Journal of Organometallic Chemistry, 166 (1979) 281—291

ADDITION COMPOUNDS OF ALKALI METAL HYDRIDES

XVII *. AN UNUSUAL REACTION OF TRIALKYLBORANES WITH LITHIUM TRI-t-BUTOXYALUMINOHYDRIDE IN TETRAHYDROFURAN

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(Received August 22nd, 1978)

Summary

Addition of equimolar or catalytic quantities of trialkylboranes to a tetrahydrofuran solution of lithium tri-t-butoxyaluminohydride results in rapid loss of active hydride with the concurrent formation of 1-butanol (from the reductive cleavage of tetrahydrofuran). The rate of reductive cleavage decreases with increasing steric requirements of the trialkylborane. In contrast to the tetrahydrofuran, tetrahydropyran is cleaved sluggishly. Consequently, this solvent can be utilized to follow the course of the reaction of lithium tri-t-butoxyaluminohydride with representative trialkylboranes by ^{11}B NMR. Chemical and spectral evidence suggest the intermediacy of lithium trialkylborohydrides and aluminum-t-butoxide in these reactions.

Introduction

Both lithium trimethoxyaluminohydride [LTMA] and lithium tri-t-butoxyaluminohydride [LTBA] [1] have been utilized to achieve the carbonylation of organoboranes (eq. 1).

$$R_3B + CO + LiAlH(OR')_3 \rightarrow R_2B\underset{\underset{OAl(OR')_3]Li}{|}}{\overset{\overset{H}{|}}{C}}R \xrightarrow{[O]} RCHO \qquad (1)$$

R′ = Me, t-Bu

In the case of LTMA, it has been established that there occurs a rapid transfer

* For part XVI see ref. 2.

of hydride from LTMA to the organoborane [2]. It is probable that the trialkylborohydride is intimately involved in the reaction with carbon monoxide [3].

It was of interest to examine LTBA to determine whether this reagent also transfers hydride to the organoborane as an essential step in the carbonylation reaction. There is already evidence of a major difference in the behavior of the two reagents in the presence of organoboranes [4]. Thus, rapid reductive cleavage of THF occurs in the presence of LTBA and Et_3B, whereas such cleavage does not occur in the presence of LTMA and Et_3B. Accordingly, we decided to examine the reaction in THF of LTBA with three trialkylboranes of markedly different steric requirements: triethylborane (Et_3B, unhindered), tri-s-butylborane (s-Bu_3B, hindered), and trisiamylborane (Sia_3B, highly hindered).

Results and discussion

We used three general techniques to follow the course of the reaction. First, we mixed an equivalent amount of trialkylborane (R_3B) with LTBA in tetrahydrofuran (THF) and observed the rate at which reductive opening of the THF occurred [5]. Second, we treated the solutions with 2-methylcyclopentanone in order to detect the presence of the trialkylborohydrides through the highly stereospecific reduction of ketones of this type. Third, we examined the ^{11}B NMR spectra for the disappearance of R_3B and the appearance of the corresponding LiR_3BH.

Reaction of LTBA with trialkylboranes in THF. Effect of the structure and stoichiometry

A standard solution of LTBA in THF was placed in a typical reaction flask maintained at room temperature (ca. 25°C) under a dry nitrogen atmosphere. A known quantity of a suitable internal standard (n-alkane) was added. The reaction was initiated by adding an equivalent or a catalytic amount of the desired trialkylborane as a neat liquid (Et_3B and s-Bu_3B) or as a standard solution in THF (Sia_3B prepared in situ by hydroboration). The resulting mixture was stirred well.

With Et_3B an immediate exothermic reaction occurred, raising the temperature to approximately 40°C. Unlike the LTMA reaction, the reaction mixture, in all three cases examined, did not become viscous or form a gel. However, as the reaction proceeded, a white precipitate formed.

The progress of the reaction was monitored by analyzing the mixture at appropriate intervals of time for the disappearance of the active hydride and for the formation of 1-butanol (after hydrolysis).

