ADDITION COMPOUNDS OF ALKALI METAL HYDRIDES

XVIII *. REACTION OF TRIALKYLBORANES WITH t-BUTYLLITHIUM. A GENERAL, CONVENIENT METHOD FOR THE PREPARATION OF LITHIUM TRIALKYLBOROHYDRIDES

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Summary

The reaction of t-butyllithium with representative trialkylboranes possessing widely differing steric requirements was examined. This reaction occurs rapidly in ether solvents, even at —78°C, with formation of the corresponding lithium trialkylborohydride in quantitative yield. This synthesis is highly general, accomodating even strongly hindered trialkylboranes such as tris(*trans*-2-methylcyclopentyl)borane and trisiamylborane. The only by-product is isobutylene, which is generally innocuous and easily removed. The lithium trialkylborohydrides were characterized by hydride analyses, infrared spectra, and ^{11}B NMR spectra. The formation of the trialkylborohydrides appears to be due to kinetic, rather than thermodynamic, factors. This reaction provides a highly general, facile, and quantitative route to the lithium trialkylborohydrides.

Introduction

The utility of alkali metal trialkylborohydrides as chemo-, regio-, and stereo-selective reducing agents [1], in new carbon—carbon bond forming reactions [2], for syntheses of transition metal carbonyl complexes [3], and in other valuable transformations [4] has aroused much interest in methods for their preparation. In recent years several important routes to these powerful, yet selective, reducing agents have been developed [5].

Lithium trialkylborohydrides have been prepared by direct reaction of trialkylboranes with lithium hydride [5a] (eqn. 1).

$$R_3B + LiH \xrightarrow[0.25-6\ h]{THF,\ 65°C} LiR_3BH \qquad (1)$$
$$(>95\%)$$

This synthesis is limited to the preparation of relatively unhindered lithium trialkylborohydrides. Hindered (s-Bu$_3$B) and highly hindered (Sia$_3$B) * trialkylboranes are essentially inert toward lithium hydride.

A general synthesis of lithium trialkylborohydrides is provided by the reaction of even highly hindered trialkylboranes with lithium trimethoxyaluminohydride [5c] (eqn. 2).

$$R_3B + Li(MeO)_3AlH \xrightarrow[30\ min]{THF,\ 25°C} LiR_3BH + Al(MeO)_3 \qquad (2)$$
$$(>95\%)$$
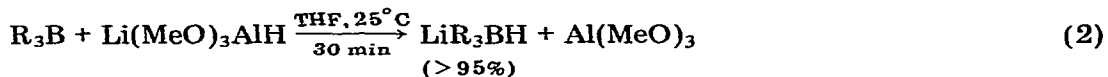
Unfortunately, the aluminum methoxide by-product complicates the workup and isolation of the pure reagent.

Corey and coworkers have reported that the reaction of thexyllimonylborane with lithium hydride fails to give a trialkylborohydride. However, treatment of the same organoborane with t-butyllithium at −40°C gives the desired lithium thexyllimonylborohydride [6] (eqn. 3).
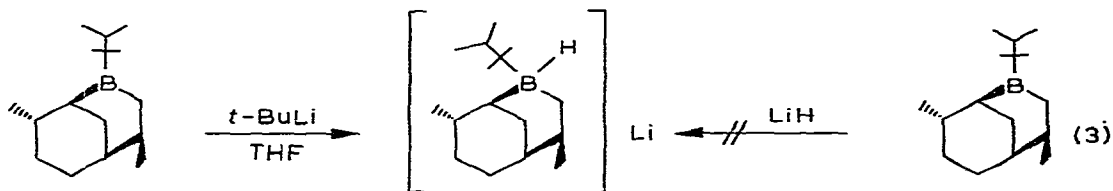
This reagent was used in the selective reduction of prostaglandin intermediates, but few experimental details concerning its preparation were presented. Other trialkylborohydrides were prepared and used in a similar manner; again, little experimental information was provided [7].

