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MONO- AND DIALKYLBORANE REAGENTS FROM SILYLAMINE-BORANES

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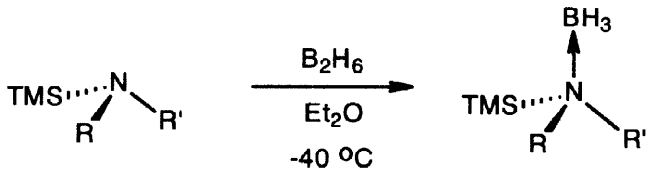
Abstract: *New procedures for the simple, efficient preparation of thexylborane ($ThxBH_2$), disiamylborane ($Siam_2BH$), 9-borabicyclo[3.3.1]nonane (9-BBN-H) and diisopinocampheylborane (Ipc_2BH) are described employing silylamine-boranes (1). By selecting a less reactive reagent, dicyclohexylborane (Chx_2BH), was prepared directly from hydroboration in crystalline form for the first time. These new methods demonstrate that the silylamine by-products (2) neither interfere with subsequent reactions or purification of the borane reagents, nor pose any difficulties in their separation from the borane-derived products.*

One of the most important features of the Brown hydroboration reaction is its ability to prepare organoboranes stereoselectively for use in the many subsequent conversions which are characteristic of this important functionality.[1] To produce only a single regioisomeric product and avoid wasting valuable alkenes in these subsequent conversions, Brown developed a series of highly selective partially alkylated boranes which include thexylborane ($ThxBH_2$),[2a] disiamylborane ($Siam_2BH$),[2b] dicyclohexylborane (Chx_2BH),[2c] 9-borabicyclo[3.3.1]nonane (9-BBN-H)[2d] and diisopinocampheylborane (Ipc_2BH),[2e] all of which exist mainly as dimers.[1] Employing borane-THF solutions, the formation of microcrystalline products with minor amounts of occluded impurities is commonplace, and with borane-dimethyl sulfide (BMS), the dimethyl sulfide by-product can be difficult to remove from contaminated reaction solvents.[1,3]

In the preceding Letter,[4] we described the preparation of a new class of amine-boranes (*i. e.* **1**) which were derived from diborane and silylated 1°- and 2°-amines (**2**).[5] With the introduction of the trimethylsilyl (TMS) substitution, the Lewis basicity of the amine is markedly decreased. Consequently, their borane complexes are weak enough so that they provide stable borane sources for a wide range of hydroboration reactivities at room temperature ranging from minutes to days. Moreover, **2** exhibits no tendency to form complexes with the organoborane products and is readily hydrolyzed to water-soluble and/or volatile by-products which are easily separated from reaction solvents and borane-derived products. In the present work, we describe new procedures for the preparation of the above important alkylborane reagents which take full advantage of these unique features of **1**.



2 **1**

To compare our new process to existing procedures, we chose to employ **1a** (R = H; R' = *t*-Bu) for the preparation of $ThxBH_2$ through the hydroboration of 2,3-dimethyl-2-butene which is complete in diethyl ether

