

pound was once formed. A sample of the N,N-dimethyl derivative was heated directly up to 100°. Such behavior contrasts sharply with explosive decomposition of methoxyamine boranes¹ in which smooth B-O bond formation was restricted by the methyl group.

The explosion of the diborane-hydroxylamine mixture at low temperatures can be attributed to sudden vigorous interaction of previously unreacted condensed phases or perhaps to impurities. Hydroxylamine itself will detonate if subjected to sudden intense heating, but the free base is much less subject to the detonation if coordinated.¹

In Table I are summarized the approximate temperatures at which 50% of the hydroxylamine-borane adducts are decomposed through loss of hydrogen from the original reaction mixtures. The data suggest that the OH hydrogen in hydroxylamine is the most acidic, that in the N-methyl is next and that in the N,N-dimethyl derivative is least acidic. This interpretation would be consistent with the assumed inductive effect of the methyl groups.

The displacement of N,N-dimethylhydroxylamine by trimethylamine is consistent with the fact that the latter is the stronger base.⁶

Experimental

a. **Materials.** 1. **Hydroxylamine.**—Free anhydrous hydroxylamine was prepared and handled as described elsewhere.⁶ In order to estimate the accuracy in the weighing and handling of hydroxylamine by the previously described techniques, weighed samples of the free base were titrated with standard acid. Results of several experiments indicated that the weight of the sample was reproducibly about 8% above the theoretical weight obtained from the titration. The discrepancy undoubtedly is due to ether adhering to the crystals. An 8% correction was applied to the weights of all samples handled in the above manner.

(6) T. C. Bissot, R. W. Parry and D. H. Campbell, *THIS JOURNAL*, **79**, 796 (1957).

2. **N-Methyl- and N,N-Dimethylhydroxylamines.**—The preparation and properties of these free bases are described elsewhere.⁶

3. **Diborane.**—Prepared from LiAlH₄ and BF₃ etherate.

4. **Diethyl Ether.**—See reference 1.

b. **Procedure.** 1. **Of Diborane.**—A procedure analogous to that previously described¹ was employed except for a few essential modifications. All reactions were conducted at -112°. The free hydroxylamine, which was insoluble in ether, required approximately 20 hr. for nearly complete reaction. The more ether soluble methyl and dimethyl derivatives gave complete reaction in 2 hr. or less at -112°.

The rate of absorption of B₂H₆ by an ether suspension of hydroxylamine was studied at -112°. At definite time intervals unreacted B₂H₆ was distilled from the system, purified, measured and returned to the reactor. The rate of complex formation was slow, but the ratio of B₂H₆ to NH₂-OH approached the theoretical value of 0.5 as a limit. More detailed data are available elsewhere.⁴

2. **N,N-Dimethylhydroxylamine in Excess.**—In a typical run a 5-mmole sample of HON(CH₃)₂ was weighed out and dissolved in 3 ml. of diethyl ether. After adding 2.39 mmoles of B₂H₆, the system was warmed to -112° and stirred for 45 minutes. The mixture was separated by distillation through a trap at -63° which retained the compound and the excess amine. In this preparation only 0.11 of a mmole of H₂ was obtained. The excess amine and the borane complex were separated by fractionation in the vacuum system.

c. **Thermal Decomposition of the Borane Adducts.**—After the excess B₂H₆ and solvent separated at -78°, the temperature of the complex was raised to -64°; after the rate of hydrogen evolution dropped almost to zero, the gas was removed, purified and measured. This procedure was repeated at regular temperature intervals up to 220°. At some of the higher temperatures volatile products such as methylamine or pure N,N-dimethylhydroxylamine-borane separated. These were trapped and purified in the vacuum system and identified by physical and chemical properties.

d. **Analytical Methods.**—These are described elsewhere.¹

Acknowledgment.—This research was conducted under Contract AF 23(616)-8 with the United States Air Force, the sponsoring agency being the Aeronautical Research Laboratory of the Wright Air Development Center, Air Research and Development Command.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

The Reaction of Lewis Acids of Boron with Sodium Hydride and Borohydride¹

BY HERBERT C. BROWN AND PAUL A. TIERNEY³

RECEIVED AUGUST 16, 1957

In the presence of diglyme, sodium hydride absorbs diborane to form sodium borohydride. In the presence of excess diborane, additional diborane is absorbed to yield NaBH₄·BH₃. In diglyme solution boron trifluoride readily reacts with sodium hydride to form diborane. Diglyme solutions of sodium borohydride react readily with boron trifluoride in either stoichiometric or excess amounts to liberate diborane quantitatively. Boron trichloride also can be used in stoichiometric amount; however, excess boron trichloride reacts with diborane to form chloroborane etherates, resulting in reduced yields of diborane. Dimethoxyboron chloride reacts with sodium borohydride in diglyme to give diborane and methyl borate. Methyl chloride is reduced to methane by sodium borohydride in diglyme.

The discovery that lithium hydride reacts readily with diborane in ethyl ether solution to form lithium borohydride provided a greatly improved

synthetic route to lithium borohydride and other metal borohydrides (through metathesis).^{4,5} Similarly, the discovery that both lithium hydride and lithium borohydride reacted readily with boron trifluoride in ether solution to form diborane pro-

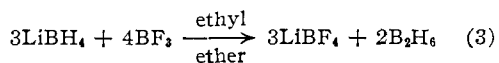
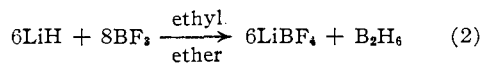
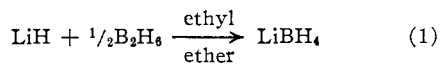
(1) Addition Compounds of the Alkali Metal Hydrides. IX.
(2) Based upon a thesis submitted by Paul A. Tierney in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Standard Oil Research Foundation Fellow, 1955-1956; Parke, Davis and Co. Fellow, 1956-1957.