The rate of reductive cleavage is strongly influenced by the steric requirements of the trialkylborane. The reaction of Et_3B (unhindered) with LTBA (1/1) is exceedingly rapid. In 5 min over 70% of the hydride is lost and the reaction is essentially complete in 1 h. With s-Bu_3B (hindered) the rate of reductive cleavage is considerably slower, 87% of 1-butanol (based on LTBA concentration) being realized in 12 h. The reaction of Sia_3B (highly hindered) is very sluggish, with only 9% reductive cleavage of THF observed in 12 h.

Further, even a catalytic quantity of trialkylborane is effective. The addition of 10 mol% of Et_3B to a THF solution of LTBA results in the rapid and essen-

TABLE 1

REACTION OF LITHIUM TRI-t-BUTOXYALUMINOHYDRIDE WITH REPRESENTATIVE TRIALKYLBORANES IN TETRAHYDROFURAN AT 25°C [a]

R_3B	Reductive cleavage (%) [b]						
	5 min	0.25 h	0.5 h	1.0 h	3.0 h	6.0 h	12.0 h
Triethylborane	73 (72)	(75)	(83)	80 (85)	92 (95)		
Triethylborane [c]	16 (18)	(40)	55 (60)	(82)	90 (95)	93 (95)	
Tri-s-butylborane		6	21	42	79	85	87
Trisiamylborane					3	7	9

[a] Unless otherwise stated, solutions were 0.5 *M* in LTBA and R_3B. [b] The values in parentheses show the hydride utilized at the time indicated. The other values show the yield of 1-butanol at that time. [c] Catalytic amount (10 mol%, 0.05 *M*) of triethylborane.

tially quantitative reductive cleavage of THF in 3 h. The results are summarized in Table 1 and represented graphically in Fig. 1.

It was of major interest to learn how minor quantities of a trialkylborane can transform the mild reducing agent LTBA which is indefinitely stable in THF [6] into a reagent capable of cleaving THF reductively with remarkable ease.

Stereoselective reduction of 2-methylcyclopentanone with representative LTBA/trialkylborane mixtures in tetrahydrofuran

The stereoselectivity realized in the reduction of a cyclic ketone such as 2-methylcyclopentanone is strongly influenced by the nature of the reducing agent. LTBA is a reducing agent of low stereoselectivity [7], whereas trialkylborohydride exhibits excellent stereoselectivity in this reaction [8]. 2-Methylcyclopentanone was treated with representative LTBA/R_3B mixtures (2 min after mixing) at 0°C in THF for 1 h. The resulting mixtures were analyzed by GC for the *cis/trans* ratio in the 2-methylcyclopentanol product.

With the LTBA/Et_3B mixture, the stereoselectivity (57.6% *cis*) realized was essentially the same as that of pure lithium triethylborohydride $LiEt_3BH$ (60.5% *cis*) *. Consequently, the hydride transfer from LTBA to Et_3B is essentially complete to form $LiEt_3BH$. The stereoselectivity of the LTBA/s-Bu_3B mixture was considerably lower (37% *cis*) than that of pure lithium tri-s-butylborohydride (Li-s-Bu_3BH) [8] (98% *cis*) indicating only partial hydride transfer in ca. 2 min. The LTBA/Sia_3B mixture exhibits stereoselectivity identical to that of pure LTBA (28% *cis*), indicating the absence of any significant hydride transfer (in 2 min) from LTBA to Sia_3B.

The results of this study clearly indicate that only in the case of Et_3B does a complete hydride transfer from LTBA to form $LiEt_3BH$ occur rapidly. The

* The stereoselectivity realized in the reduction of 2-methylcyclohexanone by LTBA/Et_3B and $LiEt_3BH$ is identical (75% *cis*).

