Aminoborohydrides. 4. The Synthesis and Characterization of Lithium Aminoborohydrides: A New Class of Powerful, Selective, Air-Stable Reducing Agents

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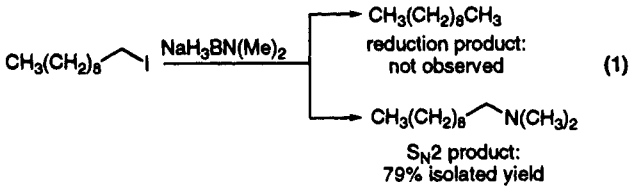
Received April 12, 1994®

Lithium aminoborohydrides ($LiABH_3$) are a new class of powerful yet selective reducing agents that reproduce, in air, virtually all of the transformations for which lithium aluminum hydride is now used. $LiABH_3$'s can be readily prepared as solids or generated *in situ*, are nonpyrophoric, and liberate hydrogen only slowly with protic solvents above pH 4. $LiABH_3$'s can be handled in dry air as easily as sodium borohydride and retain their chemical activity for at least 6 months when stored under nitrogen or dry air at 25 °C. $LiABH_3$'s can be synthesized from any primary or secondary amine, thus allowing control of the steric and electronic environment of these reagents.

Introduction

Since the discovery of lithium aluminum hydride ($LiAlH_4$) in 1947,[1] enormous effort has been invested in the development of safe and convenient alternatives[2] to this useful but highly reactive reagent.[3] Unfortunately, any increase in the stability of the new hydride reagents was accompanied by an even greater decrease in reactivity. Vitride,[4] developed in 1969, is a significant improvement over $LiAlH_4$. Vitride is nonpyrophoric, yet retains the reactivity of $LiAlH_4$. Unfortunately, the byproduct of Vitride, monomethoxyethanol is a known teratogen.[4c]

Recently, the synthesis and characterization of the reducing properties of sodium aminoborohydrides was reported.[5] Most of the functional groups reduced by $LiAlH_4$ were also reduced by sodium aminoborohydrides. However, the ^{11}B-NMR data for the reagents suggested an aminoborane structure rather than an aminoborohydride structure.[5] Additionally, reaction of these reducing reagents with 1-iododecane gave the S_N2 substitution product, 1-aminodecane, rather than decane, the expected reduction product (eq 1).[5] Similarly, the attempted reduction of 1,2-dodecene epoxide gave an 87% isolated yield of the corresponding amino alcohol with only a trace of 2-decanol.[5] The latter result suggests a borane-promoted, Lewis acid-catalyzed nucleophilic opening of the epoxide ring rather than a hydride reduction. Herein, we report the serendipitous discovery[6a,7b] and characterization of the reducing properties of lithium aminoborohydrides, a new class of powerful, air-stable reducing agents.



(1)

Results and Discussion

The Discovery of Lithium Aminoborohydrides. During the hydroboration of β,β-disubstituted enamines, we observed the formation of dihydridoaminoboranes.[7a,b] In order to obtain an authentic sample of these aminoboranes, we developed a new method for the synthesis of dihydridoaminoboranes (eq 2).[7b]

By reacting *n*-butyllithium or methyllithium with amine–borane complexes, $H_3B{:}NHR_2$, in tetrahydrofuran

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® Abstract published in *Advance ACS Abstracts,* September 15, 1994.

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(5) (a) The first synthesis of *sodium* aminoborohydrides was reported in 1961. Aftandilian, V. D.; Miller, H. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1961**, *83*, 2471. (b) Hutchins, R. O.; Learn, K.; El-Telbany, F.; Stercho, Y. P. *J. Org. Chem.* **1984**, *49*, 2438. Hutchins, *et al.*, reported the synthesis and use of sodium (dimethyl- and *tert*-butylamino)borohydrides. However, Hutchins reported ^{11}B-NMR chemical shifts of δ +43 (br s) for both of these sodium aminoborohydrides. The shift value and multiplicity do not correspond to aminoborohydrides. See refs 6a, 7a,b, and Keller, P. C. *J. Am. Chem. Soc.* **1969**, *91*, 1231.

(6) (a) Fisher, G. B.; Harrison, J.; Fuller, J. C.; Goralski, C. T.; Singaram, B. *Tetrahedron Lett.* **1992**, *33*, 4533. (b) Fuller, J. C.; Stangeland, E. L.; Goralski, C. T.; Singaram, B. *Tetrahedron Lett.* **1993**, *34*, 257. (c) Fisher, G. B.; Fuller, J. C.; Harrison, J.; Goralski, C. T.; Singaram, B. *Tetrahedron Lett.* **1993**, *34*, 1091. (d) Under conditions of extremely high humidity (90–100%), lower molecular weight $LiABH_3$'s were found to smoulder and, occasionally, catch fire. However, the pyrophoricity is due to residual *n*-BuLi present in the $LiABH_3$ acting as a "fuse" on exposure to moist air rather than to any inherent pyrophoricity of the $LiABH_3$. (e) For an excellent review of the factors affecting the stereochemistry of hydride reductions of substituted cyclohexanones, see Wigfield, D. C. *Tetrahedron* **1979**, *35*, 449. (f) Lithium triethylborohydride gives predominantly C–N bond cleavage for only aromatic *N,N*-dimethylamides.

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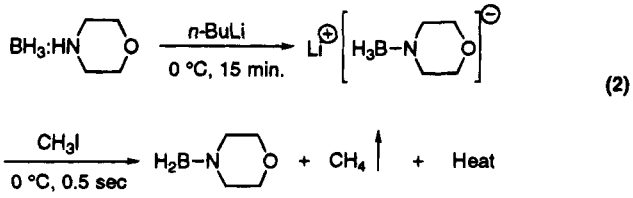


(2)

(THF), the corresponding $LiABH_3$'s were synthesized in quantitative yields. When these $LiABH_3$'s were quenched with methyl iodide at 0 °C, a violent, exothermic reaction ensued with every $LiABH_3$ that was tested and afforded the corresponding aminoboranes in high purity as determined by ^{11}B-NMR. The only other reagents with which methyl iodide was known to react in such a vigorous fashion were $LiAlH_4$ and lithium triethylborohydride ($LiEt_3BH$, SuperHydride).[2e] This reaction suggested that the $LiABH_3$'s were a new type of powerful reducing agent, comparable in reducing power to $LiAlH_4$.

Characterization of Spectral and Physical Properties. The method used for synthesizing $LiABH_3$'s, shown in eq 2, is general, and a wide variety of amino groups are readily accommodated. Following this procedure, several representative $LiABH_3$'s were prepared (Figure 1). The THF solutions of the $LiABH_3$'s so synthesized proved to be stable compounds. Many were stored under nitrogen at 25 °C for six months without undergoing any decomposition or loss of hydride activity.

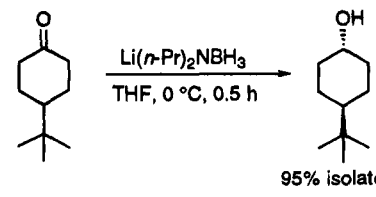
We have found two diagnostic criteria for the purity of $LiABH_3$'s: ^{11}B-NMR coupling constants and the reaction of $LiABH_3$'s with methyl iodide. Although both $LiABH_3$'s and the corresponding amine–boranes from which they are synthesized appear as sharp quartets with virtually identical chemical shifts in their respective ^{11}B-NMR spectra, the coupling constants of the $LiABH_3$'s and the corresponding amine-boranes are quite different. The $LiABH_3$'s exhibit ^{11}B-NMR J-values of between 82 and 87 Hz. In contrast, all amine–boranes have coupling constants ranging from 95–98 Hz. Additionally, all of the $LiABH_3$'s synthesized reacted vigorously and exothermically with methyl iodide to liberate methane and the corresponding aminoborane. Amine–borane complexes, however, are unreactive toward methyl iodide.