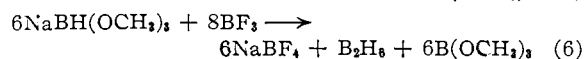
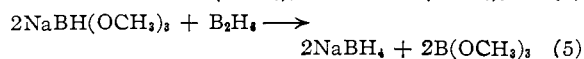
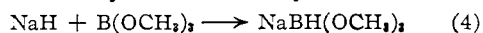
(4) H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. R. Rapp, *THIS JOURNAL*, **75**, 199 (1953).

(5) H. I. Schlesinger, H. C. Brown and E. K. Hyde, *ibid.*, **75**, 209 (1953).

vided a new practical route to this interesting substance.^{4,6}



Attempts to utilize the more economical sodium hydride and sodium borohydride were less successful. The reactions were sluggish and the yields were poor.⁷ By treating the sodium hydride with methyl borate a new compound, sodium trimethoxyborohydride, was obtained.⁸ This substance served as an active form of sodium hydride and rendered practical those reactions which could not be attained readily with sodium hydride itself.



Presumably, the difference in the behavior of the lithium and sodium derivatives arises from the ready solubility of lithium borohydride in ethyl ether⁹ and the lack of solubility of sodium borohydride in this solvent.⁴ The observation that sodium borohydride is readily soluble in diglyme (diethylene glycol dimethyl ether) and triglyme (triethylene glycol dimethyl ether)¹⁰ suggested a re-examination of the reactions of sodium hydride and borohydride with diborane, boron trifluoride and boron trichloride in these solvents.¹¹

Results

In the presence of diglyme, sodium hydride readily reacts with diborane to form sodium borohydride. In early experiments, in which excess diborane was utilized, it was observed that not one but two moles of "borane" were absorbed per mole of sodium hydride present. The first mole was strongly retained; however, the second mole could be removed by evacuating the reaction vessel to low pressures.

This phenomenon was examined further by treating sodium borohydride in diglyme solution with small increments of diborane, observing the equilibrium pressure of the gas in the system. Typical experimental data are presented in Table I.

A plot of these data indicates an essentially horizontal portion, with a slight rise, until the $\text{B}_2\text{H}_6/\text{NaBH}_4$

(6) H. I. Schlesinger, H. C. Brown, J. R. Gilbreath and J. J. Katz, *THIS JOURNAL*, **75**, 195 (1953).

(7) In the original publication (ref. 4), the formation of diborane by the reaction of sodium borohydride with boron trifluoride-ethyl etherate was described. The sodium borohydride used in these experiments was a highly active material prepared from diborane and sodium trimethoxyborohydride. Later attempts to utilize commercial sodium borohydride in this reaction gave unsatisfactory results.

(8) H. C. Brown, H. I. Schlesinger, I. Sheft and D. M. Ritter, *THIS JOURNAL*, **75**, 192 (1953).

(9) H. I. Schlesinger and H. C. Brown, *ibid.*, **62**, 3429 (1940).

(10) H. C. Brown, E. J. Mead and B. C. Subba Rao, *ibid.*, **77**, 6209 (1955).

(11) A study of the reaction of sodium hydride with methyl borate in ether solvents has been reported recently. H. C. Brown, E. J. Mead and P. A. Tierney, *ibid.*, **79**, 5400 (1957).

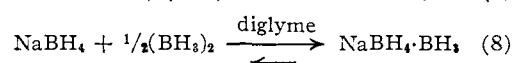
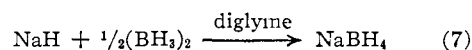
TABLE I

PRESSURE-COMPOSITION DATA FOR DIBORANE AND SODIUM BOROHYDRIDE IN DIGLYME AT 0°

Mole ratio $\text{B}_2\text{H}_6/\text{NaBH}_4$	Pressure, mm.	Mole ratio $\text{B}_2\text{H}_6/\text{NaBH}_4$	Pressure, mm.
0.143	0.7	0.596	86.2
.428	1.5	.620	108.0
.505	5.4	.638	123.1
.550	44.4	.692	172.0
.573	65.1		

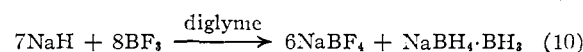
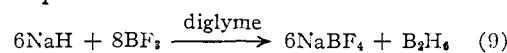
NaBH_4 mole fraction is 0.5, followed by a steep linear rise beyond mole fraction 0.5. The slope of this portion of the curve corresponds to the solubility of diborane in diglyme. These results point to the absorption of one "borane" by each sodium borohydride molecule in solution, with no significant further absorption, at least at the pressures which were here investigated.

These results are in accord with equations 7 and 8.

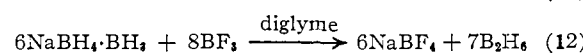
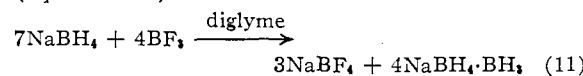


The borane addition compound of sodium borohydride, $\text{NaBH}_4 \cdot \text{BH}_3$ or NaB_2H_7 , may conveniently be termed "sodium borohydride-borane" or "sodium diborohydride."

Boron trifluoride is absorbed readily by diglyme to form an addition compound of high stability toward decomposition. Such solutions have been kept in sealed ampoules for over six months without evidence of any change. Treatment of sodium hydride with excess boron trifluoride in diglyme results in a smooth evolution of diborane. A deficiency of boron trifluoride is unsatisfactory since it results in the retention of diborane by the system in the form of sodium borohydride and its borane addition product.



