

of $C_2B_4H_8$ to the unique but somewhat delocalized B-B single bond in B_4H_{10} . Also included in Table I are previous results³ for B_5H_9 , which we may now interpret in terms of fractional three-center bonds. We introduce the notation of a dotted component of the bond at the appropriate atom in order to distinguish this new bonding situation from the earlier notations for bonds in boron hydrides and carboranes. It is interesting, and somewhat unexpected, that the molecular bonding localizes symmetrically to a structure containing fractional three-center bonds, instead of to the very nearly equivalent resonance hybrid shown, for example, for the $C_2B_4H_8$ molecule in Figure 2a, or to one of the previously considered⁴ symmetrical structures shown in Figure 2b and c. Of course, similar structures can be written for 2,4- $C_2B_5H_7$ and 1,6- $C_2B_4H_6$.

Recognition of these fractional three-center bonds allows unique, or symmetry equivalent, single valence structures to be drawn for at least these carboranes, in such a way that a common feature of bonding is preserved. These results, together with the uniquely localized bonds in the boron hydrides listed above, suggest that similar simplified bonding diagrams may emerge from more complex boranes, carboranes, carboronium-like compounds, and their metal derivatives.

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A Remarkably Facile Reductive Opening of Tetrahydrofuran and Related Ethers by Lithium *tert*-butoxyaluminumhydride in the Presence of Triethylborane

Sir:

Lithium tri-*tert*-butoxyaluminumhydride is stable indefinitely in tetrahydrofuran at 25°. ^{1,2} The addition of 1 mol equiv of triethylborane induces a rapid opening of the tetrahydrofuran ring, essentially complete within 3 hr, with the formation of 1-butanol. Even a catalytic quantity of triethylborane (10 mol %) is effective. With this new reagent 2,5-dihydrofuran is readily converted into *cis*-crotyl alcohol and the bicyclic ring system of 7-oxabicyclo[2.2.1]heptane is readily opened to form cyclohexanol. Consequently, it appears that this reducing system is one of the most active currently available.

We recently reported that the reaction of B-alkyl-9-BBN derivatives with carbon monoxide in the presence of lithium trimethoxyaluminumhydride (LTMA) provides a major new route from olefins to the corresponding aldehydes.³ In extending this synthesis to olefins containing reducible functional groups it proved advantageous to shift to the milder reducing

(1) H. C. Brown and R. F. McFarlin, *J. Amer. Chem. Soc.*, **80**, 5372 (1958).

(2) H. C. Brown and P. M. Weissman, *Israel J. Chem.*, **1**, 430 (1963).

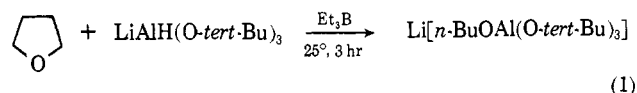
(3) H. C. Brown, E. F. Knights, and R. A. Coleman, *J. Amer. Chem. Soc.*, **91**, 2144 (1969).

agent, lithium tri-*tert*-butoxyaluminumhydride⁴ (LTBA). However, we observed a puzzling feature in applying this last reagent. To obtain a good yield it was important that the reagent be added concurrently with the uptake of carbon monoxide. If the reagent were added to the organoborane prior to the introduction of carbon monoxide, the yield decreased sharply.

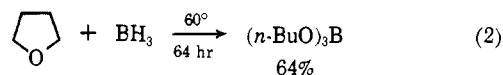
Investigation soon revealed that such solutions of LTBA and organoboranes rapidly lost active hydride with the concurrent formation of 1-butanol from reductive opening of the tetrahydrofuran (THF), utilized as solvent. For example, a 0.5 M solution of LTBA in THF appears to be stable indefinitely at 25°. Addition of an equimolar amount of triethylborane to such a solution results in a very rapid loss of hydride, with 72% of the active hydride disappearing in 5 min. Upon hydrolyzing the reaction mixture, an equivalent quantity of 1-butanol is found.

