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HYDRIDES AND BOROHYDRIDES OF LIGHT WEIGHT ELEMENTS AND RELATED COMPOUNDS

Final Report

for the Period July 1, 1949-July 31, 1950
on contract
N6ori-20, I.O. X.

By

H. I. SCHLESINGER and THOMAS WARTIK

in collaboration with

R. E. MOORE, RILEY SCHAEFFER, M. STEINDLER, and G. URRY

THE UNIVERSITY OF CHICAGO

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The University of Chicago

1) This contract is an extension of contracts N173-S, 9058; N173s-9820; and N173s-10421. The abbreviation F.R., followed by a numeral, refers to final reports of the period ending June 30 of the year indicated by the numeral; P.R. refers to progress reports. In the case of progress reports of years preceding 1949-50, the date of the report is given.

FINAL REPORT
for the period July 1, 1949 - July 31, 1950

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Introduction.

As in past years, four detailed progress reports (P.R., numbered XXXV to XXXVIII inclusive) have been submitted. The last of these covers a four month period, April 1 to July 3, 1950, and bears the same date as this final report. Copies of these quarterly reports are appended to this final report; the latter consists of summaries of the various phases of the work undertaken, together with references to the more detailed description in the Progress Reports.

I. Borazole Studies.

A. Preparation of Borazole.

Although, as reported in the work of the year 1948-49, a method for the preparation of borazole more convenient than the interaction of ammonia with diborane was found in the reaction of solid ammonium chloride with solid lithium borohydride (P.R. XXXI, p 6, Sept 1948), the procedure is not completely satisfactory. There seemed to be two principal causes for the difficulties encountered, namely, a secondary reaction between ammonium chloride and borazole (P.R. XXXII, pp 5-6, December, 1948) and the caking of the reaction mixture (P.R. XXXIII, p 8, March 1949).

As a possible alternative method of preparation, reduction of trichloroborazole seemed feasible, since Laubengayer and C. A. Brown had developed a procedure for the preparation of the latter. It was first shown that in the interaction of solid lithium aluminum hydride with solid trichloroborazole, borazole was obtained. At room temperature the yields were very small; at higher temperatures they were even less, apparently due to the intermediate formation of B-mono and probably also B-dichloroborazole--compounds less stable than borazole itself (P.R. XXXVI, p 4, Dec. 1949).

A great deal of time has been devoted to the study of reduction by lithium aluminum hydride in a variety of solvents. It was found that diethyl ether (the best solvent for this reducing agent) could not be used because it forms an azeotrope with borazole (P.R. XXXVII p 2). Borazole may be separated from dimethylcellosolve, but only by the addition of aluminum chloride to the mixture, a procedure which is disadvantageous because the chloride causes decomposition of borazole if the two are in contact for any length of time. (P.R. XXXVI, p 4, and P.R. XXXVII, p 3).

A number of other solvents were investigated, with either lithium aluminum hydride or lithium borohydride or with both. Among them were phenyl chloride, which gave very low yields (P.R. XXXVI, p 5), and methyl cyclohexane and borazole itself, in neither of which solvents did the desired reaction occur (P.R. XXXVI, p 5). The most favorable solvents were n-butyl ether and n-hexyl ether, of which the latter was less frequently employed. (P.R. XXXVII, p 2 and XXXVIII, p 1).

It is not necessary to review the many experiments (P.R. XXXVIII, p 1) carried out to ascertain why, although lithium aluminum hydride undoubtedly reduces trichloroborazole to borazole the latter cannot be recovered from the solutions of those ethers which proved the most satisfactory solvents. Suffice it to say that it

F. R. 2 Borazole Studies

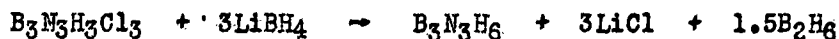
now appears as if the formation of aluminum hydride is the disturbing factor, whether initially present in impure lithium aluminum hydride or whether formed as a step in action of this compound on trichloroborazole, as illustrated by the hypothetical equation:



Two experiments serve as evidence for this interpretation of the difficulties encountered. When a mixture of pure borazole and butyl ether was evaporated and the vapor condensed, from 87 to 92% of the borazole was found to be present in the condensate; furthermore, about 80% of the original borazole could be separated from the butyl ether by use of a small, glass helix-filled column (P.R. XXXVIII, p 2). But when lithium aluminum hydride, containing an excess of aluminum hydride, was added to the butyl ether solution of borazole, less than 1% of the latter appeared in the volatile material. Equally significant is the fact that when lithium aluminum hydride alone was used to reduce trichloroborazole, less than 1% of the expected borazole could be volatilized with the butyl ether in which the reaction was carried out, but that when lithium hydride was added to the reaction mixture, yields of from 80-90% have been obtained. This result is readily explained on the interpretation under discussion, since it is well known that lithium hydride reacts with aluminum hydride in ether suspensions to form lithium aluminum hydride.

Thus far, however, the use of a mixture of lithium aluminum hydride and lithium hydride in butyl ether has been successful only when small (m mole) quantities of trichloroborazole were involved, and when the reaction was carried out in the vacuum system. When larger quantities were used and the reaction was carried out under nitrogen, the products obtained have thus far proved difficult to separate. There is evidence that under these conditions, which require longer time and higher temperatures, interaction of the lithium aluminum hydride with the ether occurs, and gives rise to products difficult to separate (P.R. XXXVIII, p 3).

Use of lithium borohydride as a reducing agent now appears more promising. It was to be expected that in its reaction with trichloroborazole, diborane would be liberated, possibly according to the equation



It was originally assumed that this reaction would have as its chief value the fact that measurement of the quantity of diborane evolved would prove a rapid and convenient method of determining the most favorable conditions for the reduction of trichloroborazole. Although initial experiments in phenyl chloride as a solvent gave unsatisfactory results (P.R. XXXVI, p 5), later experiments in n-butyl ether, carried out at room temperature, liberated an amount of diborane in 2 hours indicating 95% reduction, and produced 91% of the theoretical borazole. Of the latter, approximately 60% was isolated, and the remainder shown to be present in the residual ether (P.R. XXXVII, p 3).

The preceding experiment involved only about 5 m moles of trichloroborazole; it has hitherto not been repeated with larger quantities because the evolution of 1.6 moles of diborane per mole of borazole theoretically obtainable seemed a serious disadvantage of the procedure, implying the necessity of using vacuum procedures

F. R. 3 Borazole Studies

unsatisfactory for large quantities. But since the substitution of lithium aluminum hydride for the borohydride has caused so many difficulties, we are now investigating the effectiveness of the addition of lithium hydride to the borohydride to prevent the escape of diborane. Should this procedure prove effective, as seems possible in view of the corresponding experiments with lithium aluminum hydride, our long continued efforts to reduce trichloroborazole will have led to a satisfactory conclusion.

Additional work on the preparation of borazole consisted of attempts to reduce tribromoborazole, which was especially prepared for this purpose by the interaction of ammonium bromide and boron bromide in phenyl bromide (P.R. XXXVII p 2). Reduction with lithium borohydride in n-hexyl ether gave 87% of the theoretical diborane and 83% of borazole (loc. cit.). With lithium aluminum hydride, the results were like those obtained with the trichloro derivative. Hence, there appeared no advantage in the use of the bromine compound.

I. B. Mono and Di-halogenoborazoles.

Mono and dichloroborazole were prepared and described in the year 1948-49 (P.R. XXXII, p 5, Dec. 1948, and XXXIII, p 8, March, 1949). The work on the corresponding bromine compounds begun in that period (P.R. XXXIV, p 3, June, 1949) was completed in the current year, as described in P.R. XXXV, pp 4-6, where a summary of all of the physical constants of these compounds is given. As in the case of the trihalogenoborazoles, reduction by lithium borohydride was more successful than with the aluminum compound (P.R. XXXV, p 6). The reactions were not further studied.

I. C. Thermal Decomposition of Borazole.

One additional experiment on the very slow spontaneous decomposition of borazole was carried out. The results indicate a somewhat complex reaction for the study of which larger amounts of the starting material will be required (P.R. XXXV, p 6-7). Now that such amounts can be made available, the study, temporarily discontinued, will be undertaken again.

II. Further Studies on Tetrachlorodiborine and Related Compounds.

A. Tetrachlorodiborine.

1. Preparation. A number of efforts to improve the yield of tetrachlorodiborine in the mercury arc process for its preparation (F.R. 1948, pp 21-24) by changes in dimensions of the apparatus, and by the use of aluminum as an added reducing agent, were unsuccessful (P.R. XXXV, p 2). An improvement in the convenience, though not in the yield or conversion per pass, was effected by the use of a mechanical recirculation of the unchanged boron trichloride (P.R. XXXVII, p 3). It was also shown that carbon monoxide does not react appreciably with boron trichloride even at 350° C. (P.R. XXXV, p 3).

2. Reactions of Tetrachlorodiborine.

a. The compound under discussion absorbs hydrogen with remarkable rapidity at room temperature without the use of catalysts. In the original experiments (P.R. XXXI, p 4, Sept. 1948) it seemed that all of the chlorine of the tetra-

F. R. 4 Tetrachlorodiborine and Related Compounds.

chloro derivative was converted to boron chloride, and the remaining boron to solid hydrides. In later experiments with larger quantities, it became apparent that diborane is one of the products of the interaction and that its quantity, as well as that of the solid products obtained, depended on the experimental conditions (P.R. XXXV, p 2).

A previous observation on the behavior of liquid tetrachlorodiborine toward diborane (P.R. XXXIII, p 4, March, 1949) suggested that the products of the initial reaction between hydrogen and the chlorodiborine might be chlorodiboranes (e.g. $B_2Cl_4H_2$) which almost immediately and nearly completely disproportionate to boron trichloride and diborane. The solid products observed would then be explained by a secondary interaction of diborane with excess tetrachlorodiborine.

Thoroughly satisfactory confirmation of this interpretation was obtained by a study of the reaction under conditions such that all of the reactants were present in the gas phase at moderately low pressures. Under these conditions the major products were diborane and boron chloride, together with small amounts of monochlorodiborane and only traces of solid hydrides (P.R. XXXVI, pp 2,3,7).

These observations suggested that the preparation of diborane by the passage of a mixture of hydrogen and boron trichloride through an electric discharge might proceed through the initial formation of tetrachlorodiborine which would then react with excess of hydrogen as has just been described. To test this possibility, a mixture of hydrogen with an excess of boron trichloride was subjected to the arc discharge. Small amounts of tetrachlorodiborine were actually obtained under these conditions. The procedure does not, however, seem a desirable one for the preparation of this compound (P.R. XXXVI, p 3 and P.R. XXXVII, p 5).

Although the experiment supports the interpretation just discussed, another, very similar one, is conceivable. One might assume that, in the discharge, boron trichloride is dissociated to BCl_2 and chlorine atoms. The latter react equally readily with hydrogen or with mercury, and are thus removed whether the boron trichloride is passed through the arc in the presence of mercury or of hydrogen. The fragment BCl_2 may, however, be able to react with hydrogen but not with mercury. Hence in the presence of the former the main boron containing product may be $HBCl_2$ which polymerizes and then disproportionates, whereas in the presence of mercury the BCl_2 fragments polymerize to the diborine derivative. Data are lacking to ascertain which of the two possibilities is thermodynamically the more likely.