Synthesis of Solid Lithium Aminoborohydrides. Solid $LiABH_3$'s were readily obtained by performing the synthesis shown in eq 2 in anhydrous diethyl ether (Et_2O) or hexanes followed by removal of the solvent under high vacuum (1 Torr, 40 °C). Such $LiABH_3$'s are stable in dry air; several representative $LiABH_3$'s were stored under dry air in a closed vial for over a month without loss of their hydride activity. $LiABH_3$'s are not pyrophoric either in solid form or as THF solutions. However, when synthesizing solid $LiABH_3$'s, it is essential that *no trace of n-BuLi remains* in the $LiABH_3$; residual n-BuLi acts as a "fuse" and will cause the $LiABH_3$ to ignite in air. We have found that using a substoichiometric amount of n-BuLi (0.95 equiv) ensures that the solid $LiABH_3$ is completely nonpyrophoric. $LiABH_3$'s liberate hydrogen vigorously with acidic compounds which have a pK_a < 4.0. However, unlike the violent and potentially dangerous reaction of $LiAlH_4$ with water or methanol, hydrogen is liberated only slowly during the reaction of $LiABH_3$'s with water or methanol. Further, $LiABH_3$'s are converted to the unreactive amine–borane complex on addition to either of these protic solvents, as indicated by ^{11}B-NMR spectra. $LiABH_3$'s that have been deliberately allowed to revert to the corresponding amine–boranes by prolonged exposure to airborne moisture were readily regenerated by simple deprotonation with n-BuLi to again yield the desired $LiABH_3$.

Attempts to obtain melting point data on the solid $LiABH_3$'s were not successful. However, $LiABH_3$'s displayed remarkable thermal stability, with gradual decomposition occurring above 200 °C. The thermal stability of $LiABH_3$'s is notable when compared to the explosive decomposition that results from heating $LiAlH_4$ above 100 °C.

Characterization of Reducing Properties. After optimizing the synthesis of $LiABH_3$'s, we began a systematic study of their reducing properties. Lithium pyrrolidinoborohydride ($LiPyrrBH_3$) was used for this initial study. A wide variety of functional groups were readily reduced. The products from these reactions were easily isolable in both high yield and high purity, although successful product isolations were found to require prior acid hydrolysis to eliminate contamination by boron-containing materials. Further, unlike other powerful reducing agents, once the $LiABH_3$ has been generated, either *in situ* or in solid form, no precautions to exclude air were needed when the reduction was performed. However, we have found that the exclusion of adventitious moisture was essential to maximize the yields in reductions that require more than 1 h to complete, such as the reduction of azides or nitriles. Thus, we recommend carrying out such reductions under nitrogen or an atmosphere of dry air. Further, recent work using solid $LiABH_3$'s has demonstrated that these reagents can be handled in dry air with the same ease as sodium borohydride ($NaBH_4$). Whether generated *in situ* or used in solid form, most reductions with $LiABH_3$'s were complete in 2–3 h at ambient temperature, although some very hindered substrates required refluxing for 2–3 h to achieve a reasonable yield of the desired product.

Reduction of Aldehydes and Ketones. The reduction of aldehydes and ketones proved to be quite rapid. Generally, such reductions were complete in 15–30 min at 0 °C (Table 1). Aromatic ketones were reduced with similar ease. Whether aliphatic or aromatic, both ketones and aldehydes required only 1 equiv of $LiABH_3$ to effect their quantitative reduction to the corresponding alcohol. The stereoselectivity of $LiABH_3$ reductions of 4-substituted cyclohexanones indicates that the $LiABH_3$'s behave like unhindered hydride reagents, regardless of the size of the amine moiety (Table 1). Thus, the reduction of 4-*tert*-butylcyclohexanone using lithium (di-n-propylamino)borohydride ($Li(n\text{-}Pr)_2NBH_3$) gave 99% *trans*-4-*tert*-butylcyclohexanol in 95% isolated yield (eq 3).



(3)

Reduction of α,β-Unsaturated Aldehydes and Ketones. The regioselectivity demonstrated by $LiABH_3$'s in reductions of α,β-unsaturated aldehydes and ketones was particularly noteworthy: with all substrates investigated, $LiABH_3$'s gave exclusive 1,2-reduction of α,β-unsaturated aldehydes and ketones to the corresponding

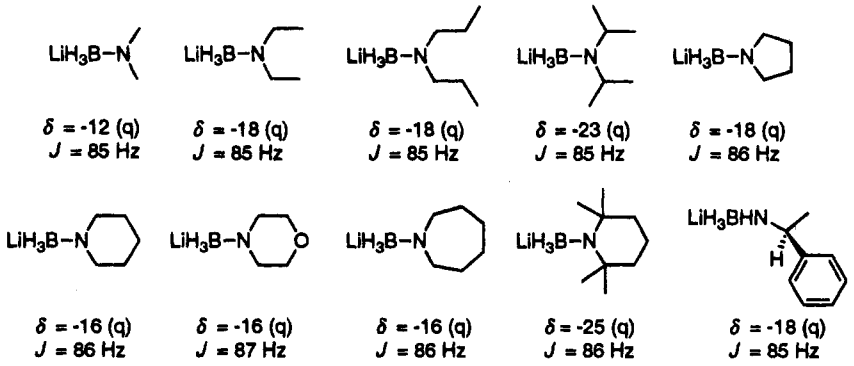


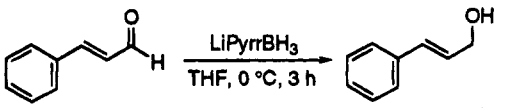
Figure 1. ^{11}B-NMR shifts of representative lithium aminoborohydrides. Note that, although the chemical shifts of the corresponding amine–borane complexes are virtually identical to those of the $LiABH_3$'s, the J-values of the amine–borane complexes are different and range from 95–98 Hz.

Table 1. Reduction of Representative Aldehydes and Ketones with 1 M THF Solutions of Lithium Aminoborohydrides[a–c]

ketone/aldehyde	product[d]	yield, %[e]
benzaldehyde[f]	benzyl alcohol	98
acetophenone[f]	1-phenylethanol	98
2-methylcyclohexanone[g]	2-methylcyclohexanol[h]	95
3-methylcyclohexanone[g]	*cis*-3-methylcyclohexanol[i]	95
4-methylcyclohexanone[g]	*trans*-4-methylcyclohexanol[j]	95
4-*tert*-butylcyclohexanone[g]	*trans*-4-*tert*-butylcyclohexanol[k]	95

[a] Reductions performed as follows: (1) 10 mmol of ketone or aldehyde, 20 mL of THF, 0 °C; (2) 12 mL of 1 M THF solution of $LiABH_3$, 0 °C, 1 h. [b] Synthesized as follows: (1) 12 mmol of amine + 12 mL of 1 M BH_3·THF, 1 h, 0 °C; (2) 12 mmol of 2.5 M *n*-BuLi, 30 min., 0 °C. [c] Purity determined by ^{11}B-NMR of the THF solution of $LiABH_3$. [d] Product purity determined by 250 MHz ^{1}H- and ^{13}C-NMR and FT-IR. [e] Isolated yields. [f] Reduction performed with $LiPyrrBH_3$. [g] Reduction performed with $Li(n\text{-}Pr)_2NBH_3$ at 0 °C for 30 min. [h] Isolated as a 40:60 ratio of *cis*- and *trans*-2-methylcyclohexanols. [i] Isolated as a 90:10 ratio of *cis*- and *trans*-3-methylcyclohexanols. [j] Isolated as a 14:86 ratio of *cis*- and *trans*-4-methylcyclohexanols. [k] Isolated as an 1:99 ratio of *cis*- and *trans*-4-*tert*-butylcyclohexanols.

