Pergamon

Tetrahedron 55 (1999) 5991–6000

TETRAHEDRON

Molecular Addition Compounds . 14. Convenient Preparations of Representative Dialkylborane Reagents Using The New, Highly Reactive *N*-Ethyl-*N*-Isopropylaniline-Borane Reagent (BACH-EI™)

Herbert C. Brown,*[†] Josyula V. B. Kanth[†‡] and Marek Zaidlewicz[‡]

[†]*H. C. Brown and R. B. Wetherill Laboratories of Chemistry, 1393 Brown Building, Purdue University, West Lafayette, IN 47906, USA*
[‡]*Institute of Chemistry, Nicolaus Copernicus University, 87-100 Torun, Poland*

Received 17 February 1999; revised 19 March 1999; accepted 23 March 1999

Abstract: Convenient procedures for the preparation of representative dialkylborane reagents, diisopinocampheylborane, [1S]-2-diisocaranylborane, 9-borabicyclo[3,3,1]nonane, dicyclohexylborane and disiamylborane, using the new, highly reactive *N*-ethyl-*N*-isopropylaniline-borane reagent (BACH-EI™) in dioxane and tetrahydrofuran are described.

Keywords: amine-boranes, hydroboration, dialkylboranes

The importance of borane reagents in modern organic synthesis is reflected in an increasing number of large scale applications of borane and its derivatives. The well established borane-tetrahydrofuran (BH_3:THF) and borane-dimethyl sulfide (BMS) are excellent, widely used reagents.[1] However, they are not free from certain inconveniences. Thus the commercial borane-tetrahydrofuran is in a tetrahydrofuran solution of relatively low concentration (1.00 *M*) and has limited stability. Borane-dimethyl sulfide is almost ideal, highly concentrated and stable indefinitely, but suffers from high volatility, flammability, and an unpleasant stench-like odor of dimethyl sulfide. Hence there is a need for the development of more convenient borane carriers. Amine-boranes offer a promising alternative, since they are less sensitive to moisture and air, readily soluble in various solvents and, more importantly, the amine carriers can be readily recovered and recycled.[2]

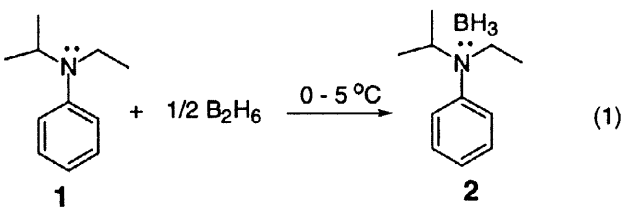
Recently, we[3-5] and others[6] developed a number of new, highly reactive borane adducts with aromatic, aliphatic hindered tertiary amines and *N*-silylamines showing excellent reactivity for the hydroboration of olefins. The reactions can be carried out in a number of readily available solvents at room temperature. Similar

* Fax: 765-494-0239, e-mail: hcbrown@chem.purdue.edu

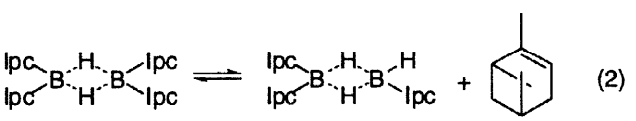
0040-4020/99/$ - see front matter
PII: S0040-4020(99)00272-0

to the behavior of BH_3:THF and BMS, the hydroborations of certain moderately hindered olefins with these amine-boranes proceed rapidly to the mono- or dialkylborane stage, with further reaction being slow.[4,6] Among these new amine-boranes, *N*-ethyl-*N*-isopropylaniline-borane (**2**) showed reactivities very similar to those of BH_3:THF. In order to further establish the synthetic potential of this new reagent and to develop an environmentally benign alternative to the existing BH_3:THF and BMS reagents, we undertook a study on the preparation of several valuable dialkylboranes,[7] such as the isomeric diisopinocampheylboranes (^{d}Ipc$_2$BH or ^{l}Ipc$_2$BH), (1S)-2-diisocaranylborane (^{d}Icr$_2$BH), 9-borabicyclo[3,3,1]nonane (9-BBN), dicyclohexylborane (Chx$_2$BH) and disiamylborane (Sia$_2$BH), using the new, highly reactive, environmentally benign amine-borane reagent, *N*-ethyl-*N*-isopropylaniline-borane (**1**), in dioxane and tetrahydrofuran.

