

ADDITION COMPOUNDS OF ALKALI METAL HYDRIDES

XVI. FACILE REACTION OF TRIALKYLBORANES WITH LITHIUM TRIMETHOXYALUMINOHYDRIDE TO FORM LITHIUM TRIALKYLBOROXYDRIDES. RAPID AND QUANTITATIVE TRANSFER OF HYDRIDE FROM ALUMINUM TO BORON

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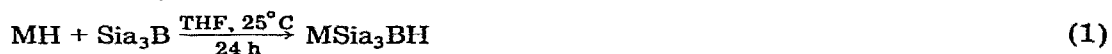
Summary

Addition of one mole equivalent of trialkylborane to a tetrahydrofuran (THF) solution of lithium trimethoxyaluminumhydride (LTMA) at room temperature results in a facile and rapid displacement of aluminum methoxide as a polymeric gel, producing the corresponding lithium trialkylborohydride in quantitative yield. The reaction is quite general and applicable to trialkylboranes of widely varied structural requirements. The trialkylborohydrides thus produced can be directly utilized for the stereoselective reduction of organic functional groups without the necessity of removing aluminum methoxide. The present reaction provides a general, convenient in situ synthesis of lithium trialkylborohydrides where this is required in synthetic transformations.

Introduction

Recent developments in the area of alkali metal trialkylborohydrides have revealed that their chemical characteristics such as reactivity and stereoselectivity are strongly influenced by the steric bulk of the alkyl group on boron [1]. This observation has aroused intense interest in the exploration of various synthetic procedures for the synthesis of such derivatives bearing alkyl groups of differing steric requirements. Recently we examined the reaction of representative trialkylboranes of increasing steric requirements with lithium and sodium hydrides in tetrahydrofuran (THF) [2]. Lithium hydride reacts with unhindered trialkylboranes quantitatively. However, it is essentially inert towards hindered trialkylboranes. The more reactive sodium hydride reacts completely with all of the unhindered and hindered trialkylboranes. A similar study with potassium hydride

indicated it to be far more reactive than the lithium and sodium analogs [3]. However, all three alkali metal hydrides failed to react with the highly hindered trialkylborane, trisiamylborane (eqn. 1).

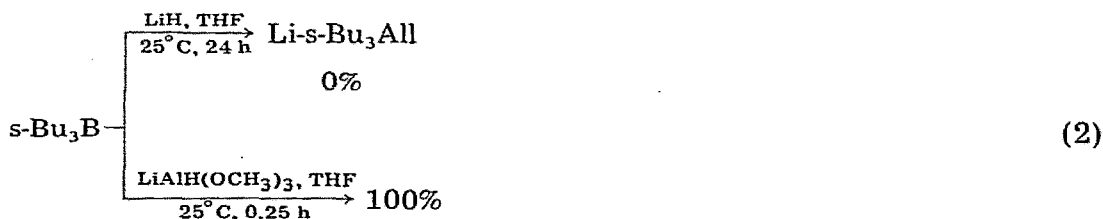


0–10%

(M = Li, Na or K)

Investigations in our laboratory and elsewhere have established the importance of hindered and highly hindered trialkylborohydrides for stereoselective reduction of ketones [1,4]. The lithium hydride route provided a convenient entry only to the unhindered lithium trialkylborohydrides (e.g., LiEt_3BH). Consequently, we became interested in exploring various procedures for the general synthesis of lithium trialkylborohydrides, applicable to unhindered, hindered, and highly hindered trialkylboranes.

