a perspective drawing of **10b** (Figure 1), and the plant growth response of **10b** and **11b** (Figure 2) (9 pages). Ordering information is given on any current masthead page.

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Rapid Reaction of Trialkylboranes with Lithium Aluminum Hydride in the Presence of Triethylenediamine. Facile and Quantitative Synthesis of Lithium Trialkylborohydrides Including Derivatives with Exceptionally Large Steric Requirements

Summary: Addition of 1 mol equiv of lithium aluminum hydride to a diethyl ether (EE) solution of trialkylborane, in the presence of 1 mol equiv of triethylenediamine (TED) at 0 °C, results in a facile and rapid transfer of hydride to form the corresponding lithium trialkylborohydride in quantitative yield, with concurrent precipitation of aluminum hydride–triethylenediamine. The reaction is general, applicable even to the synthesis of lithium trialkylborohydrides with exceptionally large steric requirements.

Sir: Investigations in our laboratory and elsewhere have established the importance of hindered and highly hindered trialkylborohydrides for the stereoselective reduction of ketones.[1,2] The trialkylborohydrides also react with carbon monoxide to give a highly reactive intermediate which can be converted into a variety of valuable compounds.[3,4] Another application of trialkylborohydrides is their addition to styrene and its derivatives,[5] providing a convenient synthesis of Markownikoff organoboranes. The most direct way to form such borohydrides is by the direct reaction of trialkylboranes and alkali metal hydrides. Such reactions have been carried out with lithium,[6] sodium,[6] and potassium[7] hydrides. However, all of the three alkali metal hydrides fail to react satisfactorily with highly hindered trialkylboranes, such as trisiamylborane (eq 1). Yet these are reagents of exceptional promise.

$$\mathrm{MH} + \mathrm{Sia_3B} \xrightarrow[24\ \mathrm{h}]{\mathrm{THF,\ 25\ °C}} \underset{0\text{–}10\%}{\mathrm{MSia_3BH}} \qquad (1)$$
$$\mathrm{M = Li, Na, K}$$

The lithium hydride route provides a convenient entry only to the relatively unhindered lithium trialkylborohydrides. A general synthesis of lithium trialkylborohydrides has been developed using lithium trimethoxyaluminohydride (LTMA)[8] (eq 2). However, this suffers from the difficulty of separating the product from the aluminum methoxide formed concurrently.

$$\mathrm{R_3B} + \mathrm{LiAl(OCH_3)_3H} \xrightarrow[15\ \mathrm{min}]{\mathrm{THF,\ 25\ °C}} \underset{100\%}{\mathrm{LiR_3BH}} + \mathrm{Al(OCH_3)_3} \qquad (2)$$

An alternative synthesis which avoids this difficulty is the reaction of *tert*-butyllithium with trialkylboranes at low temperature[2c,9] (eq 3). However, this suffers from the cost of *tert*-butyllithium for the preparation of the reagent in quantity.

$$\mathrm{R_3B} + \mathrm{(CH_3)_3CLi} \xrightarrow{\mathrm{THF,\ -78\ °C}} \mathrm{LiR_3BH} + \mathrm{(CH_3)_2C{=}CH_2} \qquad (3)$$

More recently, lithium aluminum hydride was evaluated for its applicability in the hydride-induced carbonylation of organoboranes.[10] The subsequent discovery that other complex hydrides used in this reaction transfer alkali metal hydride to the trialkylborane[8,11,12] generated interest in a systematic investigation of the reaction of lithium aluminum hydride with representative trialkylboranes[13] as a potential route to the lithium trialkylborohydrides.