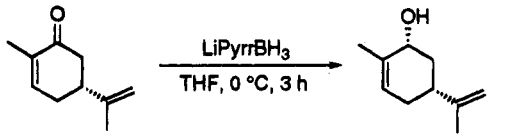
allylic alcohols (Table 2). Although other reagents are known that give high 1,2:1,4-reduction ratios,[8] $LiABH_3$'s are the only reducing agents that give exclusive 1,2-reduction of both α,β-unsaturated aldehydes and ketones. Thus, these results compliment those obtained using $LiAlH_4$ and the Luche reagent.[8p] For example, the $LiAlH_4$ reduction of cinnamaldehyde gave the corresponding saturated alcohol exclusively.[8q] Further, although the Luche reagent ($NaBH_4/CeCl_3$) gives exclusive 1,2-reduction of α,β-unsaturated ketones, this reagent does not reduce α,β-unsaturated aldehydes.[8p] The use of the Lewis-acidic lanthanide reagent catalyzes the formation of an acetal that is unreactive to further reduction.[8f] In contrast, reduction of cinnamaldehyde with $LiPyrrBH_3$ gave exclusively the 1,2-reduction product in 95% isolated yield (eq 4).



(4)

95% isolated yield

(*R*)-(−)-carvone was reduced to the corresponding allylic alcohol, (*1R,5R*)-(−)-*cis*-carveol, in 96% isolated yield (eq 5). Similarly, (*R*)-(+)-pulegone was reduced to

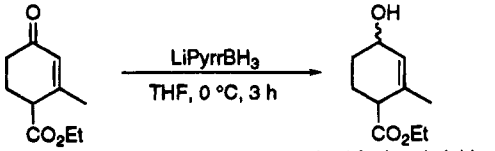


(5)

96% isolated yield

(*1R,3R*)-(−)-*cis*-pulegol. The stereochemical assignments of *cis*-carveol[8r] and *cis*-pulegol[8s] were based on chiroptical comparison.

The chemoselectivity of $LiABH_3$'s was demonstrated in the reduction of Hagemann's ester (4-carbethoxy-3-methyl-2-cyclohexen-1-one) with 1 equiv of $LiPyrrBH_3$: the ester moiety was not reduced while the more reactive α,β-unsaturated ketone functionality was reduced exclusively to the corresponding *cis*–*trans* mixture of allylic alcohols in 94% isolated yield (eq 6).



(6)

94% isolated yield

Reduction of Carboxylic Acid Esters. Although a wide variety of reducing agents will convert esters to the corresponding alcohols,[9] all except $NaBH_4$[10] require the rigorous exclusion of air during the reduction. In contrast, the reduction of both aliphatic and aromatic esters

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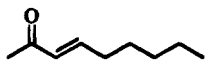
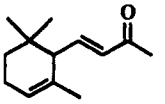
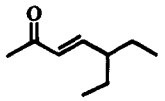
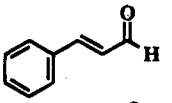
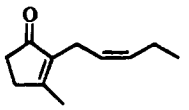
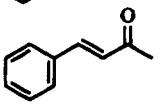
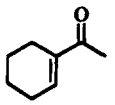
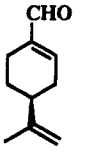
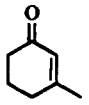
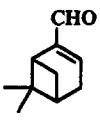
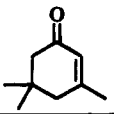
(9) (a) Brown, H. C.; Choi, Y. M.; Narasimhan, S. *J. Org. Chem.* **1982**, *47*, 3153. (b) Brown, H. C.; Narasimhan, S. *J. Org. Chem.* **1982**, *47*, 1604. (c) Brown, H. C.; Mathew, C. P.; Pyun, C.; Son, J. C.; Yoon, N. M. *J. Org. Chem.* **1984**, *49*, 3091. (d) Yoon, N. M.; Brown, H. C. *J. Am. Chem. Soc.* **1968**, *90*, 2927. (e) Nystrom, R. F.; Brown, W. G. *J. Am. Chem. Soc.* **1947**, *69*, 1197.

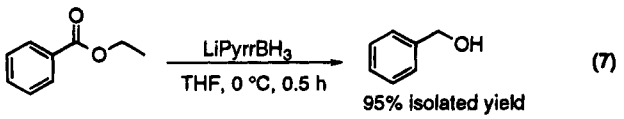
(10) The in-air reduction of esters has also been carried using $NaBH_4$ in refluxing methanol. See: Brown, M. S.; Rapoport, H. *J. Org. Chem.* **1963**, *28*, 3261.

Table 2. Reduction of α,β-Unsaturated Carbonyl Compounds with Lithium Pyrrolidinoborohydride

substrate[a]	1,2: 1,4[b]	yield, %[c,d,e]	substrate[a]	1,2: 1,4[b]	yield, %[c,d,e]
	>99:1	96		>99:1	94
	>99:1	90		>99:1	91
	>99:1	98		>99:1	95
	>99:1	89[e]		>99:1	97
	>99:1	92		>99:1	89
	>99:1	92[e]			

[a]Reduction done with $LiPyrrBH_3$ for 3 h at 25 °C unless specified otherwise. [b]Product purity determined by 250 MHz ^1H- and ^{13}C-NMR and capillary GC analyses. [c]Isolated overall yield. [d]Determined by capillary GC comparison with authentic samples. [e]Reduction done with $LiPyrrBH_3$ for 3 h at 65 °C.

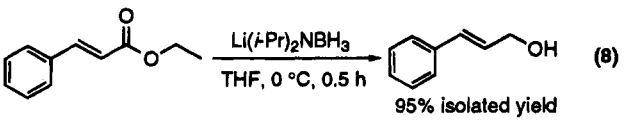
with $LiABH_3$'s proved to be a very rapid reaction. Ethyl benzoate was reduced, in air, to benzyl alcohol in 0.5 h at 0 °C in 95% isolated yield (eq 7; Table 3). Similar



(7)

results were obtained for the reduction of ethyl octanoate.

Reduction of ethyl cinnamate to the corresponding saturated alcohol in air has been achieved using excess $NaBH_4$ in refluxing methanol.[10] Our results with $LiABH_3$'s compliment this procedure. For example, reduction of ethyl cinnamate with lithium (diisopropylamino)borohydride ($Li(i\text{-}Pr)_2NBH_3$) at 0 °C is complete in 30 min and affords exclusively the 1,2-reduction product, cinnamyl alcohol, in 95% isolated yield (eq 8).



