hydrolyzed species) in the range of interest (335–365 nm), it is unfortunately not possible to decide with certainty from the observation of the UV spectra whether 1:3 complexes form at all.

The fact that 1,2-dihydroxynaphthalene-4-sulfonic acid does not form 1:3 complexes below pH 7 seems to be a favorable factor for subsequent studies on catalytic properties of the complex $Fe^{III}P_2$ in the oxidation of certain organic compounds by oxygen. Two of the coordination sites on Fe(III) are available for reaction with oxygen as shown in the scheme proposed by Tyson and Martell[3] for certain diphenolic complexes of Mn(II) and for the Fe(III)- and Cu(II)-catalyzed oxidation of ascorbic acid. Such a complex might then act as an intermediate for electron transfer to oxygen. This conclusion seems to be confirmed by some results already obtained in the preliminary studies in this field.[5]

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Registry No. PH_2, 16223-99-7; Fe(II), 15438-31-0; Fe(III), 20074-52-6.

References and Notes

(1) M. M. T. Khan and A. E. Martell, *J. Am. Chem. Soc.*, **89**, 4176, 7104 (1967); **90**, 3386 (1968).
(2) K. Eckschlager, I. Horsak, and J. Veprek-Siska, *Collect. Czech. Chem. Commun.*, **39**, 2353 (1974).
(3) C. A. Tyson and A. E. Martell, *J. Am. Chem. Soc.*, **94**, 939 (1972).
(4) J. Buffle, report to Fonds Philippe Chuit (unpublished work), 1973.
(5) J. Buffle and A. E. Martell, *Inorg. Chem.*, preceding paper in this issue.
(6) R. M. Smith and A. E. Martell, "Critical Stability Constants", Vol. III, Plenum Press, New York, N.Y., 1977.
(7) A. Willi and G. Schwarzenbach, *Helv. Chim. Acta*, **34**, 528 (1951).
(8) Y. Murakami and K. Nakamura, *Bull. Chem. Soc. Jpn.*, **36**, 1408 (1963).
(9) G. Heller and G. Schwarzenbach, *Helv. Chim. Acta*, **35**, 812 (1952).

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Addition Compounds of Alkali Metal Hydrides. 13. Reactions of Alkali Metal Hydrides with Trialkylboranes. Synthesis and Dissociation of Alkali Metal Trialkylborohydrides. Ethyl Ether–Organoborane as a Reversible "Solvent" for Lithium Hydride[1]

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Lithium hydride reacts with trimethyl- and triethylborane in ethereal solvents to give the corresponding lithium trialkylborohydrides as monoetherates. Removal of the solvent from the monoetherate adduct is possible leaving behind the solvent-free alkali metal trialkylborohydrides. These can be reversibly decomposed by heating to yield "activated" lithium hydride and trialkylborane. Sodium hydride reacts with trialkylboranes in the absence of solvents yielding sodium trialkylborohydrides. The corresponding reactions with commericial lithium hydride do not proceed. However, the "activated" lithium hydride does react with trialkylboranes in the absence of solvents to form unsolvated lithium trialkylborohydrides. Thus, a mixture of trialkylborane and ethyl ether can be considered to be a reversible "solvent" for lithium hydride, permitting its solution and recovery in active form.

Introduction

Addition compounds of alkali metal hydrides with trialkylboranes were first discovered during the course of war research (1942–1943).[3] Except for their brief observation, very little attention was devoted to exploring the chemistry of these derivatives in preference to matters which were more important at the time. This study revealed that lithium hydride in ether reacts with trimethylborane to form a solid etherate of lithium trimethylborohydride which reversibly decomposes at elevated temperature to give back the ether, lithium hydride, and trimethylborane. It was also noted that lithium hydride in the absence of ether would not react with trimethylborane. However, triethylborane reacted vigorously with sodium hydride in the absence of solvents to form an acid–base adduct, unsolvated sodium triethylborohydride ($NaEt_3BH$). The synthesis and properties of alkali metal triphenylborohydrides were briefly explored in ethereal solvents.[4] More recently, reaction of alkali metal hydrides with trialkylboranes has been examined in considerable detail.[5] Unfortunately, the majority of these reactions have been carried out under drastic reaction conditions, resulting in rather poor yields of the trialkylborohydrides. Thus a lack of systematic and organized research on these derivatives was evident. Consequently, we undertook a systematic study of the reaction under mild standardized conditions of alkali metal hydrides with trialkylboranes. The results of this investigation are reported in the present paper.