Recently, we reported that the reductive cleavage of THF and related ethers by lithium tri-*t*-butoxyaluminumhydride (a mild reducing agent) induced by triethylborane [5] proceeds through the formation of lithium triethylborohydride and possibly the hitherto unknown monomeric aluminum *tert*-butoxide [6]. We also observed that the addition of a molar amount of triethylborane to a THF solution of lithium trimethoxyaluminumhydride (LTMA), a powerful reducing agent [7], results in an instantaneous, vigorous, exothermic reaction forming a gel. However, no reductive cleavage of THF or loss of active hydride was noted. Analysis of the reaction mixture indicated that a displacement reaction had taken place to form the corresponding lithium triethylborohydride and a polymeric gel of aluminum methoxide [5]. Our preliminary studies with other trialkylboranes indicated that even with hindered trialkylboranes the reaction was essentially complete in ca. 15 min at 25°C , the rate being far faster than that involving the direct reaction with lithium hydride [4a] (eqn. 2).



Encouraged by the results of our preliminary studies, we undertook to examine the reaction of LTMA with a representative series of trialkylboranes.

Results and discussion

Representative trialkylboranes including unhindered, hindered, and highly hindered derivatives, previously examined in the direct reaction with the alkali metal hydrides [2,3] were utilized in this study. Their reaction with LTMA in

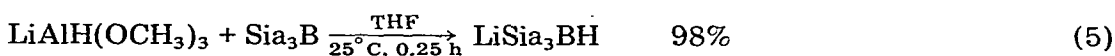
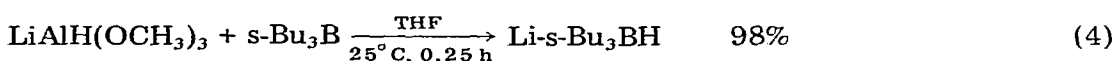
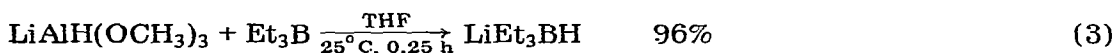
THF was examined with respect to rates and products. The product of interest, the lithium trialkylborohydride, was identified by its spectral and chemical characteristics.

Rates of reaction of LTMA with representative trialkylboranes in THF

Freshly prepared LTMA solution [7] in THF was placed in a typical reaction flask maintained at room temperature (ca. 25°C) under an inert atmosphere. An equivalent amount of the desired trialkylborane was added as a neat liquid or as a standard solution in THF (prepared in situ by hydroboration). An immediate vigorous exothermic reaction (ca. 35°C) was observed. The reaction mixture became viscous or was transformed into a gel, presumably due to the formation of polymeric aluminum methoxide. Thick gel formation was noted in the case of the unhindered and hindered trialkylboranes. In the case of the highly hindered trialkylboranes, the mixture became only slightly viscous and remained clear. The resulting mixture was stirred as efficiently as possible using an ovoid Teflon-coated magnetic stirring bar.

The rate of transfer of hydride from the LTMA to the trialkylborane was followed by an analysis for the trialkylborohydride formed after an appropriate interval of time. The reaction of LTMA with epoxides is very slow [7]. On the other hand, the reaction of lithium trialkylborohydrides with epoxides is very rapid [8]. Consequently, adding a controlled amount of a suitable epoxide to the reaction mixture, followed by hydrolysis after 15 min and GC analysis for the reduced epoxide (alcohol) established the concentration of the trialkylborohydride formed.

The results summarized in Table 1 clearly indicate that the hydride transfer from LTMA to trialkylboranes is exceedingly rapid, essentially complete in less than 15 min at room temperature. All of the trialkylboranes examined, unhindered, hindered, and highly hindered, underwent rapid and essentially quantitative hydride transfer (eqns. 3–5).



Previously, we reported that lithium hydride reacts with unhindered trialkylboranes quantitatively in refluxing THF. It was also found that lithium hydride reacts sluggishly and incompletely with hindered trialkylboranes and is essentially inert toward highly hindered trialkylboranes [2]. The greatly enhanced reactivity of LTMA over lithium hydride may be attributed to the solubility of the former in THF. Since lithium hydride is insoluble in THF, reactions with trialkylboranes involve a heterogeneous system. The LTMA solution in THF can be considered a soluble complex of lithium hydride. Similarly, a copper(I) hydride complex has been successfully prepared recently using LTMA in place of lithium hydride as the hydride source [9].