It is apparent that the reaction of trialkylboranes with t-butyllithium is potentially an extremely important method for the preparation of lithium trialkylborohydrides. In view of our interest in these reagents, we undertook a systematic study of this reaction to determine its scope and limitations.

Results and discussion

Representative trialkylboranes of varying steric requirements, unhindered, hindered, and highly hindered, were selected for this study. The trialkylborohydrides resulting from the reaction with t-butyllithium were characterized by hydride analyses, infrared spectra and ^{11}B NMR spectra. The by-product of the reaction was identified. The influence of solvent and temperature on the course of the reaction was examined. It was shown that the products are a consequence of kinetic rather than thermodynamic control. A number of lithium

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* Sia$_3$B = trisiamylborane.

trialkylborohydrides were synthesized on preparative scale (10—500 mmol) to demonstrate the utility of the reaction.

General procedure for the reaction of representative trialkylborane with t-butyllithium and characterization of the hydride product

A 0.5 M solution of trialkylborane in THF was introduced into a reaction flask fitted with a reflux condenser and a magnetic stirring bar. The flask was immersed in a dry ice-acetone bath at —78°C. A slight excess (~5%) of t-butyl-lithium in pentane was added dropwise with vigorous stirring. This produced a visibly exothermic reaction. With certain trialkylboranes, the addition of the t-butyllithium produced an intense yellow to yellow-orange colored solution. With other organoboranes, as the t-butyllithium was added dropwise, only a transient yellow color was observed. Organoboranes bearing unsaturated or aromatic groups usually gave more orange color. The reaction mixture was allowed to warm to room temperature, and the yellow color usually disappeared. The resulting solution was examined by ^{11}B NMR. The results are summarized in Table 1. In all but two cases, the spectra showed a clean, quantita-

TABLE 1

^{11}B NMR SPECTRA OF THE PRODUCTS FROM REACTION OF t-BUTYLLITHIUM WITH REPRESENTATION TRIALKYLBORANES

Trialkylborane	δ(ppm) [a]	Multiplicity	$J_{(B—H)}$(Hz) [b]
Triethylborane	—12.1	d	61
Tri-n-butylborane	—14.4	d	75
Tri-i-butylborane	—17.3	d	80
Tri-s-butylborane	—6.7	d	71
Tricyclopentylborane	—9.3	d	62
Tricyclohexylborane	—5.7	d	57
Tri-*exo*-2-norbornylborane	—8.0	d	67
Perhydro-9b-boraphenalene [c]	—10.2	d	58
	—11.1	d	58
Tris(*trans*-2-methylcyclopentyl)borane [d]	—12.6	d	75
	—14.2	d	75
Trisiamylborane [e]	—12.5	d	78
	—13.9	d	79
Thexyllimonylborane [f]	—11.0	d	75
	—11.6	d	75
Triphenylborane	—8.4	d	78
Trimesitylborane [g]	—	—	—
B-Methyl-9-BBN	—16.0	d	60
B-Cyclopentyl-9-BBN	—9.2	d	75
B-Isopinocampheyl-9-BBN	—6.5	d	78
B-Thexyl-9-BBN	—11.6	d	75
B-Allyl-9-BBN [h]	—13.2	d	70
	—16.7	s	—
B-Crotyl	—13.2	d	68
B-Phenyl-9-BBN	—13.9	d	55
B-*p*-Tolyl-9-BBN	—14.5	d	53

[a] Relative to $BF_3 \cdot OEt_2$, downfield resonances positive. [b] Minimal value (see text). [c] Probably isomeric pair of borohydrides; area of δ —10.2 to area of δ —11.1 is approximately 1 : 1. [d] Diastereometic pair of borohydrides; area of δ —12.6 to area of δ —14.2 is approximately 3 : 1. [e] Diastereomeric pair of boro-hydrides; area of δ —12.5 to area of δ —13.9 is approximately 3 : 1. [f] Probably isomeric pair of boro-hydrides; area of δ —11.0 to area of δ —11.6 is approximately 1 : 1. [g] No [11]B resonance observed, how-ever, strong EPR signal seen. [h] See text.