Boron trifluoride in diglyme also reacts readily with sodium borohydride to liberate diborane. If the boron trifluoride is added in increments to the sodium borohydride in diglyme, only traces of diborane are liberated until the $\text{BF}_3/\text{NaBH}_4$ molar ratio is greater than 0.57. This corresponds exactly to the ratio $4\text{BF}_3/7\text{NaBH}_4$ called for by equation 11. In experiments where the ratio exceeds 0.57, the amount of diborane evolved corresponds to that estimated on the basis of the reaction of boron trifluoride with sodium diborohydride (equation 12).



From these results it was apparent that in order to achieve a smooth regular evolution of diborane it would be necessary to avoid the presence of unreacted sodium borohydride in the reaction mixture. It appeared that this objective might be ac-

complished by reversing the mode of addition. This was tested. A solution of sodium borohydride in diglyme was added in increments to a solution of boron trifluoride in the same solvent. After each addition, the diborane evolved was recovered and measured. The results, summarized in Table II, are in accord with equation 13.

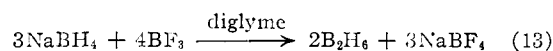


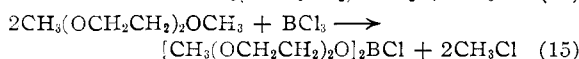
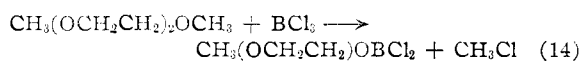
TABLE II
ADDITION OF SODIUM BOROHYDRIDE TO EXCESS BORON TRIFLUORIDE IN DIGLYME

NaBH ₄ added, mmoles	Diborane yield, mmoles	
	Expt.	Calcd.
0.60	0.38	0.40
1.20	0.81	0.80
1.80	1.19	1.20
2.40	1.61	1.60

It is evident that by this expediency a quantitative yield of diborane may be realized, regularly and smoothly evolved in accordance with the precise amount of sodium borohydride added to the solution.

Boron trifluoride also can be utilized in the form of its ethyl etherate dissolved in diglyme. Indeed, the most convenient procedure we have found for the generation of diborane on a laboratory scale involves dropping a solution of sodium borohydride in diglyme into a slight excess of boron trifluoride-ethyl etherate in the same solvent. This procedure has been utilized extensively in our laboratory in studying the utility of diborane in the hydroboration of olefins and the selective reduction of functional groups.¹²

In contrast to the apparent stability of boron trifluoride solutions in diglyme, the corresponding solutions of boron trichloride are relatively unstable. On standing at room temperature or at 0°, the solutions evolve methyl chloride, presumably accompanied by the formation of the corresponding mono- and dichloroboronates.



The boron trichloride addition compounds of methyl ether¹³ and ethyl ether¹⁴ are stable under these conditions. On the other hand, tetrahydrofuran has been reported to undergo ring opening under the influence of boron trichloride.¹⁵

In an effort to find a solvent system which would minimize the extent of this undesirable reaction of boron trichloride with the solvent, we examined the behavior under standard conditions of boron trichloride with diethyl ether, tetrahydrofuran, tetrahydropyran, monoglyme, diglyme and diethylcarbitol. Solutions of boron trichloride in ethyl ether and tetrahydropyran showed no evidence of chemical change in 24 hr. at room temperature (24°).

(12) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1135, 1136 (1957).

(13) E. Wiberg and W. Sutterlin, *Z. anorg. allgem. Chem.*, **202**, 22 (1931).

(14) W. Nespital, *Z. physik. Chem.*, **B16**, 153 (1932).

(15) J. D. Edwards, W. Gerrard and M. F. Lappert, *J. Chem. Soc.*, 1470 (1955).

Under the same conditions tetrahydrofuran showed 93% and diglyme showed 67% reaction.¹⁶ Mixtures of diglyme and tetrahydropyran exhibited somewhat decreased instability, 7-10% reaction in 1-3 hr. at 24°.

Unfortunately, sodium borohydride is not significantly soluble in either ethyl ether or tetrahydropyran. It was therefore apparent that the reactions of boron trichloride with sodium hydride and with sodium borohydride would be feasible in diglyme only if they proceeded faster than the side-reaction with the solvent.

The direct reaction of boron trichloride with sodium hydride proved to be far too slow to be useful. Presumably the vast difference in the ease of reaction of boron trifluoride and boron trichloride with sodium hydride is the result of the marked difference in the solubility of the reaction products in the solvent. The boron trifluoride reaction produces sodium fluoroborate, readily soluble in diglyme, whereas the boron trichloride reaction would be expected to yield sodium chloride, of very low solubility in the solvent.

On the other hand, boron trichloride reacts rapidly with sodium borohydride in diglyme to yield diborane. The use of stoichiometric amounts of boron trichloride ($\text{BCl}_3 + 3\text{NaBH}_4$) resulted in essentially quantitative yields of diborane.

Just as in the analogous reaction with boron trifluoride, the use of boron trichloride in deficiency resulted in low yields of diborane, presumably due to the reaction of diborane with the excess sodium borohydride. Unexpectedly, in contrast to the behavior of boron trifluoride, an excess of the boron trichloride was deleterious. Thus, the use of equimolar amounts of sodium borohydride and boron trichloride resulted in no diborane evolution from the reaction mixture.

These results are summarized in Table III.