Results and Discussion

Trimethyl- and triethylborane were selected as representative trialkylboranes. Their reactivity toward lithium hydride and sodium hydride in the absence and presence of various ethereal solvents was investigated. The majority of these reactions were carried out in vacuum lines, and the course of the reaction was monitored by vapor pressure–composition measurements.

Table I. Pressure–Composition Data for the Lithium Hydride–Trimethylborane–Ethyl Ether System at 0 °C[a]

Me_3B added,[b] mmol	Mole ratio Me_3B/LiH	Total pressure, mm
0	0	186
0.454	0.288	185
0.728	0.461	182
1.36	0.857	177
1.56	0.982	173
2.38	1.51	228
2.99	1.89	261
3.48	2.20	301

[a] Initial amounts of lithium hydride and ethyl ether were 1.58 and 10.3 mmol, respectively. [b] The numbers indicate the cumulative amount added.

Vapor Pressure–Composition Studies. Lithium Hydride–Trimethylborane–Ethyl Ether System. Lithium hydride reacts with trimethylborane in the presence of ethyl ether at 0 °C to form the 1:1 complex lithium trimethylborohydride (eq 1).

$$\mathrm{LiH} + \mathrm{Me_3B} \xrightarrow[0\,^{\circ}\mathrm{C}]{\mathrm{Et_2O}} \mathrm{LiMe_3BH} \qquad (1)$$

The addition of incremental amounts of trimethylborane to a mixture of lithium hydride and ethyl ether results in a gradual but slow decrease in the total pressure of the system

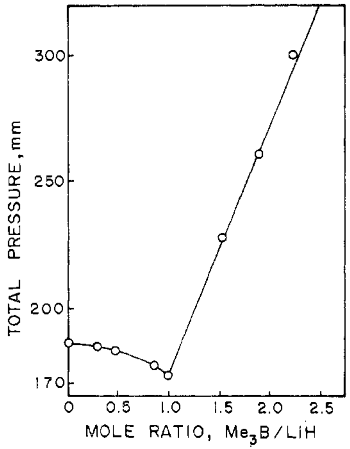

Figure 1. Pressure-composition plot for the lithium hydride–trimethylborane–ethyl ether system at 0 °C.

Table II. Pressure-Composition Data for the Lithium Trimethylborohydride-Ethyl Ether System at 0 °C[a]

Et_2O removed, mmol	Et_2O remaining, mmol	Mole ratio $Et_2O/LiMe_3BH$	Pressure, mm
3.29	9.89	3.90	156
5.87	7.31	2.88	114
7.65	5.53	2.18	73
10.2	2.95	1.16	27
10.8	2.36	0.93	3
11.0	2.14	0.85	2[b]
11.1	2.08	0.82	2
11.2	1.96	0.77	2
11.7	1.45	0.57	2
12.0	1.13	0.44	2
12.2	1.03	0.41	0.5
12.3	0.93	0.37	0.3

[a] Initial amounts of $LiMe_3BH$ and Et_2O were 2.6 and 13.2 mmol, respectively. [b] White solid, presumably $LiMe_3BH·Et_2O$.

until the ratio of Me_3B/LiH is one. The slight decrease in pressure over the value for ethyl ether itself is attributed to the solubility of the lithium trimethylborohydride in the ether. Further addition of trimethylborane results only in an increase in pressure, the slope corresponding to the solubility of trimethylborane in ethyl ether. The results are summarized in Table I and represented graphically in Figure 1.

A study of the lithium trimethylborohydride–ethyl ether system clearly indicated the existence of a monoetherate of lithium trimethylborohydride as a white solid, readily isolated upon removal of measured amounts of ether from the system. Removal of the ethyl ether results in a decrease of pressure until a ratio of $Et_2O/LiMe_3BH = 1$ is reached. Thereafter a constant pressure of 2.0 mm is maintained until the ratio of $Et_2O/LiMe_3BH$ reaches 0.5. The pressure then drops to 0.4 mm (eq 2–4). The data, Table II, are represented graphically in Figure 2.

$$2LiMe_3BH·Et_2O \rightarrow [LiMe_3BH]_2·Et_2O + Et_2O \quad (2)$$

$$[LiMe_3BH]_2·Et_2O \rightarrow 2LiMe_3BH + Et_2O \quad (3)$$

$$LiMe_3BH \xrightarrow{50\ ^\circ C} LiH + Me_3B \quad (4)$$

These results and interpretations are further supported by a study involving the removal of volatile vapors from the lithium hydride–trimethylborane–ethyl ether system. It is evident from the results summarized in Table III that ether can be essentially removed at 0 °C to give unsolvated lithium trimethylborohydride, a white solid at room temperature. Some trimethylborane can be slowly removed at 0 °C. However, the removal is facilitated at 50 °C and essentially all of the trimethylborane can be readily recovered at that temperature.