(8)

Thus, for the reductions of aliphatic or aromatic esters with $LiABH_3$'s, the mild reaction conditions, short reaction times, and chemoselectivity of $LiABH_3$'s make these reagents attractive alternatives to the reagents currently available for carrying out this transformation.[9]

Reduction of Tertiary Amides. Current methods for the reduction of tertiary amides require the rigorous exclusion of air.[11] Although reductions of primary and secondary amides with $LiABH_3$'s resulted in the recovery of the unreduced amides, a wide variety of tertiary amides were reduced in excellent yield in dry air with $LiABH_3$'s.[6c] The crude products of these reductions were often of analytical purity and required no further purification. The reduction of relatively unhindered tertiary amides, such as *N,N*-dimethylbenzamide, yielded benzyl alcohol regardless of the steric environment of the $LiABH_3$'s. However, for more sterically demanding tertiary amides, selective C—O or C—N bond cleavage[6c,11h] was achieved by varying the steric environment of the amine moiety of the $LiABH_3$ used in the reduction. Thus, reduction of 1-pyrrolidinooctanamide with $Li(i\text{-}Pr)_2NBH_3$

Table 3. Reduction of Representative Esters with Lithium Aminoborohydrides[a,b]

ester	product[c]	yield, %[d]
ethyl decanoate[e]	1-decanol	90
ethyl benzoate[e,f]	1-benzyl alcohol	95
phthalide[e]	1,2-benzenedimethanol	95
ethyl cinnamate[e,f]	cinnamyl alcohol[g]	95

[a] Synthesized as follows: (1) 12 mmol of amine + 12 mL of 1 M BH_3·THF, 1 h, 0 °C; (2) 12 mmol of 2.5 M *n*-BuLi, 30 min., 0 °C. (3) Vacuum-removal of solvent, 0.1 Torr, 1 h. [b] Purity determined by ^{11}B-NMR of the THF solution of $LiABH_3$. [c] Product purity determined by 250 MHz ^1H- and ^{13}C-NMR and FT-IR. [d] Isolated yields. [e] Reduction performed at 0 °C with 10 mmol of ester using 10 mL of 1 M $LiPyrrBH_3$ in THF. [f] Reduction performed at 0 °C with 10 mmol of ester in THF and 12 mmol of solid $LiPyrrBH_3$ added directly to the ester. [g] 1,2-reduction product isolated exclusively.

(11) $LiAlH_4$: (a) Uffer, H.; Schlitter, E. *Helv. Chim. Acta* **1948**, *31*, 1397. (b) Gaylord, N. G. *Reductions With Complex Metal Hydrides*; Wiley-Interscience: New York, 1956; p 544–592. Borane: (c) Brown, H. C.; Heim, P. *J. Am. Chem. Soc.* **1964**, *86*, 3566. (d) Brown, H. C.; Heim, P. *J. Org. Chem.* **1973**, *38*, 912. (e) Brown, H. C.; Narasimhan, S.; Choi, Y. M. *Synthesis* **1981**, 441. $NaBH_4$: (f) Borch, R. F. *Tetrahedron Lett.* **1968**, 61. (g) Satoh, T.; Suzuki, S. *Tetrahedron Lett.* **1969**, 4555. (h) Rahman, A. U.; Basha, A.; Waheed, N. *Tetrahedron Lett.* **1969**, 219. $LiEt_3BH$: (i) Brown, H. C.; Kim, S. C. *Synthesis* **1977**, 635. This paper also reported the first observation of competing C—O vs C—N bond cleavage in the reduction of tertiary amides. Also see ref 5b.

Table 4. Reduction of Aliphatic and Aromatic Tertiary Amides with Lithium Aminoborohydrides[a-c]

amide	$LiABH_3$ (eq)	product[d]	yield, %[e]	bp (Torr)[f]
1-pyrrolidinooctanamide	$Li[H_3BPyrr]$ (1.2)	1-octanol	77	93–95 (10)
1-pyrrolidinooctanamide	$Li[H_3BN(i\text{-}Pr)_2]$ (1.7)	1-octylpyrrolidine	95	44–45 (0.3)
N,N-diethyldodecanamide	$Li[H_3BN(i\text{-}Pr)_2]$ (1.2)	*N,N*-diethyldodecanamine	98	99–100 (0.5)
N,N-diisopropylcyclohexanamide	$Li[H_3BN(i\text{-}Pr)_2]$ (1.7)[g]	[(*N,N*-diisopropylamino)methyl]cyclohexane	64[h]	45–47 (0.6)
N,N-diethyl-*m*-toluamide	$Li[H_3BPyrr]$ (1.2)	3-methylbenzyl alcohol	95	52–54 (0.2)
N,N-diethyl-*m*-toluamide	$Li[H_3BN(i\text{-}Pr)_2]$ (1.2)	3-methyl-*N,N*-diethylbenzylamine	99	136–138 (100)
N,N-diisopropylbenzamide	$Li[H_3BPyrr]$ (1.2)[i,j]	benzyl alcohol	99	50–52 (1)
N,N-diisopropylbenzamide	$Li[H_3BN(i\text{-}Pr)_2]$ (1.2)	*N,N*-diisopropylbenzylamine	98	40–41 (0.1)

[a] Reactions run with $LiABH_3$ generated *in situ* at 25 °C unless otherwise noted. [b] Generated by (1) 12 mmol of amine + 12 mL of 1 M BH_3·THF, 1 h, 0 °C; (2) 12 mmol of 2.5 M *n*-BuLi, 30 min., 0 °C. [c] Purity determined by ^{11}B-NMR of the THF solution of $LiABH_3$. [d] Product purity determined by 250 MHz ^1H- and ^{13}C-NMR and FT-IR. [e] Isolated yields. [f] Bp/mp are uncorrected. [g] Quantitative recovery of starting material with $LiPyrrBH_3$ at 25 °C or 65 °C. [h] Reduction done at 65 °C for 2 h. [i] Quantitative recovery of starting material with $LiPyrrBH_3$ at 25 °C. [j] Reduction done at 65 °C for 2 h.

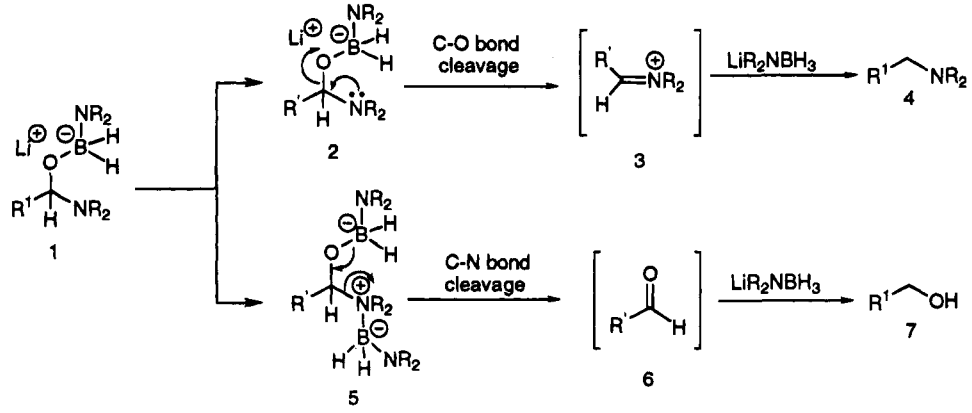
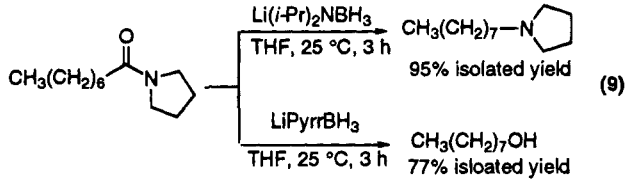


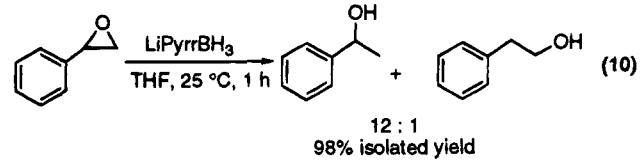
Figure 2. Mechanism to account for the selective C—O or C—N bond cleavage in $LiABH_3$ reductions of tertiary amides.