The borane adduct of *N*-ethyl-*N*-isopropylaniline (**1**) was prepared following the literature procedure,[3] by passing a slight excess of diborane gas into the neat amine at 0-5 °C (eq 1). The concentration of the adsorbed borane was established to be 5.00 *M* by hydride analysis of an aliquot, using a 2.00 *M* HCl-glycerol-water mixture, and measuring the hydrogen evolved. In ^{11}B NMR the adduct showed a peak at δ −14.4 (CCl_4, $_qJ_{B\text{-}H}$ 98.6 Hz). At room temperature, the adduct thus obtained, maintained under nitrogen, is stable indefinitely.



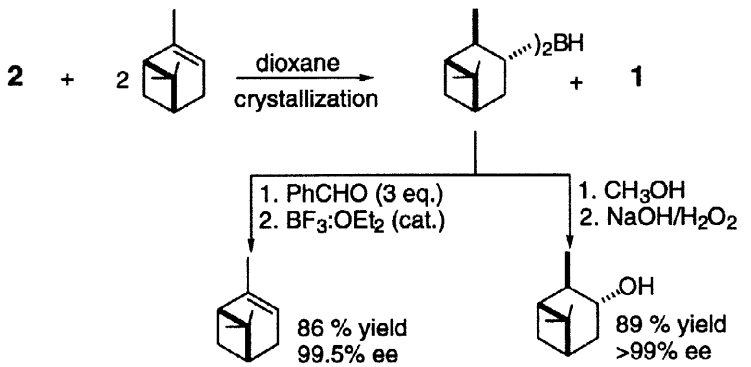
Preparation of Diisopinocampheylborane, ^{d}Ipc$_2$BH. The reaction of borane with α-pinene, not optically pure, was originally studied in diglyme and THF.[8] Asymmetric hydroboration of *cis*-2-butene with ^{d}Ipc$_2$BH thus formed and not isolated, yielded 2-butanol in 87% and 78%, ee respectively. The lower ee in THF compared to that in diglyme was attributed to greater solubility of tetraisopinocamphyldiborane in THF and hence to more dissociation of the reagent to triisopinocampheyldiborane and α-pinene. (eq 2)



In recent years, it has been demonstrated that both ^{d}Ipc$_2$BH and ^{l}Ipc$_2$BH approaching almost 100% ee can be prepared by hydroboration of (+)- and (-)-α-pinene with borane-tetrahydrofuran or BMS. Several procedures[9,10] have been developed, the most convenient one starting with (+)-α-pinene of 91% ee gives ^{d}Ipc$_2$BH of >99% ee in 91% yield (based on the borane reagent).[11] The reagent hydroborates *cis*-2-butene to afford after oxidation, 2-butanol in 97.2% ee. Hence, it was interesting to use the new amine-borane for the preparation of this remarkable reagent.

A significant increase in the yield of $^{d}Ipc_2BH$ was observed when the hydroboration of (+)-α-pinene with **2** was carried out in dioxane. Thus, when (+)-α-pinene (87.3% ee) in 25% excess was added to **2** in dioxane (1.25*M* in borane) at 0 °C and the reaction mixture was left at room temperature for 15 h, a white crystalline $^{d}Ipc_2BH$ was obtained in essentially quantitative yields (99%), based on the amount of amine-borane used. The supernatant solution did not show the presence of active hydride. The (+)-α-pinene was liberated from the product by the addition of benzaldehyde in the presence of catalytic amounts of boron trifluoride-etherate.[11] It was obtained in 86% yield and 99.5% ee, indicating effective upgradation during the crystallization of the Ipc_2BH (eq 3). Further confirmation was obtained by recovering (+)-α-pinene of 78% ee from the supernatant dioxane solution. The $^{d}Ipc_2BH$ thus obtained was free from amine. Methanolysis followed by the oxidation of $^{d}Ipc_2BH$, provided (-)-isopinocampheol in 89% yield and >99% optically purity.