TABLE 2

INFRARED SPECTRA OF THE PRODUCTS FROM REACTION OF t-BUTYLLITHIUM WITH REPRESENTATIVE TRIALKYLBORANES

| Trialkylborane	$\nu(B-H)$ cm^{-1} [a]
Triethylborane	2050
Tri-n-butylborane	2040
Tri-i-butylborane	2050
Tri-s-butylborane	2030
Tricyclopentylborane	2050
Tricyclohexylborane	2020
Tri-exo-2-norbornylborane	2030
Perhydro-9b-boraphenalene	2030
Tris(trans-2-methylcyclopentyl)borane	2060
Trisiamylborane	2150

[a] All spectra of THF solutions at 25°C.

tive formation of the lithium trialkylborohydride. Where comparisons were possible, the spectra were virtually identical to those obtained when the trialkylborohydrides were prepared by other methods [5a,c]. Unlike the spectra of the lithium trialkylborohydrides synthesized by the lithium hydride route, the spectra of the products formed via t-butyllithium were always well-resolved doublets, an indication of complete reaction with no trace of trialkylborane remaining to undergo hydride exchange with the borohydride. Such exchange has been shown to cause coalescence of the doublet [8,11].

The infrared spectra of a number of the products, summarized in Table 2, exhibit the characteristic B—H absorption near 2000 cm^{-1}. Comparison of these spectra with those of the lithium trialkylborohydrides prepared by other routes showed complete agreement.

Overall yields from each reaction were determined by hydrolysis of measured aliquots in a 1 : 1 : 1 solution of THF : glycerin : water and measurement of the hydrogen evolved. Except in two cases, quantitative yields of the lithium trialkylborohydrides were observed.

Trimesitylborane failed to form a lithium trialkylborohydride on treatment with t-butyllithium, giving instead a deep purple solution. Examination of this reaction mixture by ^{11}B NMR failed to show any detectable boron resonances! However, an EPR spectrum of the solution showed a very strong signal. Apparently, the well known trimesitylborane radical anion is produced [9] (eqn. 4).
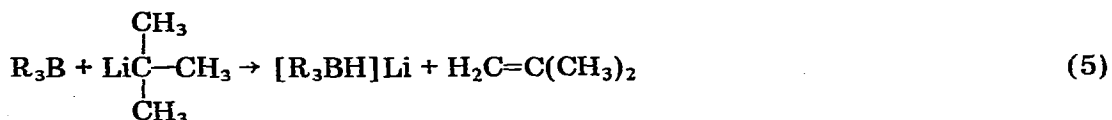

(4)
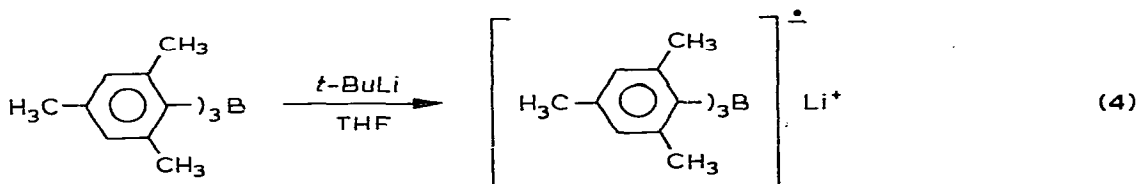
Treatment of triphenylborane with t-butyllithium produced a faint purple solution. Accordingly, it is probable that a small amount of its corresponding radical anion was formed. However, ^{11}B NMR spectra showed a sizable amount of the expected lithium triphenylborohydride to be present.