gave 1-octylpyrrolidine in 95% isolated yield; reduction of the same amide with $LiPyrrBH_3$ gave 1-octanol in 77% isolated yield (eq 9, Table 4). The selectivity of this



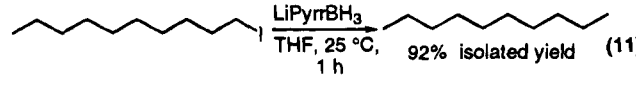
reduction appears to involve a common intermediate, **1**, obtained as the initial reduction product of the amide (Figure 2).[5b,11k] Two possible pathways from **1** lead to the corresponding amine or alcohol. In the first, the nitrogen lone pair expels the lithium dihydridoaminoborinate **2** to yield an iminium species, **3**. This iminium group is then rapidly reduced to the corresponding amine **4** by the remaining $LiABH_3$. The second pathway postulates the complexation of an aminoborane to the nitrogen of **1**, thereby converting the amine to an ammonium moiety, **5**, a better leaving group. Cleavage of the B—O bond and subsequent expulsion of the diaminodihydridoborohydride moiety results in the formation of an aldehyde, **6**, which is rapidly reduced by one of the many borohydride species present in the reaction mixture to the corresponding alcohol **7**. In all of the tertiary amide reductions that we have carried out, we have found that, as the groups bonded to the amide or $LiABH_3$ nitrogen are made more sterically demanding, amine formation through C—O bond cleavage is favored, apparently due to the unfavorable steric interactions between the $LiABH_3$ and the amide nitrogen. Whereas reductions performed with $LiAlH_4$ give mainly C—O bond cleavage and those carried out with $LiEt_3BH$[6f] give C—N bond cleavage, $LiABH_3$'s give selective C—O or C—N bond cleavage by simply altering the steric environment of the amine moiety of the $LiABH_3$.

Reduction of Epoxides. Isolation-scale reductions of epoxides were also investigated (Table 5). Epoxides were readily reduced with $LiPyrrBH_3$. Styrene oxide gave predominantly 1-phenylethanol in 98% overall isolated yield (eq 10). Similarly, cyclohexene oxide was



reduced to cyclohexanol in 93% isolated yield.

Reduction of Alkyl Halides. The reduction of alkyl halides with $LiABH_3$'s gave the corresponding alkanes in excellent yields. Thus, benzyl bromide was cleanly reduced to toluene and 1-iododecane to decane (eq 11, Table 5).



Reduction of Azides. The reduction of azides to the corresponding amines is an important transformation in synthetic organic chemistry for the introduction of the amino functional group.[12] The most commonly utilized methodologies for carrying out this transformation em-

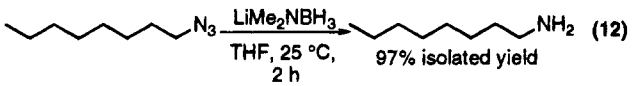
Table 5. Reduction of Miscellaneous Functional Groups with Lithium Aminoborohydrides[a,b]

substrate	product[c]	yield, %[d]
cyclohexene oxide[e]	cyclohexanol	90
styrene oxide[e]	1-phenylethanol	98
1-iododecane[e]	*n*-decane	92
benzyl bromide[e]	toluene	95[f]
1-octyl azide[g]	1-octylamine	97
benzyl azide[g]	benzylamine	85

[a] Synthesized as follows: (1) 12 mmol of amine + 12 mL of 1 M BH_3·THF, 1 h, 25 °C; (2) 12 mmol of 2.5 M *n*-BuLi, 30 min., 0 °C. [b] Purity determined by ^{11}B-NMR of the THF solution of $LiABH_3$. [c] Product purity determined by 250 MHz ^{1}H and ^{13}C-NMR and FT-IR. [d] Isolated yields. [e] Reduction performed at 0 °C with 10 mmol of substrate using 10 mL of 1 M LiPyrrBH_3 in THF. [f] Yield determined by capillary GC with internal standards. [g] Reduction performed at 25 °C with 10 mmol of substrate using 15 mL of 1 M $LiMe_2NBH_3$ in THF.

ploy either $LiAlH_4$[13] or catalytic hydrogenation,[14] although numerous other methods have been developed.[12]

The reductions of both aliphatic and aromatic azides to the corresponding primary amine with $LiABH_3$'s were carried out under mild conditions: 1.5 equiv of $Li(Me)_2NBH_3$ in THF at 25 °C. The reaction progress was conveniently monitored by IR by following the disappearance of the strong azide absorption peak (2100–2000 cm^{-1}). Azide reductions were generally complete within 2–5 h, depending on the electronic and steric environment of the azide. Thus, the reduction of 1-octyl azide afforded a 95% isolated yield of 1-octylamine (eq 12, Table 5). Similarly, benzyl azide was reduced to benzylamine



(12)

in 85% isolated yield.

Conclusion

The survey of the chemistry of $LiABH_3$'s presented here represents only our initial studies with these reagents. The implications of these new reducing agents for both industry and academia appear to be quite promising. In undergraduate teaching laboratories, transformations that would seldom be attempted due to the need to use $LiAlH_4$, such as the reduction of esters, may become routine experiments with the use of $LiABH_3$'s. For example, for the past three years, students in the U. C. Santa Cruz introductory organic chemistry laboratory class have employed both solid and 1 M THF solutions of $LiABH_3$'s to reduce aliphatic, aromatic, and α,β-unsaturated esters to the corresponding aliphatic, aromatic, and allylic alcohols, in air, in 70–98% isolated yields without incident or difficulty. In academic research laboratories, the short reaction time, ease of generation and handling, and the simple workup procedures for performing reductions with $LiABH_3$'s make these new reagents attractive alternatives to $LiAlH_4$ or $LiEt_3BH$ ("SuperHydride") reductions (Figure 3).

The reactivity of $LiABH_3$'s is comparable to the reactivity of both $LiAlH_4$ and Vitride. $LiABH_3$'s are air-stable, nonpyrophoric, thermally stable, and, with the exception of carboxylic acids and primary and secondary amides, cleanly reduce essentially every functional group that $LiAlH_4$ and Vitride reduce. Solid $LiABH_3$'s can be handled in air with the same ease and convenience as sodium borohydride, yet reductions performed with these reagents are generally complete in 1–3 h. Moreover, the reactivity of $LiABH_3$'s can be sterically modified by altering the amine moiety, a feature that enhances the versatility of $LiABH_3$'s.

Currently, our research group is conducting a comprehensive investigation of the reducing properties of $LiABH_3$'s containing an optically active amine moiety.

Experimental Section

All operations were carried out under a nitrogen atmosphere. All glassware, syringes, and needles were oven-dried at 120 °C and cooled to room temperature with nitrogen gas before use. Tetrahydrofuran (THF) was freshly distilled from sodium and benzophenone ketyl. Anhydrous diethyl ether (Et_2O) was purchased from Fisher Scientific and used directly. Borane–dimethyl sulfide (BMS, 10.2 M), *n*-butyllithium (2.5 M, in hexanes), and all of the amines used in this study were purchased from the Aldrich Chemical Co., stored under nitrogen, and used without further purification. ^{11}B-NMR spectra were obtained on a Bruker ACF MultiProbe 250 MHz NMR; the chemical shifts are in δ relative to Et_2O·BF_3 with chemical shifts downfield from Et_2O·BF_3 assigned as positive. ^{1}H-NMR and ^{13}C-NMR spectra were obtained on a Bruker ACF MultiProbe 250 MHz NMR. Chemical shifts are in δ relative to internal Me_4Si. Gas chromatographic analyses were carried out with a Hewlett-Packard 5890 Series II chromatograph using a 60M Methylsilicone capillary column.

