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Ready Preparation of Trialkoxyboranes and Dialkoxyboranes by $LiBEt_3H$-Promoted Reaction of BH_3 in Tetrahydrofuran with Alcohols

Yuzuru MASUDA,* Yutaka NUNOKAWA, Masayuki HOSHI, and Akira ARASE*
Department of Industrial Chemistry, Kitami Institute of Technology, 165 Koencho, Kitami 090

A catalytic amount of $LiBEt_3H$ (1%) promoted markedly the reactions of BH_3 in tetrahydrofuran (THF) with stoichiometric amounts of alcohols (1:2 and 1:3) to provide corresponding trialkoxyboranes and dialkoxyboranes quantitatively under mild reaction conditions.

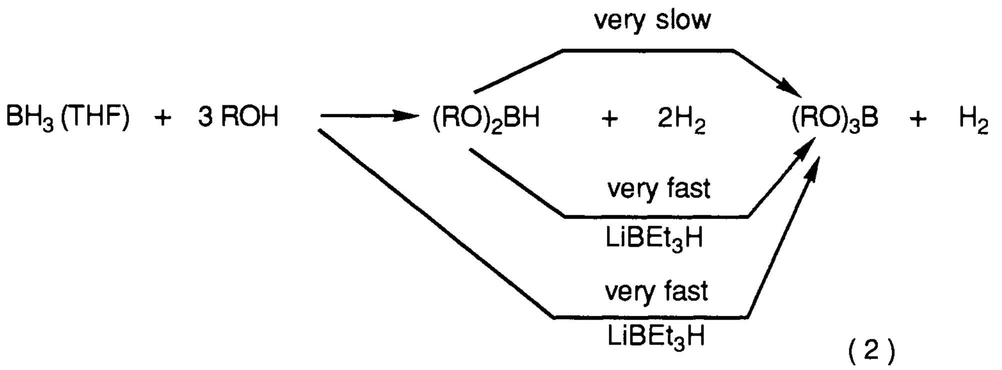
Recently we reported a procedure for the low temperature hydroboration of alkenes with catecholborane[1)] using a small amount of $LiBH_4$ as the promoter of the reaction.[2)] During above study, we found that a very small amount of lithium borohydride compounds, especially $LiBEt_3H$, promoted the reaction of BH_3 in THF with catechol and alcohols. We wish to report here a $LiBEt_3H$-promoted reaction of BH_3 in THF with alcohols, leading to dialkoxyboranes or trialkoxboranes quantitatively.

Previously it has been reported that the gas phase reaction of an excess amount of diborane, B_2H_6, with methanol proceeded rapidly to provide dimethoxyborane which decomposed readily to B_2H_6 and trimethoxyborane at 0 °C.[3)]

$$6\,(CH_3O)_2BH \rightleftharpoons B_2H_6 + 4\,(CH_3O)_3B \qquad (1)$$

However in THF solution, dialkoxyboranes might be present in a relatively stable state. For example, the reaction of 2 mmol of BH_3 in THF with 6 mmol of BuOH at 20 °C, monitored by estimation of the volume of hydrogen evolved, showed considerable retardation when the amount of hydrogen approached to 4 mmol, and no more progress of the reaction was observed after it reached to 4 mmol . An addition of 0.02 mmol (1%) of $LiBEt_3H$ (1 M-sol. in THF) to the above reaction mixture caused spontaneous evolution of additional 2 mmol of hydrogen (Fig. 1A-a). And

2 mmol of BH_3 in THF containing 0.02 mmol of $LiBEt_3H$ reacted with 6 mmol of BuOH at 20 °C evolving 6 mmol of hydrogen spontaneously, indicating that tributoxyborane was formed quantitatively (Fig. 1A-b).