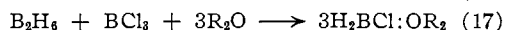
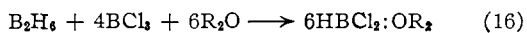
TABLE III
REACTION OF BORON TRICHLORIDE WITH SODIUM BOROHYDRIDE IN DIGLYME

NaBH ₄ , mmoles	BCl ₃ , mmoles	Molar ratio BCl ₃ /NaBH ₄	Diborane yield, mmoles		CH ₄ , mmoles
			Expt.	Calcd. ^a	
0.66	1.06	1.60	0.00	0.00	0.15
2.00	0.66	0.33	1.29	1.32	.18
1.64	1.01	0.62	0.55	0.64	.29
1.64	1.65	1.01	.03	.00	.48
1.54	1.04	0.68	.42	.49	.40
1.76	0.58	.33	1.06	1.16	^b
2.4	.80	.33	1.52	1.60	^b
2.1	.70	.33	1.34	1.40	^b
2.0	.65	.33	1.29	1.30	^b
3.8	1.27	.33	2.40	2.54	^b
3.2	1.07	.33	2.00	2.14	^b

^a Calculated assuming that diborane reacts with excess boron chloride in a molar ratio of 1:1. ^b Methane not measured.

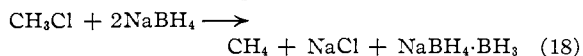
In examining the reason for this behavior, we established that solutions of boron trichloride in ethers absorb diborane readily to form a new class of compounds, the mono- and dichloroborane etherates.

(16) The reaction was followed by measuring the change in hydrochloric acid formed in hydrolysis of the reaction mixture at 0°.

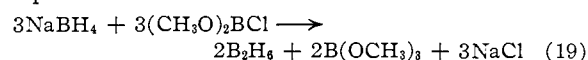


Thus an excess of boron trichloride over the stoichiometric quantity required to react with sodium borohydride decreases the amount of diborane evolved from the reaction mixture. Excellent agreement was realized between the experimental yields of diborane and those calculated on the assumption that diborane reacts with excess boron trichloride in a 1:1 molar ratio to form the monochloroborane etherate (Table III). We established that diborane does not undergo a similar reaction with solutions of boron trifluoride in ethers.

We had anticipated that the formation of diborane in this reaction of sodium borohydride with boron trichloride would be accompanied by the formation of small quantities of methyl chloride from the side reaction of the boron halide with diglyme. However, no methyl chloride was identified in the product. Instead the formation of small quantities of methane was noted. It was established that methyl chloride reacts relatively rapidly with sodium borohydride in diglyme, in accordance with the equation



Dimethoxyboron chloride, prepared by the reaction of methyl borate with boron trichloride,¹⁷ does not split diglyme. A solution of dimethoxyboron chloride in diglyme reacts readily with sodium borohydride to evolve diborane, in accordance with equation 19



It was not necessary to prepare the dimethoxyboron chloride in a separate operation. The introduction of boron trichloride to diglyme containing methyl borate ($1\text{BCl}_3/2\text{B}(\text{OCH}_3)_3$) yields stable solutions which react readily with sodium borohydride to liberate diborane.

Discussion

The ready reaction of sodium hydride with diborane in diglyme to form sodium borohydride (7) is primarily of theoretical interest in view of the present commercial availability of the product. However, the ready absorption of a second mole of "borane" (8) is highly unexpected and of both practical and theoretical interest.

The borane addition compound of sodium borohydride, $\text{NaBH}_4\cdot\text{BH}_3$ or NaB_2H_7 , appears to be a member of a numerous class of electron-deficient molecules containing single bridges,^{18,19} related to the more generally recognized doubly-bridged systems, such as aluminum methyl, gallium chloride and diborane itself. These singly-bridged molecules are under investigation in our laboratories, and discussion is best deferred until complete results are available for publication.

The observation that the addition of small amounts of boron trifluoride to sodium borohydride

(17) E. Wiberg and H. Smedsrud, *Z. anorg. allgem. Chem.*, **202**, 1 (1931).

(18) R. E. Rundle, *J. Chem. Phys.*, **17**, 671 (1949).

(19) H. C. Brown, P. F. Stehle and P. A. Tierney, *THIS JOURNAL*, **79**, 2020 (1957).

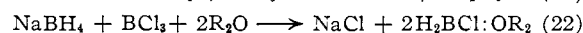
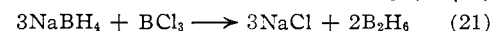
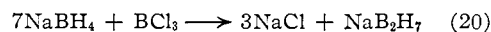
in diglyme did not result in the evolution of diborane is reasonably attributed to the formation of the relatively stable sodium diborohydride. However, the addition of limited amounts of boron trifluoride to lithium borohydride in ethyl ether has been reported to result in the immediate evolution of diborane.²⁰ This marked difference in the two results led us to examine the behavior of lithium borohydride in this reaction. In diglyme, lithium borohydride readily absorbs a second mole of "borane" at 0°. However, in ethyl ether no reaction was observed at this temperature. Because of the decreasing solubility of the salt, lower temperatures could not be employed.²¹

Upon addition of boron trifluoride to sodium hydride or borohydride in diglyme, the diborane evolved is accurately given by equations 10, 11 and 12. In accordance with these equations, no diborane is liberated from sodium borohydride until the mole ratio of boron trifluoride to sodium borohydride exceeds the value 0.57 (eq. 11). The addition of more boron trifluoride results in the evolution of diborane in the amounts indicated by equation 12. At a mole ratio of 1.33, all of the sodium borohydride present is transformed into diborane. Excess boron trifluoride has no effect upon the yield.

These complications are avoided by adding a solution of sodium borohydride in diglyme to an excess of boron trifluoride (or boron trifluoride-ethyl etherate) in the same solvent. In this way the presence of unchanged sodium borohydride in the reaction solution is avoided and the evolution of diborane may be smoothly and quantitatively controlled.

Presumably, the reaction between boron trichloride and sodium borohydride in diglyme follows the same course as that described above until all of the diborane has been liberated. However, in the presence of excess boron trichloride the yield of diborane is decreased. With a mole ratio of boron trichloride to sodium borohydride of one, no diborane is evolved. This behavior has been established as being due to the formation of relatively stable chloroborane etherates.

