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One-Pot Synthesis of Ammonia–Borane and Trialkylamine–Boranes from Trimethyl Borate

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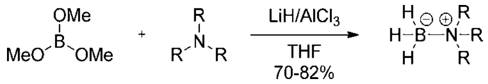
ABSTRACT



A one-pot procedure for the preparation of ammonia borane from trimethyl borate in 90% yield and >99% purity has been reported. This methodology has been modified to prepare a series of trialkylamine–boranes in 70–82% yields from trimethyl borate and lithium hydride/aluminum chloride in the presence of the corresponding trialkylamine.

Amine–boranes, with their wide range of reactivity, have found numerous applications in organic synthesis.[1,2] Apart from their traditional use as reagents for the reduction of carbonyls,[3] reductive amination,[4] hydroboration of alkenes,[5] and transfer hydrogenation,[6] amine–boranes have also been employed as curing agents or accelerators for the preparation of epoxy resins,[7] as reductive bleaching agents,[8] and in electroless plating applications.[9] More recently, the synthesis of nanoparticles using amine–boranes has attracted substantial attention from materials chemists.[10] Their use as borane carriers for exchange reactions has also been demonstrated.[11]

Additionally, ammonia–borane (AB) and other amine–boranes have received enormous attention as hydrogen carriers for energy storage applications because of their high hydrogen content and recycling prospects.[12] A practical, energy efficient, and cost-effective synthesis remains a significant challenge for these amine–boranes to realistically become an energy carrier. Various methods have been reported for the preparation of AB[13] and amine–boranes,[14]

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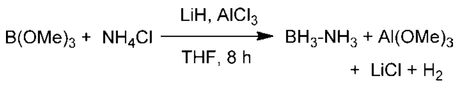
mostly using either diborane or metal borohydrides. One of these[13a] describes a large-scale preparation of ammonia–borane using sodium borohydride ($NaBH_4$), which in turn, is industrially prepared using Schlesinger's protocol from trimethyl borate [$B(OMe)_3$] and sodium hydride (NaH) at 270 °C.[15] We have since reported a one-pot $AlCl_3$ mediated formation of $NaBH_4$ and $LiBH_4$ from $B(OMe)_3$ in the presence of the appropriate metal hydride (MH) under ambient conditions.[16] Herein, we report a novel, one-pot synthesis of AB and other trialkylamine–boranes directly from $B(OMe)_3$.

Table 1. Examination of Ammonium Salts for the Preparation of AB from $B(OMe)_3$ and $LiH/AlCl_3$



$$B(OMe)_3 + NH_4Cl \xrightarrow[\text{THF, 8 h}]{\text{LiH, AlCl}_3} BH_3\text{-}NH_3 + Al(OMe)_3 + LiCl + H_2$$

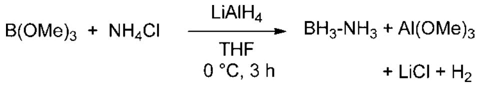
entry	NH_4X	yield[a] (%)
1	NH_4Cl	68
2	NH_4F	54
3	$(NH_4)_2SO_4$	59
4	$(NH_4)_2CO_3$	63
5	NH_4OAc	NR[b]
6	NH_4NO_3	NR[b]

[a] Isolated yield. [b] NR = no reaction.

On the basis of our one-pot synthesis of $NaBH_4$ and $LiBH_4$ from $B(OMe)_3$,[16] coupled with our synthesis of AB from $NaBH_4$,[13a] we envisaged a one–pot synthesis of AB from $B(OMe)_3$. Accordingly, $AlCl_3$ dissolved in tetrahydrofuran (THF) was added to a suspension of $B(OMe)_3$, lithium hydride (LiH), and ammonium chloride (NH_4Cl) in dry THF at room temperature (rt). The reaction, monitored by ^{11}B NMR spectroscopy, was complete within 8 h. Extraction with diethyl ether provided a 68% yield of analytically pure AB. Other ammonium salts, such as ammonium fluoride, sulfate, and carbonate, afforded only moderate yields of AB (Table 1). Ammonium nitrate and acetate failed to provide any of AB. The corresponding reaction with NaH and ammonium chloride provided only poor yields (< 25%) of AB.

With an aim to improve upon this result, we replaced $LiH/AlCl_3$ with lithium aluminum hydride (LAH). However, the addition of $B(OMe)_3$ to a solution of LAH and NH_4Cl in THF at rt resulted in the formation of AB in only 46% yield. Changing the solvent to diethyl ether did not improve the yield. A careful analysis revealed that the low yield might be due to the reaction of LAH and NH_4Cl to produce aluminum nitride and LiCl, with the concurrent liberation of hydrogen. Consequently, the temperature and mode of addition were modified.