TABLE 1

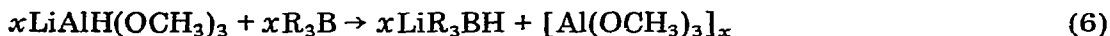
REACTION OF LITHIUM TRIMETHOXYALUMINOHYDRIDE WITH REPRESENTATIVE TRIALKYLBORANES IN TETRAHYDROFURAN AT 25°C^a

R ₃ B	LiR ₃ BH formed (%) ^b	
	0.25 h	1.0 h
Triethylborane ^c	95	
Tri-n-butylborane ^c	99	
Triisobutylborane ^d	94	98
Tri-s-butylborane ^d	98	98
Tricyclopentylborane ^d	100	100
Tricyclohexylborane ^d	98	
Tri-exo-2-norbornylborane ^d	100	100
Tris(trans-2-methylcyclopentyl)borane ^e	98	
Trisiamylborane ^e	99	

^a Solutions were equimolar in concentrations, approximately 0.5 M. ^b Monitored by GC by measuring the cyclohexanol or 2-butanol formed after quenching with cyclohexene oxide or 1,2-epoxybutane, respectively. ^c Thick gel. ^d Viscous and forms gel on standing. ^e Clear non-viscous solution.

Products of the reaction

Addition of trialkylboranes to a THF solution of LTMA results in a vigorous exothermic reaction, forming the trialkylborohydride and aluminum methoxide (eqn. 6).



In view of the high viscosity or gel-like characteristics of these solutions, it is probable that the aluminum methoxide is present in some polymeric form. However, we did not attempt to isolate and examine this product. Rather, we undertook to examine the LTMA/trialkylborane mixtures for the presence of lithium trialkylborohydrides by spectral and chemical methods.

Infrared and ¹¹B NMR spectra. Representative lithium trialkylborohydrides exhibit a strong IR absorption, due to the boron-hydrogen bond, at approximately 2000 cm⁻¹ [2]. The solutions formed in the reaction of equimolar amounts of the representative organoboranes with LTMA reveal the same absorption.

Lithium trisiamylborohydride in THF exhibits a ¹¹B NMR spectrum with a pair of doublets, due to diastereomers, at δ -13.3 (*J* 75 Hz, three parts) and -14.5 ppm (*J* 75 Hz, one part) [4b]. The solution obtained from the reaction of equimolar quantities of trisiamylborane and LTMA exhibits a similar ¹¹B NMR spectrum: δ -13.0 (d, *J* 78 Hz, three parts), -14.2 ppm (d, *J* 78 Hz, one part).

From such comparisons we conclude that the reaction proceeds with quantitative transfer of hydride from LTMA to R₃B to form the corresponding lithium trialkylborohydride. The spectroscopic data are summarized in Table 2.

Stereoselective reduction of cyclic ketones. The stereochemical course of the reduction of cyclic ketones such as 2-methylcyclohexanone by trialkylborohydrides is highly sensitive to the nature of the alkyl group on boron. Representative reaction mixtures were quenched with cyclic ketones and the *cis/trans* isomer ratios of the resulting alcohols determined by GC. The isomer ratios