On this basis the complete behavior of the boron trichloride-sodium borohydride system can be understood in terms of the three equations 20-22.



The reactions of boron trifluoride and boron trichloride with sodium borohydride are summarized in Fig. 1. The solid line gives the yield of diborane predicted by equation 13 in the case of boron trifluoride and by equation 21 in the case of the chloride. The dashed lines indicate the calculated yields based upon equations 11 and 20 for the borohydride in excess and upon equation 22 for boron trichloride in excess. It is evident that the experimental points are in good agreement with the predicted values.

(20) J. R. Elliott, E. M. Boldebeck and G. F. Roedel, *ibid.*, **74**, 5047 (1952).

(21) A detailed description of these experiments will be reported in a later publication.

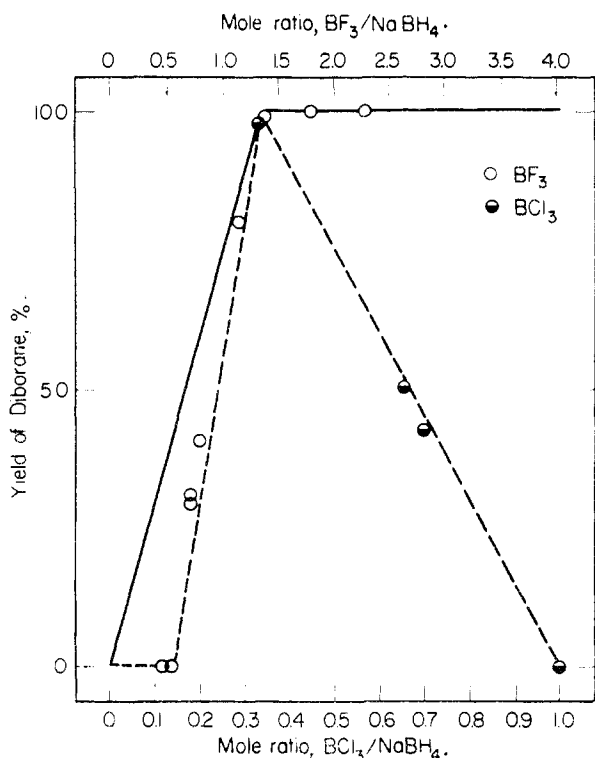
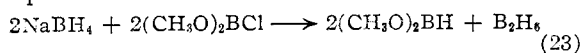


Fig. 1.—Reaction of sodium borohydride with boron trifluoride and trichloride in diglyme.

The chloroborane etherates are interesting new substances. We are examining their physical and chemical properties, and especially their applicability as new, selective reducing agents.

The unusual results realized with dimethoxyboron chloride merit consideration. Originally we attributed the stability of solutions of this substance in diglyme to its weak coordination tendencies, approaching those of methyl borate. However, we anticipated that this substance would react with sodium borohydride to form both dimethoxyborane and diborane, in accordance with equation 23



In actual fact we realized a nearly quantitative yield of diborane with no dimethoxyborane detected (eq. 19). The products are suggestive of a reaction of boron trichloride (eq. 21), rather than of dimethoxyboron chloride. Indeed, identical results have been obtained by utilizing both preformed dimethoxyboron chloride in diglyme and by adding methyl borate and boron trichloride individually to diglyme. This suggests that dimethoxyboron chloride may disproportionate in diglyme to methyl borate and boron trichloride. If so, methyl borate apparently serves to stabilize the solutions and to reduce or to eliminate the side reaction of boron trichloride with diglyme. Alternatively, the solvent may serve to catalyze greatly the usually slow disproportionation of dimethoxyborane. It is planned to investigate this system further in order to clarify the precise composition of the methyl borate-boron trichloride-diglyme reaction mixtures.

Finally, the relatively fast reaction of methyl chloride with sodium borohydride in diglyme suggests that this reaction may be quite useful in replacing halogen atoms by hydrogen in organic molecules which contain functional groups which are not attacked by sodium borohydride in diglyme. We plan to examine this reaction in detail.

Experimental Part

Materials.—Sodium hydride was obtained from Metal Hydrides, Inc.; the product analyzed 92% sodium hydride. Sodium borohydride was obtained from Metal Hydrides, Inc. and from Callery Chemical Co. The commercial products were recrystallized from diglyme¹⁰ and exhibited a purity of 99.8%. Diborane was prepared as required by the reaction of boron trifluoride with sodium borohydride in diglyme.

Boron trifluoride (Matheson) was purified through the preparation and subsequent thermal dissociation of the anisole addition compound.²² Boron trichloride (Matheson) was similarly purified through the nitrobenzene addition compound.²³ Methyl borate (Metal Hydrides) was purified by distillation.

The diglyme was a sample provided by the Ansul Chemical Co. The product was twice distilled from small quantities of lithium aluminum hydride under reduced pressure (b.p. 64° at 16 mm., n_D^{20} 1.4087). Diglyme used in experiments in the vacuum apparatus was further purified by treatment with small amounts of diborane for periods of 4 to 12 hr. The diglyme was then distilled away from the non-volatile products and separated from residual diborane by trapping the distillate at -78° .

Tetrahydropyran (du Pont) was placed over calcium hydride for 24 hr. and then twice distilled from lithium aluminum hydride under nitrogen (b.p. 86–87° at 742 mm., n_D^{20} 1.4203). Tetrahydrofuran, monoglyme, diethyl ether of diethylene glycol and ethyl ether were previously purified samples available in the laboratory. They were treated with lithium aluminum hydride for 24 hr. and distilled directly from this material directly into the high vacuum system.