Scheme 1

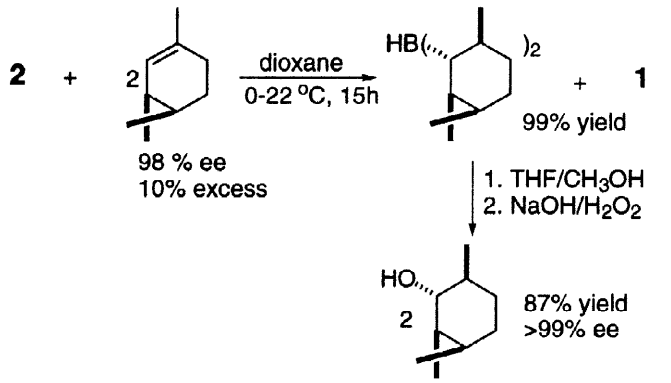


In tetrahydrofuran, the adduct **2** also gave $^{d}Ipc_2BH$ of >99% ee. However, the yield was lower (90%), similar to that reported for borane-tetrahydrofuran and BMS. Similarly, starting from (-)-α-pinene, $^{l}Ipc_2BH$ was obtained in 99% and 91% yields in dioxane and THF respectively.

Preparation of (1S)-2-Diisocaranylborane, 2-$^{d}Icr_2BH$. Recently, it was reported that 2-$^{d}Icr_2BH$ hydroborates prochiral *cis*-disubstituted olefins, giving the corresponding alcohols in high enantiomeric excess.[12] Its *B*-allyl derivative proved to be a highly enantioselective allylborating reagent for aldehydes.[13] Accordingly, the synthesis of this important chiral auxiliary using the new amine-borane, **2** was examined.

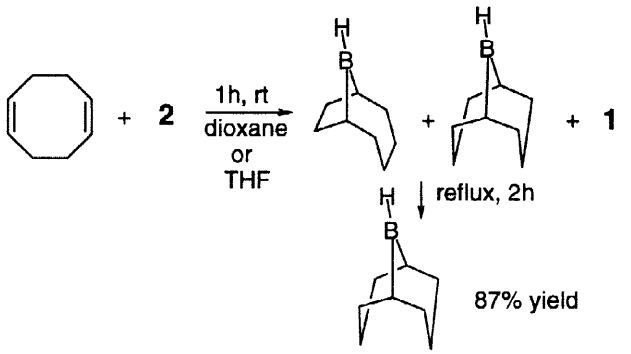
It was prepared by the addition of (+)-2-carene, 98% ee (10% excess) to a dioxane solution of **2** at 0 °C and keeping the mixture undisturbed at room temperature for 15 h. A white crystalline precipitate of 2-$^{d}Icr_2BH$ started separating out from the dioxane solution even during the addition of the (+)-2-carene. The reaction mixture after 15h was centrifuged and the supernatant solution was separated using a double ended needle. The precipitate was further washed with pentane and centrifuged to remove trace amounts of carrier amine. Thus, amine-free 2-$^{d}Icr_2BH$ was obtained in excellent yields (99%). Enantiomeric purity of the product was checked

by oxidation, which gave (-)-2-isocaranol of >99% ee (eq 3). In tetrahydrofuran, 2-^{d}Icr$_2$BH was obtained in lower yields (86%).