(2)

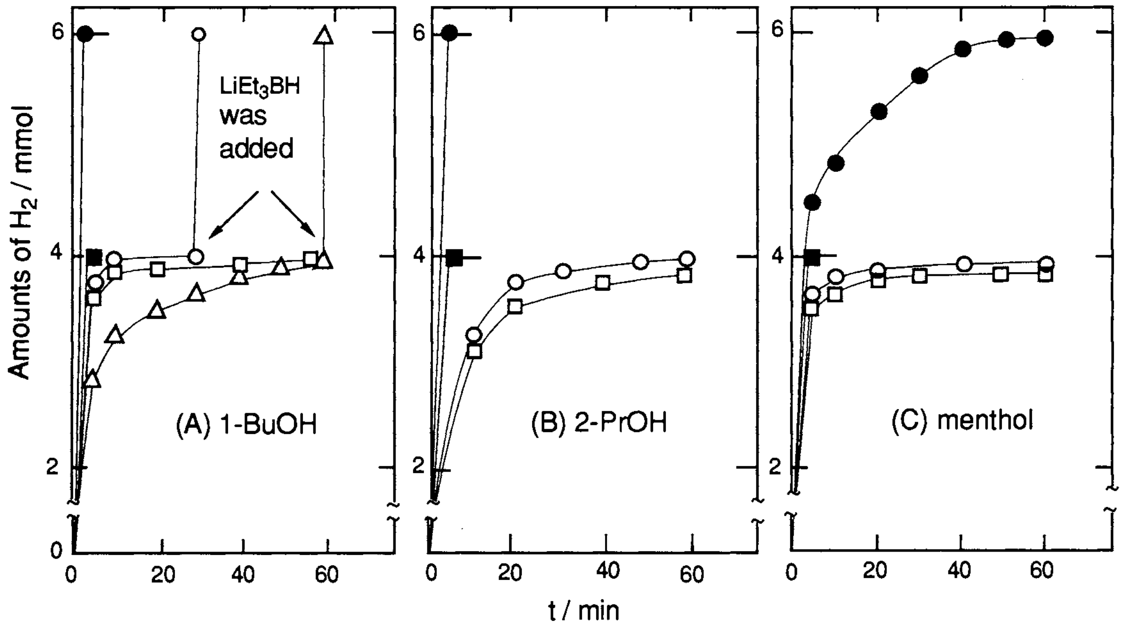


Fig.1. Amount of H_2 evolved in the reaction of 2 mmol of BH_3 in THF with 1-BuOH, 2-PrOH and menthol at 20 °C. (a) ○ ; 6 mmol of alcohol, (b) ● ; 6 mmol of alcohol and $LiBEt_3H$ (1%), (c) □ ; 4 mmol of alcohol, (d) ■ ; 4 mmol of alcohol and $LiBEt_3H$ (1%), (e) △ ; 6 mmol of 1-BuOH and 2 mmol of $H_3B{\bullet}S(CH_3)_2$.

Indeed the ^{11}B NMR spectrum of the reaction mixture showed the presence of tributoxyborane (a broad singlet peak, δ=18.3, relative to $BF_3{\bullet}Et_2O$) almost uncontaminated by other borane derivatives. From the solution obtained by a large-scaled reaction in a similar manner as above, tributoxyborane was distilled directly in 95% yield [bp 111 °C/13 mmHg, n_D^{21} 1.4088; lit., bp 115 °C/15 mmHg, n_D^{20} 1.4085 [4]] indicating that the presence of $LiBEt_3H$ did not interfere the isolation by distillation.

With other primary and relatively unhindered secondary alcohols, similar results were obtained. In Fig. 1B-a and b, the results obtained in similar reactions with 2-propanol are shown. With hindered alcohol, such as menthol, the reaction with the third hydrogen of BH_3 was sluggish under similar reaction conditions. However a prolonged reaction time led easily to the formation of the trialkoxyboranes (Fig. 1C-b).