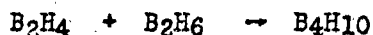
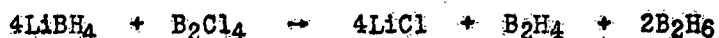
b. One mole of tetrachlorodiborine reacts with 8 moles of dimethylamine to form a new compound of empirical formula $B(NR_3)_2$, which in all probability is tetramethylaminodiborane, i.e., $B_2(NR_2)_4$ in which $R = CH_3$. The preparation analysis and a few of the properties of the compound are described in P.R. XXXVII, p 4, and P.R. XXXVIII, pp 4-5.

c. One mole of tetrachlorodiborine reacts with two moles of trimethylamine to form a product of empirical formula $BCl_2 \cdot NR_3$ (in which $R = CH_3$), as has been shown by analysis (P.R. XXXVII, p 4). It was anticipated that the compound is an addition product of 2 moles of trimethylamine with one of the chloroborane, i.e., $B_2Cl_4 \cdot 2NR_3$. However, a determination of the molecular weight by the freezing point lowering method, using benzene as a solvent, gave a value of 1105, which is almost four times the expected value of 279. Experiments are under way to ascertain whether this unexpected result is real or is due to the formation of solid solutions of benzene and the compound.

F. R. 5 Tetrachlorodiborine and Related Compounds

The compound is a white, very stable solid which, though it sinters somewhat at 125° C and shows signs of softening at 195° C, melts without noticeable decomposition at about 228° C if heated in an atmosphere of nitrogen. It is soluble in benzene and in diethyl ether; its solubility in isopentane is so slight that efforts to obtain the molecular weight in this solvent were unsuccessful (P.R. XXXVIII, p 5). It is far less reactive than tetrachlorodiborine itself. Thus, it does not react with hydrogen nor with diborane, as does tetrachlorodiborine; instead of liberating hydrogen chloride when treated with ethyl alcohol, it absorbs two moles of the latter. (P.R. XXXVII, p 4).

The possibility of hydrogenation of the compound $B_2Cl_4 \cdot 2NR_3$ has been investigated. Before discussing this aspect of our present work, it is desirable to review what had been done on the hydrogenation of tetrachlorodiborine itself. In earlier reports (P.R. XXXIII, pp 3-4, March, 1949, P.R. XXXIV, pp 5-7, June, 1949, P.R. XXXV, p 1) it was pointed out that neither lithium hydride nor lithium aluminum hydride in the presence of diethyl ether reacts with either tetrachloro or tetrabromodiborine. When the investigation of the latter reaction was planned, it was thought that the initial products might be diborane and the hypothetical diborine, and that these might react with each other to form dihydrotetraborane:



Actually, some dihydrotetraborane was obtained, but the amount of this compound was much smaller, and the amount of diborane produced was much greater than these equations demand. Lowering the temperature at which the reaction was carried out decreased the relative amount of diborane and increased that of the tetraborane. At still lower temperatures, achieved by the use of aluminum borohydride, the ratio of diborane to tetraborane was still further decreased.

These observations could be interpreted on the basis of the preceding equations provided it is assumed that the excess of diborane and the deficiency of tetraborane are due to the great instability of the latter. The appearance of still smaller amounts of pentaborane and decaborane might be similarly interpreted. The data obtained were, however, not sufficient to serve as a confirmation or denial of the hypothesis.

Further work on this reaction was deferred because of its complicated course, until a study could be made of the reduction (hydrogenation) of the compound $B_2Cl_4 \cdot 2NR_3$. The greater stability of the latter makes the study simpler, and the presence of trimethylamine might stabilize any initial reaction products, which might otherwise disproportionate or decompose. The first such reaction studied was its behavior toward lithium aluminum hydride (P.R. XXXVII, pp 4-5). A volatile crystalline product of 1 - 2 mm vapor tension at room temperature was obtained, but was obviously not homogeneous because it contained aluminum and boron in variable proportions. It may have been a mixture of the compound $AlH_3 \cdot NR_3$ with some unidentified boron compound, an assumption made plausible by the fact that the sample of lithium aluminum hydride used was later found contaminated with aluminum hydride.

The reaction should be studied further, but this work was postponed to allow time for the investigation of the behavior of the compound $B_2Cl_4 \cdot 2NR_3$ toward lithium borohydride. The initial experiment produced diborane, trimethylamine borine, and as yet unidentified nonvolatile materials. It is evident that there was not enough tri-

F.R. 6. Tetrachlorodiborine and Related Compounds.

methyllamine to convert all of the diborane to trimethylamine borine or to react completely with either the hypothetical B_2H_4 or the B_4H_{10} . Further studies in the presence of excess trimethylamine are in progress (P.R. XXXVIII, pp 5-6).

d. Tetrachlorodiborine does not react with methane or with hydrogen chloride at room temperature (P.R. XXXV p 3).

e. Summaries of reactions of tetrachlorodiborine studied in preceding years are found in F.R. 1948 p 26 and F.R. 1949 pp 4-6.

II. B. Subchlorides other than Tetrachlorodiborine. Little progress has been made in the study of the trace of volatile crystalline white material often observed as a very minor contaminant of tetrachlorodiborine. Thus far the amount collected has proved to be too small for even a qualitative analysis; in other words, it is not yet even certain that it is a boron compound. Efforts to improve the yield of the material have been unsuccessful (P.R. XXXV, p 2).

Enough of the slightly volatile, viscous red decomposition product of tetrachlorodiborine (P.R. XXXII, p 10, Dec. 1948) has been obtained for a preliminary analysis, as is true also of the nonvolatile white solid decomposition product. For the red material the B:Cl ratio was 1.0:0.91, or nearly 1:1; for the white, 5.1:3.0 (P.R. XXXVII pp 5-6). When attempts were made to determine the molecular weight of the red material in solution, it was discovered that it undergoes slow decomposition even at room temperature. There are indications that this decomposition may be inhibited by the pressure of boron trichloride, a possibility now being explored. These observations, however, throw doubt on the reliability of the analytical data, since the material analyzed may not have been homogeneous.

III. The Preparation of Calcium and of Sodium Aluminum Hydrides.

After long continued and unsuccessful efforts, satisfactory procedures for the preparation of both calcium and sodium aluminum hydrides have finally been developed. It is quite possible that the preparation of the former compound may be still further improved by applying to it the ideas developed in connection with the sodium compound, as will be described below.

III. A. Calcium Aluminum Hydride.

The best procedure so far developed for the preparation of this compound is still that described in P.R. XXXII, p 11, Dec. 1948. It consists of the treatment of calcium hydride with the diethyl etherate of aluminum chloride in dimethyl ether, followed by evaporation of the dimethyl ether and extraction of the residue with tetrahydrofuran. The procedure suffers from the slowness of the reaction and a moderately low yield.

Attempts to improve the procedure by carrying the reaction out in tetrahydrofuran were unsuccessful. At ordinary temperatures there was no appreciable reaction; at reflux temperature reaction occurred, but the product was impure, because, as was shown experimentally, metal aluminum hydrides react with this solvent at reflux temperatures. Other solvents were dimethylcellosolve, dioxane, and n-ethyl morpholine; none of these was satisfactory (P.R. XXXV, pp 3,8).

F. R. 7 Preparation of Calcium and of Sodium Aluminum Hydride.

It seems more than likely that the addition of small amounts of calcium chloride or of lithium chloride may improve the result, as is described below for the case of sodium aluminum hydride.

III. B. Sodium Aluminum Hydride.

Sodium aluminum hydride was initially prepared by the reaction of aluminum bromide on sodium hydride in the presence of dimethyl ether. A pure product in from 60-65% yield was obtained, but the reaction was not considered a desirable one because of the use of the relatively expensive aluminum bromide, and the necessity of carrying out the reaction and the filtrations under the 6-7 atmospheres pressure of dimethyl ether at room temperature.

The numerous unsuccessful efforts to obtain satisfactory results with aluminum chloride instead of the bromide need not be recounted. The most recent of them are reviewed in P.R. XXXVIII, pp 6-7. Recently, however, success has been obtained as a result of the consideration that the reagent actually reacting with the metal hydride is the AlX_4^- ion ($X = Cl$ or Br) rather than the simple halide AlX_3 .

To implement this hypothesis sodium hydride was treated with aluminum chloride and a small amount of lithium chloride in tetrahydrofuran. (Lithium chloride was employed because it is known to dissolve in ethers containing aluminum chloride, whereas that is not true of sodium chloride.) In the absence of lithium chloride, the corresponding reactions do not occur at all or are slow or incomplete, and fail to produce a pure product. But in the presence of lithium chloride a pure product was obtained in what was probably a short time, although the reaction was allowed to continue for 3 days to assure completion.

The details of the reaction are given in P.R. XXXVIII, pp 7-8, where also the details still to be settled before the solution of the sodium aluminum hydride problem may be considered complete are discussed, as well as the contributions of these observations to an understanding of the "induction period" in the reaction between lithium hydride and aluminum chloride.

IV. Thermal Decomposition of Lithium Borohydride and of Monomethyl Lithium Borohydride.

Repeated inquiries from individuals working on a variety of government supported investigations, about the observation reported by Schlesinger and Brown, JACS 62, 3429 (1940) that the early stages of the thermal decomposition of lithium borohydride is reversible, led us to reinvestigate the reaction. We were unable to confirm the earlier observation although we studied the decomposition under a variety of conditions. It was also shown that the decomposition of the monomethyl derivative, i.e. $Li(BH_3CH_3)$ is a continuous, nonreversible process (P.R. XXXV, pp 3-4, and P.R. XXXVI, p 6).

Catalysts greatly accelerate the decomposition. It seems possible that the very small quantity of lithium borohydride (6 mg) used by Schlesinger and Brown may have contained an impurity which acted as a catalyst, and thus formed traces of lithium hydride to which the reversibility observed may have been due.

F. R. 8 Reaction of Lithium Borohydride with Hydrazine Hydrochloride.

V. Reaction of Lithium Borohydride with Hydrazine Hydrochloride.

It is reasonable to hope that the reactions of hydrazine and its derivatives with diborane and its derivatives might lead to interesting new types of boron-nitrogen-hydrogen compounds. The work has at present just begun.

Because of the ready availability of the starting materials, we began the work with a preliminary study of the reaction between lithium borohydride and hydrazine dihydrochloride, both in the absence of solvents and in diethyl ether. As was to be expected from the behavior of amine hydrochlorides toward the borohydride, about 1 mole of hydrogen was evolved per mole of the borohydride at room temperature, and about 2 moles at higher temperatures. The study is complicated by the fact that aside from hydrogen and traces of diborane, no other volatile products are obtained. We are, therefore, postponing the further study of this reaction until we have investigated the presumably simpler one between diborane and hydrazine. The latter reagent was supplied to us through the courtesy of the Naval Research Laboratory.

Publications.

1. A paper by T. Wartik, R. E. Moore, and H. I. Schlesinger on tetrachlorodiborane is to be presented at the September meeting of the American Chemical Society, and will be submitted for publication before long.

2. Two papers by T. Wartik and H. I. Schlesinger on the reactions of lithium aluminum hydride on alkyl compounds of the metals are being prepared for publication.