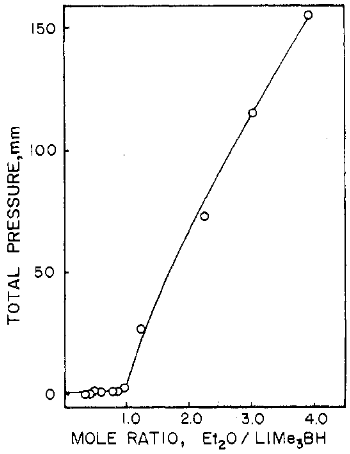

Figure 2. Pressure-composition plot for the lithium trimethylborohydride–ethyl ether system at 0 °C.

Table III. Reversibility of the Lithium Hydride-Trimethylborane-Ethyl Ether System

Compd	Initial amount, mmol	Amount removed at 0 °C, mmol	Amount removed at 50 °C, mmol
LiH	0.88		
Me_3B	0.88	0.12	0.77
Et_2O	7.30	7.04	0.21

Table IV. Pressure-Composition Data for the Lithium Hydride-Trimethylborane-*n*-Butyl Ether System at 0 °C[a]

Me_3B added, mmol	Mole ratio, Me_3B/LiH	Total Pressure, mm
0.540	0.231	1.19
1.13	0.485	1.11
1.71	0.732	1.15
2.29	0.978	1.18
2.54	1.09	23.7
2.91	1.25	47.5
3.62	1.55	97.3

[a] Initial amounts of lithium hydride and *n*-butyl ether were 2.34 and 17.1 mmol, respectively.

Lithium Hydride–Trimethylborane–*n*-Butyl Ether System. In *n*-butyl ether lithium hydride readily reacts with trimethylborane at 0 °C to form lithium trimethylborohydride (eq 5). As trimethylborane is added in incremental amounts, the total pressure remains essentially constant until the ratio Me_3B/LiH exceeds 1, whereupon it increases, corresponding to the solubility of trimethylborane in *n*-butyl ether. A study of the reversibility of the lithium hydride–trimethylborane–*n*-butyl ether system by collecting volatile vapors when the system was heated showed that a yield of 96% of the trimethylborane initially present could be recovered easily at about 150 °C.

$$LiH + Me_3B \underset{150\ ^\circ C}{\overset{0\ ^\circ C}{\rightleftharpoons}} LiMe_3BH \quad (5)$$

The data are summarized in Table IV.

Lithium Hydride–Triethylborane–Ethyl Ether System. In the presence of excess ethyl ether, lithium hydride reacts with triethylborane and ethyl ether in a ratio of 1:1:1 to form the monoetherate of lithium triethylborohydride at 0 °C (eq 6).

$$LiH + Et_3B + Et_2O \xrightarrow[Et_2O]{0\ ^\circ C} LiEt_3BH·Et_2O \quad (6)$$

The removal of the ether from the adduct, a liquid at room

Table V. Pressure-Composition Data for the Lithium Triethylborohydride-Ethyl Ether System at 0 °C

Et_2O removed, mmol	Et_2O remaining, mmol	Et_3B removed, mmol	Et_3B remaining, mmol	Mole ratio $Et_2O/LiEt_3BH$	Pressure, mm
0	15.4	Trace[a]	4.07	3.80	128
2.57	12.9	Trace	4.07	3.16	108
2.57	10.3	Trace	4.07	2.53	76
2.29	8.01	Trace	4.07	1.97	32
0.58	7.43	Trace	4.07	1.82	19
2.17	5.26	0.09	3.98	1.32	5.0
1.17	4.09	Trace	3.98	1.03	1.4
1.39	2.70	Trace	3.98	0.68	0.6
0.95	1.75	Trace	3.98	0.44	0.6
0.66	1.09	Trace	3.98	0.27	0.6
1.12	0	Trace	3.98	0	0.1

[a] These trace amounts were stored until enough was collected to be measured.