B-Allyl-9-BBN * failed to undergo quantitative conversion to the corresponding trialkylborohydride on treatment with t-butyllithium. When this organoborane was treated with t-butyllithium at −20°C, the resulting ^{11}B NMR spectrum consisted of a relatively sharp singlet at δ −16.0 ppm. Addition of even a large excess of t-butyllithium did not alter the spectrum. When the reaction was repeated at −78°C, the ^{11}B NMR spectrum consisted of a doublet at δ −13.2 ppm (*J* 70 Hz) and a singlet at δ −16.7 ppm. The reason for this behavior was not pursued; however, all other *B*-allyl-9-BBN derivatives behaved normally when treated with t-butyllithium, giving the expected lithium trialkylborohydride.

Identification of the by-product resulting from the reaction of t-butyllithium with trialkylboranes

Tri-n-butylborane was treated with t-butyllithium on a 10-mmol scale, as previously described. The reaction mixture was warmed to 35°C, and the gas evolved was collected in a dry ice-acetone cooled trap. Examination of this gas by VPC and infrared showed the major constituent to be isobutylene. Thus, the overall reaction must be as shown in eqn. 5. There were minor amounts of iso-

$$R_3B + Li\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{-}CH_3 \rightarrow [R_3BH]Li + H_2C{=}C(CH_3)_2 \tag{5}$$

butane, ethylene, and 2-methylbutane. The former gases are probably formed by metallation-cleavage of the THF (eqn. 6), while the latter is a constituent in

$$\tag{6}$$
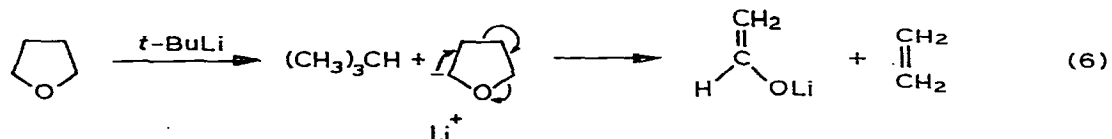
the pentane solvent of the t-butyllithium.

Effect of temperature

The reaction of triethylborane with t-butyllithium was examined in THF at various temperatures. The yield of lithium triethylborohydride was determined by quenching the reaction mixture with a known quantity of 2-methylcyclohexanone and analyzing the quantity of 2-methylcyclohexanol produced by VPC. When the addition of t-butyllithium was carried out at −78°C or −40°C, essentially quantitative yields of the trialkylborohydride were realized. However, increasing the temperature of the reaction sharply decreased the yield of the triethylborohydride (0°C = 90%, 25°C = 80%). Further, it was found that the ^{11}B NMR coupling constants of the lithium trialkylborohydrides formed at −78°C were consistently larger than those of hydrides formed at −25°C. This implies a slightly incomplete formation of the borohydride, some free tricoordinate boron species, and chemical exchange leading to partial coalescence of

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* 9-BBN = 9-borabicyclo[3.3.1]nonane.

the doublet. (Since even slight traces of tricoordinate boron species can lead to partial coalescence of the doublets in the ^{11}B NMR spectra, the values given for the coupling constants of the trialkylborohydrides in Table 1 should be taken only as lower limits of the true values.)
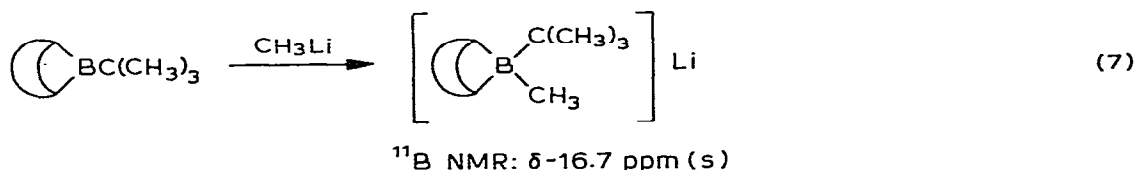
Apparently this decrease in yield is a result of a side reaction of the t-butyllithium with the THF. Below about −20°C, t-butyllithium does not appear to react with THF [10] except to form a bright yellow solution. Accordingly, it is necessary to maintain reaction temperatures below−20°C to preserve the quantitative formation of the trialkylborohydride. Since the hydride formation is an exothermic reaction, the t-butyllithium must be added dropwise with vigorous stirring to avoid local overheating which could decrease the yields.
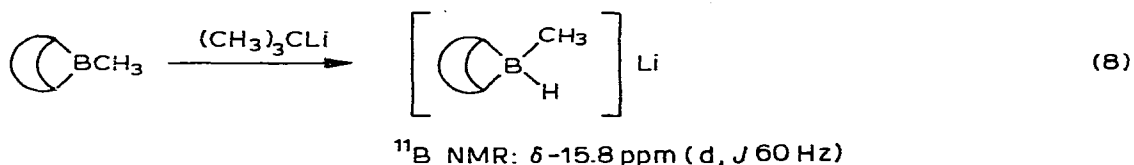
Effect of solvent