3. A paper by G. W. Schaeffer, Riley Schaeffer and H. I. Schlesinger on the preparation of borazole by the action of ammonium chloride on lithium borohydride and on the action of boron halides on borazole has been submitted for publication.

4. The work on the preparation of sodium and calcium aluminum hydrides by T. Wartik, G. Urry, and H. I. Schlesinger should soon be in shape for publication.

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by

H. I. Schlessinger and T. Wartik

in collaboration with

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The period covered by this report includes the vacations due the members of the staff as University employees. Furthermore, a large part of the work undertaken is experimentally difficult and time-consuming. For both of these reasons, progress has been relatively slow.

The work undertaken has covered:

I. Further borazole studies:

(a) Additional data on the physical constants of mono and dichloro, and of mono and dibromoborazoles have been obtained. The present report includes, in addition to the new data, a summary of all of the data hitherto reported.

(b) The mono and dichloroborazoles may be reduced to borazole by either lithium aluminum hydride or lithium borohydride.

(c) A few additional data are reported on the slow room temperature decomposition of borazole. As explained in the experimental part of the report, these data have proved themselves difficult of interpretation.

II. Further studies on halogeno diborines and on other subchlorides of boron.

(a) All efforts to hydrogenate chloro and bromodiborines by lithium aluminum hydride and lithium hydride have failed. The latest experiment, that is, the treatment of tetrabromodiborine with lithium hydride in the presence of diethyl ether, led to no result. Details of the experiment need not be reported. Attention is called to the hydrogenation of tetrachlorodiborine by lithium borohydride, and the complications involved in this reaction (P. R. XXXIII, pp 3 - 5, and XXXIV, pp 5 - 7).¹⁾

1) The abbreviation P. R. refers to progress reports, the abbreviation F. R. to final reports. Progress Reports I to XI, inclusive, are bound with the final report for the year, July 1, 1944 to June 30, 1945 (F. R. 45); P. R. XII through XXIII with F. R. 46; P. R. XXIII through XXVI with F. R. 47; P. R. XXVII through XXX with F. R. 48; and P. R. XXXI through XXXIV with F. R. 49.

(b) Reaction of tetrachlorodiborine with hydrogen.

In an earlier experiment in which only 6 mg. of tetrachlorodiborine were treated with hydrogen, the data indicated that all (or nearly all) of the chlorine (98%) was converted to boron trichloride (P. R. XXXI, p. 4). Repetition of the experiment on a considerably larger scale has thus far led to only 80% recovery of the chlorine as boron chloride. It is conceivable that, because of the very small quantities involved in the earlier experiment, the data are in error. It is equally likely that the difference between the earlier experiment and the one on a somewhat larger scale is due to some difference in the conditions. Obviously, if all of the chlorine can be converted to boron trichloride, analysis of the residue and the interpretation of the results will be greatly simplified. Although some time was devoted to an attempt to separate the several products obtained in the larger scale experiment, the data will not be reported further until it is definitely ascertained that the earlier results are not reproducible.

(c) Among the reactions of tetrachlorodiborine reported in preliminary fashion was its behavior toward ammonia, which appeared to be complex (P. R. XXXI, p. 8). The reaction with trimethylamine has now been shown to be simpler, in that approximately 2 moles of the amine react with one mole of the tetrachloride. An interpretation of this observation and its bearing on the ammonia reaction are discussed later in this report.

(d) In the preparation of tetrachlorodiborine by the arc process (F. R. 48, pp 22 - 24) very small amounts of products less volatile than the tetrachloro compound have been observed. It seems likely that these are homologues of tetrachlorodiborine, such as B_3Cl_5 , B_4Cl_6 etc. A little of these products has now been collected from the byproducts in the preparation of the tetrachloro compound. A white solid, readily sublimable in vacuo (vapor tension at about 30° C. approximately 0.5 mm), and at least moderately stable, has been isolated. Further description is deferred to a later report, since analyses and further studies are now in process.

(e) Attempts to improve the yields of the "subchlorides" of boron.

(1) A mixture of boron trichloride and tetrachlorodiborine was passed through the discharge apparatus (F. R. 48, pp 22 - 24) in an attempt to prepare the hypothetical higher chloroborines. None of the desired compounds was obtained; the only result was the complete disappearance of the tetrachloro compound. In another experiment, the tetrachloro compound, unaccompanied by boron trichloride, was subjected to the discharge. On a single pass, all but 3.1 cc of 30.5 cc (gas at S. C.) had been converted to an orange brown deposit and to 29.0 cc of boron trichloride. Evidently, these methods of securing larger quantities of the desired products are not feasible, and there is no reason for reciting details.

(2) As a result of the failures reported in the preceding paragraph, efforts have been and still are directed toward improving the yields of the tetrachloro derivative. Among these was the use of powdered aluminum in the discharge tube as a means (in addition to the mercury vapor) for removing the chlorine probably formed from boron trichloride under the influence of the discharge. The yields (average of two runs, 45%) and conversion (average of two runs, 3.1%) were of the same order of magnitude as were obtained in the absence of aluminum, and the procedure has the great disadvantage that the aluminum greatly retards the rate of flow through the discharge tube. No further details about these experiments are to be given.

(3) Carbon monoxide failed to reduce boron trichloride to a borine homologue under a variety of conditions, e. g., at room temperature, at 110° C, and 350° C, or under the influence of ultraviolet light.

(f) Methane and hydrogen chloride have been shown not to react appreciably with tetrachlorodiborine, since the only changes observed were those which might have resulted from the spontaneous decomposition of the tetrachloro derivative under the conditions of the experiment. The experiments were carried out at room temperature over periods of from 20 - 40 minutes.

III. Preparation of Calcium Aluminum Hydride.

(a) The reaction of calcium hydride on the diethyletherate of aluminum chloride in tetrahydrofuran as a solvent has been studied further. At room temperature no appreciable amount of calcium aluminum hydride was obtained after ten days stirring of the mixture. At reflux temperature of the mixture, however, reaction occurred after a two hour treatment, as shown by the fact that the solution contained calcium, aluminum and hydrogen in the atomic ratio $\text{Ca}_1\text{Al}_{2.08}\text{H}_{6.26}$. An additional 2 hour heating at reflux temperature improved the result in that the ratio had become $\text{Ca}_1\text{Al}_{2.08}\text{H}_{6.72}$. But a further heating period of about 12 hours caused a diminution of the active hydrogen content as seen from the observed ratio $\text{Ca}_1\text{Al}_{2.11}\text{H}_{4.86}$. The fact that the ratio Ca/Al remained practically constant while the relative amount of active hydrogen decreased, suggests that at reflux temperature tetrahydrofuran is reduced by aluminum hydrides, presumably to compounds of ions of the type $(\text{AlH}_x(\text{OR})_{4-x})^-$. Such a reaction would obviously decrease the H/Al ratio without altering the Ca/Al ratio in the reaction under discussion. This suggestion has been confirmed by showing that hydrogen is lost when solutions of lithium aluminum hydride in tetrahydrofuran are maintained at reflux temperatures, as described in the experimental part of the report.

The reactions of calcium hydride with aluminum chloride in the presence of dimethyl cellulose, in dioxane and in N-ethyl morpholine at about 60° C were also studied. In no case was evidence for the formation of calcium aluminum hydride obtained. In the reaction in N-ethyl morpholine, considerable cleavage of the ether by aluminum chloride seemed to occur, whether the latter was added directly or as a diethyl etherate.

It is proposed to carry out only one further set of experiments on this reaction, in order to ascertain whether there is a temperature below that of reflux, at which reaction occurs without appreciable reduction of the solvent. Should no improvement result, we shall let the matter rest with the procedure described in P. R. XXXII, p. 11, which, though not convenient in glass apparatus can be very easily carried out in a metal reactor capable of withstanding from 5 - 10 atmospheres pressure.

IV. Thermal Decomposition of Lithium Borohydride.

Schlesinger and H. C. Brown, in their original paper on lithium borohydride (J.A.C.S. 62, 3429 (1940)), reported that at from 275° - 280° C, the compound loses about one half of its hydrogen. Further loss of hydrogen was reported as being very slow. It was further reported that hydrogen was

reabsorbed by the residue when the temperature was lowered. It was recognized at the time that these observations needed verification, since only one experiment was carried out, and involved only 6 mg. of the borohydride, which might not have been pure.

Attempts to repeat this observation have been unsuccessful thus far. In the absence of catalysts the loss of hydrogen is very slow at about 280° C, and there is no evidence of a change of rate at any concentration. In the presence of Raney nickel the decomposition sets in at lower temperature and goes to completion without any noticeable break at any point.

V. Publications.

A preliminary paper, "Derivatives of Diborane" by Thomas Bartik, R. Moore and H. I. Schlesinger, J. A. C. S. 71, 3265 (1949) has resulted from the work on the project. Other papers are in preparation.

Experimental Data

Experimental data are given only for experiments in which definite positive results have been obtained. In the case of negative results, descriptions of procedures are unnecessary because they have not differed from those described in earlier reports. In the case of experiments still under way, such data as necessary will be reported later.

I.(a) B-dibromo borazole was prepared by treatment of borazole with boron tribromide (P. R. XXXIV, p. 2). The volatile solid products obtained were fractionated through -22° C and -30° C traps. The white crystalline solid retained in the -30° C melted at 49.5° - 50.0° C. Analysis by the hydrolytic methods previously used for halogenoborazoles gave the results recorded in Table I.

Table I
Analysis of B-Dibromo Borazole

B ₃ N ₃ H ₄ Br ₂ Weight of sample (mg.)	Hydrolyzable H ₂ (m.moles)		NH ₃ (m.moles)		B ₂ O ₃ (m.moles)		Br (m.moles)	
	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
9.0	0.038	0.038	0.113	0.114	0.092	0.114	0.070	0.076
9.0	0.032	0.038	0.110	0.114	0.120	0.114	--	--

The agreement between observed and calculated values is good in view of the small samples available. Vapor tension measurements were made at elevated temperatures. The data above 50° C. are expressed by the equation:

$$\log P = 9.352 - \frac{2849}{T}$$

which was obtained by the method of least squares. The extrapolated boiling point is 167° C; the heat of vaporization, 13,037 cal./mole; and the Trouton constant, 29.6. Vapor tension data and temperatures calculated for each pressure from the above equation are recorded in Table II for comparison.

Table II

Vapor Tensions of B-Dibromo Borazole

P mm.	T _{obs.}	T _{calc.}
<chem>B3N3H4Br2</chem>		
0.9	303.8	---
2.2	316.7	---
3.4	323.0	---
4.3	326.3	326.7
5.7	331.2	331.4
9.3	340.9	339.8
18.2	353.4	352.1
31.5	362.3	362.7
122.4	390.3	392.1

} at or below
melting point.

Monobromo borazole has been found to be somewhat less stable than the corresponding chloro compound. Thus a sample of monobromo borazole decomposed over a period of five days at room temperature to give hydrogen, a nonvolatile white solid and a material more volatile than bromoborazole, presumably borazole itself.

Table III contains a summary of the physical properties of halo borazoles. Melting points of chloro borazoles are recorded in addition to data previously reported.