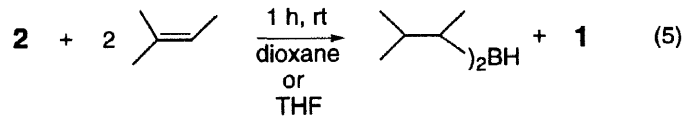
(3)

Preparation of 9-Borabicyclo[3,3,1]nonane, 9-BBN. The hydroboration of 1,5-cyclooctadiene with **2** in dioxane[14] and tetrahydrofuran was carried out at room temperature. The reaction was complete in 1 h, as revealed by estimation of residual hydride. Oxidation of an aliquot with alkaline hydrogen peroxide gave 1,4- and 1,5-cyclooctanediol (29% and 71%), corresponding to the formation of both borabicyclo[4,2,1]- and -[3,3,1]-nonane, respectively (eq 4). Thermal isomerization of the mixture of organoboranes in refluxing dioxane was complete in 2 h. After cooling, 9-BBN was obtained as a pure crystalline solid, free from amine, in 87% yield.



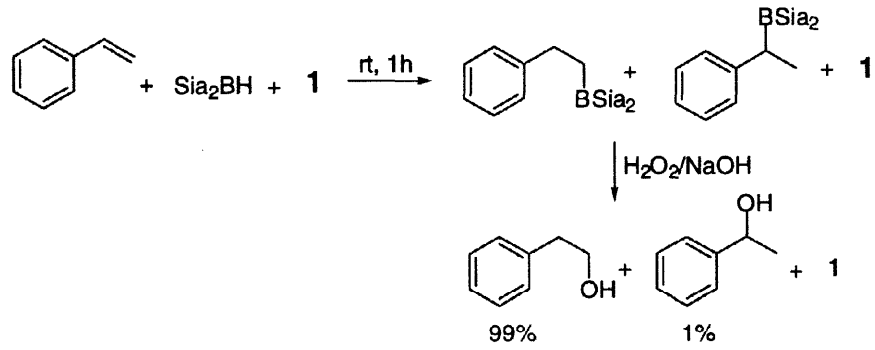
(4)

Preparation of Disiamylborane, Sia$_2$BH. The reaction of 2-methyl-2-butene with **2** in dioxane and tetrahydrofuran was complete within 1 h at room temperature (eq 5). The formation of disiamylborane was confirmed by ^{11}B NMR, from the disappearance of a peak at δ -14.4 corresponding to **2** and the appearance of absorption at δ +31.1. The reagent thus prepared can be utilized for hydroborations or can be converted by methanolysis to methyl disiamylborinate, valuable for the synthesis of unsymmetrical diynes.[15] Oxidation of the reaction mixture gave 3-methyl-2-butanol in quantitative yields.



(5)

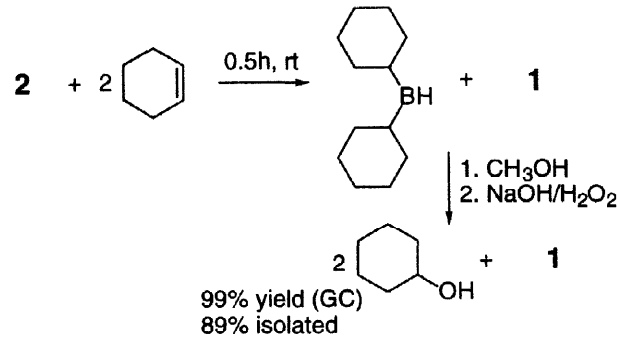
Application of Disiamylborane for Regiospecific Hydroboration of Styrene. The reagent prepared as described above was reacted with styrene at room temperature. The reaction was complete in 1 h both in dioxane and THF (eq 6). Oxidation of the product with alkaline hydrogen peroxide gave 2-phenylethanol (99%) and 1-phenylethanol (1%).



(6)

Clearly, the amine present in the reaction medium does not interfere in the subsequent hydroborations. The amine can be readily separated from the product alcohol by simple acid-base manipulations.

Preparation of Dicyclohexylborane. The hydroborations of cyclohexene with **2** in 2:1 ratio were complete within 1 h at room temperature in both dioxane and tetrahydrofuran (eq 7). Dicyclohexylborane precipitated from the solution and was isolated in 89% yield.



(7)

Oxidation of the methanolized solution in THF using alkaline hydrogen peroxide afforded cyclohexanol in quantitative yields (99% by GC), which was also isolated, free of amine by simple acid-base manipulations, in 89% yield.