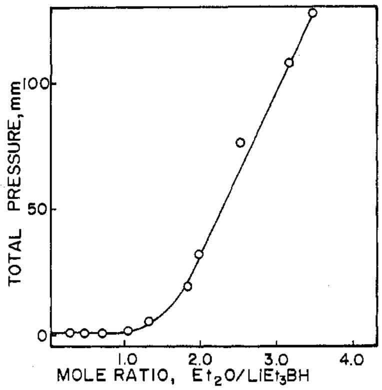

Figure 3. Pressure–composition plot for the lithium triethylborohydride–ethyl ether system at 0 °C.

temperature, can be accomplished slowly at 0 °C and faster at higher temperatures (eq 7). The white solid adduct, lithium triethylborohydride, melts around 85 °C where it is partially dissociated into lithium hydride and triethylborane (eq 8).

$$LiEt_3BH{\cdot}Et_2O \xrightarrow{25\,^\circ C} LiEt_3BH + Et_2O \tag{7}$$

$$LiEt_3BH \xrightarrow{85\,^\circ C} LiH + Et_3B \tag{8}$$

This was verified by reacting lithium hydride with triethylborane in a ratio of 1:1 with an excess measured amount of ethyl ether present. Ethyl ether was then removed in incremental measured amounts, accompanied by only trace amounts of triethylborane. It is evident from the results summarized in Table V and Figure 3 that removing ethyl ether results in a drop in pressure until the ratio $Et_2O/LiEt_3BH$ is 1, whereupon a constant pressure is attained. The remaining ether can be removed with only traces of triethylborane being present. Continued collection of vapors then results only in the removal of triethylborane.

Reaction of Lithium Hydride and Sodium Hydride with Trialkylboranes in the Absence of Solvents. In the absence of solvents, lithium hydride does not react at room temperature to any appreciable extent with either trimethylborane or triethylborane over a period as long as 24 h (eq 9).

$$LiH + Et_3B \xrightarrow[24\ h]{25\,^\circ C} \!\!\!\!\!\!\!/\!/\;\; LiEt_3BH \tag{9}$$

However, sodium hydride readily reacts under these conditions with trimethylborane and triethylborane in a ratio of 1:1 (eq 10 and 11). The reaction of trimethylborane with sodium hydride was quite sluggish, producing a white solid which melted between 75 and 80 °C. Recrystallized material exhibits mp 76 °C.[5] Upon melting, the solid turned into a dark liquid. Heating the solid to 130–140 °C resulted in the recovery of 77% of the trimethylborane originally present. Some noncondensable vapor (at–196 °C), assumed to be hydrogen, was also produced.

$$NaH + Me_3B \rightarrow NaMe_3BH \tag{10}$$

$$NaH + Et_3B \rightarrow NaEt_3BH \tag{11}$$

Sodium triethylborohydride, from the direct reaction of neat sodium hydride and triethylborane, is produced as an oily liquid. Recrystallized product exhibits mp 30 °C.[5] The liquid adduct[6] is soluble in benzene and stable at room temperature. Heating to 135–150 °C results in essentially a quantitative recovery of the triethylborane. However, a small amount of noncondensable vapor is produced along with a trace amount of an unidentified condensable vapor.

Although commercial lithium hydride does not react with trialkylboranes, lithium hydride recovered from the decomposition of either $LiMe_3BH{\cdot}Et_2O$ or $LiEt_3BH{\cdot}Et_2O$ reacts readily with both trimethylborane and triethylborane in the absence of solvents in a ratio of 1:1 to form the corresponding unsolvated lithium trialkylborohydrides. The enhanced reactivity of this "activated" lithium hydride may be attributed to two factors: (i) the cleaning of the surface of the commercial lithium hydride of oxides or other coatings; (ii) formation of the lithium hydride in an expanded state. This lowers the crystal lattice energy of the sample to a point where a reaction occurs with both trimethylborane and triethylborane in the absence of a solvent.

Preparation of Solvent-Free Lithium Triethylborohyride. Solutions of lithium triethylborohydride in ethyl ether are conveniently prepared by stirring together triethylborane and lithium hydride (moderate excess) in refluxing ethyl ether for 24 h. As stated in the earlier section, removal of ether can be easily carried out under vacuum (0.1–0.2 mm) at room temperature in about 24 h to give ether-free lithium triethylborohydride as white crystalline needles in excellent yield.

Solvent-free lithium triethylborohydride is highly reactive toward both water and atmospheric oxygen, resulting in vigorous reactions. It is not only very soluble in ethereal solvents but also moderately soluble in nonethereal solvents, such as benzene, toluene, and *n*-hexane, readily forming solutions (0.42–0.46 M) at room temperature.