A catalytic quantity of triethylborane is also effective. Thus, the addition of 10 mol % of triethylborane causes the loss of 60% of the active hydride in 30 min, with the formation of 55% of 1-butanol. The reactions are essentially complete in 3 hr (Figure 1).

Thus triethylborane induces a rapid, essentially quantitative opening of the tetrahydrofuran ring at 25° (eq 1). To our knowledge no reducing system



currently available is capable of achieving the reductive cleavage of THF so rapidly and cleanly. For example, diborane has been recommended for this purpose, but it requires 64 hr at 60° to achieve a 64% conversion to 1-butanol (eq 2).⁵



Surprisingly, triethylborane fails to induce a similar reductive cleavage of THF by the otherwise more powerful reducing agent, lithium trimethoxyaluminumhydride.⁶

It would, of course, be very desirable to have an understanding of the mechanism of this reaction which would provide a reasonable explanation for the remarkable reducing capability exhibited by the system and for the marked difference in behavior of the methoxy and *tert*-butoxy derivatives. However, it appeared more timely to explore the utility of this new reduction for desired transformations in synthetic operations.

Monoglyme dissolves LTBA and the addition of triethylborane results in a rapid evolution of a gas, presumably methane. In 1 hr at 25° there was identified the formation of 47% of 2-methoxyethanol. The reagent is also soluble in tetrahydropyran (THP). However, reductive cleavage of this ether is much slower. We found only 17% of 1-pentanol after 24 hr. Consequently, we adopted this solvent for a survey of certain interesting possibilities for reductive cleavages.

The reaction of cyclohexene oxide with LTBA is very slow.² Yet the addition of triethylborane causes

(4) H. C. Brown and R. A. Coleman, *ibid.*, **91**, 4606 (1969).

(5) J. Kollonitsch, *ibid.*, **83**, 1515 (1961).

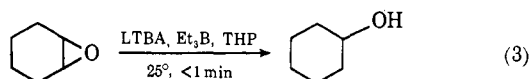
(6) H. C. Brown and P. M. Weissman, *ibid.*, **87**, 5614 (1965).

Table I. Reaction of Lithium Tri-*tert*-butoxyaluminumhydride-Triethylborane with Representative Cyclic Ethers in Tetrahydrofuran at 25°^a

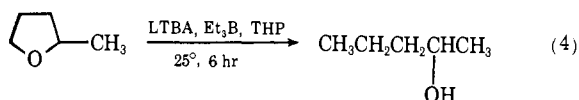
Compound	[LTBA], M	[Et ₃ B], M	Time, hr	Product	Yield, ^b %
Cyclohexene oxide	1.0	0.00	0.25	Cyclohexanol	4
	1.0	0.1	0.01	Cyclohexanol	100
	1.0	1.0	0.01	Cyclohexanol	100
Tetrahydrofuran	1.0	0.1	24.0	1-Butanol	100
	1.0	1.0	0.5	1-Butanol	98
2-Methyltetrahydrofuran	2.0	2.0	6.0	2-Pentanol	95
2,2-Dimethyltetrahydrofuran	2.0	2.0	24.0	2-Methyl-2-pentanol	4
2,5-Dihydrofuran	1.0	0.1	24.0	<i>cis</i> -Crotyl alcohol	91
	1.0	1.0	2.0	<i>cis</i> -Crotyl alcohol	95
7-Oxabicyclo[2.2.1]heptane	2.0	2.0	3.0	Cyclohexanol	97

^a In all cases the reaction mixture was 0.5 M in the cyclic ether. In reactions involving longer reaction times, some amount of 1-pentanol is also formed from THF. ^b The yields reported were determined by glpc utilizing a suitable internal standard.

an almost instantaneous opening of the epoxide ring (eq 3).