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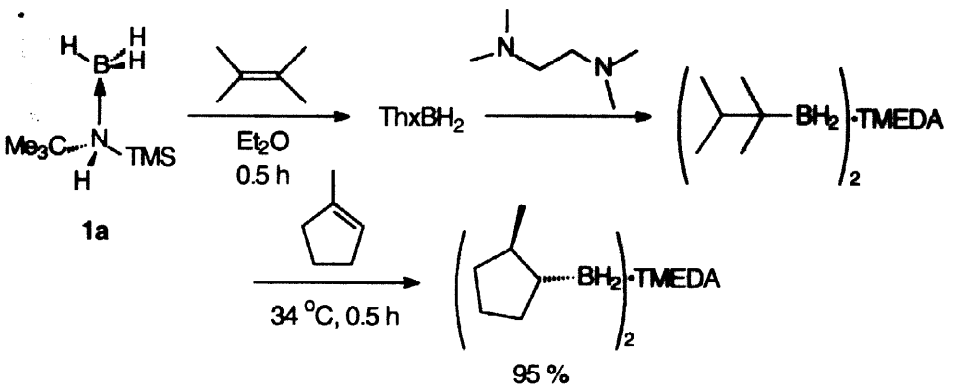
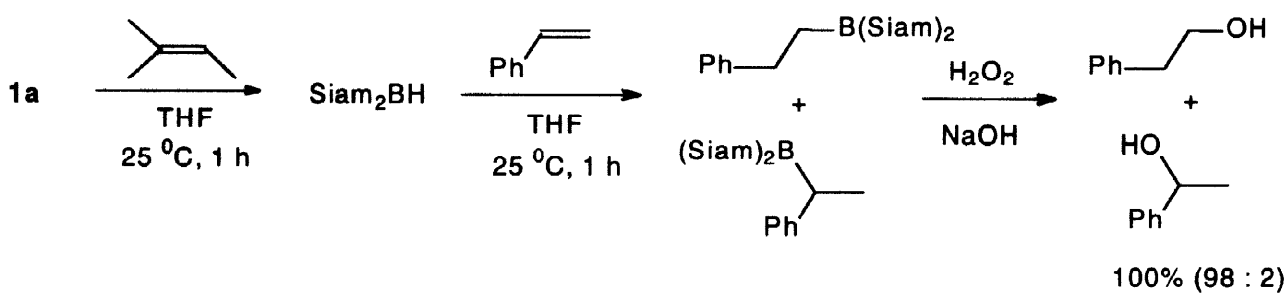
in 0.5 h at 25 °C.[1a,b,2a] This was converted to its *bis*-(thexylborane)-TMEDA complex with the addition of *N,N,N',N'*-tetramethylethylenediamine (TMEDA, 0.5 mol equiv). Following the reported procedure, this complex was allowed to react with 1-methylcyclopentene in refluxing diethyl ether, to afford *bis*-[*trans*-(2-methylcyclopentyl)borane]-TMEDA adduct in 95% yield (Scheme 1).[6]

Scheme 1



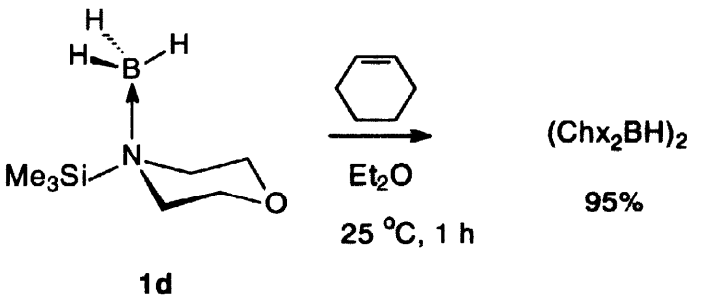
Having satisfied ourselves that **1** provides a very useful entry to $ThxBH_2$, we turned our attention to the preparation of dialkylboranes beginning with $Siam_2BH$ whose preparation from the hydroboration of 2-methyl-2-butene with **1a** (2:1) in THF at 25 °C is complete in one hour (^{11}B NMR, δ 31.6).[1a,b,2b] Because the hydroboration of styrene with borane itself gives a ~4:1 mixture of terminal and internal borane adducts, the greater regioselectivity of $Siam_2BH$ (98:2) provides a useful demonstration of the value of this reagent. The *in situ* reaction is complete in 1 h at 25 °C (^{11}B NMR, δ 86.8) and the oxidation of the intermediate boranes results in the quantitative formation of a 98:2 mixture of 1- and 2-phenylethanols. This demonstrates both the utility of **1** for the preparation of this reagent and that the presence of **2a** in solution with disiamylborane does not interfere with its subsequent hydroborations (Scheme 2).