Synthesis of Lithium Piperidinoborohydride. The following procedure for the synthesis of a 1 M THF solution of lithium piperidinoborohydride is representative. A 1000-mL round-bottom flask equipped with a magnetic stirring bar and fitted with a rubber septum was charged by cannula with piperidine (34.1 g, 39.6 mL, 400 mmol) and THF (anhydrous, 160.4 mL) and cooled under nitrogen to 0 °C. BMS (10 M, 40 mL, 400 mmol) was added dropwise, the stirring, over a 30 min period. The reaction mixture was stirred for an additional 1 h at 0 °C. The reaction mixture was charged dropwise by cannula with *n*-butyllithium (2.5 M, 160 mL, 400 mmol) over a 90 min period. The reaction was stirred at 0 °C for 1 h and then allowed to come to room temperature. The reaction mixture was stirred for an additional 1 h at 25 °C to afford lithium piperidinoborohydride. ^{11}B-NMR (THF): δ −16 (q, J = 86 Hz); IR (THF): 2235 (B–H str), 1468 (B–N str), 1377 (B–N str), cm^{-1}.

Synthesis of Solid Lithium (*N,N*-Diethylamino)borohydride. The following procedure for the synthesis of solid lithium (diethylamino)borohydride is representative. A 250-mL round-bottom flask equipped with a magnetic stirring bar and fitted with a rubber septum was charged with BMS (10 M, 5 mL, 50 mmol) and hexane (anhydrous, 100 mL) and cooled under nitrogen to 0 °C. Diethylamine (3.6 g, 5.2 mL, 50 mmol) was added dropwise, with stirring, over a 2 min period. The reaction mixture was stirred for an additional 1 h at 0 °C. The reaction mixture was charged dropwise by cannula with *n*-butyllithium (2.5 M, 19 mL, 47.5 mmol) *(The use of a substoichiometric amount of n-BuLi is essential to insure that the solid $LiABH_3$'s synthesized are nonpyrophoric! See ref 6d)* over a 15 min period. The reaction was stirred at 0 °C for an additional 1 h and allowed to come to room temperature. The reaction mixture was stirred for an ad-

(12) (a) Sheradsky, T. *The Chemistry of the Azido Group*; Patai, S., Ed.; Wiley-Interscience: New York, 1971; Chapter 6. (b) Mungall, W. S.; Greene, G. L.; Heavner, G. A.; Letsinger, R. L. *J. Org. Chem.* **1975**, *40*, 1659. (c) Vaultier, M.; Knouzi, N.; Carrie, R. *Tetrahedron Lett.* **1983**, *24*, 763. (d) Rolla, F. *J. Org. Chem.* **1982**, *47*, 4327. (e) Samano, M. C.; Robins, M. J. *Tetrahedron Lett.* **1991**, *32*, 6293. (f) Adachi, T.; Yamada, Y.; Inoue, I.; Saneyoshi, M. *Synthesis* **1977**, 45. (g) Sarma, J. C.; Sharma, R. P. *Chem. Ind.* **1987**, *21*, 764. (h) Pei, Y.; Wickham, B. O. S. *Tetrahedron Lett.* **1993**, *34*, 7509.

(13) (a) Boyer, J. H. *J. Am. Chem. Soc.* **1951**, *73*, 5865. (b) Boyer, J. H.; Canter, F. C. *Chem. Rev.* **1954**, *54*, 1. (c) Hojo, H.; Kobayashi, S.; Soai, J.; Ikeda, S.; Mukaiyama, T. *Chem. Lett* **1977**, 635. (d) Kyba, E. P.; John, A. M. *Tetrahedron Lett.* **1977**, 2737.

(14) Corey, E. J.; Nicolaou, K. C.; Balanson, R. D.; Machida, Y. *Synthesis* **1975**, 590.

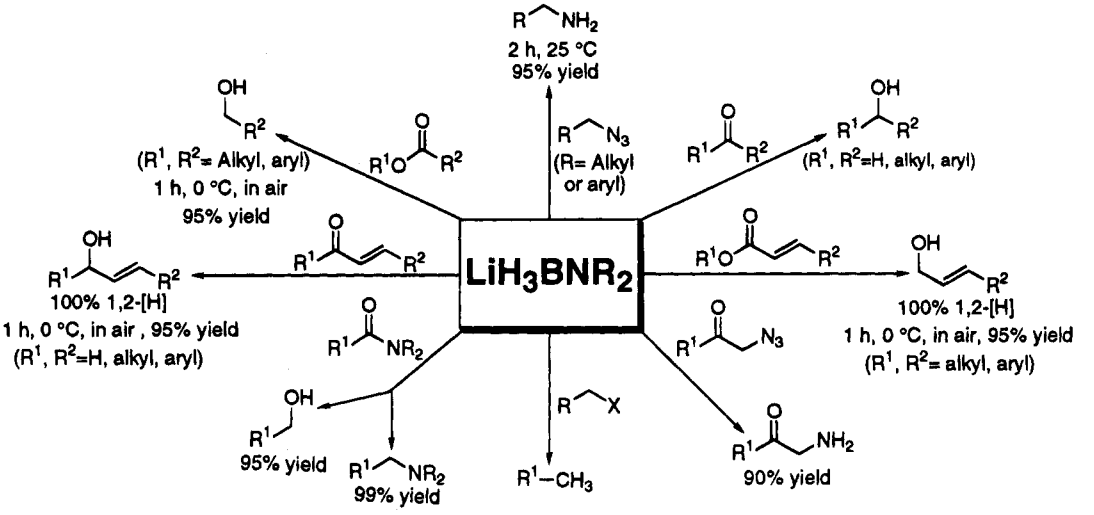


Figure 3. Representative functional groups reduced by lithium aminoborohydrides.

ditional 1 h at 25 °C. The solvent was removed in vacuo at 40 °C (1 Torr) to yield (*N,N*-diethylamino)borohydride as a white powder. ^{11}B-NMR (THF): δ −18 (q, J = 85 Hz); IR (THF): 2205 (B−H str), 1462 (B−N str), 1372 (B−N str) cm^{-1}.

General Procedure for Alkylcyclohexanone Reductions. Reduction of 4-*tert*-Butylcyclohexanone to 4-*tert*-Butylcyclohexanol. A 100 mL flask was charged with 4-*tert*-butylcyclohexanone (1.5 g, 10 mmol) and THF (10 mL) and cooled to 0 °C. Li(*n*-Pr)$_2$NBH$_3$ (solid, 1.7 g, 12 mmol) was added with stirring in small portions and the reaction mixture was stirred for an additional 1 h. The solution was quenched by addition of 3 M HCl (16 mL, 48 mmol) and the solution stirred for 1 h [*Caution: Hydrogen evolution*]. The reaction solution was then extracted with ether (3 × 20 mL) and the combined ether extracts were washed with 3 M NaOH (1 × 20 mL). The organic phase was washed with water (1 × 10 mL) and dried over anhydrous MgSO$_4$. The solvent was evaporated under reduced pressure (25 °C, 20 Torr) to yield crude *trans*-4-*tert*-butylcyclohexanol as a low-melting solid; 1.2 g, 95% isolated yield of pure product. ^{1}H-NMR ($CDCl_3$): δ 0.8 (s, 9H), 0.9−2.1 (m, 10H), 3.5 (m, 1H); ^{13}C-NMR ($CDCl_3$): δ 25.6, 27.7, 36.1, 47.2, 71.2.