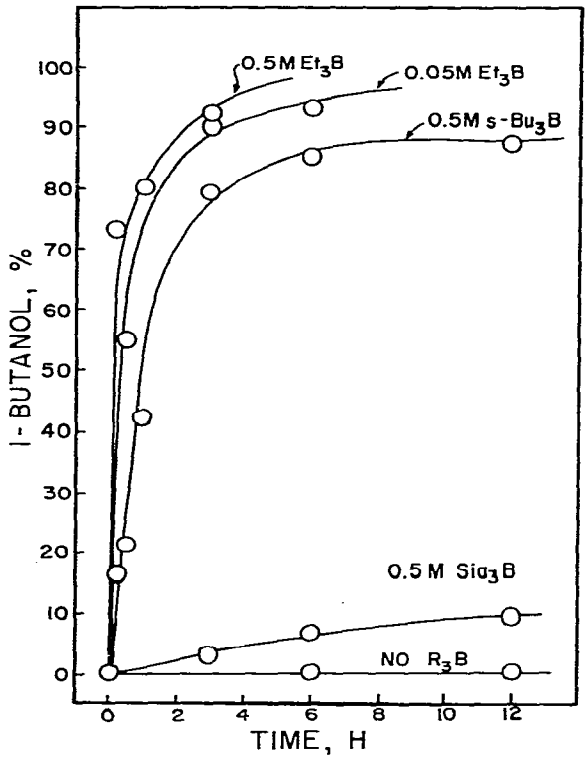


Fig. 1. Reductive cleavage of tetrahydrofuran at 25°C by lithium tri-t-butoxyaluminohydride (0.5 *M*) in the presence of representative trialkylboranes.

results are summarized in Table 2 along with the isomer ratios realized with pure lithium trialkylborohydrides.

^{11}B NMR studies of the reaction between LTBA and trialkylboranes in tetrahydropyran with time

Recently, ^{11}B NMR has emerged as an excellent tool for monitoring and understanding a number of fascinating reactions involving borohydrides [9]. The fast reductive cleavage of tetrahydrofuran by LTBA and Et_3B prevents the

TABLE 2

STEREOSELECTIVE REDUCTION OF 2-METHYLCYCLOPENTANONE WITH LITHIUM TRI-t-BUTOXYALUMINOHYDRIDE/TRIALKYLBORANE MIXTURES IN TETRAHYDROFURAN AT 0°C [a,b]

R_3B	*cis*-2-Methylcyclopentanol (%) [c]	
	LiR_3BH	LTBA + R_3B [d]
Triethylborane	60.5	57.6
Tri-s-butylborane	98.0	37.0
Trisiamylborane	99.5	28.0

[a] Hydride/ketone = 2.0. [b] Ketone was added 2 min after the addition of trialkylborane to LTBA. [c] Analysis by GC. [d] Pure LTBA gives 28% *cis* alcohol.

use of this solvent for such NMR studies. Fortunately, the reductive cleavage of tetrahydropyran (THP) is much slower (17% in 24 h) permitting the use of this solvent for ^{11}B NMR [5].

The addition of one equivalent of Et_3B to LTBA in THP results in a rapid reaction. Examination of the solution by ^{11}B NMR immediately following mixing of the reagents (ca. 15 min) revealed the complete absence of the resonance of Et_3B at δ +80 ppm. Unexpectedly, the resonance of $LiEt_3BH$ at δ —12 ppm is also absent.

However, there is a broad singlet at δ +48 ppm. We attribute this singlet to a complex of $LiEt_3BH$ and aluminum-t-butoxide (eq. 2).

$$LiAlH(O\text{-}t\text{-}Bu)_3 + Et_3B \rightarrow Li[Et_3BHAl(O\text{-}t\text{-}Bu)_3] \quad (2)$$

The fact that we realized almost the same stereoselectivity in the reduction of 2-methylcyclopentanone with this reagent as with $LiEt_3BH$ suggests that the reduction must proceed through a slight dissociation of the complex into $LiEt_3$-BH, which achieves the reduction.

On standing, there appears after approximately 30 min a complex resonance in the "ate" complex region (δ —15 to —19 ppm). It initially increased slowly with time but then decreased after 24 h. Evidently, a secondary reaction slowly occurs. However, we did not explore this side reaction further.

The reaction of s-Bu_3B with LTBA is much slower. Thus, after mixing the reagents, the ^{11}B NMR resonance of s-Bu_3B at δ +85 ppm appears essentially unchanged and there is no other resonance evident. With time the resonance at δ +85 ppm slowly decreases and a resonance characteristic of Li-s-Bu_3BH appears at δ —8.05 ppm. The observation of a singlet rather than the expected doublet is attributed to a very slow interaction between Li-s-Bu_3BH and aluminum-t-butoxide or s-Bu_3B (unreacted). After 24 h, the reaction has proceeded approximately 50% to completion.