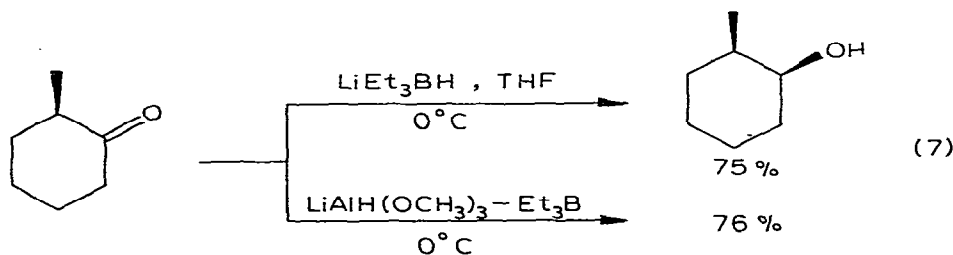
TABLE 2

SPECTRAL CHARACTERISTICS OF LITHIUM TRIMETHOXYALUMINOHYDRIDE/TRIALKYLBORANE MIXTURES IN TETRAHYDROFURAN

Reaction mixture	IR $\nu(\text{B-H})$ (cm^{-1})	^{11}B NMR ^a	
		δ (ppm)	J (Hz)
LiEt_3BH	2060	-12.3(d)	55
$\text{LiAlH}(\text{OCH}_3)_3 + \text{Et}_3\text{B} + \text{LiOCH}_3$		-11.7(s)	
$\text{Li-s-Bu}_3\text{BH}$	2070	-6.52(d)	70
$\text{LiAlH}(\text{OCH}_3)_3 + \text{s-Bu}_3\text{B}$	2020	-8.04(d)	73
$\text{LiAl}(\text{OCH}_3)_4 + \text{Li-s-Bu}_3\text{BH}$	2050	-8.05(d)	66
$\text{Li} \left[\text{HB} \left(\text{Cyclopentyl} \right)_3 \right]^b$	2060	-12.5(d, 3 parts) -14.2(d, 1 part)	75 75
$\text{LiAlH}(\text{OCH}_3)_3 + \text{Cyclopentyl}_3\text{B}^b$	2060	-13.2(d, 3 parts) -14.9(d, 1 part)	75 70
LiSi_3BH^b	2150	-13.3(d, 3 parts) -14.5(d, 1 part)	75 75
$\text{LiAlH}(\text{OCH}_3)_3 + \text{Si}_3\text{B}^b$	2150	-13.0(d, 3 parts) -14.2(d, 1 part)	78 78
$\text{LiAlH}(\text{OCH}_3)_3 + \text{Si}_3\text{B} + \text{LiOCH}_3^b$		-12.7(d, 3 parts) -13.9(d, 1 part)	80 78

^a ^{11}B NMR chemical shifts are relative to $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (δ 0 ppm) with chemical shifts upfield assigned as negative. ^b Diastereomeric pairs.

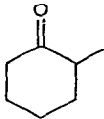
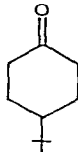
realized with LTMA/trialkylborane mixtures were essentially identical to the ratios realized with trialkylborohydrides prepared by independent routes (eqn. 7) [4]. The results are summarized in Table 3.



It is also evident from the results that the presence of aluminum methoxide does not interfere significantly with the stereoselective property of the trialkylborohydride anion. Further, the present reaction provides a general and convenient in situ synthesis of lithium trialkylborohydrides which can be utilized for further reactions without the necessity of removing polymeric aluminum methoxide.

TABLE 3

STEREoselective REDUCTION OF CYCLIC KETONES WITH LITHIUM TRIMETHOXY-ALUMINOHYDRIDE/TRIALKYLBORANE MIXTURES IN TETRAHYDROFURAN

Reaction mixture	<i>cis</i> -Alcohol, (%) ^a	
	 , 0°C	 , -78°C
LiEt ₃ BH ^b	75.0	
LiAlH(OCH ₃) ₃ + Et ₃ B	76.0	
LiAlH(OCH ₃) ₃ + Et ₃ B + LiOCH ₃	76.0	
Li- <i>s</i> -Bu ₃ BH ^c	>99.0	97.0
LiAlH(OCH ₃) ₃ + <i>s</i> -Bu ₃ B	>99.0	96.5
LiSi ₃ BH ^d	≥99.5	99.4
LiAlH(OCH ₃) ₃ + Si ₃ B + LiOCH ₃	96.0	95.0
LiAlH(OCH ₃) ₃ + Si ₃ B + LiOCH ₃ + <i>n</i> -BuNH ₂ ^e		99.0

^a Analysis by GC. ^b Ref. 6. ^c Ref. 4a. ^d Ref. 4b. ^e 20 mol % of *n*-BuNH₂ was added to destroy selectively minute amounts of the less selective aluminohydrides present.