Apparatus and Techniques.—Except for the laboratory-scale preparations of diborane, all experiments were carried out in an all-glass high vacuum system using techniques common to experimentation in this area.²⁴

Analyses.—Diborane prepared in the vacuum apparatus was measured as a gas in the standard calibrated volume. Its purity was established by vapor pressure measurement, v.p. 225 mm. at -111.8° , and by the homogeneity of individual fractions. Volumes of gases are all given for standard conditions (0° , 760 mm.).

Diborane prepared in large scale experiments was passed into dry acetone and aliquots of the acetone removed, hydrolyzed and analyzed for boric acid.

Sodium borohydride was analyzed for hydrogen as hydrogen gas after hydrolysis, sodium as sodium hydroxide and boron by titration as boric acid in the presence of mannitol.

Diborane and Sodium Hydride.—Sodium hydride (0.0986 g., 3.81 mmoles, based upon 92% purity), was introduced into a tube fitted with a manometer. Diglyme (2.0 ml.) was introduced, followed by 119 cc. (5.30 mmoles) of diborane. The reaction mixture was allowed to stand at room temperature. Diborane was absorbed slowly, as indicated by the decreasing pressure on the manometer. The residual pressure in the tube corresponded to the absorption of 1.0 mole of diborane per mole of sodium hydride.

The tube was warmed and the diglyme and diborane removed by distillation, the last traces by maintaining the reaction tube and its contents at 70° . There was collected 79 cc. of diborane (3.35 mmoles). Thus, 1.95 mmoles of diborane had reacted with 3.81 mmoles of sodium hydride.

A sample of the white solid in the flask was analyzed for boron and hydride.

Anal. Calcd. for 0.0064 g. of NaBH₄: B, 0.170 mmole; H, 0.68 mmole. Found: B, 0.165 mmole; H, 0.63 mmole.

(22) R. A. McNeese, M.S. Thesis, Purdue University, 1949.

(23) H. C. Brown and R. R. Holmes, *THIS JOURNAL*, **78**, 2173 (1956).

(24) R. T. Sanderson, "Vacuum Manipulations of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

To test the absorption of a second mole of "borane," the remaining product (3.64 mmoles NaBH_4) was again dissolved in diglyme and treated with 44 cc. (1.96 mmoles) of diborane. Excess diborane (3.6 ml.) was removed until the residual pressure, 4.0 mm. at 25°, was not markedly altered by further removal of small quantities of the gas. Thus the product, 3.64 mmoles NaBH_4 , had absorbed 40.0 cc. (1.79 mmoles) of diborane.

Diborane and Sodium Borohydride.—A sample of sodium borohydride (0.1134 g., 3.00 mmoles) was introduced into a reaction tube, fitted with a manometer, together with 4.52 g. (33.8 mmoles) of diglyme. Small amounts of diborane were introduced and the equilibrium pressure measured at 0° after each addition. The data are summarized in Table I.

Boron Trifluoride and Sodium Hydride.—A 250-ml. flask was fitted with a dropping funnel, an inlet for nitrogen, an outlet for diborane and a magnetic stirrer. In the flask was placed 4.40 g. (0.169 mole) of sodium hydride and 50 ml. of diglyme. The flask was flushed out with nitrogen and 64.7 g. (0.337 mole) of freshly distilled boron trifluoride etherate was added slowly through the dropping funnel. The solution became warm and diborane was evolved. The gas was passed into a gas absorption bottle containing 100 ml. of dry acetone. As the reaction proceeded, the sodium hydride in the flask dissolved and a white crystalline material replaced it. After 4 hr., the acetone in the gas absorption bottle was diluted with water to 500 ml. and a 10-ml. aliquot was analyzed for boric acid. The 1.03 mmoles of boric acid found indicated a yield of 92% of diborane, based on sodium hydride.

Boron Trifluoride and Sodium Borohydride.—The following procedure is typical of the experiments carried out to study the reaction of boron trifluoride with sodium borohydride. Three ml. of a 1.07 *M* solution of sodium borohydride in diglyme was introduced into a 120-ml. reaction flask fitted with a manometer and magnetic stirrer. Into the degassed flask and solution was condensed 78.4 cc. (3.5 mmoles) of boron trifluoride. Rapid reaction was observed at room temperature. After 2 hr., the gas was removed from the flask at -78°. There was obtained 1.74 mmoles of diborane. The results of this and similar experiments are summarized in Table IV.

TABLE IV
REACTION OF BORON TRIFLUORIDE WITH SODIUM BOROHYDRIDE IN DIGLYME

NaBH_4 , mmoles	BF_3 , mmoles	Molar ratio ^a $\text{BF}_3/\text{NaBH}_4$	Diborane yield, mmoles	
			Expt.	Calcd.
5.3	2.6	0.49	0.02	0.00
3.2	1.7	.53	.01	.00
3.2	1.8	.56	.08	.00
3.2	2.3	.72	.67	.40
3.2	2.3	.72	.63	.40
5.3	4.2	.79	1.65	1.02
3.2	3.5	1.09	1.74	1.45
4.2	5.7	1.36	2.78	2.80
3.2	5.0	1.56	2.00	2.08

^a Calculated ratio for $3\text{NaBH}_4 + 4\text{BF}_3$ (eq. 13) is 1.33.