Table III

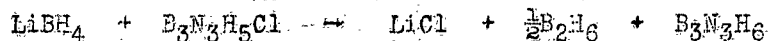
Physical Properties of Halo Borazoles.

Formula	m.w. calc.	m.w. obs.	m.p. ° C.	Normal b.p. ° C.	H Vap. cal./mol.	Trouton Constant	Log P _{mm} A	B - A/T
<chem>B3N3H5Cl</chem>	114.9	117.5	-34.6	109.5	8,445	22.1	1,846	7.703
<chem>B3N3H5Br</chem>	159.4	153	-32.8	122.3	9,939	25.1*	2,172	8.373
<chem>B3N3H4Cl2</chem>	149.4		33.5	151.9	9,125	21.5	1,994	7.572
<chem>B3N3H4Br2</chem>	238.4		50.0	167.1	13,037	29.6*	2,349	9.352

*The unusually high value for Trouton's constant probably has no important significance. The extrapolation for the boiling point is large (about 50° C) and a slight error in the slope of the vapor tension curve would produce a large error in the value of the constant.

(b) Reduction of B-monochloro Borazole

The reaction of 8.6 cc. of monochloro borazole with an excess of lithium borohydride at room temperature for twenty-one hours in the absence of solvent gave 7.5 cc. of borazole and 4.3 cc. of diborane. These data fit the equation of the expected reaction



Lithium aluminum hydride appears to be equally effective as a reducing agent but this experiment has not as yet been completed. A small amount of hydrogen was produced in the reaction and the zero vapor tension of the product was 89 mm. in contrast to that of pure borazole, 84.8 mm. Since the lithium aluminum hydride was deposited from an ether solution and the solid heated only one hour at 60 - 65° C, a trace of residual ether may be present in the product, accounting for the high vapor tension.

The reduction of dichloro borazole with lithium aluminum hydride appears to take place in the absence of solvent, but a complete report of this reaction cannot be made at the present time.

(c) The Slow Decomposition of Borazole

As reported in P. R. XXXIV, p. 4, about 4 g. of borazole decomposed in about two months to give 452 cc. of hydrogen and 34.5 cc. of diborane. The remaining mixture was fractionated through traps kept at -11° C, -45° C, and -196° C. Borazole and traces of diborane were retained in the latter trap. On warming, the -45° C trap was found to contain a liquid, while a white solid was retained in the -11° C trap. Attempts to purify the former were unsuccessful, due to a moderately rapid decomposition at room temperature to give diborane and a nonvolatile white solid. The vapor tension of this material at room temperature was about ten mm., but more than doubled during a ten minute period at room temperature. Attempts to measure the gas density were unsuccessful. The solid retained in the -11° C trap also decomposed slowly during attempts at purification giving diborane and a nonvolatile white solid.

Both fractions were purified as much as possible and hydrolyzed. Analytical data for these fractions and for the nonvolatile white solid produced in the initial decomposition of borazole are given in Table IV.

Table IV

Compound	Sample weight (mg.)	Boron (mr. at. wts.)	Nitrogen (mr. at. wts.)	Hydrolysable Hydrogen (mr. at. wts.)
volatile liquid	...	4.53	3.98	4.12
volatile solid	...	1.85	1.76	1.50
nonvolatile solid	28.9	1.15	1.12	0.59
	50.9	1.98	2.02	1.09
	27.8	...	...	0.59

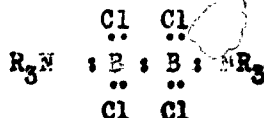
It is interesting to note that in the nonvolatile solid, the atomic ratio B:N:H in two experiments averages 1.00:0.995:0.53, or very nearly $B_2N_2H_4$. Furthermore, the sum of the weights of the nitrogen, the boron and the hydrogen constitutes over 99% of the weights of the material analyzed. Nevertheless, it does not seem permissible to assume that the formula is that indicated by the analysis, since the analytical procedure yields only the amount of hydrogen attached to boron, and does not show the hydrogen attached to nitrogen. It is therefore not yet demonstrated that the nonvolatile solid is a homogeneous material. Similar comments apply to the analyses of the two other products, except that in the analyses of these, the weight of sample was not obtained because of their rapid decomposition.

II (b) In approximately 1 1/2 hours, 38.2 cc. of B_2Cl_4 (gas at S. C.) absorbed 15.1 cc. of hydrogen, and produced 40.8 cc. of boron trichloride. Had all of the chlorine been converted to boron trichloride, the quantity of the latter would have been approximately 51 cc; in other words, only 80% of the expected amount of boron chloride was obtained. Similarly, the amount of hydrogen absorbed is only about 85% of that expected for a reaction exactly like the smaller scale experiment initially carried out (P. R. XXXI, p. 4). Furthermore, the original experiment gave rise to a small quantity of a sublimable white solid; no corresponding material was observed in the present experiment. In the latter, a number of volatile products containing boron, chlorine and hydrogen were obtained.

Experiments are under way to ascertain whether the difference in the results are due to incompleteness of reaction in the more recent experiment, or whether in it conditions were such that partial chlorination of an initially produced borane occurred.

(c) Trimethylamine was purified by treatment with phosphorus pentoxide in a sealed tube at $100^\circ C$ for 15 hours. Of the purified material ($0^\circ C$ tension, 698 mm, accepted value 681 mm), 54.5 cc. (gas at S. C.) was condensed on 9.13 cc. of tetrachlorodiborine. A vigorous reaction, coating the walls of the reaction vessel with a white deposit, set in before the mixture had warmed to room temperature. The mixture was nevertheless allowed to stand for 24 hours at room temperature, after which time the volatile contents were removed. The vapor tension of the volatile material was 178.7 mm at $-30^\circ C$ (melting bromobenzene) whereas the accepted value for trimethylamine is 179 mm. The volume of gas was 37.0 cc. showing that 17.5 cc. of the amine had reacted with the 9.13 cc. of B_2Cl_4 , a ratio of $N(CH_3)_3/B_2Cl_4 = 1.92/1.00$.

It, therefore, seems probable that an addition reaction yielding the product:



had been obtained. The corresponding reaction with ammonia might initially have formed a similar addition product, which could, however, have reacted further with ammonia according to the equation:



This equation accounts for the fact that one mole of tetrachlorodiborine absorbs (approximately) 6 moles of ammonia (P. R. XXXI, p. 8). It has been shown that the product of the ammonia reaction contains ammonium chloride, but further study of the nonvolatile residue is needed to confirm the observation. It will be especially interesting to ascertain whether this product is the same as the substance (BNH)_x reported by Stock and Pohland, Ber. 59B, 2215 (1926).

The trimethylamine addition product seems very stable at room temperature and is sublimable without decomposition when gently warmed. Because of this stability, it was thought that the relatively unstable tetrachlorodiborine might be stored as the aminate. It is, however, impossible to regenerate the simple chloro compound by treatment of the aminate with either boron trichloride or trifluoride.

It is considered unnecessary to discuss further the details of items II (a), (d) (e) and (f) of this report.

III. Preparation of Calcium Aluminum Hydride. Action of lithium aluminum hydride on tetrahydrofuran.

The experiments on the reaction of calcium hydride with the diethyl etherate of aluminum chloride in tetrahydrofuran need no further description, but it seems desirable to describe the evidence supporting the conclusion, discussed earlier, that aluminohydrides reduce tetrahydrofuran. A solution of lithium aluminum hydride in that solvent was prepared by dissolving a sample of a commercial product in the solvent and then removing the insoluble residue by filtration. Two aliquots of approximately 10 ml. were taken; one was analyzed as a blank and the other was heated at reflux temperature for four hours. The blank generated 58.9 cc. of hydrogen per gram of sample, whereas the refluxed aliquot generated only 28.8 cc. of hydrogen when hydrolyzed in the usual way. The approximately 50% decrease in active hydrogen is adequate evidence that our interpretation of the difficulty in the preparation of calcium aluminum hydride in tetrahydrofuran is a valid one. Some curious observations in connection with the rate of loss of active hydrogen are being studied further and, if confirmed, will be described in later reports.

IV. The lithium borohydride used in this study of its thermal decomposition was a sample recrystallized from ether, and was shown by the volume of hydrogen evolved to be of 98.4% purity. A 0.1117 g. sample of the product was slowly heated to about 270° C in an evacuated system. At 200° C a small pressure (2 mm) developed but remained constant. The temperature was maintained at from 268° C to 287° C for 19 hours during which time the pressure slowly rose to 70 mm. Cooling of the reaction vessel to room temperature produced only a small pressure decrease, indicating that no reabsorption of hydrogen occurred. The hydrogen obtained was then removed by a Toepler pump; its volume proved to be 15.4 cc. (S. C.), which corresponds to only a little over 6% of the amount contained in the borohydride used.

The residual material was reheated several times at temperatures varying from about 273° to 298° C. Between each heating period, the reaction vessel was cooled before removal of the hydrogen, to ascertain whether reabsorption occurred, but at no time was the decrease in pressure which accompanied lowering of the temperature greater than that due to the normal contraction of the gas volume. During a total of about 200 hours of heating the material, only a total of 53.7 cc., or about 2.4 m.moles of gaseous hydrogen were obtained. This quantity is only about 25% of the total hydrogen of the original sample of lithium borohydride. The product remaining in the reaction vessel contained yellowish solids in addition to the white unchanged borohydride, but it was not further investigated.

The slowness of the decomposition and the small amount of hydrogen obtained were in marked contrast to the observations reported by Schlesinger and Brown (op. cit). Since in the latter's experiment, a catalytic impurity might have been present, lithium borohydride was next mixed with Raney nickel, prepared by the method of Pavlic and Adkins (J.A.C.S. 68, 1471 (1946)). The sample contained about 74% of nickel and 24% of aluminum; it was dried and heated under vacuum for 10 hours at 130° C.

In the first experiment, a sample of lithium borohydride was mixed in a dry box under nitrogen with an approximately equal volume of the catalyst. After the reaction vessel containing the mixture had been attached to the line and evacuated, it was heated to 225° C. in vacuo. Noncondensable gas was rapidly evolved. The heating was discontinued several times, but no reabsorption of gas was observed. Since the volume of gas collected exceeded the total hydrogen contained in the borohydride used, it was evident that the Raney nickel had either not been degassed completely, or that it had adsorbed nitrogen in the dry box. For this reason, further details of the experiment are not given.

In the next experiment, a side arm was attached to the reaction vessel in such a way that the contents of the side arm could be added to those of the reaction tube in vacuo. The catalyst was placed into the side arm, and the borohydride (1.25 m.moles) into the bottom of the reaction tube. The former was heated to 290° C. for 19 hours in vacuo, during which time the reaction vessel itself was at room temperature. When the system had become evacuated, the catalyst (after it was cooled) was allowed to fall on the borohydride, and the two were mixed with the aid of two magnets. The material was then heated. Evolution of gas seemed to begin at about 219° C. The sample was kept at 225° C for about 2 hours, and then at 290° C for about 48 hours. The gas collected at the end of this heating period had a volume of 48.7 cc (2.17 m moles) and, except for a trace of material, was completely noncondensable. The volume of gas corresponded to about 85% of the hydrogen to be expected from complete decomposition of the borohydride. No reabsorption occurred when the residue was cooled in contact with the gas. After further heating at about 290° to 297° C over a period of 70 1/2 hours, the total gas evolved amounted to 2.74 m. moles (about 10% more than expected from complete decomposition). The excess of gas might have been due to a slow leak in the system.