The reaction involving Sia_3B, the highly hindered trialkylborane, is even slower than s-Bu_3B. Immediately after mixing, examination of the LTBA/Sia_3B mixture by ^{11}B NMR reveals only one resonance, a broad singlet at δ +86 ppm corresponding to that of pure Sia_3B. However, after 1 h, there appears an additional resonance two pairs of doublets at δ —12.7 (d, J 80 Hz) and —13.9 ppm (d, J, 77 Hz). This resonance is attributed to the formation of a small quantity of $LiSia_3BH$ [10]. After 24 h, there was 36% of hydride transfer to form $LiSia_3$-BH.

Thus, the ^{11}B NMR studies of the LTBA/R_3B reaction have provided important evidence about the intermediates involved in the reductive cleavage of ethers. The results clearly reveal that the transfer of hydride from LTBA to R_3B is rapid and essentially complete only with the unhindered Et_3B. Further, it is also evident that $LiEt_3BH$ and aluminum-t-butoxide produced in the reaction form a 1/1 complex. With trialkylboranes of higher steric requirements, s-Bu_3B and Sia_3B, the rate of hydride transfer is sluggish and incomplete. Further, Li-s-Bu_3BH and $LiSia_3BH$ produced in these reactions do not form a complex with aluminum-t-butoxide.

The results of the ^{11}B NMR studies of the LTBA/R_3B mixtures are similar to those realized with KR_3BH/R_3B mixtures on THF by C.A. Brown [9a]. His results clearly indicate that the exchange of s-Bu_3B with K-s-Bu_3BH and Sia_3B

with $KSia_3BH$ are negligible on the NMR time scale, in contrast to the fast exchange observed in the KEt_3BH/Et_3B system.

Mechanistic considerations

The ^{11}B NMR studies of $LTBA/R_3B$ mixtures together with the stereoselective reduction of 2-methylcyclopentanone with these reaction mixtures clearly indicate the formation of lithium trialkylborohydrides in these reactions. However, the trialkylborohydrides alone cannot be responsible for the reductive cleavage of THF; a large number of such derivatives have now been synthesized in THF by independent routes. In all cases such solutions have proved to be stable indefinitely with no evidence of the reductive cleavage of THF detected [11].

Consequently, the reaction muxt also involve aluminum-t-butoxide in some way. Accordingly, we undertook to test this possibility by adding freshly sublimed aluminum-t-butoxide (a dimer) [12] to $LiEt_3BH$ solution in THF. The mixture remained clear and no exothermic reaction was noticed. The reaction was monitored with time by analyzing for 1-butanol. In a 24 h period, no 1-butanol was detected and 98% of the original hydride activity remained. This clearly indicates that the aluminum-t-butoxide generated in the reaction of $LTBA/R_3B$ may be entirely different and more reactive than the commercial dimer.

Previously, based on the stereoselectivity evidence, we had suggested the possibility that the reaction may involve lithium triethylborohydride and monomeric aluminum-t-butoxide, an exceptionally powerful Lewis acid, coordinated with THF [4]. However, our recent ^{11}B NMR studies of the $LTBA/Et_3B$ system clearly indicated the absence of any free $LiEt_3BH$ but the presence of $LiEt_3BH$ complexed with the freshly generated aluminum-t-butoxide. Based on this, we must slightly modify our original conclusions. It is possible that LTBA reacts with unhindered trialkylboranes such as Et_3B to form aluminum-t-butoxide complexed with trialkylborohydride which is slightly dissociated and in equilibrium with aluminum-t-butoxide—THF complex and free trialkylborohydride. The position of this equilibrium is strongly influenced by the steric requirements of the trialkylborane (eq. 3 and 4).

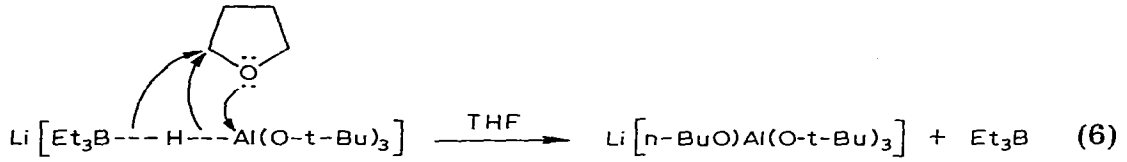
$$LiAlH(O\text{-}t\text{-}Bu)_3 + R_3B \xrightarrow{THF} Li\left[R_3B\text{---}H\text{---}Al(O\text{-}t\text{-}Bu)_3\right] \quad (3)$$

$$Li\left[R_3B\text{---}H\text{---}Al(O\text{-}t\text{-}Bu)_3\right] \underset{}{\overset{THF}{\rightleftharpoons}} LiR_3BH + \overset{\bar{A}l(O\text{-}t\text{-}Bu)_3}{\underset{}{O^+}} \quad (4)$$