The significance of this procedure is that it provides a simple, convenient procedure for the preparation of unsolvated lithium triethylborohydride without the drastic conditions previously required.[5] For instance, we have observed that commercial lithium hydride fails to react with triethylborane to any significant extent in benzene in 24 h at 80 °C (eq 12). Thus, preparation of lithium triethylborohydride in ethyl ether and removal of the solvent to produce the unsolvated salt, followed

$$LiH + Et_3B \xrightarrow[80\,^\circ C,\ 24\ h]{C_6H_6} \!\!\!\!\!\!\!/\!/\;\; LiEt_3BH \tag{12}$$

by solution of the salt in benzene or related solvents, provide solutions of the adduct in various solvents difficult to achieve by direct procedures.

Conclusion

Both trimethylborane and triethylborane react readily with finely divided sodium hydride to produce the corresponding sodium trialkylborohydrides, $NaMe_3BH$ and $NaEt_3BH$. However, these boranes fail to react with finely divided lithium hydride under comparable conditions. In the presence of ether solvents, such as ethyl ether and *n*-butyl ether, reaction readily occurs to give the corresponding lithium trialkylborohydrides, $LiMe_3BH$ and $LiEt_3BH$, in solution. These can be isolated as 1:1 solvates with the ether solvents.

In the case of the ethyl ether derivatives, the solvents can be removed by pumping at moderate temperatures without loss of the organoboranes, providing the corresponding unsolvated trialkylborohydrides, $LiMe_3BH$ and $LiEt_3BH$. These materials can be dissolved in solvents such as benzene, toluene, and *n*-hexane to give solutions which cannot be obtained directly by the reaction of lithium hydride with the trialkylboranes in these solvents.

Finally, the unsolvated lithium trimethylborohydride and lithium triethylborohydride readily dissociate into lithium hydride and the corresponding organoborane at moderate temperatures. Lithium hydride thus prepared is enormously more active than the commercial material and readily reacts with the trialkylboranes in the absence of solvents to form the unsolvated trialkylborohydrides.

In a sense, then, a mixture of trialkylborane and ethyl ether can be considered to be a reversible "solvent" for lithium hydride, permitting its solution and recovery in active form.

Experimental Section

Materials. The lithium hydride and sodium hydride were obtained from Ventron Corp. The lithium hydride was a gray, finely divided powder which analyzed 93.9% based upon the hydrogen released on hydrolysis. In several experiments which were carried out in initial phases of this program, the lithium hydride was less pure, 88.5%. The sodium hydride was a dark, fairly coarse material which analyzed 93.1% based upon the hydrogen evolved on hydrolysis. The lithium hydride and sodium hydride were introduced into the reaction system by means of small glass ampules. The method of preparing them involved the utilization of small rubber-stoppered glass ampules which were dried and weighed empty. The hydride was then placed in the ampules through a small funnel in a dry, nitrogen-filled glovebox. The use of the funnel ensured that the hydride would settle to the bottom of the ampules and would prevent loss in the subsequent seal-off operation. The ampules were then unstoppered and sealed off under a nitrogen atmosphere. In the seal-off operation the glass was pulled thin so that the ampule could be broken in the reaction system by dropping a Teflon stirring bar on it. Trimethylborane was prepared by reacting boron trifluoride with methylmagnesium iodide in *n*-butyl ether. The material was purified by releasing the gas from the trimethylamine adduct with hydrogen chloride.[7,8] The vapor pressure of the tensimetrically pure material was 29 mm at −80 °C. Boron trifluoride used in the preparation of trimethylborane was purified through the preparation and subsequent thermal dissociation of the anisole addition compound.[9] The tensimetrically pure material had a vapor pressure of 305 mm at −111.8 °C. Trimethylamine was placed over phosphorus pentoxide[10] for about a day before storage and subsequent usage. The vapor pressure of the tensimetrically pure amine was 681 mm at 0 °C. Hydrogen chloride was prepared by adding hydrochloric acid to sulfuric acid.[8] The tensimetrically pure material had a vapor pressure of 125 mm at −111.8 °C. Triethylborane was obtained from the Callery Chemical Co. The material obtained directly from the tank was impure and contained both high volatile and low volatile contaminants. It was generally necessary to fractionate small portions just before usage. The vapor pressure of triethylborane was 12–13 mm at 0 °C. The ethyl ether employed was from a freshly opened can from Mallinckrodt, Inc. It was distilled into the vacuum line from lithium aluminum hydride. The vapor pressure at 0 °C was 189 mm. The *n*-butyl ether was distilled twice from calcium hydride (bp 140.2–140.3 °C, 746 mm). It was transferred into the vacuum line by distilling out of lithium aluminum hydride. The vapor pressure was 1.1 mm at 0 °C.