Conclusion

The present study demonstrates the usefulness of the new *N*-ethyl-*N*-isopropylaniline-borane(**2**) for the preparation of well established dialkylborane reagents. In certain cases the adduct showed advantages over borane-tetrahydrofuran and BMS. For example $^{l}Ipc_2BH$ or $^{d}Ipc_2BH$ and 2-$^{d}Icr_2BH$ were prepared in higher yields and excellent optical purity. Other partially substituted boranes, such as disiamylborane, dicyclohexylborane, 9-BBN can also be prepared conveniently. The dialkylboranes examined do not coordinate with the carrier amine, so crystalline products are readily isolated free of amine. Soluble dialkylboranes can be used for further hydroborations in the presence of the amine. However, additional studies are needed to establish the scope of such applications.

Experimental Section

Methods. All manipulations and reactions with air-sensitive compounds were carried out in an atmosphere of dry nitrogen. The special techniques employed in handling air-sensitive materials are described elsewhere.[1a] The glassware was oven-dried for several hours, assembled while hot, and cooled in a stream of dry nitrogen gas. ^{1}H, ^{13}C and ^{11}B NMR spectra were recorded on a 200 MHz multinuclear instrument. The ^{11}B NMR chemical shifts δ are in ppm relative to BF_3:OEt_2. GC analyses were carried out on a chromatograph equipped with FID and a CI-100A integrator. The following columns were used, 6 ft x 0.125 in, 15 % Carbowax 20M on Chromosorb W, 9 ft x 0.125 in, 3% OV-17 on Chromosorb-G and 3 ft x 0.125 in, 10% SE 30 on Chromosorb W. Optical rotations were measured on a polarimeter. The hydride analysis studies were carried out using the gasimeter.[1a]

Materials. *N*-Ethyl-*N*-isopropylaniline and its borane adduct was prepared following the reported procedure.[3] All solvents were purified according to literature procedures and stored under nitrogen. Tetrahydrofuran and dioxane were freshly distilled from benzophenone ketyl before use. All olefins were distilled from a small amount of lithium aluminum hydride and stored under nitrogen. (+)-α-Pinene, $[\alpha]^{22}_{D}$ +45.2° (87.3% ee) and (+)-2-carene, $[\alpha]^{22}_{D}$ +92.0° (Camphor and Allied Products, India) were used. Aldrich Chemical Co. was the souce of materials not otherwise identified.

Preparation of Diisopinocampheylborane, $^{d}Ipc_2BH$. An oven-dried RB flask provided with a septum inlet was cooled to 0 °C under a stream of nitrogen gas. (+)-α-Pinene (8.52g, 62.5 mmol, 87.3% ee) was added with stirring to a solution of **2** (5.0 mL, 25 mmol) in dioxane (5.0 mL) over 5 min. at 0 °C. The ice-bath was removed and the solution was left undisturbed. After 30 min. crystals started separating out. The mixture was left for 15 h at room temperature and the supernatant solution was removed from the crystals with a double-

ended needle. The crystalline mass was broken, washed with pentane, kept under reduced pressure to remove the remaining solvent and solid $^{d}Ipc_2BH$: 6.98g, 99% yield was obtained.

Methanol (1.0 mL) was slowly added to a mixture of $^{d}Ipc_2BH$ (5.72g, 20.0 mmol) in tetrahydrofuran. The hydrogen evolved was vented out and 3.0*M* sodium hydroxide (6.8 mL, 20.0 mmol) was added followed slowly by hydrogen peroxide (4.0 mL, 30%, 40.0 mmol) at 10-20 °C. The mixture was stirred at room temperature and 1 h at 45 °C. It was cooled to room temperature, saturated with potassium carbonate and extracted with ether. The combined organic extracts were dried over anhydrous magnesium sulfate. GC analysis did not show the presence of **1**. Evaporation of the solvent afforded (-)-isopinocampheol, which was further purified by column chromatography on silica gel using hexane/ethyl acetate (8:2) as an eluant, 5.47g, 89% yield, $[\alpha]^{22}_{D}$ -34° (c 20, EtOH), >99% ee (lit.[9c] $[\alpha]^{22}_{D}$ -34° (c 20, EtOH))