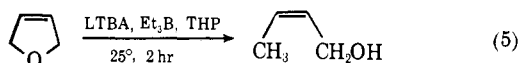


This reductive cleavage could be readily applied to tetrahydrofuran and 2-methyltetrahydrofuran (in THF solution) (eq 4). On the other hand, the reaction with

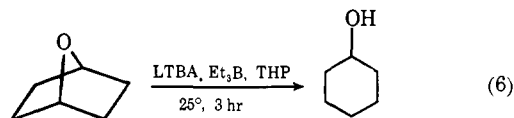


2,2-dimethyltetrahydrofuran failed to proceed.

2,5-Dihydrofuran is readily converted to *cis*-crotyl alcohol in 95% yield (eq 5).



Finally, we observed that the bicyclic ring system of 7-oxabicyclo[2.2.1]heptane readily undergoes this reductive ring cleavage (eq 6).



The experimental results are summarized in Table I.

The following procedure is representative. An oven-dried 50-ml flask, equipped with a side arm fitted with a silicone rubber stopple, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler, was cooled to room temperature under nitrogen. In the flask was placed 2.54 g of lithium tri-*tert*-butoxyaluminumhydride (10 mmol) and 2.6 ml of THF. The flask was immersed in a water bath at 25°. Then 0.5 ml of a 5.0 M solution in THF of 7-oxabicyclo[2.2.1]heptane (2.5 mmol) was injected into the reaction flask, followed by 0.5 ml of a 2.0 M solution in THF of *n*-tridecane (1.0 mmol) to serve as internal standard, followed by 1.42 ml of triethylborane (10 mmol). The mixture was stirred vigorously. After 1 hr, 0.5 ml of the reaction mixture was withdrawn with a syringe, and quenched with a mixture of water and ether. The aqueous phase was saturated with anhydrous potassium carbonate. Glpc analysis of the dry ethereal layer revealed the presence of 91% cyclohexanol. In 3 hr, a 97% yield of cyclohexanol was realized.

In conclusion, it should be pointed out that the reaction evidently involves an S_N2 displacement on carbon. Consequently, the use of lithium tri-*tert*-

butoxyaluminumdeuteride should make available the corresponding monodeutero derivatives. Even more promising is the attainment of an understanding of the mode of operation of this system and the extension

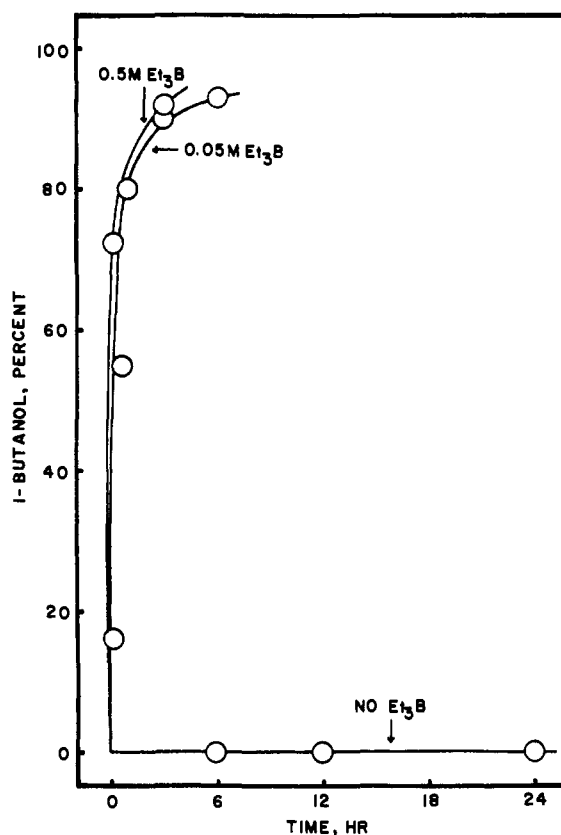


Figure 1. Reductive cleavage of tetrahydrofuran at 25° by lithium tri-*tert*-butoxyaluminumhydride (0.5 M) in the absence and presence of triethylborane.

of this extraordinarily powerful system to other compounds not easily handled by lithium aluminum hydride and other previously available reducing agents. We are continuing our explorations in this area.

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