The trialkylborohydride formed next reacts with the polarized carbon—oxygen bond of the aluminum-t-butoxide—THF complex (eq. 5).

$$LiR_3BH + \overset{\bar{A}l(O\text{-}t\text{-}Bu)_3}{\underset{}{O^+}} \longrightarrow Li\left[(n\text{-}BuO)Al(O\text{-}t\text{-}Bu)_3\right] + R_3B \quad (5)$$

Alternatively, a direct four-center reaction between the 1/1 complex of $LiEt_3BH$ and aluminum-t-butoxide with THF is also conceivable (eq. 6).



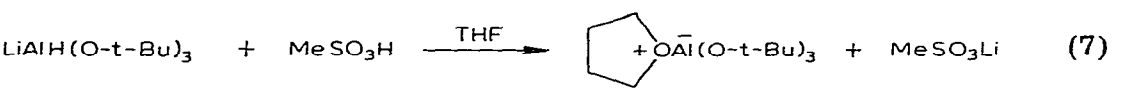
(6)

The hydrolysis of the lithium tetraalkoxyaluminate formed gives 1-butanol (with THF). The overall rate of the reductive cleavage of THF or THP is dependent on two factors: (1) the rate of hydride transfer from LTBA to R_3B (eq. 2). Increasing the steric requirement of trialkylboranes decreases this rate; (2) the reactivity of the trialkylborohydride formed (eq. 5 or 6). There are indications that increasing the steric requirements of trialkylborohydrides significantly reduces their hydride transfer ability [10,13]. Both of these factors contribute to the overall decrease in the rate of reductive cleavage as the size of the alkyl substituent on boron increases.

Our observation that the reductive cleavage can be brought about even by catalytic quantities of trialkylborane can be explained by the regeneration of trialkylborane in eq. 5 or 6.

Generation of active aluminum-t-butoxide from LTBA and methanesulfonic acid in THF. Contact time experiment

Addition of one equivalent of methanesulfonic acid ($MeSO_3H$) to a THF solution of LTBA results in rapid and quantitative evolution of hydrogen (eq. 7).



(7)

We undertook to investigate whether such freshly generated aluminum-t-butoxide induces the reductive cleavage of THF (by LiR_3BH). To an equimolar mixture of LTBA and methanesulfonic acid was added an equivalent quantity of lithium triethylborohydride solution in THF. The reaction mixture was monitored for the reductive cleavage with time. The cleavage was rapid in the

TABLE 3

REDUCTIVE CLEAVAGE OF TETRAHYDROFURAN BY LITHIUM TRIETHYLBOROHYDRIDE AND FRESHLY GENERATED ALUMINUM-t-BUTOXIDE AT 25°C [a]

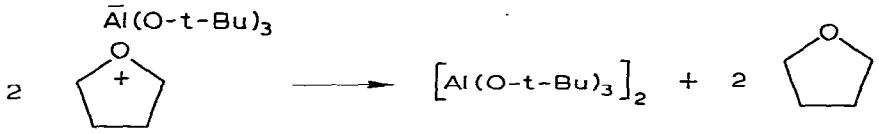
Contact time (min) [b]	Reductive cleavage (%) [c]
5	27
15	13
30	7
720	1

[a] Aluminum-t-butoxide was generated by mixing equimolar quantities of LTBA in THF and methanesulfonic acid. [b] The time the LTBA/methanesulfonic acid mixture was allowed to react before adding lithium triethylborohydride in THF. [c] Monitored by analyzing for 1-butanol produced at 15 min after the addition of borohydride.

initial phases of the reaction (5 min, 19%; 30 min, 31%) and decreased rapidly in rate with time (24 h, 45%).