The following procedure was utilized to examine the reaction of sodium borohydride with excess boron trifluoride in diglyme. The apparatus consisted of a reaction flask fitted with a manometer, magnetic stirrer and a buret extending to the bottom of the flask. Sufficient mercury was placed in the flask to cover the tip of the buret. A solution of 0.1136 g. (3.00 mmoles) of sodium borohydride in 5 ml. of diglyme was prepared in the vacuum apparatus using utmost caution to exclude moisture. This solution was introduced into the buret in a stream of dry nitrogen. Into the flask was placed 211.9 cc. (9.46 mmoles) of boron trifluoride and 5.0 ml. of diglyme. The stopcock of the buret was carefully opened and 1 ml. of the sodium borohydride was permitted to pass down the tip, through the mercury, and up into the boron trifluoride solution. The diborane formed was recovered and measured. Additional aliquots of the sodium borohydride solution were introduced and the diborane formed determined in the same manner. The results are summarized in Table II.

Boron Trifluoride and Sodium Diborohydride.—Into the usual reaction flask was placed 0.0795 g. (2.0 mmole) of so-

dium borohydride and 2.0 ml. of diglyme. The solution was treated with 22.4 cc. (1.0 mmole) of diborane. The gas was absorbed, the pressure dropping to less than 2.0 mm. at 0°. Samples of boron trifluoride were introduced into the reaction flask. After 30 minutes, the diborane was collected and measured. The data are summarized in Table V.

TABLE V
REACTION OF BORON TRIFLUORIDE WITH THE BORANE ADDITION COMPOUND OF SODIUM BOROHYDRIDE IN DIGLYME

$\text{NaBH}_4\cdot\text{BH}_3$, mmoles	BF_3 , mmoles	Molar ratio $\text{BF}_3/\text{NaBH}_4\cdot\text{BH}_3$	Diborane yield, mmoles	
			Expt.	Calcd.
2.00	0.35	0.175	0.47	0.31
2.00	.46	.23	.61	.40
2.00	.79	.40	.97	.70
2.00	1.40	.70	1.35	1.23
2.00	2.03	1.02	1.81	1.78
2.00	2.72	1.36	2.28	2.34

Preparative Procedure for Diborane.—The following procedure proved to be highly convenient for the generation of diborane on a laboratory scale. In cases where it was desired to isolate pure diborane, a solution of boron trifluoride in diglyme was prepared and used. In cases where diborane was to be utilized as a reagent and the presence of minor amounts of ethyl ether was not deleterious, the boron trifluoride was conveniently utilized in the form of the commercially available ethyl etherate.

The generator consisted of a 250-ml. distilling flask equipped with a pressure-equalized dropping funnel, an inlet for nitrogen, an outlet for the diborane and a magnetic stirrer. The diborane outlet was fitted with a T-tube dipping into mercury to serve as a safety release valve. For safety, any gas bubbling through the mercury was conducted into running water to destroy the diborane. To determine the yield, the diborane was led into a gas absorption flask containing 100 ml. of dry acetone. The diborane rapidly reacts with acetone to form diisopropoxyborane, $[(\text{CH}_3)_2\text{CHO}]_2\text{B}_2\text{H}_6$.²⁶ The yield was based upon an analysis for boron in the acetone (as boric acid, after hydrolysis).

A 1.0 *M* solution of boron trifluoride in diglyme was prepared by passing boron trifluoride directly into freshly purified diglyme maintained at 0°. Similarly, a 1.25 *M* solution of sodium borohydride was prepared by dissolving the salt in freshly purified diglyme.

In the distilling flask was placed 150 ml. (0.15 mole) of the boron trifluoride solution. The sodium borohydride solution, 80 ml. (0.10 mole) was placed in the dropping funnel. Stirring now was initiated, then the system was flushed with nitrogen and the borohydride solution then added dropwise to the boron trifluoride solution in the flask. Diborane evolution began immediately. A slow stream of nitrogen was maintained to carry the diborane out of the flask and into the gas absorption vessel containing the acetone. The reaction was complete in 1 hr. Analysis of the acetone solution showed the presence of 120 mmoles of boric acid, indicating a yield of 90%.

Similar results were realized by using 0.267 mmole of freshly distilled boron trifluoride-ethyl etherate dissolved in 80 ml. of diglyme in place of the boron trifluoride-diglyme solution.

Reaction of Boron Trichloride with Ethers.—A solution of boron trichloride in diglyme rapidly evolves methyl chloride, and the reaction may be followed readily by recovering and measuring the methyl chloride. Hydrolysis of the residual reaction product followed by titration for ionic chloride indicated that methyl chloride is the sole product containing non-ionizable chlorine.

In a typical experiment 5.0 ml. of diglyme (*ca.* 40 mmoles) was placed in a reaction tube fitted with a manometer. To this was added 47 cc. (2.1 mmoles) of boron trichloride. After 6.0 hr. at room temperature, 24°, the volatile gas was recovered and measured. There was obtained 78.5 cc. (3.5 mmoles) of gas identified as methyl chloride by its v.p. of 32 mm. at -78°. After 24 hr., a total of 107.3 cc. (4.8 mmoles) was recovered. The residue was hydrolyzed and analyzed. It contained 2.01 mmoles of boron and 1.62 mmoles of chloride, as compared with 2.1 mmoles of boron

(25) H. C. Brown, A. B. Burg and H. I. Schlesinger, *THIS JOURNAL*, **61**, 873 (1939).

and 1.5 mmoles of chloride estimated on the basis of equations 14 and 15.

In an attempt to find stable solvents for boron trichloride, a number of ethers were allowed to stand in a sealed tube with boron trichloride and the extent of reaction determined as above by hydrolysis and titration for ionic chloride. Consistent results could be realized only by carrying the hydrolysis out in a sealed vessel. Accordingly, the following procedure was utilized.

A small sealed ampule of water was introduced into the reaction tube. A weighed sample of ether was introduced into the dried tube, which was then attached to the high vacuum system and degassed. A measured amount of boron trichloride, measured as a gas, was introduced into the tube, which was then sealed. After an appropriate time, the ampule of water was broken by shaking the tube vigorously. The tube was then opened carefully and the contents analyzed for boric acid and ionic chloride.