Scheme 1. Preparation of AB from $B(OMe)_3$ Using $LiAlH_4$



$$B(OMe)_3 + NH_4Cl \xrightarrow[\text{THF, 0 °C, 3 h}]{LiAlH_4} BH_3\text{-}NH_3 + Al(OMe)_3 + LiCl + H_2$$

Table 2. Examination of Ammonium Salts for the Preparation of AB from $B(OMe)_3$ and LAH

entry	ammonium salt	yield[a] (%)
1	NH_4Cl	90
2	NH_4F	67
3	$(NH_4)_2SO_4$	59
4	$(NH_4)_2CO_3$	63
5	NH_4NO_3	47
6	NH_4OAc	42

[a] Isolated yield.

Thus, LAH in THF was added to a mixture of $B(OMe)_3$ and NH_4Cl in THF at 0 °C over a period of 1 h and stirred for 3 h at the same temperature to obtain, after ethereal extraction, 90% isolated yield of AB (Scheme 1). A ^{11}B NMR spectroscopic analysis as well as hydrogen estimation via hydrolysis revealed > 99% chemical purity. Again, other ammonium salts, such as ammonium fluoride, sulfate, nitrate, carbonate, and acetate, provided poorer yields of AB (Table 2).

We surmised that the poor yields obtained earlier during the $AlCl_3$-mediated reaction of trimethyl borate, LiH, and NH_4Cl (Table 1) could be due to the liberation of gaseous diborane from the presumed intermediate $LiBH_4$ and/or a lack of reactivity of the ammonium salts under the reaction conditions. This prompted us to capture the liberated diborane as a trialkylamine–borane complex by conducting the reaction in the presence of trialkylamines to achieve a novel *one-pot* synthesis of such amine–boranes.

To our delight, a reaction of trimethyl borate with $LiH/AlCl_3$ in the presence of triethylamine provided the corresponding amine–borane in 70% isolated yield (Scheme 2).[17] The increased yield is attributed to the instant capture of the diborane generated from the borohydride in the presence of $AlCl_3$. In an optimized reaction, $B(OMe)_3$ was added to the suspension of LiH (5.5 equiv) in THF followed by the addition of Et_3N (0.75 equiv). The reaction mixture was

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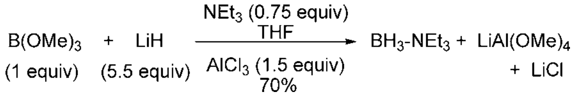
(17) A similar reaction of $B(OMe)_3$ and LAH in the presence of triethylamine provided only 45% isolated yield of triethylamine–borane.

Scheme 2. Preparation of Triethylamine Borane



$$\underset{\text{(1 equiv)}}{B(OMe)_3} + \underset{\text{(5.5 equiv)}}{LiH} \xrightarrow[\substack{AlCl_3\text{ (1.5 equiv)} \\ 70\%}]{\substack{NEt_3\text{ (0.75 equiv)} \\ THF}} BH_3\text{-}NEt_3 + LiAl(OMe)_4 + LiCl$$

vigorously stirred at rt for 1 h and was monitored by ^{11}B NMR spectroscopy for the chemical shift change from δ (ppm) 19 to 3.[18] Aluminum chloride (1.5 equiv) dissolved in THF was then added, dropwise, at 0 °C, over a period of 1 h, and the stirring was continued at rt until the reaction was complete, as determined by the change in ^{11}B NMR spectroscopic chemical shift to −13.3 (q). The solvent was removed under reduced pressure, and the residue was stirred in anhydrous pentane for 1 h and filtered through Celite under inert atmosphere. Removal of pentane in vacuo provides the amine−borane complex. The reaction was repeated with other metal hydrides such as NaH and calcium hydride to obtain triethylamine−borane in 66% and 68% yields, respectively. Magnesium hydride did not provide the amine−borane. A brief screening of Lewis acids showed that zinc chloride and zirconium tetrachloride were equally effective under similar conditions.

With the optimal procedure in hand, we turned our attention to the preparation of a series of trialkylamine−boranes.

Table 3. Preparation of Amine−Boranes via the Reaction of $B(OMe)_3$ with LiH and $AlCl_3$ in the Presence of Amines

entry	amine−borane	^{11}B NMR[a] (δ) (ppm)	yield[b] (%)
1	BH_3-NEt_3	−13.3 (q)	70
2	i-Pr_2NEt-BH_3	−13.4 (q)	73
3	DMAP-BH_3	−13.7 (q)	72
4	2,6-Lutidine-BH_3	−17.9 (q)	74
5	2,6-Lutidine-BH_3	−17.9 (q)	77[c]
6	2,4,6-Collidine-BH_3	−18.4 (q)	82
7	DABCO-$(BH_3)_2$	−11.0 (q)	80

[a] Multiplicity q = quartet. [b] Isolated yield. [c] 20 g scale reaction.