Attempted removal of aluminum methoxide from the reaction mixture

Earlier it was pointed out that the mixtures of lithium trialkylborohydrides and aluminum methoxide are sometimes quite viscous or become gels due to the formation of aluminum methoxide polymer. Occasionally we also encountered difficulties in stirring the reaction mixtures efficiently.

Consequently, it was desirable to explore possible means for removal of aluminum methoxide from trialkylborohydrides. Accordingly, we explored the feasibility of simply precipitating aluminum methoxide selectively by (a) allowing the reaction mixture to stand at room temperature for an extended period of time; (b) heating the reaction mixture to reflux; (c) utilizing *n*-pentane or toluene as cosolvent (5–30%); (d) complexing with ethylenediamine, *n*-butylamine, 1,4-diazabicyclo[2.2.2]octane, or *N,N,N',N'*-tetramethylethylenediamine; (e) adding the dilithio salt of ethylene glycol. None of these methods was entirely successful.

Finally, we examined the addition of lithium methoxide in an attempt to precipitate aluminum methoxide gel as lithium tetramethoxyaluminate [10,11]. To our surprise, this caused dissolution of the gel resulting in a clear solution. Control experiments indicated that lithium tetramethoxyaluminate is indeed formed but is solubilized by lithium trialkylborohydride. Examination of the resulting clear solution by IR, ¹¹B NMR and for stereoselectivity revealed no significant changes from the characteristics of the pure lithium trialkylborohydride solutions. Consequently, this provides a satisfactory procedure for circumventing difficulties associated with the formation of the thick gel.

Conclusions

LTMA reacts rapidly and quantitatively with all of the trialkylboranes examined, including the ones bearing highly hindered alkyl substituents, to give

the corresponding lithium trialkylborohydrides. The reaction is far faster than the corresponding reaction involving lithium hydride. Consequently, this provides a convenient entry into hindered and highly hindered lithium trialkylborohydrides which are especially useful for the stereoselective reduction of ketones. The other product of the reaction, presumably polymeric aluminum methoxide, appears to be inert and does not interfere in the further reactions of the trialkylborohydride.

Experimental

General comments

All glassware was dried at least 4 h at 140°C, assembled hot, and cooled under a stream of prepurified nitrogen. All reactions were carried out under a dry nitrogen atmosphere. Additions of solvents and liquid reagents were carried out with oven-dried, nitrogen-purged hypodermic syringes fitted with stainless steel needles.

Materials

THF, trialkylboranes, and clear solutions of lithium aluminum hydride (LiAlH_4) in THF were stored under a nitrogen atmosphere. THF was distilled from excess LiAlH_4 . Methanol (J.T. Baker spectrophotometric grade) was dried over 4 Å molecular sieves and kept under a nitrogen atmosphere. The procedures for the synthesis and distillation of trialkylboranes used in this study are as described in our previous papers [2,3]. LTMA was prepared fresh before use by the addition of three equivalents of methanol to one equivalent of LiAlH_4 in THF [7].

Spectra

Spectra were obtained under inert atmosphere using apparatus and techniques described elsewhere [12]. Infrared spectra were obtained with either Perkin-Elmer 137 or 700 spectrometers using sealed liquid cells and the two-syringe technique. ^{11}B NMR spectra were recorded on a Varian FT-80A spectrometer with a broadband probe fitted with a Hewlett-Packard 3335A Synthesizer. The spectra were recorded in the FT mode using a ^2H internal lock. All chemical shifts are relative to BF_3/OEt_2 (δ 0 ppm) with those downfield assigned as positive.

GC analyses

GC analyses were carried out with Varian Model 1200 FID or Hewlett-Packard 5752B chromatographs.