In general, the reaction of t-butyllithium with trialkylboranes is carried out in THF since the organoboranes are usually prepared via the hydroboration reaction in this solvent. This hydride formation reaction also occurs normally in diethyl ether. However, when the preparation of the lithium borohydride from *B*-methyl-9-BBN was attempted in hydrocarbon solvent, no visible reaction occurred at −78°C. On warming to room temperature, a white precipitate formed. ^{11}B NMR showed no boron resonances in the supernatant liquid. When THF was added, the usual yellow color appeared, and the precipitate dissolved. ^{11}B NMR then showed a mixture of "ate" complexes including a borohydride (doublet δ −8.9 ppm, J 70 Hz). This problem was not further examined other than to note that ethers seem to be necessary for formation of the desired lithium trialkylborohydride.

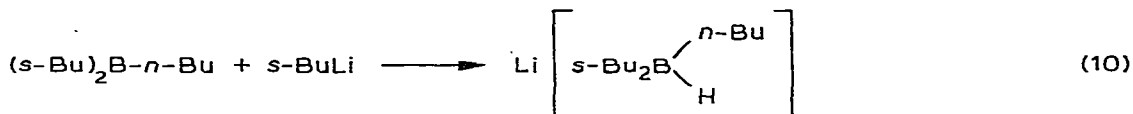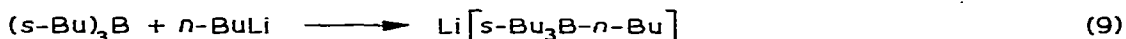*Kinetic versus thermodynamic control of the reaction*

It was of interest to understand whether the transfer of hydride from t-butyllithium to trialkylboranes was due to thermodynamic or kinetic phenomena. For this purpose, we examined two systems by ^{11}B NMR. Addition of methyllithium to *B*-t-butyl-9-BBN results in the formation of the corresponding "ate" complex (eqn. 7).

$$\text{(9-BBN)}BC(CH_3)_3 \xrightarrow{CH_3Li} \left[\text{(9-BBN)}B\begin{smallmatrix}C(CH_3)_3\\CH_3\end{smallmatrix} \right] Li \tag{7}$$

^{11}B NMR: δ −16.7 ppm (s)

No trialkylborohydride is observed. However, attempts to synthesize the same compound via treatment of *B*-methyl-9-BBN with t-butyllithium produced exclusively the corresponding *B*-methylborohydride (eqn. 8).

$$\text{(9-BBN)}BCH_3 \xrightarrow{(CH_3)_3CLi} \left[\text{(9-BBN)}B\begin{smallmatrix}CH_3\\H\end{smallmatrix} \right] Li \tag{8}$$

^{11}B NMR: δ −15.8 ppm (d, J 60 Hz)

Consequently, the pathway of these reactions is not determined by the nature of the products formed (thermodynamic control), but by the properties of the reactants (kinetic control). Similar phenomena have been observed with lithium tri-s-butyl-n-butylborate [12] (eqns. 9, 10).