Accordingly, *N*,*N*-diisopropylethylamine, 4-dimethylaminopyridine, 2,6-lutidine, 2,4,6-collidine, and 1,4-diazabicyclo[2.2.2]octane (DABCO) were utilized to prepare the corresponding amine-boranes from $B(OMe)_3$ in the presence of LiH and $AlCl_3$ in good to excellent yields (Table 3). While the bisborane−DABCO adduct was formed cleanly (entry 7), the monoborane−DABCO adduct was not pure. The ^{11}B NMR spectral data is also summarized in Table 3.

After demonstrating the generality of the reaction, we examined the feasibility of this protocol for large-scale applications. Accordingly, the reaction was repeated with 20 g (0.192 mol) of $B(OMe)_3$ in the presence of 2,6-lutidine and LiH, which provided 2,6-lutidine−borane in 77% yield.

In summary, we have reported a new and economical procedure for the preparation of ammonia borane and trialkylamine−boranes from trimethyl borate. The known procedures for preparation of trialkylamine−borane involve reaction of (i) other complexes of borane, such as BH_3-SMe_2 or BH_3-THF or in situ generated gaseous diborane with trialkylamine,[19,20] (ii) lithium borohydride with ammonium salt,[21] or (iii) transamination of existing amine−borane.[22] The advantage of our protocol is that the preparation begins with the precursor of the borohydrides $B(OMe)_3$. The reaction has been demonstrated on a molar scale. The optimal yield for AB is achieved using LAH as the hydride source, whereas the LiH/$AlCl_3$ combination provided optimal yields of trialkylamine boranes. Utilization of either LAH or LiH/$AlCl_3$ under mild conditions, in contrast to the relatively expensive NaH[23] and energy-intensive reaction (high temperature) conditions used in the industrial protocol,[24] makes this scalable process[25] more economical. We believe that this synthesis will find applications in organic synthesis[1−10] and the efficient synthesis of ammonia−borane will aid in hydrogen storage research.

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Supporting Information Available. Experimental procedures and compound characterization data/spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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(18) Vigorous stirring and the purity of LiH is crucial for the complexation, which is critical for good yields of the amine−boranes Additional time (up to 4 h) and lower yields are observed otherwise.

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(25) **Preparation of AB from $B(OMe)_3$ Using $LiAlH_4$.** Trimethyl borate (0.5 g, 0.0048 mol) was added under nitrogen atmosphere to a suspension of ammonium chloride (0.518 g, 0.0096 mol) in THF (24 mL) at 0 °C. Under vigorous stirring, lithium aluminum hydride (0.23 g, 0.0057 mol) in THF (12 mL) was added, dropwise, over a period of 1 h at the same temperature. The reaction mixture was warmed to room temperature and stirred for 2 h. The ^{11}B NMR shows the formation of AB (δ (ppm): −21.6 (q). The solvent was distilled under reduced pressure at rt to obtain a powdery solid residue, which was suspended in cold diethyl ether at 0 °C and stirred for 30 min. The cold ether layer was filtered and the solvent was removed in vacuo to obtain 0.133 g (90%) of ammonia-borane as a white crystalline solid in >99% purity. **Representative Procedure for the Preparation of Amine−Boranes.** Trimethyl borate (0.5 g, 0.0048 mol) was added, under nitrogen atmosphere at rt, to a suspension of lithium hydride (0.210 g, 0.0264 mol) and triethylamine (0.5 mL, 0.0036 mol) in THF (10 mL) contained in an oven-dried round-bottom flask. The reaction mixture was stirred for 1 h and was monitored by ^{11}B NMR spectroscopy (change in chemical shift δ (ppm) from +19 to +3). (Note: Depending on the vigor of stirring this may take up to 4 h.) Aluminum chloride (0.960 g, 0.0072 mol) dissolved in THF (10 mL) was then added, dropwise, over a period of 1 h, at 0 °C, and the stirring was continued at rt until the reaction was judged to be complete by ^{11}B NMR spectroscopy (chemical shift δ (ppm): −13.3 (q)). The solvent was removed under reduced pressure via cannula distillation under inert atmosphere, the residue was stirred with anhydrous pentane for 1 h and filtered through Celite under nitrogen atmosphere, and the solvent was removed in vacuo to obtain triethylamine−borane complex as a colorless liquid, 289 mg, 70%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.79 (q, J = 7.3 Hz, 6H), 0.75−2.00 (broad q, BH_3), 1.19 (t, J = 7.3 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 52.1, 8.3. ^{11}B NMR (96 MHz, $CDCl_3$) δ (ppm): −13.32 (q, J = 95.0 Hz).