Thus, in an experiment involving 40 mmoles of tetrahydropyran and 2.10 mmoles boron trichloride, after 24 hr. at 24° there was found 2.05 mmoles of boric acid and 6.19 mmoles of chloride. Evidently no significant reaction had occurred. On the other hand, in an identical experiment involving 40 mmoles of tetrahydrofuran and 2.06 mmoles of boron trichloride there was found 2.01 mmoles of boric acid and 0.46 mmole of chloride. In this case the splitting of the ether was estimated to be 93% complete.

The experimental results are summarized in Table VI.

TABLE VI
REACTION OF BORON TRICHLORIDE WITH SOME ETHERS AND MIXED ETHERS

Ether	Ether, mmoles	BCl ₃ , mmoles	Temp., °C.	Time, hr.	Reaction, %
Ethyl ether	40	2.0	24	24	0
Tetrahydrofuran	40	2.1	24	24	93
Tetrahydropyran	40	2.1	24	24	0
Monoglyme	40	2.2	24	24	57
Diglyme	40	2.1	24	6	57
Diglyme	40	2.1	24	12	67
Diglyme	40	2.1	24	24	73
Diglyme	40	1.7	0	23	63
Diethylcarbitol	40	1.9	24	24	27
Diglyme-ethyl ether	^a	0.86	24	24	47
Diglyme-tetrahydropyran	^a	1.30	24	24	28
Diglyme-tetrahydropyran	^a	1.92	0	24	10
Diglyme-tetrahydropyran	^a	1.36	24	1	7

^a Mixture of 2.5 ml. each of the two ethers.

Boron Trichloride and Sodium Borohydride.—The following procedure was utilized in determining the yields of diborane with varying quantities of boron trichloride. A solution of sodium borohydride was prepared in the vacuum apparatus by transferring 3 ml. of purified diglyme into the reaction vessel containing a weighed amount of sodium borohydride. A measured amount of boron trichloride was condensed into the vessel and the flask was permitted to warm to room temperature. Magnetic stirring was utilized. It was observed that the pressure reached a maximum in approximately 20 min. from the time the liquid nitrogen-bath was removed. In experiments in which the BCl₃/NaBH₄ mole ratio is greater than 0.33, the pressure was ob-

served to decrease gradually, attaining a constant value in approximately 1 hr. Diborane was recovered and measured as a gas in the usual manner.

The experimental results are summarized in Table III.

Diborane and Boron Trichloride in Diglyme.—In a reaction flask attached to the vacuum apparatus was added 2.5 ml. of diglyme and 11.2 cc. (10.5 mmole) of diborane. The pressure in the flask at room temperature was 71 mm. Boron trichloride, 11.2 cc. (0.5 mmole), was condensed into the flask. The pressure at room temperature was observed to fall. After 24 hr., the pressure had dropped to approximately 2 mm.

Diborane and Boron Trifluoride in Ethyl Ether.—A sample of 4.5 mmoles of ethyl ether (v.p. 189 mm. at 0°) and 7.6 cc. (0.34 mmole) of diborane was placed in the above reaction flask. The pressure was 217 mm. at 0° and 35 mm. at -78°. Upon addition of 11.2 cc. (0.50 mmole) of boron trifluoride, the pressure remained essentially constant at 216 mm. at 0° and 35 mm. at -78°. It was concluded that no reaction occurs between boron trifluoride and diborane.

Methyl Chloride with Sodium Borohydride.—In a typical experiment, 2.5 ml. of diglyme, 2.33 mmoles of sodium borohydride and 8.5 cc. (0.38 mmole) of methyl chloride were permitted to stand for 1 hr. The volatile products were recovered. There was collected 7.8 cc. (0.35 mmole) of methane and 0.7 cc. (0.03 mmole) of methyl chloride. The solution was hydrolyzed. The analysis indicated 1.91 mmoles Na, 2.29 mmoles B and 8.8 mmoles H as compared with the values 1.95 Na, 2.29 B and 8.8 H estimated on the basis of equation 19.

Rough kinetic experiments indicated that the rate shows a marked decrease following conversion of the sodium borohydride to sodium diborohydride.

Dimethoxyboron Chloride and Sodium Borohydride.—Dimethoxyboron chloride was synthesized from methyl borate and boron trichloride.¹⁷

A 1.0-ml. sample of diglyme and 8.3 cc. (0.37 mmole) of dimethoxyboron chloride was mixed and allowed to stand at room temperature. The pressure at 25° was 14 mm. and it exhibited no change at 24 hr. It was concluded that methyl chloride was not formed.

A solution of 0.451 g. (1.19 mmoles) of sodium borohydride in 2.0 ml. of diglyme was treated with 26.7 cc. (1.19 mmoles) of dimethoxyboron chloride. As the solution warmed to room temperature, the pressure in the flask was observed to increase and a white precipitate formed. After 1 hr., the pressure had reached a maximum value of 110 mm. The materials volatile at -79° were recovered and measured. There was obtained 17 cc. (0.76 mmole) of diborane. From the solution there was obtained a fraction, 8.3 cc. (0.37 mmole), with a v.p. of 118 mm. at 25°. Hydrolysis gave only traces of hydrogen and 0.35 mmole of boric acid. It was concluded that no significant amount of dimethoxyborane is formed in the reaction.

Boron chloride, 1.20 mmoles, was added to 2.40 mmoles of methyl borate in 5.0 ml. of diglyme. No methyl chloride was evolved from the solution over a period of 2 hr. at room temperature. To this solution was added 5.0 ml. of diglyme containing 3.60 mmoles of sodium borohydride. Diborane was evolved. A total of 50.3 ml., a yield of 93%, was recovered.

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