Rates of reaction of LTMA with trialkylboranes in THF at 25°C

Triethylborane. A 50-ml flask, equipped with a sidearm fitted with a silicone rubber stopple, a magnetic stirring bar, and connected to a mercury bubbler, was cooled to room temperature under a stream of dry nitrogen. The flask was immersed in a water bath (ca. 25°C). In the flask was placed 2.2 ml

of tetrahydrofuran and 4.1 ml of 1.23 M LiAlH_4 (5 mmol) in THF. Then 3 ml of 5 M methanol (15 mmol) in THF was introduced into the reaction flask dropwise and the resulting solution was stirred for 30 min. To the resulting homogeneous solution of LTMA was added 0.72 ml triethylborane (5 mmol) with vigorous stirring. There was observed an instantaneous and vigorous exothermic reaction (temperature rose to 33°C) and the mixture became a viscous gel. Fifteen minutes after the addition of triethylborane, a THF solution containing 5 mmol of cyclohexene oxide and 2.5 mmol of n-dodecane was introduced. After stirring for 15 min, the reaction was quenched with water and the organoborane oxidized ($\text{NaOH}/\text{H}_2\text{O}_2$). The aqueous layer was saturated with anhydrous potassium carbonate and the dry THF layer was subjected to GC analysis (6 ft. \times $\frac{1}{8}$ in. stainless steel column filled with 5% Carbowax 20M on AW DMCS 100/120 Chromosorb W). A 95% yield of cyclohexanol corresponded to the presence of 95% lithium triethylborohydride. Also detected was 4–5% of unreacted cyclohexene oxide.

An identical reaction of LTMA with triethylborane was carried out and this mixture was cooled to 0°C (ice bath) and reacted with 5 mmol of 2-methylcyclohexanone. After the usual workup, GC analysis of the reaction mixture (8 ft. \times $\frac{1}{8}$ in. stainless steel column filled with 5% Quadrol on AW DMCS 100/120 Chromosorb W) indicated the presence of *cis*-2-methylcyclohexanol in 76% isomeric purity.

Tri-s-butylborane. The apparatus was the same as in the previous experiments. LTMA (5 mmol) in THF was generated in situ from LiAlH_4 (5 mmol) and methanol (15 mmol). Then 1.25 ml tri-s-butylborane (5 mmol) was injected with rapid stirring. Immediately a vigorous, exothermic reaction was observed and the reaction mixture became viscous. Fifteen minutes after the addition of tri-s-butylborane, the reaction mixture was analyzed by the cyclohexene oxide reduction technique, indicating the presence of lithium tri-s-butylborohydride in 98% yield. Additional experiments were carried out to monitor the reaction at 1 h (98%) and 3 h (99%).

The mixture of LTMA and s-Bu₃B exhibited the following spectral characteristics. ¹¹B NMR: δ -8.04 ppm (d, *J* 73 Hz); IR (THF): 2020 cm⁻¹ (B-H).

Separate mixtures of LTMA and s-Bu₃B were quenched with 2-methylcyclohexanone (at 0°C) and 4-t-butylcyclohexanone (at -78°C). After the usual workup, GC analysis of the reaction mixtures indicated the presence of >99.0% of *cis*-2-methylcyclohexanol and 96.5% of *cis*-4-t-butylcyclohexanol, respectively [4a].

Trisiamylborane. To 1.23 ml of 0.81 M LTMA (1 mmol) in THF was added 2 ml of 0.5 M trisiamylborane (1 mmol) in THF at 25°C. After 15 min the mixture was quenched with 0.09 ml 1,2-epoxybutane (1 mmol). Following the usual oxidative workup, GC analysis (6 ft. \times $\frac{1}{4}$ in. stainless steel column filled with 10% Carbowax 20M on AW DMCS 60/80 Chromosorb W) indicated a 98% yield of 2-butanol, corresponding to essentially quantitative formation of lithium trisiamylborohydride.

Mixtures of LTMA and trisiamylborane exhibited spectral characteristics essentially identical to those for lithium trisiamylborohydride prepared using t-butyl lithium [4b]. ¹¹B NMR: δ -13.0 (d, *J* 78 Hz, three parts), -14.2 ppm (d, *J* 78 Hz, one part). IR (THF): 2150 cm⁻¹ (B-H).

