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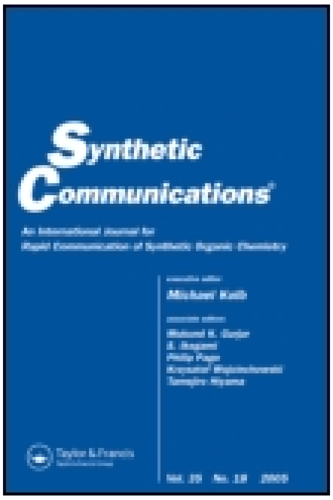

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PREPARATION OF TRIBUTYLBORANE FROM BUTYLLITHIUM AND BORON TRIFLUORIDE ETHERATE

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PREPARATION OF TRIBUTYLBORANE FROM BUTYLLITHIUM AND BORON TRIFLUORIDE ETHERATE

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ABSTRACT

A convenient laboratory synthesis of tributylborane from commercially available *n*-butyllithium and boron trifluoride etherate is developed.

Tributylborane is one of the trialkylboranes that have found wide application[1] in organic synthesis. It is for instance a versatile reagent for butylation of aryl aldehyde tosylhydrazones[2] or trifluoroethyl tosylate,[3] conversion of methylsulfones to sulfonamides,[4] and the preparation of ^{15}O-labelled butanol.[5]

This compound caught our attention because of its ability to form $(n\text{-Bu})_2$BOTf on treatment with trifluoromethanesulfonic acid.[7] This triflate

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is an excellent[6] reagent for asymmetric aldol condensation. However, it is rather expensive and commercially available only as 1.0 M solutions in low boiling organic solvents. Its high sensitivity to air also causes additional difficulty in storage. For these reasons, we chose to prepare n-Bu$_2$BOTf from triethylborane ourselves. In literature searching, we found, to our surprise, that despite its broad utility and the long history, essentially all the tributylborane used in organic synthesis over the last 60 years was prepared by Johnson's procedure using butyl Grignard reagent (Eq. 1),[8] and no-one seemed to have tried using n-butyllithium in preparation of tributylborane, although since the late 1970s n-butyllithium has been the most widely and most frequently used organometallic compound, and can be found practically in every synthetic laboratory.

$$n\text{-BuMgX} + \text{F}_3\text{B}\cdot\text{OEt}_2 \rightarrow n\text{-Bu}_3\text{B} + \text{MgXF} \qquad \text{(Eq. 1)}$$

It appears to be rather rare in organic chemistry that the preparation of a given compound essentially relies on one single procedure over some 60 years. In further literature studies we found that Brown did mention in 1986 that lithium was not suitable for preparing tributylborane,[9] when he reported a one-pot protocol. However, judging from the reaction conditions employed there, this failure to obtain tributylborane from lithium does not necessarily suggest that butyllithium could not react with boron trifluoride to form the desired alkylborane in synthetically useful yields. This consideration and the potential convenience of preparing tributylboron from n-butyllithium encouraged us to examine the reaction of commercially available n-butyllithium with boron trifluoride (Eq. 2).

$$3n\text{-BuLi} + \text{F}_3\text{B}\cdot\text{OEt}_2 \rightarrow n\text{-Bu}_3\text{B} + 3\text{LiF}. \qquad \text{(Eq. 2)}$$

Similarly to the Grignard reagent, n-butyllithium reacts violently with boron trifluoride. However, the reaction phenomenon was somewhat different from that with the Grignard reagent, where the inorganic salt formed during the reaction precipitates from solution. In some runs we obtained substantial amounts of "ate" compound, which mixed with the inorganic salt to give a sticky paste. On contact with water in the work-up, a violent exothermic reaction took place, giving off large amounts of gas (butane). This led to drastically reduced yields of tributylborane. By changing the amount of ether and the method of mixing the reactants, we obtained the most satisfactory results by adding an ethereal solution of freshly distilled boron trifluoride to n-butyllithium.[10] In this way, tributylborane can be obtained on a 30 mmol scale in *ca.* 64% distilled yield with rather narrow boiling point range.

Although using butyllithium to replace butyl Grignard reagent to react with boron trifluoride is unremarkable in theory, this work may clear the myth that the Grignard reagent must be used in this reaction. It also offers a handy route to tributylborane, which is particularly convenient for occasional small scale preparation of n-Bu$_2$BOTf.[7]

EXPERIMENTAL

BBu$_3$ is highly sensitive to air (but not sensitive to water) and therefore all operations must be carried out under N$_2$. With stirring, a solution of $BF_3 \cdot OEt_2$ (4.0 mL, 31.8 mmol) in dry ether (8 mL) was added to n-BuLi (1.5 M in hexanes, 96.0 mmol) at such a rate that the reaction mixture gradually warmed up to gentle boiling. The reaction mixture was then heated to reflux for 2 h. After cooling to rt 3 N HCl (20 mL, exothermic) was introduced, followed by more water (20 mL). The mixture was transferred *via* a cannula into a separating funnel. The lower (aqueous) phase and precipitates were separated and the upper (organic) phase was transferred into a flask containing anhydrous Na$_2$SO$_4$. The supernatant was transferred into a distillation flask and all low-boiling solvents were distilled off. The remainder was then distilled *in vacuo* (bp 70–71°C/4 mmHg) to give BBu$_3$ as a colorless liquid (3.683 g, 63.8%).

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