$$(s\text{-Bu})_3B + n\text{-BuLi} \longrightarrow Li[s\text{-Bu}_3B\text{-}n\text{-Bu}] \qquad (9)$$

$$(s\text{-Bu})_2B\text{-}n\text{-Bu} + s\text{-BuLi} \longrightarrow Li\left[s\text{-Bu}_2B \left\langle \begin{array}{l} n\text{-Bu} \\ H \end{array} \right. \right] \qquad (10)$$

Conclusion

The reaction of t-butyllithium with trialkylboranes provides a general procedure for the synthesis of lithium trialkylborohydrides. Even highly hindered trialkylboranes, such as trisiamylborane, react rapidly under very mild conditions, giving quantitative yields of the desired trialkylborohydride. The only by-product, isobutylene, can be removed easily. Lithium trialkylborohydrides, such as those preparable by this method, have been used for selective [1b] and asymmetric [1c] reductions of organic functional groups. Accordingly, the present reaction appears to be the method of choice for preparing these versatile reagents in the laboratory and should find wide applicability in syntheses.

Experimental

General comments

The techniques described in Chapter 9 of ref. 13 were used extensively. All glassware was dried at 140°C for at least 4 h, assembled hot, and cooled under a stream of prepurified nitrogen. The reaction flasks were fitted with sidearms capped with rubber septa. All reactions were carried out under a static pressure of nitrogen and were stirred magnetically using oven-dried, Teflon-coated stirring bars. All transfers of liquids and solutions of organometallics were done with oven-dried, nitrogen-purged hypodermic syringes fitted with stainless steel needles or with double-ended needles [14].

Materials

THF and diethyl ether were distilled under nitrogen from lithium aluminum hydride and then stored under nitrogen in large ampoules fitted with Teflon stopcocks. The organoboranes used in this study were prepared by methods described previously [5,13,15] except the following, which were commercial materials: triethylborane, tri-n-butylborane, tri-i-butylborane (all from Callery Chemical Corp.), triphenylborane (Ventron-Alfa), and trimesitylborane (Willow Brook Labs.). The commercial materials were used as received, except tri-n-butylborane, which was distilled prior to use. The t-butyllithium in pentane (Foote Mineral Co., Ventron-Alfa, or Aldrich) was used as received after careful standardization [13,16].

Analyses

Infrared spectra were recorded on Perkin-Elmer IR-137 or 700 spectrometers. Liquid samples were contained in sealed cells using the two-syringe technique [13], while gas samples were contained in a 10 cm cell under reduced pressure [11]. VPC analyses were carried out on either Hewlett-Packard 5752B or Varian 1200 chromatographs fitted with strip chart recorders and Disc mechanical integrators. The internal standard technique was used for quantitative analyses. ^{11}B NMR spectra were recorded on either a Varian XL-100-15 spectrometer (32.1 MHz) fitted with a Nicolet 1080 data system (CW signal-averaged or FT modes) or a Varian FT 80-A spectrometer (25.517 MHz) (FT mode only). In either case, the samples were contained in 5 mm sample tubes mounted coaxially in larger tubes containing a perdeuteroacetone lock sample. All chemical shifts are relative to boron trifluoride etherate (δ 0 ppm) with downfield resonances defined as positive.

General procedure for the reaction of trialkylboranes with t-butyllithium

The following procedures demonstrate the applicability of these reactions for the syntheses of lithium trialkylborohydrides on typical laboratory scales. No difficulties were found in scaling up these methods to preparative (100 mmol to 1 mol) batches.