Consequently, we undertook to examine whether the unusual reactivity of freshly generated aluminum-t-butoxide changes with time. Accordingly, 1/1 mixtures of LTBA and $MeSO_3H$ were allowed to stand for various intervals of time (contact time) and the reductive cleavage was induced by adding an equivalent quantity of lithium triethylborohydride in THF. Each of these mixtures was stirred well for 15 min. The mixtures were analyzed for 1-butanol.

The results summarized in Table 3 reveal that the reductive cleavage sharply decreases with increasing contact time. Consequently, the freshly generated aluminum-t-butoxide in the absence of a trapping agent must be converted into the inactive dimer (eq. 8).



(8)

Conclusions

Addition of trialkylboranes to THF solutions of LTBA induces a facile reductive cleavage of the solvent. The rate of reductive cleavage is strongly influenced by the steric requirements of R_3B (Et_3B > s-Bu_3B > Sia_3B). Chemical (stereoselective reduction of 2-methylcyclopentanone in THF) and ^{11}B NMR (in THP) studies of this reaction clearly indicate the intermediacy of LiR_3BH and aluminum-t-butoxide. The results of these studies also reveal that the rate of hydride transfer from LTBA to R_3B decreases with increasing size of the alkyl substituent on boron. $LiEt_3BH$ and aluminum-t-butoxide form a complex. However, Li-s-Bu_3BH and $LiSia_3BH$ do not form such a complex with aluminum-t-butoxide. The present study has led to a better understanding of this unusual reaction.

Experimental

General comments

All glassware was dried at least 4 h at 140°C, assembled hot, and cooled under a 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 using oven-dried, nitrogen-purged hypodermic syringes fitted with stainless steel needles.

Materials

THF and THP (Aldrich) were distilled from excess lithium aluminum hydride and stored under nitrogen. Solutions of LTBA in THP solvent were prepared by dissolving the commercial material (Ventron/Alfa) or by dissolving freshly prepared material [6] after removal of THF. Aluminum-t-butoxide (Ventron/Alfa) was sublimed (135°C at 0.1 Torr). All other materials were described previously [2].

^{11}B NMR spectra

^{11}B NMR spectra were obtained using a Varian FT-80A spectrometer fitted with a Hewlett—Packard 3335A synthesizer. The spectra were recorded at 25.517 MHz using a ^{2}H internal lock. All chemical shifts are relative to $BF_3 \cdot OEt_2$ (δ 0 ppm) with those downfield assigned as positive.

GC analyses

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

Reaction of trialkylboranes with LTBA in THF

The procedure using tri-s-butylborane is representative. A dry 50-ml flask with a septum inlet and magnetic stirring bar was connected to a mercury bubbler, and the apparatus was purged with nitrogen. The flask was immersed in a water bath (ca. 25°C) and 5.0 ml of 1.0 *M* LTBA (5.0 mmol) in THF was introduced, followed by 2.8 ml of THF and 0.975 ml of n-dodecane (internal standard). Then 1.20 ml of tri-s-butylborane (5.0 mmol) was added, giving a solution 0.5 *M* in both LTBA and the organoborane. There was no vigorous reaction, but after 1 h, a white precipitate, presumably $Li[(n\text{-}BuO)Al(O\text{-}t\text{-}Bu)_3]$, had begun to form. At appropriate intervals, 0.5-ml aliquots were removed and quenched in 0.2 ml of 3 *N* aqueous sodium hydroxide, followed by oxidation using 0.2 ml of 30% hydrogen peroxide. To the resulting mixture was added 0.5 g of anhydrous potassium carbonate. The organic phase was dried over pulverized 3 Å molecular sieves, and the yield of 1-butanol was determined by GC (6 ft. × 1/4 in. stainless steel column filled with 10% Carbowax 20M on AW DMCS 60/80 Chromosorb W). The results are summarized in Table 1 and in Figure 1.