Addition of lithium tri-s-butylborohydride to lithium tetramethoxyaluminate

A 50-ml flask with a septum inlet and magnetic stirring bar was fitted with a dry condenser connected to a mercury bubbler, and the apparatus was purged with nitrogen. The flask was immersed in an ice-water bath and 0.50 ml of 1.99 M LiAlH_4 (1.0 mmol) in THF was introduced. Then 0.96 ml of 4.15 M methanol (4.0 mmol) in THF was added dropwise. A white precipitate of lithium tetramethoxyaluminate formed. To this was added 1.0 mmol of lithium tri-s-butylborohydride prepared by addition of 0.57 ml of 1.76 M *t*-butyllithium (1.0 mmol) in pentane to 2.0 ml of 0.5 M tri-s-butylborane (1.0 mmol) in THF [4]. The white precipitate immediately dissolved and a clear, colorless, non-viscous solution resulted. ^{11}B NMR: δ -8.05 ppm (d, J 66 Hz).

Reaction of triethylborane with LTMA followed by addition of lithium methoxide

In a 50-ml flask, fitted with a septum inlet and magnetic stirring bar and connected to a mercury bubbler, was placed 10 ml of 0.5 M triethylborane (5 mmol) in THF. The flask was immersed in a water bath and 6.2 ml of 0.82 M LTMA (5 mmol) in THF was added. A viscous, turbid mixture resulted. To this was added a suspension of 5 mmol lithium methoxide prepared by addition of 1.20 ml of 4.15 M methanol (5 mmol) in THF to 2.06 ml of 2.43 M *n*-butyllithium (5 mmol) in hexane. After stirring overnight, a clear, non-viscous solution was formed. ^{11}B NMR: δ -11.8 ppm (s).

Reaction of trisiamylborane with LTMA followed by addition of lithium methoxide

The previous procedure was followed using 10 ml of 0.5 M trisiamylborane (5 mmol) in THF. Again, a clear, non-viscous solution was formed. The solution was transferred to a dry, nitrogen-flushed, Teflon-stopcock protected 50-ml volumetric flask with a double-ended needle and diluted to the mark with THF. ^{11}B NMR: δ -12.7 (d, J 80 Hz, three parts), -13.9 ppm (d, J 78 Hz, one part).

Reduction of 4-t-butylcyclohexanone by trisiamylborane-LTMA- lithium methoxide

In a 50-ml flask, fitted with a septum inlet and magnetic stirring bar and connected to a mercury bubbler, was placed 5 ml of the solution prepared in the previous reaction (1 mmol of hydride). The flask was immersed in a dry ice/acetone bath at -78°C , followed by addition of 0.3 ml of 2.42 M 4-*t*-butylcyclohexanone (0.67 mmol) in THF. After allowing the solution to warm to room temperature, oxidation of the organoborane was accomplished by addition of 0.5 ml of 3 N aqueous sodium hydroxide and 0.5 ml of 30% hydrogen peroxide. To the aqueous layer was added 1 g anhydrous potassium carbonate. The THF layer was separated and dried over 3 Å molecular sieves. GC analysis (6 ft. \times $\frac{1}{4}$ in. stainless steel column filled with 10% Carbowax 20M on AW DMCS 60/80 Chromosorb W) showed a 95/5 ratio of *cis*- and *trans*-4-*t*-butylcyclohexanols.

Reaction of trisiamylborane-LTMA-lithium methoxide with n-butylamine followed by reduction of 4-t-butylcyclohexanone

The procedure was the same as for the previous reaction except that 0.02 ml

n-butylamine (ca. 0.2 mmol) was added to the hydride and the solution was stirred 2 h at room temperature before cooling to -78°C and addition of the ketone. GC analysis after oxidation showed a 99/1 ratio of *cis*- and *trans*-4-t-butylcyclohexanols.

Acknowledgement

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