Addition of a THF solution of lithium aluminum hydride to triethylborane resulted in a rapid, moderately exothermic reaction. Examination of the clear, colorless solution by ^{11}B NMR unexpectedly revealed a triplet (δ −16.7, J = 67 Hz), instead of the anticipated doublet. Other trialkylboranes with primary alkyl groups gave similar results. Evidently, the reaction proceeds as shown in eq 4. Reaction 4 was carried out at −78 °C and the solution examined as rapidly as possible by ^{11}B NMR. The results established that the reaction proceeds with the initial formation of the desired trialkylborohydride (eq 5 and 6).

$$\mathrm{LiAlH_4} + \mathrm{R_3B} \xrightarrow[15\ \mathrm{min}]{\mathrm{THF,\ 25\ °C}} \mathrm{LiR_2BH_2} + \mathrm{RAlH_2} \qquad (4)$$
$$\mathrm{R} = \mathrm{Et}, n\text{-}\mathrm{Bu}, i\text{-}\mathrm{Bu}$$

$$\mathrm{LiAlH_4} + \mathrm{R_3B} \xrightarrow{\mathrm{THF,\ -78\ °C}} \mathrm{LiR_3BH} + \mathrm{AlH_3} \qquad (5)$$

$$\mathrm{LiR_3BH} + \mathrm{AlH_3} \xrightarrow[\mathrm{fast}]{\mathrm{THF,\ 25\ °C}} \mathrm{LiR_2BH_2} + \mathrm{RAlH_2} \qquad (6)$$

This study indicated that a new synthesis of lithium trialkylborohydride might be achieved if the aluminum hydride could be trapped as soon as formed so as to avoid the fast subsequent reaction. We had recently observed that triethylenediamine (TED) rapidly and quantitatively precipitates aluminum hydride as TED·AlH$_3$ from both diethyl ether (EE) and THF.[14] Accordingly, the lithium aluminum hydride solution (EE) was added to an EE solution of the trialkylborane containing 1.0 equiv of TED at 0 °C. A voluminous white precipitate of TED·AlH$_3$

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Table I. Infrared and ^{11}B NMR Spectra of the Products from Reactions of Lithium Aluminum Hydride with Representative Trialkylboranes in the Presence of Triethylenediamine

trialkylborane	ν_{B-H}, cm^{-1}	δ^a (multiplicity)	J_{B-H}, Hz
triethylborane	2010	−13.4 (d)	61
tri-*n*-butylborane	2010	−15.4 (d)	60
triisobutylborane	1990	−18.2 (d)	61
tri-*sec*-butylborane	2000	−6.3 (d)	58
tricyclopentylborane	2050	−9.3 (d)	65
tricyclohexylborane	2020	−5.9 (d)	59
tri-*exo*-2-norbornylborane	2030	−7.9 (d)	68
perhydro-9b-boraphenalene[b]	2025	−10.2 (d)	59
		−11.1 (d)	59
tris(*trans*-2-methylcyclopentyl)borane[c]	2100	−12.4 (d)	75
		−14.3 (d)	75
trisiamylborane[d]	2060	−12.6 (d)	77
		−13.9 (d)	78

[a] All chemical shifts relative to $Et_2O \cdot BF_3$ with those upfield assigned as negative. [b] Probably isomeric pair of borohydrides; (area δ −10.2)/(area δ −11.1) ~ 1/1. [c] Diastereomeric pair of borohydrides; (area δ −12.4)/(area δ −14.3) ~ 3/1. [d] Diastereomeric pair of borohydrides; (area δ −12.6)/(area δ −13.9) ~ 3/1.

formed rapidly. The supernatant liquid, examined by ^{11}B NMR and IR spectroscopy, revealed the quantitative formation of trialkylborohydride. Initially, the precipitate is present as a voluminous gel which is difficult to separate from the solution. However, on standing for approximately 12 h, it becomes a granular precipitate, easily centrifuged from the reaction mixture.[15] The resulting solution contains the product in pure form. The results are summarized in Table I.