Reduction of 2-methylcyclopentanone by trialkylborane/LTBA mixtures in THF

The following procedure involving tri-s-butylborane is representative. A dry 50-ml flask with a septum inlet and magnetic stirring bar was connected to a mercury bubbler and purged with nitrogen. The flask was immersed in an ice-water bath (ca. 0°C) and 7.5 ml of THF was introduced, followed by 2.44 ml of tri-s-butylborane (10 mmol). To this was added 14.5 ml of 0.69 *M* LTBA (10 mmol) in THF. After stirring for 2 min, 0.54 ml of 2-methylcyclopentanone (5 mmol) was added. After 1 h the mixture was oxidized by successively adding 3.5 ml of 3 *N* aqueous sodium hydroxide and 4 ml of 30% hydrogen peroxide. After 1 h, 7.5 g of anhydrous potassium carbonate was added. The organic phase was separated and dried over anhydrous magnesium sulfate. A portion of this was dried further over pulverized 3 Å molecular sieves and analyzed by GC (12 ft. × 1/4 in. stainless steel column filled with 10% Quadrol on AW DMCS 60/80 Chromosorb W). A 37/63 ratio of *cis*- and *trans*-2-methylcyclopentanols was observed. This indicates that reduction was due mainly to LTBA, since lithium tri-s-butylborohydride gives a 98/2 ratio of the *cis* and *trans* isomers under these conditions [8].

^{11}B NMR observation of the reaction of trialkylboranes with LTBA in THP

The procedure using trisiamylborane is representative. A dry 50-ml flask with

a septum inlet and magnetic stirring bar was connected to a mercury bubbler, the apparatus was purged with nitrogen, and 4.0 ml of 0.5 *M* trisiamylborane (2 mmol) in THF was introduced. The THF was removed using a water aspirator (ca. 20 Torr). To the resulting neat trisiamylborane was added 0.33 ml of 2-methyl-2-butene (ca. 3 mmol) to insure that there would be no dehydroboration, followed by addition of 2.41 of 0.83 *M* LTBA (2.0 mmol) in THP. Immediately 0.5 ml of the resulting solution was placed in a dry, nitrogen-filled 5-mm NMR tube. ^{11}B NMR spectra were recorded at appropriate intervals by completing approximately 5000 transients, ending after the time specified. The extent of trialkylborohydride formation was determined by electronically integrating the resonances for the product and unreacted organoborane.

Reaction of commercial aluminum-t-butoxide with lithium triethylborohydride in THF

A typical reaction setup was assembled and 1.85 g of freshly sublimed aluminum-t-butoxide (7.5 mmol) was placed in the flask. Tetrahydrofuran (9 ml) was injected into the flask followed by 1.0 ml of a 2.0 *M* solution of n-tridecane (2 mmol) in THF (internal standard). The aluminum-t-butoxide completely dissolved in THF. Then 5 ml of a 1.5 *M* solution of lithium triethylborohydride (7.5 mmol) in THF was introduced into the reaction flask and stirred well. The resulting mixture was 0.5 *M* each in aluminum-t-butoxide and lithium triethylborohydride. At appropriate intervals of time, a suitable aliquot of the reaction mixture was withdrawn by a syringe, hydrolyzed with water, and analyzed by GC for the formation of 1-butanol. The reaction was followed for 24 h. No 1-butanol was detected. The solution retained 98% of the original hydride activity after 24 h.

Reaction of freshly generated aluminum-t-butoxide with lithium triethylborohydride in THF

Tetrahydrofuran (0.6 ml), lithium tri-t-butoxyaluminohydride, 10 ml (10 mmol), of 1 *M* in THF, and 2 ml of 2 *M* n-tridecane (4 mmol) in THF were placed in a reaction flask in the order indicated. Then 0.66 ml methanesulfonic acid (10 mmol) was added and vigorous hydrogen evolution was observed. After 5 min, 6.8 ml of 1.5 *M* lithium triethylborohydride (10 mmol) was introduced and stirred well. The reaction was monitored by analyzing 1-butanol formed with time by GC: 5 min (19%), 30 min (31%) and 24 h (45%).

Contact time experiments

Fresh aluminum-t-butoxide (2.5 mmol) was generated as in the previous experiment (LTBA + methanesulfonic acid) in four different reaction flasks and allowed to stir for different intervals of time (5, 15, 30, and 720 min). Then, 1.7 ml of 1.5 *M* lithium triethylborohydride (2.5 mmol) in THF was introduced in each of these flasks and the resulting mixtures were allowed to stir for 15 min. Then the mixture was hydrolyzed, oxidized, and analyzed for 1-butanol. The results are summarized in Table 3.

Acknowledgement

The authors thank the U.S. Army Research Office for support of this research provided by Grant DAAG-29-76-G-0218.

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