Scheme 2

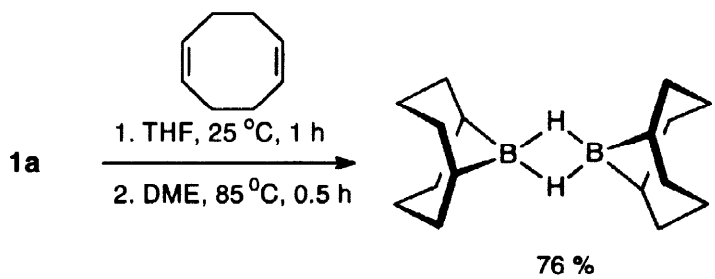


With the preparation of dicyclohexylborane, we were afforded a unique opportunity to demonstrate the advantages of having the spectrum of reactivities offered by **1**. We have had considerable previous experience with its preparation both from borane-THF and BMS, finding both to produce a microcrystalline powdery product which contains borane and cyclohexylborane impurities. We reasoned that a reagent which would release borane more slowly should provide a pure crystalline product. This expectation was

spectacularly achieved with *N*-TMS-morpholine-borane (**1d**) which, after the addition of cyclohexene (2 equiv) to its ether solution at 25 °C and cessation of stirring, produces large pure Chx_2BH dimer crystals which fall gently from solution much like snowflakes on a winter day. The procedure gives a very pure product (mp 106.5-108°C, lit[2c] 103-105°C) in 95% yield. This material is quantitatively converted to pure MeO-B(Hx-*c*)$_2$ (98% yield) upon methanolysis.



1d

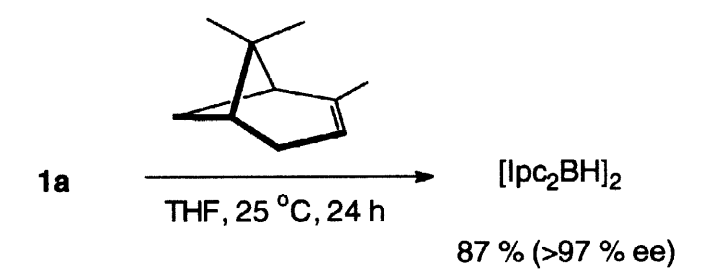


76 %

The preparation of 9-BBN-H dimer was carried out performing the hydroboration of 1,5-cyclooctadiene with **1a** in THF at 25°C. The solvent and **2a** were removed *in vacuo* (0.1 Torr) at room temperature and DME was added. After heating at reflux for 30 min, slow cooling to 0°C, afforded crystalline 9-BBN-H dimer (76%, mp 153-155°C, lit[2d] 153-155°C). While this process is somewhat less efficient than our BMS-based process,[3b] it has the advantage of being operationally simpler, particularly for smaller scale preparations of the reagent.

The reaction of (1*R*)-(+)-α-pinene (91% ee) with **1a** in a 2.5:1 ratio in THF at 25 °C for 24 h afforded Ipc_2BH in 87% yield.[2e] This procedure allows the equilibration of the initially formed material with the excess of α-pinene to result in Ipc_2BH dimer of higher enantiomeric purity than the original α-pinene used. The optical purity of our product was >97% ee as established by the optical rotation of the α-pinene (82%, $[\alpha]_D^{23}$ +50.2 (neat)) which is displaced from this material upon heating with benzaldehyde.[7,8]

In the above paragraphs, we have described new, efficient procedures for the preparation of five (5) of the important partially alkylated borane reagents which are commonly prepared through the simple hydroboration of readily available alkenes. Our study employed the use of novel silylamine-borane complexes (**1**) which are isolable in pure form from the reaction of diborane with a variety of silylamines (**2**). Because a wide variety of silylated amines **2** are either commercially available or are easily prepared, a broad spectrum of hydroboration reactivities is available from **1**. All of these complexes are stable solids at room temperature which can be utilized in a wide variety of solvents. Complete conversion to the corresponding alkylborane



derivative is observed in each case with the most reactive complex **1a** being the reagent of choice for the majority of these preparations. However, when a slower delivery of borane is desirable, as was the case for the preparation of Chx_2BH dimer, other reagents such as **1d** provide an exceptionally pure crystalline product. Because **2** does not interact significantly with these borane reagents, their subsequent reactions can often be carried out in the presence of **2** without consequence. The fact that **2** undergoes ready hydrolysis during the oxidation step to give volatile and/or water-soluble products, also greatly facilitates the isolation of the product derived from the organoborane when compared to bulky 3°-amine-borane complexes.[9] These new borane reagents **1** offer continued promise for future applications in boron chemistry.

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