The reaction was applied to a wide variety of trialkylboranes. Whereas the lithium trialkylborohydrides, synthesized by the lithium hydride route, exhibit only a singlet in the ^{11}B NMR spectrum,[6] the lithium trialkylborohydrides prepared by the present method exhibit sharp doublets, similar to those realized for the lithium trialkylborohydrides prepared from trialkylboranes and *tert*-butyllithium.[2c] This is evidence for the completeness of the reaction.[3]

The usefulness of this procedure as a method for formation of lithium trialkylborohydrides of high stereoselectivity depends upon whether the solution can be used directly for such stereoselective reductions. Therefore, the reduction of 4-*tert*-butylcyclohexanone was carried out as a test case using lithium trisiamylborohydride prepared by this procedure. The result was a 99:1 ratio of the *cis*- and *trans*-4-*tert*-butylcyclohexanols, essentially identical with the ratio realized with lithium trisiamylborohydride prepared by the earlier procedures (eq 2 and 3).[8,2b]

The following procedure is representative. All operations were carried out under nitrogen[16] in ethyl ether solution. An oven-dried, 50-mL centrifuge tube was charged with 10 mL of a 1.0 M solution of trisiamylborane and 10 mL of a 1.0 M solution of triethylenediamine. The clear solution was then cooled to 0 °C and 10 mL of a 1.0 M solution of $LiAlH_4$ was added slowly with vigorous stirring. A voluminous precipitate of $TED \cdot AlH_3$ separated out. The reaction mixture was stirred as efficiently as possible, using an ovoid Teflon-coated magnetic stirring bar. The reaction mixture was then set aside for 12 h at 25 °C and centrifuged to remove the granulated $TED \cdot AlH_3$. A 1.0-mL aliquot of the clear solution gave on hydrolysis 0.33 mmol (100%) of hydrogen. The supernatant liquid, 27 mL (90%), was withdrawn for further examination. The precipitate was washed with cold EE, and >95% of the lithium trisiamylborohydride was recovered: ^{11}B NMR δ −12.6 (d, J = 77 Hz), −13.9 (d, J = 78 Hz); IR 2060 cm^{-1}. 4-*tert*-Butylcyclohexanone (4.2 mmol) was reduced at −78 °C with 15.0 mL of the above solution, following the literature procedure.[2b] After the usual workup, GLC analysis indicated the presence of *cis*-4-*tert*-butylcyclohexanol, ≥99% isomerically pure.[2b,8] The volatile solvent and the siamyl alcohol were removed under reduced pressure to give 0.6 g, a yield of 90%, of pure *cis*-4-*tert*-butylcyclohexanol, mp 80–81 °C [lit.[17] mp 82 °C].

The procedure has been carried out by using both trisiamylborane from Aldrich borane and trisiamylborane prepared in situ from 2-methyl-2-butene and borane–methyl sulfide (BMS) in the usual manner.

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Registry No. 4-*tert*-Butylcyclohexanone, 98-53-3; *cis*-4-*tert*-butylcyclohexanol, 937-05-3; lithium aluminum hydride, 16853-85-3; triethylborane, 97-94-9; tributylborane, 122-56-5; triisobutylborane, 1116-39-8; tri-*sec*-butylborane, 1113-78-6; tricyclopentylborane, 23985-40-2; tricyclohexylborane, 1088-01-3; tri-*exo*-2-norbornylborane, 22801-27-0; perhydro-9*b*-bornaphenalene, 16664-33-8; tris(*trans*-2-methylcyclopentyl)borane, 40911-83-9; trisiamylborane, 32327-52-9; lithium triethylborohydride, 22560-16-3; lithium tributylborohydride, 67335-72-2; lithium triisobutylborohydride, 63717-73-7; lithium tri-*sec*-butylborohydride, 38721-52-7; lithium tricyclopentylborohydride, 61721-97-9; lithium tricyclohexylborohydride, 69786-43-2; lithium tri-*exo*-2-norbornylborohydride, 72150-24-4; lithium perhydro-9*b*-boraphenalenehydride, isomer 1; lithium perhydro-9*b*-boraphenalenehydride, isomer 2, 67392-85-2; lithium tris(*trans*-2-methylcyclopentyl)bornohydride, 60284-40-4; lithium trisiamyl bornohydride, 60217-34-7.

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