General Procedure for α,β-Unsaturated Ketone and Aldehyde Reductions. The following procedure is representative. A 100-mL round-bottom flask equipped with a magnetic stirring bar and fitted with a rubber septum was cooled under nitrogen to 25 °C. The flask was charged with (*R*)-(−)-carvone (1.5 g, 1.55 mL, 10 mmol) and THF (anhydrous, 20 mL). A 1 M solution of LiPyrrBH$_3$ (10 mL, 10 mmol) was added to the flask slowly while stirring. The reaction was stirred at 25 °C for an addition 3 h. The reaction mixture was cooled to 0 °C and quenched by the slow addition of water (2 mL), followed by 3 M HCl (14 mL, 42 mmol) *[Caution: Hydrogen evolution!]*. The aqueous and organic fractions were separated and the aqueous fraction extracted with Et$_2$O (2 × 50 mL). The combined ethereal fractions were washed with water (3 × 10 mL) and dried over MgSO$_4$. The solvent was removed at 25 °C under reduced pressure (6 Torr). Distillation of the residue yielded (*1R,5R*)-(−)-*cis*-carveol (bp 44−46 °C, 0.1 Torr; 1.46 g, 96% isolated yield. $[\alpha]_D$: −35° (*c* 4.0, MeOH). ^{1}H-NMR ($CDCl_3$): δ 1.4−2.4 (m, 6H), 1.7 (s, 3H), 1.8 (s, 3H), 4.2 (br s, 1H), 4.7 (s, 2H), 5.5 (m, 1H); ^{13}C-NMR ($CDCl_3$): δ 19.1, 20.6, 31.1, 38.0, 40.5, 70.9, 109.1, 123.8, 136.3, 149.0.

Reduction of (*R*)-(+)-Pulegone to (*1R,3R*)-(−)-*cis*-pulegol. The representative procedure was followed using a 1 M THF solution of LiPyrrBH$_3$. Bp: 54−55 °C (0.1 Torr), 1.4 g, 89% isolated yield. $[\alpha]_D$: −69° (*c* 4.0, MeOH). ^{1}H NMR ($CDCl_3$): δ 0.8−2.4 (m, 8H), 1.1 (d, J = 7 Hz, 3H), 1.6 (s, 3H), 1.8 (s, 3H), 4.7 (t, J = 5 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 19.8, 20.5, 21.6, 22.3, 26.8, 32.0, 39.6, 68.3, 126.4, 132.7.

Reduction of 3-Nonen-2-one to 3-Nonen-2-ol. The representative procedure was followed using a 1 M THF solution of LiPyrrBH$_3$. Bp: 44−45 °C (0.2 Torr), 1.4 g, 96% isolated yield. ^{1}H-NMR ($CDCl_3$): δ 0.9 (t, J = 7 Hz, 3H), 1.1−1.5 (m, 9H), 1.7 (s, 1H), 2.0 (q, J = 6 Hz, 2H), 4.2 (qnt, J = 6 Hz, 1H), 5.4−5.7 (m, 2H). ^{13}C-NMR ($CDCl_3$); δ 14.0, 22.5, 23.4, 28.9, 31.4, 32.1, 69.0, 131.2, 134.1.

The Reduction of *trans*-Cinnamaldehyde to *trans*-Cinnamyl Alcohol. The representative procedure was followed using a 1 M THF solution of LiPyrrBH$_3$. Bp: 53−55 °C (0.1 Torr), 1.2 g, 91% isolated yield; ^{1}H-NMR ($CDCl_3$): δ 2.6 (t, J = 5 Hz, 1H), 4.3 (t, J = 5 Hz, 2H), 6.3−6.5 (dt, J = 6 Hz, 16 Hz, 1H), 6.6 (d, J = 16 Hz, 1H), 7.4 (m, 5H). ^{13}C-NMR ($CDCl_3$): δ 63.6, 126.5, 127.7, 128.6, 131.0, 136.8.

The Reduction of 4-Phenyl-3-buten-2-one to 4-Phenyl-3-buten-2-ol. The representative procedure was followed using a 1 M THF solution of LiPyrrBH$_3$. Bp: 53−55 °C (0.1 Torr), 1.4 g, 95% isolated yield; ^{1}H-NMR ($CDCl_3$): δ 1.4 (d, J = 6 Hz, 3H), 2.1 (br s, 1H), 4.5 (qnt, J = 5 Hz, 1H), 6.3 (dd, J = 6 Hz, 16 Hz, 1H), 6.6 (d, J = 16 Hz, 1H), 7.3 (m, 5H). ^{13}C-NMR ($CDCl_3$): δ 23.5, 68.9, 126.5, 127.7, 128.6, 129.4, 133.7, 136.8.

General Procedure for Tertiary Amide Reductions. Reduction of 1-Pyrrolidinooctanamide to 1-Octylpyrrolidine. The following procedure is representative for all *in situ* reductions. A 50-mL serum vial equipped with a magnetic stirring bar was cooled under nitrogen and sealed with a rubber septum. The vial was charged with a 1 M solution of Li(*i*-Pr)$_2$NBH$_3$ (12 mL, 12 mmol) followed by the dropwise addition, with stirring, of neat 1-pyrrolidinooctanamide (2.0 g, 10 mmol). The reaction mixture was stirred for an additional 2 h at 25 °C. The reaction was cooled to 0 °C and quenched by the *slow* addition of 3 M HCl (17 mL, 51 mmol) *[Caution: Hydrogen evolution!]*. The aqueous fraction was separated, layered with Et$_2$O (~40 mL), and cooled to 0 °C, and NaOH (s) was added until the reaction mixture was strongly basic to litmus. The ethereal fraction was separated, the aqueous fraction was extracted with Et$_2$O (4 × 15 mL), and the ethereal fractions were combined and dried over MgSO$_4$. The solvent was removed *in vacuo* at 25 °C to yield analytically pure 1-octylpyrrolidine (bp: 44−45 °C, 0.3 Torr; 1.7 g, 95% isolated yield). ^{1}H-NMR ($CDCl_3$): δ 0.8 (t, J = 7 Hz, 3H), 1.2 (br m, 10H), 1.4 (br m, 2H), 1.7 (qnt, J = 4 Hz, 4H), 2.3 (m, 2H), 2.4 (m, 4H). ^{13}C-NMR ($CDCl_3$): δ 14.0, 22.6, 23.3, 27.7, 29.1, 29.2, 29.6, 31.8, 54.2, 56.7.

Reduction of 1-Pyrrolidinooctanamide to 1-Octanol. The representative procedure was followed using a 1 M THF solution of LiPyrrBH$_3$. Bp: 93−95 °C, 10 Torr; 1.0 g, 77% isolated yield; ^{1}H-NMR ($CDCl_3$): δ 0.8 (m, 3H), 1.2 (br m, 10H), 1.5 (m, 2H), 2.7 (s, 1H), 3.5 (t, J = 7 Hz, 2H). ^{13}C-NMR ($CDCl_3$): δ 14.0, 22.6, 25.8, 29.3, 29.4, 31.8, 32.7, 62.7.