In a final experiment, special care was taken to decrease the aluminum content of the catalyst by use of concentrated sodium hydroxide, and to avoid adsorbed gases. For the latter purpose, the catalyst was washed with alcohol, then dried at 270° C with continuous pumping, and finally heated at 340° C for 10 hours. The apparatus in which the mixing of the catalyst and the borohydride and the heating of the mixture were carried out were so constructed that each of the components of the mixture could be separately heated before mixing. The catalyst was heated for 6 hours at 310° C. in the apparatus, the lithium borohydride for 9 hours at 45° C in vacuo to remove residual ether. Mixing of the materials was carried out as previously described.

From 4.11 m.moles of the borohydride, mixed with an approximately equal volume of catalyst, 1.62 m.moles of noncondensable gas were liberated in 45 minutes at 240° C. Another heating period of 1 1/4 hours at 240° and 1/2 hour at 300° C brought the total gas evolved to 92.2 cc, or 4.12 m.moles, a quantity just 1/2 of that expected for complete decomposition. The pressure in the apparatus at room temperature was considerably higher than that in the experiment of Schlesinger and Brown (225 mm, as compared with about 22 mm); nevertheless no reabsorption of gas occurred at room temperature. Further heating at 300° C for a total of 26 hours increased the amount of collected gas to 6.78 m.moles. Evolution of gas had become slow; heating was continued at 330° C and 360° C, until, after a total heating period of 69 hours, 7.26 m.moles, or 88.4% of the total hydrogen had been evolved. Treatment of the residue with ether showed that it contained little, if any, material soluble in this solvent. This fact demonstrated conclusively that the gas evolved had resulted from decomposition of the borohydride rather than from release of adsorbed gas by the catalyst.

In none of the experiments was the reabsorption of gas reported by Schlesinger and Brown observed. The latter authors worked with minute quantities (6 mg) of the borohydride, which might have been contaminated with some impurity not present in our samples. Since ethyl lithium was used in the preparation of Schlesinger and Brown's sample, alkyl borohydrides might have been present. We are, therefore, now studying the thermal decomposition of compounds of this type.

HYDRIDES AND BOROHYDRIDES OF LIGHT WEIGHT ELEMENTS
AND RELATED COMPOUNDS

Progress Report No. XXXVI on Contract N6ori-20, T.O. X
for the period October 1, 1949 to December 31, 1949.

by

H. I. Schlesinger and T. Wartik

in collaboration with

R. E. Moore, Riley Schaeffer, Martin Steindler and G. Urry

The work undertaken during the period covered by this report included the followings:

- I. Further investigation of tetrachlorodiborine
 - (a) Attempt to analyze the slightly volatile, red decomposition product.
 - (b) Preparation and analysis of $B_2Cl_4 \cdot 2N(CH_3)_3$
 - (c) Reaction of $B_2Cl_4 \cdot 2N(CH_3)_3$ with $LiAlH_4$ and with LiH .
 - (d) Reaction of B_2Cl_4 with hydrogen.

II. Reduction of trihalogenoborazoles

- (a) Reduction of trichloroborazole with lithium aluminum hydride and with lithium borohydride in the absence of solvent and in the presence of various solvents.
- (b) Preparation of tribromoborazole
 - (1) By reaction of trichloroborazole with boron tribromide.
 - (2) By interaction of an onium bromide and boron bromide.

III. Thermal decomposition of lithium borohydride and of lithium monomethylborohydride.

IV. Modified procedures for the preparation of sodium aluminum hydride.

Of the preceding experiments only items I (d) and III are completed; on the rest there has been definite but slow progress. Only the experiments in which definite results have been obtained are reported in detail.

1. The work on tetrachlorodiborane has proved unexpectedly difficult because of the fact that the compound decomposes with appreciable speed at temperatures at which it reacts with the reagents in which we are at present interested. The compound $B_2Cl_4 \cdot 2N(CH_3)_3$ is considerably more stable and might undergo the same types of reactions which are of interest in the simple tetrachlorodiborane. For this reason, we are planning considerable work with the trimethylamine derivative, but before this is to be undertaken, we must make certain of having samples uncontaminated with the substances that might be obtained by interaction of trimethylamine with impurities in the tetrachlorodiborane. For this reason, we have spent considerable time in the purification of the chlorodiborane and the analysis of the solid trimethylamine derivative to make sure of its homogeneity. It may be added that considerable difficulties were encountered in the analysis of the trimethylamine, but it is believed that these difficulties have now been overcome. Since the analyses are not yet quite complete, details of analytical procedure and their results will be deferred until the next progress report is made.

Preliminary experiments have shown that the trimethylamine derivative reacts with lithium aluminum hydride to give a moderately volatile product which appears to contain aluminum. Neither the homogeneity of the product nor its composition have as yet been established. There are some indications that the amine derivative may react with lithium hydride, but the observations are not conclusive.

Much of the difficulty encountered in the work with tetrachlorodiborane has been due to the small quantities available. Hitherto there has been no great advantage in preparing larger quantities because of its decomposition at all temperatures not considerably below $0^\circ C$. Now that we are planning to work with the more stable trimethylamine derivative, we are seeking improved procedures for the preparation of tetrachlorodiborane. In this project, just recently undertaken, no progress has as yet been made.

During the course of the past few months, we had accumulated a small amount of the slightly volatile, red, solid decomposition product of tetrachlorodiborane, and have made an attempt to analyze it. The result is not completely satisfactory, since etching of the glass occurred during the course of the analysis. It may be stated that the Cl/B ratio, so far as can be judged from the present uncertain data, is not far from 1/1.

The most interesting development in the investigation of the tetrachloride has come out of the study of its reaction with hydrogen. It will be recalled that earlier experiments resulted in the formation of solid products, among which decaborane ($B_{10}H_{14}$) was suspected (F. R. 49, p. 4. P. R. XXXI, p. 8).¹⁾ Later

1) The abbreviation F. R. 49 refers to the final report for the year ending June 30, 1949; the abbreviation P. R. refers to progress reports.

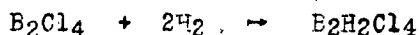
experiments, not reported in detail, led to inconsistent results (P. R. XXXV, p. 2) which suggested that diborane might be the initial product of the reaction and that the mixtures of solid and liquid products obtained might have resulted from the action of diborane on an excess of the liquid tetrachlorodiborane (F. R. 49, p. 5, P. R. XXXIII, p. 3).

This hypothesis was verified by experiments carried out in vessels large enough to allow all of the tetrachlorodiborane to be in the vapor phase at room temperature. As will be shown in the section of this report devoted to experimental details, diborane and boron chloride are the major products of the reaction, as indicated by the equation:

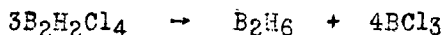


Even under these conditions, it was impossible altogether to prevent secondary reaction of diborane with the tetrachloro derivative as is shown by the facts (1) that the amount of hydrogen absorbed is less than demanded by the equation, (2) that the amount of boron chloride is greater and that of diborane less than the amounts calculated according to the equation from the amount of hydrogen consumed, and (3) that small amounts of products characteristic of the reaction of tetrachlorodiborane with diborane were observed. (see experimental details, p. 7).

The observations reported above suggest that the initial reaction between hydrogen and tetrachlorodiborane occurs according to the equation:



to be followed by the disproportionation:



The reaction is of interest in two respects. In the first place, hydrogen seldom reacts rapidly at ordinary temperatures in the absence of catalysts; although we have no measurements of the reaction rate, observation indicates that before the reactants have become diluted, the reaction proceeds with considerable speed, i.e., most of the reaction is completed in the first 30 or so minutes. It may be worthwhile to ascertain whether the reaction is photochemical.

The second point of interest is the relationship of this reaction to the preparation of diborane by the arc process (Schlesinger and Burg, JACS. 53, 4321 (1937)). It is conceivable that the first step in that process is dissociation of boron trichloride into BCl_2 fragments and chlorine atoms. The latter might then react with hydrogen to give hydrogen chloride and the former might either react directly with hydrogen to give BCl_2H which would disproportionate to diborane and boron chloride, or first polymerize to B_2Cl_4 and then react with hydrogen.

In the original experiments of Schlesinger and Burg, hydrogen was present in large excess, a condition which is desirable when the objective is the preparation of diborane. It now is desirable to repeat the experiments with the modification that boron trichloride is the component in excess, to ascertain whether in the arc method any tetrachlorodiborane is formed and, if so, whether this procedure might be an improvement over present methods of preparing tetrachlorodiborane. These experiments have just been undertaken and have not progressed far enough for a report.

II. In view of the fact that a fairly efficient method of preparing B-trichloroborazole has been developed by Brown and Laubengayer,¹⁾ its reduction might

1) Reported by Charles A. Brown and A. W. Laubengayer, on page 10P of Abstracts of Papers presented at the September meeting of the American Chemical Society at Atlantic City, 1949. See also Cornell University thesis of Charles A. Brown, June, 1948.

well prove to be a method of preparing borazole far more efficient than any now available. Such a development would be of considerable value in proposed studies of this compound.

Although Brown and Laubengayer were not successful in their efforts to prepare borazole by the reduction of the trichloro derivative by lithium hydride or by lithium aluminum hydride in the presence of n-butyl ether as a solvent, we nevertheless believe it worthwhile to reinvestigate this problem, because we have found that B-monochloro and B-dichloroborazoles may be reduced to borazole (P. R. XXXV, pp 1 and 6). It, therefore, seems possible that the trichloro derivative might also be efficiently reduced if the right conditions could be found. Our experiments in this direction have thus far merely shown that reduction by lithium aluminum hydride or by lithium borohydride does occur, but have not yet led to a solution of the problem. Consequently, the present report will only be a qualitative description of the work thus far done.

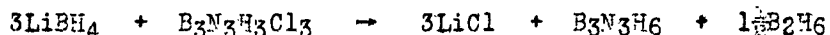
Reaction of solid B-trichloroborazole with solid lithium aluminum hydride for three days at room temperature gave a small amount of material having a zero tension of 83.5 mm, as compared with the 84.8 mm vapor tension of borazole at 0° C. Repetition of the reaction for 12 hours at 60-65° C. resulted in the formation of small amounts of B-monochloroborazole with only traces of borazole. This result is not surprising in view of our observation that after heating a mixture of 1.1 m moles of B-trichloroborazole with 1.7 m moles of borazole at 150° C. for 15 minutes, there were present 1.1 m moles of unchanged borazole, 0.24 m mole of B-monochloroborazole, together with smaller quantities of the di- and trichloro derivatives, hydrogen and a small quantity of nonvolatile solid material. Evidently, borazole undergoes disproportionation with the trichloro derivative to produce less highly chlorinated borazoles. For this reason, it does not seem likely that the solid-solid reaction between trichloroborazole and lithium aluminum hydride will become an efficient procedure for the preparation of borazole, although we have succeeded in making small amounts of borazole in this way for use in other experiments.