Liberation of (+)-α-Pinene from $^{d}Ipc_2BH$. Benzaldehyde (7.6 mL, 75.0 mmol) was cautiously added (caution! exothermic reaction) to $^{d}Ipc_2BH$ (6.91g, 24 mmol) maintaining the reaction temperature at about 50 °C. Once the initial reaction subsided, the mixture was slowly heated to 100 °C (bath temperature), boron trifluoride-etherate (0.06 mL, 0.5 mmol) was added and the mixture was stirred for 1 h at 100 °C. The liberated α-pinene was distilled off at reduced pressure. Redistillation from lithium aluminum hydride gave (+)-α-pinene: 5.59g, 86% yield, bp 50-51°C/ 17 mmHg, $[\alpha]^{22}_{D}$ +51.34° (neat), 99.5% ee, lit.[16] $[\alpha]^{22}_{D}$ +51.4°(neat).

Preparation of (1S)-Diisocaranylborane, 2-$^{d}Icr_2BH$. A 50 mL RB flask provided with a septum inlet and magnetic stirring bar was charged with **2** (3.0 mL, 15.0 mmol) in dioxane (6.8 mL). To this, (+)-2-carene (5.2 mL, 33.0 mmol) was added during 5 min. The ice-bath was removed and the reaction mixture was kept at room temperature undisturbed for 15 h. A white crystalline precipitate of $^{d}Icr_2BH$ started separating out even during the addition of the (+)-2-carene. The reaction mixture was centrifuged and the supernatant solution was separated using a double ended needle. The crystalline mass was broken, washed with *n*-pentane and kept under reduced pressure to remove solvent, yielding pure 2-$^{d}Icr_2BH$: 4.24 g, 99% yield. The solid thus obtained was suspended in 15 mL of THF and 0.8 mL (20.0 mmol) of methanol was added slowly at 0 °C. After the evolution of hydrogen ceased, the liberated hydrogen was vented, the mixture was oxidized by using 5.0 mL of 3.0*M* NaOH solution and 3.0 mL, 30% hydrogen peroxide at 30 °C for 3 h and at 50 °C for 1 h. The mixture was cooled to room temperature, saturated with potassium carbonate and extracted with ether. The combined organic extract was washed with brine and dried over anhydrous magnesium sulfate. (-)-2-Isocaranol was isolated by distillation: bp 60-62 °C/2 mmHg, 3.93g (87%), $[\alpha]^{22}_{D}$ -31.2° (neat), [lit.[12] bp 50-52 °C /0.05 mm, $[\alpha]^{22}_{D}$ -31.5° (neat).

Preparation of 9-BBN. An oven-dried RB flask provided with a septum inlet was cooled to 0 °C under a stream of nitrogen gas. The flask was charged with **2** (2.0 mL, 10.0 mmol) in 1.8 mL of dioxane at room temperature and 1,5-cyclooctadiene (1.08 g, 10.0 mmol) was added drop-wise to a well-stirred solution. The mixture was further stirred for 3 h. The reaction was complete as indicated by the estimation of residual active hydride.

An aliquot was taken and oxidized with aqueous alkaline hydrogen peroxide in THF. A few drops (0.3 mL) of this THF solution placed in a vial, dried with magnesium sulfate, and 0.3 mL of dry pyridine and 0.3 mL of N,O-bis(trimethylsilyl)acetamide (BSA) were added. The mixture was heated for 10-15 min. while shaking. The product was analyzed on GC using a SE-30 column. The isomeric distribution of 1,4- and 1,5-cyclooctanediols (29 : 71) was determined from the integration of peaks, assuming the same response factor for both diols. The dioxane solution was refluxed and the progress of isomerization was controlled by GC analysis of the oxidized product as described above. After 2 h, the isomerization was complete as indicated by the exclusive presence of 1,5-cyclooctanediol in the oxidation product.