Preparation of lithium triethylborohydride

To a dry, nitrogen-flushed, 100 ml flask fitted with a magnetic stirring bar, septum inlet, and reflux condenser connected to a mercury bubbler, there was added 2.8 ml (20.0 mmol) of neat triethylborane and 13 ml of THF. The reaction flask was immersed in a dry ice-acetone bath, and, with stirring, the contents were allowed to thermally equilibrate. The stirring speed was increased, and 14 ml (20.0 mmol) of a 1.43 M solution of t-butyllithium in pentane was added dropwise. After the addition was complete, the reaction flask was removed from the cold bath, and the pale yellow reaction mixture was allowed to warm to room temperature. ^{11}B NMR, δ —12.2 ppm (d, J 61 Hz); IR 2050 cm^{-1} (B—H). Hydride analysis indicated a 100% yield of the borohydride.

In similar fashion, lithium tri-n-butyl-, tri-i-butyl-, and tri-s-butylborohydrides were prepared in essentially quantitative yields.

Preparation of lithium tricyclohexylborohydride

Tricyclohexylborane (20 mmol) was prepared in the usual manner [13] by the hydroboration of cyclohexene (65 mmol) with borane: THF (20 mmol). About 20 ml of THF was added, and the slurry was cooled in a dry ice-acetone bath. t-Butyllithium, 14 ml of a 1.43 M solution in pentane (20 mmol), was added dropwise with vigorous stirring. After the addition was complete, the reaction mixture was allowed to warm to room temperature. ^{11}B NMR δ —5.7 ppm (d, J 57 Hz); IR 2020 cm^{-1} (B—H). Hydride analysis indicated a quantitative formation of lithium tricyclohexylborohydride.

Preparation of lithinium B-isopinocampheyl-9-borobicyclo[3.3.1]nonylhydride

d-Pinene (10 mmol), 96% optical purity, was hydroborated with 9-BBN in THF (reflux, 12 h). The formation of the borohydride was carried out as described

above using 10 mmol of t-butyllithium in pentane. ^{11}B NMR δ —6.5 ppm (d, J 78 Hz).

Preparation of lithium trisiamylborohydride

The usual reaction flask containing 20 ml of a 0.5 M (10 mmol) solution of trisiamylborane in THF was cooled in a dry ice-acetone bath. t-Butyllithium, 5.8 ml of a 1.76 M solution in pentane (10.2 mmol), was added dropwise with vigorous stirring. The resulting yellow solution was allowed to warm to room temperature by which time the yellow color faded. ^{11}B NMR δ —12.5 (d, J 78 Hz, area = 3), δ —13.9 ppm (d, J 79 Hz, area = 1); IR 2150 cm^{-1} (B—H). Hydride analysis indicated a quantitative yield of lithium trisiamylborohydride.

Identification of the by-product formed in the reaction of t-butyllithium with trialkylboranes

To an oven-dried, nitrogen-flushed apparatus consisting of a 50 ml flask, fitted with a septum inlet and a magnetic stirring bar, topped with a water-cooled condenser leading through a dry ice-acetone cooled trap to a liquid nitrogen-cooled trap, there was added 1.822 g of tri-n-butylborane (10.0 mmol) and about 5 ml of THF. The flask was immersed in a dry ice-acetone bath where 7.46 ml of a 1.34 M solution of t-butyllithium in pentane (10.0 mmol) was added dropwise with vigorous stirring. After stirring for about 5 min, the reaction mixture was allowed to warm to room temperature. Some gas evolved, which passed through the first trap (—78°C) and was caught in the second trap (—196°C). VPC and infrared analyses showed this material to be a mixture of nitrogen and ethylene. The reaction mixture was warmed to 35°C with a water bath. A copious amount of gas evolved, which was retained in the first trap. After the gas evolution ceased, the first trap was connected to a fresh trap cooled in a dry ice-acetone bath. By warming the first trap to 0°C, its contents were distilled into the fresh trap. VPC and infrared analyses showed this mixture to be mostly isobutylene, with smaller amounts of ethylene, isobutane, and 2-methylbutane. The gas in the headspace above the t-butyllithium solution was also examined by VPC and infrared and found to contain a large amount of 2-methylbutane and a smaller quantity of isobutane.

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