We next turned our attention to the use of solvents. The first one employed was dimethyl cellosolve. Like Brown and Laubengayer, in their analogous experiments in which they used n-butyl ether, we observed evidence that interaction had occurred, but were unable to isolate any borazole by fractionation of the volatile material. A subsequent test with a mixture of borazole and dimethyl cellosolve showed that the two cannot be separated by the ordinary fractionating procedures, but also demonstrated that after addition of aluminum chloride, a considerable portion of the borazole could be recovered. Evidently, borazole forms complexes with ethers; furthermore, the experiment just mentioned indicates that the ether can be removed from some such complexes by aluminum chloride.

Since ethers are the best solvents for lithium aluminum hydride, as well as good solvents for lithium borohydride and trichloroborazole, they should be the best media for the reduction of chloroborazoles. We, therefore, propose first to study the reaction between borazole and various ethers and to ascertain whether efficient methods for the removal of borazole from such ethers can be found.

Other solvents tested have been methylcyclohexane and phenylbromide. In the former, lithium aluminum hydride was the reducing agent. After three days at room temperature, some reduction to borazole seems to have occurred, since fractionation of the volatile reaction products through a -80°C . trap into one at -95°C . gave a sample of material which, according to analysis, appeared to be borazole of 90% purity. Since only a small quantity of this material was obtained, an attempt was made to hasten the reaction by raising the temperature to $70-90^{\circ}\text{C}$. After 12 hours, no borazole was found, possibly because of decomposition of the product.

In phenyl chloride, lithium hydride and lithium borohydride were the reducing agents. With the former, no evidence of interaction was observed. From 14.8 m moles of the latter, after stirring with 3.94 m moles of B-trichloroborazole in the solvent in question and fractionating the volatile products from time to time, diborane and borazole were isolated. The quantity of the latter after 11 days stirring at room temperature, was 0.48 m mole and that of diborane 3.0 m moles. Since the desired reaction is:



it is evident both that the reaction was far from complete and that it did not proceed uniquely in the desired direction. It is probable that mono- and dichloro derivatives were formed. The reaction is sufficiently promising to be worthy of further study and to justify the further search for more effective solvents. It is possible that in a solvent in which lithium borohydride is soluble, this salt might prove the most satisfactory reducing agent. Further work in this direction is contemplated.

It seemed possible that the most effective solvent for the desired reaction might be borazole itself. Our only experiment in this direction was a failure, since the borazole, added to a mixture of solid B-trichloroborazole and solid lithium aluminum hydride, almost completely disappeared when the material was heated to reflux temperature for several days. The experiment must, however, be repeated, before any conclusions should be drawn, because, in the one performed, less borazole was used as solvent than the minimum which would be necessary if its disproportionation reaction with trichloroborazole proceeds more rapidly than does reduction of the latter. We are awaiting accumulation of more borazole before proceeding to further work on this aspect of the problem.

Since we have found that bromo derivatives are, in general, more readily reduced than chloro derivatives, we are at present attempting to prepare B-tri-bromoborazole in order to study it as a possible source of borazole by reduction methods. As preparative methods, we are studying the reactions of boron tribromide with trichloroborazole and with ammonium bromide. This work has just been started. Preliminary indications are favorable, i.e., in the reaction of boron

tribromide with trichloroborazole, hydrogen chloride was formed, and in the reaction with ammonium bromide, hydrogen bromide is obtained. But the reaction products have not yet been separated into their components, and further comment is still premature.

III. As discussed in P. R. XXXV, p. 3, the thermal decomposition of lithium borohydride was undertaken to confirm observations reported by Schlesinger and H. C. Brown in JACS 62, 3429 (1940), in order to ascertain whether a compound such as LiBH_2 is formed in the reaction. It has proved impossible to repeat these earlier observations, i.e., the later experiments have given no evidence of a break in the rate of hydrogen evolution after the loss of 1 mole of hydrogen per mole of the salt, nor any evidence for the reversibility of the decomposition. The present experiments included heating of samples of pure lithium borohydride in glass and in iron vessels, as well as the heating of mixtures of lithium borohydride and Raney nickel catalyst. In glass, the decomposition at temperatures up to 290°C . was very slow from the start, and the rate decreased with continued heating. Even after 220 hours of heating at an average temperature of 280°C . only 24.2% of the total available hydrogen had been liberated.

The reaction proceeded more rapidly when the compound was contained in a Swedish iron tube, which had not previously been reduced by hydrogen, as may be seen from the fact that in 88 hours at an average temperature of 295°C ., about 65% of the total available hydrogen had been collected. But if the iron tube was heated to 800°C in an atmosphere of hydrogen before its use as a container for lithium borohydride, the decomposition of the latter was even slower than it had been in a glass vessel. Raney nickel catalyst seemed to accelerate the decomposition, but whether this effect was due to the catalyst itself or to an oxide coating which had not been completely removed by pretreatment of the catalyst, was not determined. Finally, a sample of lithium monomethyl borohydride, $\text{Li}(\text{BH}_3\text{CH}_3)$, was heated to ascertain whether any break in the decomposition rate occurs. Results were negative.

It, therefore, seemed undesirable to devote additional time to this undertaking, which has now been abandoned. It seems probable that in the experiment of Schlesinger and Brown, which was carried out with only 6 mg. of the borohydride, some trace impurity was responsible for the observations made. It is conceivable that, for this reason, some lithium was formed in the decomposition, and that this reacted reversibly with hydrogen.

IV. The preparation of sodium aluminum hydride by a modification of the original procedure, much like that used for the preparation of calcium aluminum hydride, was undertaken by a part time assistant on the project. The work is still too far from completion for a report.

EXPERIMENTAL DETAILS

The only experimental work far enough along to warrant recording of the details is that dealing with the reaction of tetrachlorodiborine with hydrogen. In one experiment, a mixture of 11.1 cc of the gaseous chloro derivative and 27.3 cc of hydrogen (prepared by thermal decomposition of lithium aluminum hydride in vacuo) was allowed to stand in a 500 cc bulb for one hour at approximately 26° C. The unchanged hydrogen (17.9 cc) was removed and collected; 9.4 cc of hydrogen was thus shown to have undergone reaction. The theoretical quantity, according to the equation: $3B_2Cl_4 + 3H_2 \rightarrow 4BCl_3 + B_2H_6$, would have been 11.1 cc. It is possible that the reaction was not complete. It is, however, much more likely that the deficiency in the amount of hydrogen which had reacted is due to loss of the tetrachloride by secondary reaction with diborane.

Fractionation of the other volatile products yielded 14.3 cc of boron trichloride (v.t. at -45.2° C, 48mm) and 3.74 cc of a gaseous material which passed through a -140° C trap and condensed at -196° C. The vapor pressure of this material at -112° C was 245 mm as compared with the value, 225 mm, for diborane, indicating that the sample was a mixture of diborane with hydrogen chloride. Hydrolysis of the sample and analysis of the hydrolysate yielded the equivalent of 5.63 cc of boron, 16.4 cc of hydrogen and 1.1 cc of hydrogen chloride. Although the boron-hydrogen ratio was 1/2.92 instead of 1/3, the results, in view of the small quantities involved, are satisfactory confirmation that the material in question consisted of 2.7 to 2.8 cc of diborane and approximately 1 cc of hydrogen chloride.

According to the equation given above, the reaction of 9.4 cc of hydrogen with tetrachlorodiborine should have produced about 12.5 cc of boron trichloride and 3.1 cc of diborane. Since 14.3 cc of boron trichloride and only 2.7-2.8 cc of diborane were actually obtained in the reaction in which 9.4 cc of hydrogen were absorbed, it is reasonable to ascribe these discrepancies to a secondary reaction in which diborane reacts with tetrachlorodiborine to give boron trichloride and other products. That such a reaction actually occurs has previously been shown (P. R. XXXIII, p. 3). Whether this reaction, or the presence of traces of moisture were responsible for the formation of the very small amount of hydrogen chloride obtained, has not been determined.

In the experiment just described, an amount of a volatile, crystalline material, too small for analysis or other characterization, was obtained. This seems to have been due to an impurity in the tetrachlorodiborine, since it was not observed in experiments in which a highly purified sample of the tetrachloride was used. It was likewise shown that this solid is not formed by the reaction of diborane with this especially carefully purified sample of the tetrachloro derivative. It might be recorded that, in this experiment, a mixture of 25.1 cc of the gaseous tetrachloride and 70.3 of diborane, was allowed to stand for 2 1/2 hours at room temperature in a 500 cc bulb before the mixture was analyzed. Of the diborane 56.4 cc was unchanged, and 30 cc of boron chloride together with 4.1 cc of a very unstable substance condensable at -80° C were formed. The latter rapidly decomposed to boron chloride and diborane. In addition to these products, 1.3 cc of hydrogen and a viscous yellowish, nonvolatile liquid were observed.

HYDRIDES AND BORO-HYDRIDES OF LIGHT WEIGHT ELEMENTS
AND RELATED COMPOUNDS

Progress Report No. XXXVII on Contract N6ori-20, T.O. X
for the period January 1, 1950 to March 31, 1950

by

H. I. Schlesinger and T. Wartik

in collaboration with

R. E. Moore, Riley Schaeffer, Martin Steindler and G. Urry

The work undertaken during this period is largely a continuation of that included in P. R. No. XXXVI¹⁾ and little of it is as yet completed. For this
1) P. R. is an abbreviation for Progress Report, and F. R. for Final Report for the year ending June 30 of the year stated in parentheses.

reason the present report is, in most instances, a brief review of the work in progress, to be amplified in later reports. In general, the investigations covered the following topics:

I. The preparation of tribromoborazole, and further studies on the reduction of trichloro and tribromoborazole to borazole.

II. Reactions of tetrachlorodiborine and of the compound $B_2Cl_4 \cdot 2N(CH_3)_3$.

III. The reaction of boron trichloride with hydrogen in the electric discharge.

IV. Other subchlorides of boron.

V. Further studies on the preparation of sodium aluminum hydride.

Ia. The Preparation of Tribromoborazole

1. Because of the difficulty of obtaining borazole by reduction of its trichloro derivative, and because of the fact that bromo derivatives are in general more easily reduced than the corresponding chloro compounds, we have prepared the bromo derivative by the type of reaction described by Laubengayer and Brown (C. S. Brown, Cornell University Ph. D. thesis, 1948), i.e., by the interaction

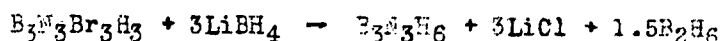
of boron bromide and ammonium bromide. The desired reaction did not occur in the absence of a solvent, but occurs when the reactants are heated in the presence of phenyl bromide at the reflux temperature of the latter (120-130° C).