Isolation of 9-BBN. In a pre-weighted 50 mL flask equipped with a reflux condenser and a magnetic stirring bar was placed **2** (2.0 mL, 10.0 mmol) in 1.8 mL of dioxane under nitrogen. The flask was placed in a water bath (20 °C) and 1,5-cyclooctadiene (1.08g, 10.0 mmol) was added slowly with stirring. The stirring was continued for another 3 h at room temperature, followed by 2 h under reflux. After cooling the reaction mixture to room temperature, the 9-BBN crystallized out. The supernatant liquid was separated using a double-ended needle, the crystals were washed with ice-cold *n*-pentane and left under reduced pressure: yield; 1.04g (87%), recrystallized from THF, mp 152 °C [lit.[17] mp 153 °C].

Preparation of Disiamylborane. An oven-dried RB flask provided with a septum inlet was cooled to 0 °C under a stream of nitrogen gas. The flask was charged with **2** (2.0 mL, 10.0 mmol) in dioxane (5.9 mL) at 0 °C and 2-methyl-2-butene (2.1 mL, 20.0 mmol) was slowly added to this solution. The reaction mixture was further stirred at room temperature. The reaction was complete within 1h as indicated by active hydride analysis and the presence of only one peak at δ+31.1 in the ^{11}B NMR spectrum. The reaction mixture was oxidized using 3.0*M* NaOH (4.0 mL) and 30% hydrogen peroxide (4.0 mL). The GC analysis of the oxidation product, using an OV-17 column, revealed the quantitative formation of 3-methyl-2-butanol.

Application of Disiamylborane in Regioselective Hydroboration of Styrene. To a solution of disiamylborane (10.0 mmol) in dioxane, prepared as described above, was added styrene (1.04 g, 10.0 mmol) at room temperature and stirring was continued at room temperature for 1 h, by which time the hydroboration

was complete. The mixture was oxidized by alkaline hydrogen peroxide and GC analysis of the oxidized product revealed the formation of 2-phenylethanol (99%) and 1-phenylethanol (1%).

Preparation of Dicyclohexylborane. An oven dried 50 mL RB flask provided with a septum inlet was cooled to 0 °C under a stream of nitrogen gas. The flask was charged with **2** (2.0 mL, 10.0 mmol) in dioxane (5.2 mL) and *n*-nonane (1.78 mL, GC standard). Cyclohexene (0.82 g, 20.0 mmol) was added slowly at 0 °C during 5 min. and the mixture was stirred at room temperature. The reaction was complete within 1 h, as indicated by the estimation of active hydride. The reaction mixture was oxidized using alkaline hydrogen peroxide. The aqueous layer was saturated with potassium carbonate and GC analysis of the organic layer using a Carbowax 20M column revealed a 99% yield of cyclohexanol.

Isolation of Dicyclohexylborane. Hydroboration of cyclohexene was carried out with **2** in 10 mmol scale in dioxane as described above in a pre-weighed centrifuge flask. After the hydroboration was complete, the reaction mixture was centrifuged and the supernatant liquid was removed using a double-ended needle. The precipitate was washed with cold *n*-pentane and kept under reduced pressure to yield 1.59 g of dicyclohexylborane: 89% yield, free from amine, mp 102-3 °C (lit.[17] mp 103-4 °C, after sublimation).

Acknowledgment. JVBK thanks the Aldrich Chemical Company, for financial support and Nicolaus Copernicus University, Poland for laboratory facilities.

References and Notes

(1) (a) Brown, H. C. *Organic Syntheses via Boranes*; Wiley: New York, **1975**, p 18. A reprinted edition, *Organic Syntheses via Boranes,* vol. 1; Aldrich Chemical Co., Inc., Milwaukee, **1997**, is currently available. (b) Pelter, A.; Smith, K.; Brown, H. C.; *Borane Reagents*; Academic Press: London, **1988**. (c)*Encyclopedia of Organic Synthesis*, Paquette, L. Ed., J. Wiely, New York, 1995.