Reduction of *N,N*-Diethyl-*m*-toluamide to 3-Methylbenzyl Alcohol. The representative procedure was followed using a 1 M THF solution of LiPyrrBH$_3$. Bp: 52−54 °C, 0.2 Torr; 1.2 g, 95% isolated yield. ^{1}H-NMR ($CDCl_3$): δ 2.4 (s,

3H), 2.9 (br s, 1H), 4.6 (s, 2H), 7.1–7.3 (m, 4H). ^{13}C-NMR ($CDCl_3$): δ 21.4, 65.1, 124.1, 127.8, 128.3, 128.5, 138.2, 141.0.

Reduction of *N,N*-Diethyl-*m*-toluamide to 3-Methyl-*N,N*-diethylbenzylamine. The representative procedure was followed using a 1 M THF solution of Li(*i*-Pr)$_2$NBH$_3$. Bp: 136–138 °C, 100 Torr; 1.8 g, 99% isolated yield. ^{1}H-NMR ($CDCl_3$): δ 1.1 (t, J = 7 Hz, 6H), 2.4 (s, 3H), 2.6 (q, J = 7 Hz, 4H), 3.6 (s, 2H), 7.1–7.2 (m, 4H). ^{13}C-NMR ($CDCl_3$): δ 11.8, 21.5, 46.8, 57.6, 126.1, 127.5, 128.1, 129.7, 137.7, 140.0.

General Procedure for Ester Reductions. Use of Solid LiABH$_3$'s. The following procedure for the reduction of ethyl benzoate with solid lithium pyrrolidinoborohydride (LiPyrrBH$_3$) is representative for reductions using solid LiABH$_3$'s (Reduction of these representative esters using a 1 M THF solution of LiABH$_3$ gave identical results). A 100-mL round-bottom flask equipped with a magnetic stirring bar was cooled under nitrogen and sealed with a rubber septum. The flask was charged with ethyl benzoate (1.5 g, 1.4 mL, 10 mmol) and THF (anhydrous, 20 mL). The flask was then cooled to 0 °C. The flask was then opened to the air and solid LiPyrrBH$_3$ (1.4 g, 12 mmol) was added with stirring over a 2–3 min period to the reaction mixture. The reaction was maintained at 0 °C and stirred for an additional 1 h. The reaction mixture was kept at 0 °C and quenched by the slow addition of 3 M HCl (17 mL, 51 mmol) *[Caution: Hydrogen evolution!]*. The aqueous and organic fractions were separated and the aqueous fraction extracted with Et$_2$O (2 × 50 mL). The combined ethereal fractions were washed with water (3 × 10 mL) and dried over MgSO$_4$. The solvent was removed at 25 °C under reduced pressure (6 Torr). The residue was distilled to yield benzyl alcohol (bp: 47–48 °C, 2 Torr, 1.0 g, 95% isolated yield). ^{1}H-NMR ($CDCl_3$): δ 3.2 (br s, 1H), 4.6 (s, 2H), 7.3 (s, 5H). ^{13}C-NMR ($CDCl_3$): δ 65.0, 127.1, 127.6, 128.6, 140.9.

Reduction of Ethyl Decanoate to Decanol. The representative procedure was followed using solid LiPyrrBH$_3$. Bp: 80–82 °C (5 Torr); 1.4 g, 90% isolated yield. ^{1}H-NMR ($CDCl_3$): δ 0.9 (t, J = 7 Hz, 3H), 1.3 (br s, 14H), 1.5 (m, 2H), 1.8 (br s, 1H), 3.6 (t, J = 7 Hz, 2H). ^{13}C-NMR ($CDCl_3$): δ 14.1, 22.7, 25.8, 29.3, 29.5, 29.6, 29.7, 31.9, 32.8, 63.0.

Reduction of Phthalide to 1,2-Benzenedimethanol. The representative procedure was followed using solid LiPyrrBH$_3$. Mp: 61–62 °C; 1.4 g, 95% isolated yield. ^{1}H-NMR ($CDCl_3$): δ 3.9 (br s, 1H), 4.6 (s, 4H), 7.3 (s, 1H). ^{13}C-NMR ($CDCl_3$): δ 64.0, 128.6, 129.7, 139.4.

Reduction of Ethyl Cinnamate to Cinnamyl Alcohol. The representative procedure was followed using solid LiPyrrBH$_3$. Bp: 53–55 °C (0.1 Torr), 1.3 g, 95% isolated yield; ^{1}H-NMR ($CDCl_3$): δ 2.2 (br s, 1H), 4.3 (d, J = 7 Hz, 2H), 6.4 (dt, J = 6 Hz, 16 Hz, 1H), 6.6 (d, J = 16 Hz, 1H), 7.4 (m, 5H); ^{13}C-NMR ($CDCl_3$): δ 63.6, 126.5, 127.7, 128.6, 131.0, 136.8.

General Procedure for Azide Reductions. The following procedure for the reduction of benzyl azide is representative. A 100-mL serum vial equipped with a magnetic stirring bar was cooled under nitrogen and sealed with a rubber septum. The vial was charged with a 1 M THF solution of LiMe$_2$NBH$_3$ (15 mL, 15 mmol) followed by the dropwise addition with stirring of benzyl azide (1.6 g, 10 mmol). The reaction mixture was stirred for 2 h at 25 °C. The reaction was cooled to 0 °C and quenched by the sequential *slow* addition of methanol (40 mmol) and 3 M HCl (20 mL, 60 mmol) *[Caution: Hydrogen evolution!]*. The reaction mixture was then stirred at 25 °C for 2 h, and the solvents were evaporated under reduced pressure (20 Torr). The aqueous residue was cooled to 0 °C and layered with Et$_2$O (~40 mL), and NaOH (s) was added until the reaction mixture was strongly basic to litmus. The ethereal layer was separated, the aqueous layer was extracted with Et$_2$O (4 × 15 mL), and the ethereal fractions were combined and dried over MgSO$_4$. The solvent was removed under reduced pressure (6 Torr) at 25 °C to yield benzylamine (0.9 g, 85% yield; crude product was not purified). ^{1}H-NMR ($CDCl_3$): δ 1.8 (br s, 2H), 3.8 (br s, 2H), 7.2 (br s, 5H). ^{13}C-NMR ($CDCl_3$): δ 46.4, 126.8, 127.1, 128.5, 144.0.

Reduction of 1-Octyl Azide. The representative procedure was followed using a 1 M THF solution of LiMe$_2$NBH$_3$. The solvent was removed under reduced pressure (6 Torr) at 25 °C to afford 1-octylamine (1.25 g, 95% yield), Bp 83–85 °C, 20 Torr. ^{1}H-NMR ($CDCl_3$): δ 0.8 (t, J = 7 Hz, 3H), 1.2 (s, 2H), 1.3 (br s, 10H), 1.4 (m, 2H), 2.6 (t, J = 7 Hz, 2H). ^{13}C-NMR ($CDCl_3$): δ 14.1, 22.7, 26.9, 29.3, 29.5, 31.8, 33.9, 42.3.

Acknowledgment. The authors would like to thank the Dow Chemical Co. for the grant of funds that made this research possible. We would also like to thank the Callery Chemical Co. for supplying us with the borane–dimethyl sulfide and *N,N*-dimethylamine–borane used in this research.

Supplementary Material Available: ^{1}H- and ^{13}C-NMR spectra of all the reduction products, and representative procedures for the reductions of ketones and aldehydes, epoxides, and halides; experimental data for those reduction products listed in Tables 1–5 but not included in the Experimental Section; ^{11}B-NMR and FT-IR spectra of all of the lithium aminoborohydrides synthesized; representative procedures and experimental data for the synthesis of all LiABH$_3$'s listed in Figure 1 but not included in the Experimental Section (109 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.