2. Procedures and Properties

It is important to use carefully purified reagents in the preparation to avoid the formation of a liquid impurity, difficult to remove from the product. Ammonium bromide was dried at 110° C, boron bromide was shaken with mercury and distilled directly into the vessel containing the ammonium bromide, and the phenyl bromide was dried with sodium hydride. Approximately 7 cc of the solvent were used per gram of ammonium bromide, and boron bromide was present in considerable, though varied, excess. The mixture was heated for approximately 8 to 12 hours to 120 - 130° C in a 500 cc flask, equipped with a reflux condenser. Completion of the reaction may be recognized by the disappearance of the solid ammonium bromide and by cessation of the evolution of hydrogen bromide. The reaction mixture was finally filtered through a fritted glass filter funnel. The tribromoborazole was purified by vacuum sublimation at 60 - 70° C. Analysis of the product of four preparations gave the following average values: boron, 11.3%, bromine, 74.6%, N 14.2%, as compared with the theoretical values, 10.2%, 75.5%, 13.3%, respectively. Departure from the theoretical values is probably due to slight hydrolysis of the product during manipulation. The melting point of one sample was 126-128° C (under nitrogen). The compound undergoes slow decomposition at temperatures as low as 90° C; at approximately 220° C, it was at least 73% decomposed in 5 hours, as judged by the amount of hydrogen bromide evolved.

Ib. Reduction of Tribromoborazole to Borazole.

Treatment of 1.35 m-mole of tribromoborazole with 0.33 g of lithium borohydride for 3 days at room temperature in the presence of dry n-hexyl ether produced 0.56 m mole of hydrogen, 1.78 m moles of diborane, and 1.13 m moles of borazole. Based on the diborane evolved, approximately 87% of the original tribromoborazole was reduced to borazole as judged by the equation:



The amount of borazole recovered was approximately 83% of the theoretical. Reductions with lithium aluminum hydride in n-hexyl ether have not as yet given satisfactory results.

These observations do not indicate any decided advantages in the use of tribromoborazole over trichloroborazole; consequently, the work with the former is being temporarily discontinued.

Ic. Reduction of Trichloroborazole.

Preliminary experiments on the reduction of trichloroborazole by lithium borohydride in diethyl ether showed that evolution of diborane and, consequently, reduction of the trichloro compound occurs. Borazole could, however, not be separated from the ether solution, probably because of the formation of an azeo-

trope, the formation of which was indicated by the fact that the vapor tension of a mixture of borazole and the ether is lower than that of either component. Separation of borazole from the ether by conversion of the latter into the etherate of aluminum chloride is impossible because the aluminum chloride reacts with borazole to decompose the latter in an as yet undetermined manner.

When the reaction was carried out in butyl ether an amount of diborane corresponding to 95% reduction of the trichloroborazole was obtained. Ordinary procedures of fractional evaporation and condensation of the solution of borazole and the ether were not effective. Partial separation was, however, effected by heating the mixture till the total vapor pressure was approximately 150 mm in a vessel separated from the vacuum line by a float valve, then opening the vessel to the vacuum line, and rapidly distilling the mixture through a -45°C trap into one at liquid nitrogen temperature. Several repetitions of this procedure accumulated a borazole-rich fraction in the low temperature trap, and left most of the ether in the -45°C trap. Slow distillation of the borazole-rich fraction through a -80°C trap led to the recovery of 2.7 m moles of pure borazole. Hydrolysis of the ether-rich fractions showed them to contain an additional 1.9 m moles of borazole. Thus, the total amount of borazole obtained from 4.97 m moles of trichloroborazole was 4.6 m moles, or 91% of the theoretical, an amount satisfactorily in agreement with the production of 95% of the theoretical diborane.

Although the reduction of trichloroborazole to borazole by lithium borohydride is thus shown to be possible, the procedure has the disadvantage of theoretically producing $1\frac{1}{2}$ moles of diborane per mole of borazole obtained. Consequently, an experiment similar to the one just described was carried out with lithium aluminum hydride plus lithium hydride as the reducing agent. The reaction proceeded smoothly at room temperature in butyl ether. By the procedure described in the preceding paragraph, 62.3% of the theoretical borazole was isolated and an additional 22% was shown by analysis to be present in the residual ether solution.

These experiments suggested that separation of butyl ether from borazole produced by reduction of trichloroborazole with lithium aluminum hydride should be possible by use of an appropriate distilling column. Thus far, however, experiments of this type with larger quantities of reagents, carried out in ordinary laboratory equipment instead of in a vacuum system, have not been successful. The reasons for the difficulty have not yet been discovered, but the problem is being actively pursued.

II. Tetrachlorodiborine and compound $\text{B}_2\text{Cl}_4 \cdot 2\text{N}(\text{CH}_3)_3$

a. Preparation of Tetrachlorodiborine

The method hitherto used to prepare tetrachlorodiborine (P. R. XXI, p. 8), is tedious because of the manual recirculation of boron chloride through the mercury glow discharge. We have recently used a two stage mercury vapor pump as a device to achieve this circulation automatically. The results indicate that such a procedure is effective, but that for best results a more efficient circulatory pump is necessary. It did not seem desirable to construct such a device for the reactive reagents involved; the details of the present experiments need not be described.

IIf. Reaction of Tetrachlorodiborine with Dimethylamine.

Preliminary experiments indicate that tetrachlorodiborine reacts with dimethylamine, but the results are not as yet clearcut. In one experiment, 8.2 moles, and in another, 7.3 moles of the amine were retained per mole of the chlorodiborine. There is some, though not definite, indication that the difference may be due to a difference in temperature resulting from a difference in rate of mixing of the reactants. Details will not be reported till more consistent results have been obtained.

IIf. Analysis of the Compound $B_2Cl_4 \cdot 2N(CH_3)_3$

The composition of the compound $B_2Cl_4 \cdot 2N(CH_3)_3$ has hitherto been derived from the relative amounts of tetrachlorodiborine and trimethylamine interacting in its formation (P. R. XXXV, p. 7). Analysis had proved difficult, because of the resistance of the compound to hydrolysis by water, and because of the fact that it dissolves so slowly in alkaline solutions that simple addition of the solid to the basic solution gives rise to fuming, which represents a loss of material.

The difficulty has now been overcome by sealing the material in a weighing tube which is broken open under the alkaline solution contained in a silver dish (to avoid contamination of the solution with boron or silicon from glass or quartz). Concentrated, heated, chloride free sodium hydroxide solution was employed. Boron was determined as boric acid, and chlorine as silver chloride. The results of such an analysis are as follows: wt. sample, 0.1503 g; boron found, 8.02%, theory, 7.69%; chlorine found 49.8%, theory 50.4%.

To complete characterization of the compound, it is intended to determine its molecular weight in diethyl ether or in benzene solution, in both of which solvents the compound is readily soluble.

IIf. Reactions of $B_2Cl_4 \cdot 2N(CH_3)_3$

The trimethylamine addition product is markedly less reactive than tetrachlorodiborine, since, unlike the latter, it does not react with hydrogen even at about 900° C (see P. R. XXXVI, pp 2-3) nor, within a 15 minute period at room temperature, with diborane (see P. R. 49, p.5, P. R. XXXIII, p. 3, and P. R. XXXVI, p. 2). Instead of evolving hydrogen chloride when treated with ethyl alcohol, the amine addition product takes up 2 moles of the alcohol, a reaction the products of which have not as yet been determined.

The amine addition product reacts with lithium aluminum hydride in ether solution at room temperatures, but the results are as yet difficult to interpret. A crystalline product, with a vapor tension of between 1 and 2 mm was obtained. Hydrolysis of the product yielded hydrogen, and the hydrolysate was shown to contain boron and aluminum. It is possible, in spite of the homogeneous appearance of the crystals and their uniform behavior on sublimation, that the material is a mixture in which the aluminum is present as an impurity. The latter might be the trimethylamine-aluminum hydride addition product, which might have been formed because of aluminum hydride present as an impurity in the lithium aluminum hydride used, or formed as an intermediate in the reaction of the latter with $B_2Cl_4 \cdot 2N(CH_3)_3$. Details will not be given till the situation is clarified.

The attempt to reduce, i.e., to hydrogenate, $B_2Cl_4 \cdot 2N(CH_3)_3$ was undertaken with lithium aluminum hydride rather than with the borohydride, because of the possibility that diborane, liberated by the reaction of the latter, would react with the $B_2Cl_4 \cdot 2N(CH_3)_3$ as it does with tetrachlorodiborine. Since it has now been shown that the amine addition product does not react rapidly with diborane, and since the use of lithium aluminum hydride leads to the complication described in the preceding paragraph, we shall study the reaction of the borohydride before returning to that of the aluminum compound.

III. The Reaction of Boron Trichloride with Hydrogen in an Electrical Discharge.

As pointed out in P. R. XXXVI, p. 3, the observation that tetrachlorodiborine reacts very rapidly with hydrogen at room temperature to produce diborane, suggests that in the procedure developed by Schlesinger and Burg for the preparation of diborane (J. A. C. S. 53, 4321, (1931)), the initial step is the formation of tetrachlorodiborine. In the original experiments a large excess of hydrogen was used, and under those conditions the chlorodiborine could not possibly have been detected.

We have now modified the Schlesinger and Burg experiment by using a considerable excess of boron trichloride. Although the main, initial product of the reaction under these conditions was still monochlorodiborane, as in the original Schlesinger and Burg procedures, the presence of tetrachlorodiborine has been definitely established. Separation of the product was difficult, but we were able to obtain a fraction which had a 0° C tension of 44.5 mm (B_2Cl_4 tension equals 44.3 mm), and in which the ratio of hydrogen, boric acid and chloride ion, resulting from hydrolysis, was 0.92:2.00:4.12, instead of the theoretical ratio 1:2:4. Another sample, by slow decomposition, produced the red product characteristic of the decomposition of pure tetrachlorodiborine.

Although not conclusive evidence, this experiment strongly supports the hypothesis that the first step in the formation of diborane by the reaction of hydrogen with boron chloride in an electric discharge is tetrachlorodiborine. For the production of the latter it does not seem likely, however, that the use of hydrogen can be made as efficient as that of mercury vapor in the discharge chamber.

IV. Other Subchlorides of Boron

As described in P. R. XXXII, p. 10, the decomposition of tetrachlorodiborine produces a viscous, liquid, red product of very low volatility and an almost white, nonvolatile solid. The two may be separated by volatilization of the red material at 90 - 100° C.

It was difficult to obtain enough of these materials by decomposition of the tetrachlorodiborine in a closed vessel because the reaction seemed to become slower as time went on. As suggested by this observation, we have hastened the decomposition by removing the boron chloride, also formed in the reactor, from time to time. By this procedure, enough material for a preliminary analysis was obtained.

The method of analysis described in section IIc of this report was not satisfactory for analysis of the other subchlorides, because the hydrolysis by sodium hydroxide is not complete, as shown by the fact that the hydrolysate still reduces silver ion. Instead, it was necessary, after the hydrolysis with sodium hydroxide by the procedure described in the earlier section, to decrease the P_h to very slight alkalinity, and then to add 90% hydrogen peroxide. The excess of the latter was decomposed by platinum black.

The results of these analyses gave a B:Cl ratio of 1.0:0.91 for the red product, and of 5.1:3.0 for the white one. It seems likely, however, that neither product was entirely pure, since decomposition may have occurred at the elevated temperature needed for the separation of the two from each other. We are, therefore, seeking a solvent by means of which the separation and purification of the two (or more) decomposition products may be effected.

V. Further Attempts to Improve the Preparation of Sodium Aluminum Hydride.

No satisfactory results have been obtained as yet. Slowness of this aspect of the project is due in part to the fact that it is in the hands of a part time assistant, but is largely due to the apparent difficulty of the problem.