Apparatus and Techniques. Except for the purification of solvents, preparation of crude trimethylborane, and titrations for lithium and sodium ions, all pressure–composition experiments were carried out in an all-glass vacuum system using standard techniques.[11] The portion of the apparatus in which most of the experiments were run consisted of a reaction flask, manometer, and trap separated from the rest of the vacuum line by two mercury valves.

Analyses. The analysis of the lithium hydride and sodium hydride was based upon the hydrogen released after hydrolysis. The analysis of the lithium hydride used in the early work was based on the hydrogen measured by displacing water in a gas burette. Later hydrogen measurements for both lithium and sodium hydride were made by means of an automatic Toepler pump. Volatile substances were generally measured as gases on the vacuum line. During the measurements, the pressure of the gases was kept around 50% of the vapor pressures at room temperature in order to prevent deviations from ideality. When a large amount of solvent was utilized, measurements were usually made by distilling out of a weighing bottle, the bottle being weighed before and after removal of solvent. Identification of volatile substances was made by vapor pressure measurements.

Reaction of Lithium Hydride with Trimethylborane in Ethyl Ether at 0 °C (Pressure–Composition Experiment). Lithium hydride, 1.58 mmol, and ethyl ether, 10.3 mmol, were placed in the reaction flask, and trimethylborane was added in increments. The equilibrium pressures at 0 °C were followed. An initial induction period of approximately 2.5 h was noted in the initial phase, presumably a consequence of surface impurities on the lithium hydride. The data are summarized in Table I and shown graphically in Figure 1.

The Lithium Trimethylborohydride–Ethyl Ether System at 0 °C. Lithium hydride, 2.54 mmol, and ethyl ether, 13.2 mmol, were introduced into the reaction flask, along with 3.26 mmol of trimethylborane. The reaction was allowed to proceed at 0 °C. After 4 h, the reaction appeared to be complete, with no further pressure decrease observed. The flask was maintained at −80 °C, as volatile materials were removed for 30 min. Trimethylborane, 0.66 mmol, was recovered. Thus, 2.60 mmol of trimethylborane had reacted with 2.54 mmol of lithium hydride. Vapors were then removed in increments at 0 °C and collected in a liquid nitrogen trap, and pressure changes were noted. Ether was separated from very small amounts of trimethylborane which accompanied the ether. The trimethylborane was then returned to the reaction flask. The data (Table II) are represented graphically in Figure 2.

Reversibility of the Lithium Hydride–Trimethylborane–Ethyl Ether System. Lithium hydride (0.88 mmol), ethyl ether (7.30 mmol), and trimethylborane (0.88 mmol) were allowed to react to completion overnight. The reaction flask was maintained at 0 °C while volatile material was distilled away, trapped out with liquid nitrogen. There were recovered 7.0 mmol of ethyl ether and 0.12 mmol of trimethylborane. The reaction flask was then brought to 50 °C and vapors were collected for a short time. Fractionation resulted in the additional recovery of 0.77 mmol of trimethylborane and 0.21 mmol of ethyl ether. The results are summarized in Table III.

Reaction of Lithium Hydride with Trimethylborane in *n*-Butyl Ether at 0 °C (Pressure–Composition Experiment). Trimethylborane, 3.62 mmol, was added to 2.34 mmol of lithium hydride and 17.1 mmol of *n*-butyl ether. The course of the reaction was followed by the pressure changes. As in the other experiments, an induction period was observed. Once the reaction had started, further additions of trimethylborane resulted in rapid reaction. The data are summarized in Table IV.

Reversibility of the Lithium Hydride–Trimethylborane–*n*-Butyl Ether System. The above system, which contained 3.62 mmol of trimethylborane, 2.34 mmol of lithium hydride, and excess *n*-butyl ether, was maintained at 0 °C. Trimethylborane was collected in a −196 °C trap (after first passing through a −80 °C trap, which took out the *n*-butyl ether). In 20 min, 1.33 mmol of trimethylborane was collected, leaving 2.29 mmol for reaction with 2.34 mmol of lithium hydride. No more trimethylborane could be collected at 0 °C.

