pinene, 80-56-8; (2,6-dimethylphenoxy)monoisopinocampheylborane, 91425-15-9.

(7) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975.

(8) Pelter, A.; Ryder, D. J.; Sheppard, J. H.; Subrahmanyam, C.; Brown, H. C.; Mandal, A. K. *Tetrahedron Lett.* **1979**, 4777.

Direct Conversion of Allylic Selenides to Protected Allylic Amines

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We have recently reported that anhydrous chloramine T (**5**) in methanol is an effective reagent for the conversion of allylic phenyl selenides **1** to the corresponding rearranged *N*-allylic *p*-toluenesulfonamides **2**.[1] Reactions of this type hold promise as a stratagem for the formation of new carbon to nitrogen bonds with high regiochemical and stereochemical control.[2] The hazards associated with

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