Trialkoxyboranes can provide metal trialkoxyborohydrides, potentially useful reducing reagents.5) Although several methods have been reported for the synthesis of trialkoxyboranes,4) the most convenient method seems to be the direct reaction of BH_3 with an alcohol in a molar ratio of 1:3.

Brown et al. have reported a procedure for the preparation of trialkoxyboranes by reactions of neat $BH_3{\bullet}S(CH_3)_2$ with alcohols at room temperature for the straight chain primary alcohols and at reflux temperature for the secondary alcohols where the third reaction was very sluggish at room temperature.6) In our experiment using $BH_3{\bullet}S(CH_3)_2$, prepared by removal of Et_2O from $BH_3{\bullet}S(CH_3)_2$ in Et_2O (2M-sol.) under reduced pressure, the most of primary alcohols, except for MeOH and EtOH, and secondary alcohols could not react with the third hydrogen of BH_3 at room temperature (Fig. 1A-e). In these cases the addition of a small amount of $LiBEt_3H$ (1%) was also very effective for the promotion of the reactions.

Thus present finding provides a facile and convenient method for the syntheses of trialkoxyboranes.

Furthermore the present reaction can provide a very simple and widely applicable procedure for the preparation of dialkoxyboranes when it was carried out by using stoichiometric amounts of BH_3 in THF and an alcohol, 1:2.

$$BH_3\,(THF) \; + \; 2ROH \xrightarrow[\text{very fast}]{LiBEt_3H} (RO)_2BH \; + \; 2H_2 \qquad (3)$$

In most stoichiometric reactions the rate of the hydrogen evolution decreased markedly and it took fairly long reaction time to complete the reaction. For example in the reaction of BuOH at 20 °C the rate of the hydrogen evolution slowed down after the amount of hydrogen became about 90 % of the theoretical amount (Fig. 1A-c,). In such reactions it required rather long reaction time or higher reaction temperature to complete the reaction. However in the presence of $LiBEt_3H$ (1%) the reaction was completed spontaneously (Fig. 1A-d). The ^{11}B NMR spectrum of the resulting solution showed the presence of dialkoxyborane itself (δ=27.4, d, J=161 Hz) almost uncontaminated by other borane compounds.

Similar results were obtained in the cases of 2-propanol and menthol (Fig. 1B-c and d, Fig. 1C-c and d).

Dialkoxyboranes have never been used practically for the hydroboration of alkenes and for the reduction of the carbonyl compounds because of their less reactive property and thus need of high reaction temperature which might cause the decomposition of dialkoxyboranes.$^{7)}$

Very recently we found that the presence of a small amount of $LiBEt_3H$ also promoted markedly the hydroboration of alkenes and the reduction of carbony compounds with dialkoxyboranes under mild reaction conditions. These results will be published elsewhere.

Although we can not clarify the reaction mechanism here, the present findings seem to provide very convenient methods for the preparation of trialkoxyboranes and dialkoxyboranes.

References

1) H. C. Brown and E. F. Knight, *J. Am. Chem. Soc.,* **90**,4439 (1968).

2) A. Arase, Y. Nunokawa, Y. Masuda, and M. Hoshi, *J. Chem. Soc., Chem. Commun.,* **1991**, 251.

3) A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.,* **55**, 4020 (1933).

4) For example: M. F. Lappert, *Chem. Rev.,* **56**, 959 (1956).

5) For example: A. Pelter, K. Smith, and H. C. Brown, "Borane Reagents," Academic, London (1988).

6) C. A. Brown and S. Krishnamurthy, *J. Org. Chem.,* **43**, 271 (1978).

7) W. G. Woods and P. L. Strong, *J. Am. Chem. Soc.,* **88,** 4667 (1966); A. Suzuki, M. Yamamoto, S. Sono, and M. Itoh, *Kogyo Kagaku Zasshi,* **72**, 804 (1969); R. H. Fish, *J. Org. Chem.,* **43**, 159 (1973).

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