Keeping the reaction flask at 0 °C, solvent was removed until a white solid appeared. The white solid adduct was then heated gradually. Melting was noticed around 45 °C. The pressure at 50 °C was 2 mm; at 60 °C it was 4 mm. The temperature was maintained at 60–70 °C for 30 min where both *n*-butyl ether and trimethylborane were collected. A total of 3.13 mmol of trimethylborane was obtained—86.5% of the 3.62 mmol initially present. After 0.5 h at 150 °C, 0.34 mmol more of trimethylborane was collected along with more *n*-butyl ether. This makes the total trimethylborane collected equal to 3.47 mmol, representing 95.8% recovery of the 3.62 mmol originally present. The *n*-butyl ether which was separated from the trimethylborane during the recovery was weighed and found to be 0.0551 g (4.22 mmol). This means that 1.81 mol of *n*-butyl ether was complexed per mole of lithium hydride, indicating the possible existence of $LiMe_3BH{\cdot}2n\text{-}Bu_2O$.

Lithium Triethylborohydride–Ethyl Ether System at 0 °C (Pressure–Composition Experiment). Lithium hydride, 4.07 mmol, 15.4 mmol of ethyl ether, and 4.07 mmol of triethylborane were allowed to react to produce lithium triethylborohydride in excess ether. Ether was then recovered by distillation, maintaining the flask at temperatures between −80 and 0 °C. The results, Table V, are represented graphically in Figure 3. The white solid adduct, lithium triethylborohydride, melted at about 85 °C (66–67 °C[5]). Continued heating at 80–90 °C resulted in the recovery of triethylborane only. Hence, the formation of ether-free lithium triethylborohydride is evident. The volatile materials were added to excess water and stirred for several hours. Only a trace of hydrogen formed. This test ensured no compounds containing active hydrogen had been evolved.

Reaction of Lithium Hydride with Trimethylborane. A sample of lithium hydride, 3.39 mmol, and trimethylborane, 0.795 mmol, in the absence of solvent, was allowed to stir for 24 h at room temperature. The observed pressure, 149 mm, did not change over this time, indicating the absence of any appreciable reaction.

Reaction of Lithium Hydride with Triethylborane. Lithium hydride, 3.29 mmol, and 4.17 mmol of triethylborane were maintained with stirring for 21 h at room temperature. With the reaction flask at 0 °C, all of the triethylborane was easily recovered. The appearance of the lithium hydride had not changed. From these results, it was concluded that no reaction had occurred.

Reaction of Sodium Hydride with Trimethylborane. Into the reaction flask was placed an ampule of sodium hydride, 2.01 mmol, and trimethylborane, 3.25 mmol. The mixture was maintained at 30 °C. A slow decrease in pressure with the appearance of a white solid was noted. After 7 days, unreacted trimethylborane was collected, 1.45 mmol. Therefore, 1.80 mmol had reacted with 1.86 mmol of sodium hydride (after correcting for 0.15 mmol of hydrogen produced in the reaction).

Properties and Reversibility of Sodium Trimethylborohydride. Sodium trimethylborohydride was a white solid of low volatility. The pressure above the compound was 1 mm at 32 °C, 14 mm at 85 °C. The reaction flask was gradually warmed and melting noticed between 75 and 80 °C. (Recrystallized material exhibits mp 76 °C[5].) Upon melting, the white solid turned into a dark black liquid. The Teflon stirring bar inside the reaction flask also turned black. At 130–140 °C, some 77% of the trimethylborane could be recovered.

Reaction of Sodium Hydride with Triethylborane. In a typical experiment, 5.01 mmol of sodium hydride was allowed to stir at room temperature with 6.74 mmol of triethylborane. After about 1 h, the mixture suddenly started clearing up, the pressure increased as the reaction vessel became warm, followed by a decrease in pressure. Keeping the reaction flask at room temperature, triethylborane, 1.48 mmol, was collected from the reaction vessel. Thus, the sodium hydride reacted with triethylborane in a ratio of 1:1.

Properties and Reversibility of Sodium Triethylborohydride. Sodium triethylborohydride was observed to be a nonvolatile, clear liquid at room temperature.[6] (Recrystallized material exhibits mp 30 °C.[5]) A sample of 1.18 mmol of sodium triethylborohydride was heated to 135–150 °C and vapors were collected in a U-trap at −196 °C. The Teflon stirring bar turned black. It was necessary to degas small amounts of noncondensable vapors. The material collected was essentially pure triethylborane (1.2 mmol) which was identified by its vapor pressure.

Reaction of "Activated" Lithium Hydride with Trimethylborane. Trimethylborane, 3.77 mmol, was added to lithium hydride produced in the dissociation of 2.54 mmol of $LiMe_3BH{\cdot}Et_2O$. The pressure decreased slowly at 0 °C, faster at room temperature. After 1.5 days, no further decrease in pressure was noted. The reaction flask was then cooled to −80 °C and 1.31 mmol of unreacted trimethylborane was removed. Hence, 2.46 mmol of trimethylborane had reacted with 2.54 mmol of lithium hydride. The product was a white solid, exhibiting a pressure of 0.6 mm at 0 °C and 1.7 mm at 27 °C.