(2) (a) Lane, C. F.; *Aldrichemica Acta*, **1973**, *6*, 51. (b) Brown, H. C.; Murry, L. T.; *Inorg. Chem.*, **1984**, *23*, 2746. (c) Hutchins, R. O.; Learn, K.; Nazer, B.; Pytlewski, D.; Pelter, A.; *Org. Prep. Proced.Int.*, **1984**, *16*, 335. (d) Narayana, C.; Periasamy, M.; *J. Organomet. Chem.*, **1987**, *145*, 323. (e) Reddy, C. K.; Periasamy, M.; *Tetrahedron*, **1993**, *49*, 8877. (f) Periasamy, M.; Kanth, J. V. B.; Reddy, C. K.; *J. Chem. Soc., Perkin Trans.*, **1995**, 427. (g) Salunkhe, A. M.; Burkhardt, E. R.; *Tetrahedron Lett.*, **1997**, *38*, 1519.

(3) Brown, H. C.; Zaidlewicz, M.; Dalvi, P. V.; *Organometallics*, **1998**, *17*, 4202.

(4) Brown, H. C.; Kanth, J. V. B.; Zaidlewicz, M.; *J. Org. Chem.*, **1998**, *63*, 5154.

(5) (a) Brown, H. C.; Zaidlewicz, M.; Dalvi, P. V.; Narasimhan, S.; Mukhopadyay, A.; *Organometallics*, **1999**, *18*, in press. (b) Brown, H. C.; Kanth, J. V. B.; Zaidlewicz, M.; *Organometallics*, **1999**, *18*, in press.

(6) (a) Soderquist, J. A.; Medina, J. R.; Huertas, R.; *Tetrahedron Lett.*, **1998**, *39*, 6119. (b) Soderquist, J. A.; Huertas, R.; Medina, J. R.; *Tetrahedron Lett.*, **1998**, *39*, 6123.

(7) All these partially substituted boranes exist mainly as diborane dimers, but the monomeric forms are shown for the sake of convenience.

(8) Brown, H. C.; Moerikoffer, A. W.; *J. Am. Chem. Soc.* **1962**, 84, 1478.

(9)(a) Braun, L. M.; Braun, R. A.; Crissman, H. R.; Opperman, M.; Adams, R. M.; *J. Org. Chem.* **1971**, *36*, 2388. (b) Lane, C. F.;*Ibid.* **1974**, *39*, 1437. (c) Brown, H. C.; Mandal, A. K.; Kulkarni, S. U.; *Ibid*, **1977**, *42*, 1392.

(10) Brown, H. C.; Yoon, N. M.; *Isr. J. Chem.* **1977**, *15*, 12.

(11) Brown, H. C.; Joshi, N. N.; *J. Org. Chem.* **1988**, *53*, 4059.

(12) Brown, H. C.; Vara Prasad, J. V. N.; Zaidlewicz, M.; *J. Org. Chem.* **1988**, *53*, 2911.

(13) Brown, H. C.; Randad, R.S.;Bhat, K. S.; Zaidlewicz, M.;Racherla, U. S.; *J. Am. Chem. Soc.* **1990**, *112*, 2381.

(14) Previously we observed that monoglyme and diglyme are superior media for obtaining high yields and high purities of 9-BBN and similar crystalline dialkylboranes. See, Soderquist, J. A.; Brown, H. C.; *J. Org. Chem.*, **1981**, *46*, 4599. The present study shows that dioxane likewise is especially favorable for the preparation and isolation of such crystalline dialkylboranes.

(15) Sinclair, J. A.; Brown, H. C.; *J. Org. Chem.* **1976**, *41*, 1078.

(16) Based on the maximum rotation reported for (+)-α-pinene, $[\alpha]^{22}_{D}$ +51.6°: Johnson, W. S.; Frei, B.; Gopalan, A. S. *J. Org. Chem.* **1981**, *46*, 1512.

(17) Brown, H. C.; Mandal, A. K.; *J. Org. Chem.* **1992**, *57*, 4970.