Reaction of "Activated" Lithium Hydride with Triethylborane. Similarly, 4.24 mmol of triethylborane was added to lithium hydride from the dissociation of 2.60 mmol of $LiEt_3BH{\cdot}Et_2O$ and the mixture allowed to stir for 18 h at room temperature. After 18 h at room temperature, excess triethylborane was collected. The results revealed that 1.41 mmol of triethylborane had reacted with 2.60 mmol of lithium hydride. The triethylborane was returned and the reaction allowed to proceed. Absorption was complete at 96% in 89 h.

The white solid adduct, lithium triethylborohydride, started melting at 80 °C. The pressure above the solid was 0.6 mm at 31 °C and 8 mm at 62 °C.

Preparation of Solvent-Free Lithium Triethylborohydride. In a clean, oven-dried, 250-mL flask fitted with rubber syringe cap on an inlet port and a magnetic stirring bar, 2.4 g (300 mmol) of lithium hydride was placed and a reflux condenser connected to a mercury bubbler was attached. After introducing 150 mL of ethyl ether, the system was thoroughly flushed with nitrogen. While stirring, 28.4 mL (19.6 g, 200 mmol) of triethylborane was introduced via hypodermic syringe and the mixture was refluxed for 24 h. The mixture was then cooled to room temperature and excess lithium hydride was removed by passing the suspension through a filtering chamber fitted with a sintered glass filter (fine-grade) under slight positive pressure of nitrogen. The resulting clear solution was concentrated using a water aspirator at room temperature and ethyl ether was further removed using a vacuum pump via a solvent trap cooled with dry ice–acetone. The resulting white cake-like material was dissolved in dry, hot *n*-hexane (20 mL) and the solvents were removed under vacuum to give white solid. Vacuum (0.2–0.1 mm) was further applied for 24 h at room temperature to give 21.2 g of lithium triethylborohydride as a white solid. This was recrystallized from benzene (50 mL), and the crystals were dried under vacuum (0.1 mm) overnight to obtain 19.35 g (182.7 mmol, 91.3%) of solvent-free lithium triethylborohydride as white crystals (needles), mp 78–83 °C (with a sign of decomposition).

The compound is moderately soluble in nonetherate solvents, such as benzene, toluene, and *n*-hexane, at room temperature. Thus saturated solutions of these solvents were 0.42–0.46 M in lithium triethylborohydride. The solid is unstable toward air, smoking when exposed. Addition of a drop of water to the solid in air caused a vigorous reaction with flame.

Registry No. $LiMe_3BH$, 63526-12-5; $LiEt_3BH$, 22560-16-3; $NaMe_3BH$, 22560-17-4; $NaEt_3BH$, 17979-81-6; LiH, 7580-67-8; NaH, 7646-69-7; Me_3B, 593-90-8; Et_3B, 97-94-9.

References and Notes

(1) Based upon a thesis submitted by Albert Khuri in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Purdue University.

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(3) H. C. Brown, H. I. Schlesinger, I. Sheft, and D. M. Ritter, *J. Am. Chem. Soc.*, **75**, 192 (1953).
(4) (a) G. Wittig, G. Keicher, A. Rückert, and P. Raff, *Justus Liebigs Ann. Chem.*, **563**, 110 (1949); (b) G. Wittig and A. Rückert, *ibid.*, **566**, 101 (1950).
(5) P. Binger, G. Benedikt, G. W. Rotermünd, and R. Köster, *Justus Liebigs Ann. Chem.*, **717**, 21 (1968).
(6) J. B. Honeycutt, Jr., and J. M. Riddle, *J. Am. Chem. Soc.*, **83**, 369 (1961).
(7) H. C. Brown, *J. Am. Chem. Soc.*, **67**, 374 (1945).
(8) R. B. Johannesen, Ph.D. Thesis, Purdue University, 1949.
(9) R. A. McNees, M.S. Thesis, Purdue University, 1949.
(10) H. C. Brown, H. Bartholomy, Jr., and M. D. Taylor, *J. Am. Chem. Soc.*, **66**, 435 (1944).
(11) R. T. Sanderson, "Vacuum Manipulations of Volatile Compounds", Wiley, New York, N.Y., 1948.