Briefly stated, we have verified the earlier observation that, although a 60% yield of the desired product in pure form can be achieved by the reaction of sodium hydride with aluminum bromide in dimethyl ether, the same result is not achieved with aluminum chloride. The reason for the difference has not been discovered. Furthermore, the procedure of extracting the reaction product of the aluminum bromide reaction with tetrahydrofuran after evaporation of the dimethyl ether (in order to avoid filtration under the high pressure of dimethyl ether) proved unsuccessful--a result entirely unexpected in view of the success of this procedure for the preparation of calcium aluminum hydride. In the case of the sodium aluminum hydride preparation, the product obtained had an aluminum-hydrogen ratio of only 1:2.86, instead of the expected 1:4.

In view of the fact that methyl borate acts catalytically in the reaction between lithium hydride and boron fluoride, and that sodium trimethoxyborohydride is more reactive than sodium hydride, we have attempted (1) the reaction of sodium hydride with aluminum chloride in the presence of an excess of methyl borate at room temperature, (2) the same reaction in the presence of a small amount of methyl borate and tetrahydrofuran, (3) the reaction of sodium trimethoxyborohydride with aluminum chloride in dimethyl ether. It was realized that sodium borohydride, or possibly even an etherate of aluminum borohydride might be formed. Thus far, none of these experiments has led to definite results. In the last one mentioned, a product very soluble in dimethyl ether was obtained. That the nature of this material is has not been ascertained, except to demonstrate that it is neither sodium borohydride, sodium aluminum hydride, nor aluminum borohydride etherate. The experiments are being continued.

**HYDRIDES AND BOROHYDRIDES OF LIGHT EIGHT ELEMENTS
AND RELATED COMPOUNDS**

**Progress Report No. XXXVIII on Contract N6ori-20, T.O. I
for the period April 1 - July 31, 1950**

by

H. I. Schlesinger and T. Wartik

in collaboration with

R. E. Moore, Riley Schaeffer, M. Steindler and G. Urry

The work of this report concerns:

- I. The reduction of Trichloroborazole to borazole
- II. Further studies on Tetrachlorodiborine and its Derivatives
- III. The preparation of Sodium Aluminum Hydride
- IV. The reaction of Lithium Borohydride with Hydrazine Hydrochloride

Because of the fact that the present contract covers a 13 month period, i.e., from July 1, 1949 to July 31, 1950, the period covered by this "quarterly" progress report is 4 rather than 3 months. References to previous final reports are indicated by the letters F.R. followed by the year in which the report was completed; references to progress reports are indicated by the letters P.R. followed by a Roman numeral. If the P. R. is of a year earlier than 1949-50, the date of issuance is given.

I. The Reduction of Trichloroborazole to Borazole.

Before describing the work of the period covered by this report, it is desirable to refer to an experiment described in P. R. XXXVII, p 3, in which trichloroborazole was treated with an n-butyl ether solution of lithium aluminum hydride in which a considerable amount of lithium hydride was suspended. The experiment was originally undertaken to ascertain whether lithium aluminum hydride could act as a carrier for hydrogen from lithium hydride as has been suggested for the types of reaction by Blizzard, Carhart, and Johnson, J.A.C.S. 70, 3684-5 (1948).

The fact that in this experiment not only was the yield of borazole much higher than in preceding ones, but that a very much larger percentage of the borazole than

in preceding experiments could be separated from the ether, suggested an explanation of the difficulties previously encountered in the use of lithium aluminum hydride as a reducing agent for the desired reaction. It seemed possible that the reduction reaction produces aluminum hydride according to an equation like the following:



and that the aluminum hydride formed in some way reacts with borazole and prevents its volatilization with the ether. The possibility that borazole forms a nonvolatile etherate was also considered.

The first step in testing these possibilities was to determine whether pure borazole and n-butyl ether would distill together from a mixture of the two. Such mixtures were sealed in bulbs equipped with break-off side arms and were heated to different temperatures for different time intervals. The bulbs were then attached to a vacuum system, the hydrogen was pumped off and measured, and the remaining volatile material was distilled into concentrated aqueous hydrochloric acid. The amount of hydrogen liberated as a result of the acid hydrolysis was taken as a measure of the quantity of borazole recovered in the volatile material. Results of two such experiments are as follows (ml refers to liquid volumes, cc to volumes of gaseous material referred to STP):

Original mixture	Conditions	Products	% $\text{B}_3\text{N}_3\text{H}_6$ recovered
10 ml $(\text{Bu})_2\text{O}$ } 28 cc $\text{B}_3\text{N}_3\text{H}_6$ }	30 minutes 100° C	1.59 cc H_2 } 24.5 cc $\text{B}_3\text{N}_3\text{H}_6$ } nonvolatile solids)	87%
5 ml $(\text{Bu})_2\text{O}$ } 31.8 cc $\text{B}_3\text{N}_3\text{H}_6$ }	2 hours 50° C	0.63 cc H_2 } 29.3 cc $\text{B}_3\text{N}_3\text{H}_6$ } nonvolatile solids)	92%

It is evident from these data that borazole is not in any way rendered nonvolatile by butyl ether (i.e., does not form a nonvolatile etherate). Furthermore, the very small amount of hydrogen and of solids obtained indicates that borazole is not extensively decomposed at higher temperatures by butyl ether.

In the preceding experiments the borazole was not separated from the butyl ether. To ascertain whether such a separation is possible, a mixture of 4.79 g of borazole and 30ml of the ether was distilled through a small column packed with glass helices. The fraction passing over between 52 and 54° C was collected and weighed. It consisted of about 3.8 g of borazole, indicating an approximately 80% recovery. Use of a more efficient column could probably improve the result, but the small amounts of borazole then available made further work along these lines undesirable until the actual results of reduction of trichloroborazole had been ascertained.

It was next shown that borazole could be recovered from its mixture with solid lithium aluminum hydride. After the mixture had stood for 10 hours at room temperature, about 85% of the borazole was regained by evaporation and condensation. It was also demonstrated that a saturated solution of lithium aluminum hydride in n-butyl ether liberates only very small quantities of hydrogen (e.g. 0.26 cc) when it is heated to 100° C for one hour. Evidently then, if aluminum hydride causes the

difficulty encountered, the hydride is a product of the interaction of lithium aluminum hydride with borazole, and not an unavoidable contaminant of the former. (It might be mentioned in this connection that only 38% of a sample of borazole could be recovered from dry, activated alumina after 3.5 hours at 25° C. Evidently exclusion of moisture is of the greatest importance in these experiments.)

The preceding experiments indicate that neither the presence of n-butyl ether nor of lithium aluminum hydride prevent the recovery of borazole from mixtures in which it is known to be present. But when a mixture of pure borazole and a butyl ether solution of lithium aluminum hydride containing an excess of aluminum hydride was evaporated, after standing one hour at room temperature, no material containing active hydrogen could be isolated in the volatile portion. The hypothesis that aluminum hydride reacts with or in some other way holds back borazole has thus received considerable support.

On the basis of these observations it is possible to explain why results obtained in the reduction of trichloroborazole with lithium aluminum hydride in the presence of an excess of lithium hydride are much better than those obtained in the absence of lithium hydride. The latter is known to react with aluminum hydride to give lithium aluminum hydride; the use of lithium hydride thus may be effective because it removes the aluminum hydride assumed to be present according to the hypothesis under discussion.

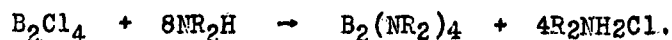
Although the procedure using lithium hydride in addition to lithium aluminum hydride has been successful in small scale experiments, carried out in the vacuum system, it has not yet proved satisfactory when attempts were made to reduce larger quantities of trichloroborazole in ordinary laboratory apparatus in an atmosphere of nitrogen. The reasons have not yet been fully ascertained. It is conceivable that because of the longer time required for larger scale experiments, difficulties are caused by secondary reactions of lithium aluminum hydride with the ether, too slow to be troublesome in small scale experiments. Support for such an explanation is found in the fact that in a larger scale experiment a gaseous product having properties not unlike those of n-butane has been obtained. This interpretation of the difficulty requires further confirmation.

Even though these experiments have thus not yet shown definitely how trichloroborazole can be reduced efficiently to borazole by lithium aluminum hydride, they have suggested a procedure by means of which the chief objection to the use of lithium borohydride as a reducing agent may possibly be overcome. The objection to the latter reagent lay in the fact that 1.5 moles of diborane are theoretically liberated per mole of borazole obtained. But diborane is known to react rapidly with evolution of considerable heat with lithium hydride in ether solutions to form lithium borohydride. Should the procedure of using a mixture of lithium hydride and lithium borohydride in this way avoid the liberation of diborane or decrease it to an insignificant amount, a satisfactory method for the preparation of borazole in larger quantities may have been achieved.

II. Further Studies on Tetrachlorodiborine and its Derivatives.

- (a) Reaction of tetrachlorodiborine with dimethylamine.

Tetrachlorodiborine reacts rapidly with dimethylamine at temperatures as low as -80°C to form the new compound tetradimethylaminodiborine according to the equation ($\text{R} = \text{CH}_3$):



The equation is an empirical one since the molecular weight of the new compound has not yet been determined. The substance is a liquid of very low vapor tension at 0°C . Only one of its reactions has as yet been studied, namely that with hydrogen chloride, and this work is as yet incomplete. The product of the reaction is a white solid from which the tetradimethylaminodiborine is recovered by addition of dimethylamine.

The details of the preparation of the new compound and of its analysis are as follows (cc refer to gases at STP, ml to liquids):

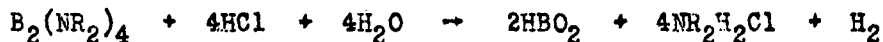
The reagents, 20.1 cc of tetrachlorodiborine and 210.5 cc of dimethylamine both tensimetrically pure, were condensed into a reaction vessel, which was then warmed to -80°C . Although reaction seemed to occur immediately, the mixture was maintained at this temperature for several hours, after which time the volatile products were distilled into the fractionating system at room temperature. The procedure required several hours because of the slight volatility of the reaction product. A small amount of solid, probably a decomposition product, deposited on the walls of the receiving vessel.

The more volatile material thus obtained was distilled through a -80°C trap into one at -196°C . The latter contained 58.0 cc of dimethylamine (v.t. at 0°C 563 mm instead of 564.5), indicating that the tetrachlorodiborine and dimethylamine had reacted in the volume ratio 1:7.59 (theory 1:8). The discrepancy is not large in view of the difficulty of handling the original chloro compound.

The material recovered in the -80°C trap was purified by distilling it through a 0°C trap into one at -196°C . The latter was found to contain a small quantity of a liquid with a vapor tension of 6.5 mm at 25°C . It is likely that this material was the compound $\text{B}(\text{NR}_2)_3$ (v.t. at $25^{\circ}\text{C} = 5\text{mm}$), contaminated with a trace of dimethylamine.

The material in the 0°C trap was then distilled into a quartz bulb containing 5 ml of 10% sodium hydroxide solution for analysis. The mixture, originally consisting of two layers, formed a homogeneous solution when it was heated for 4 hours in a steam bath. During this process 12.4 cc of hydrogen were liberated. The volatile products were distilled into 50 ml of 0.1N hydrochloric acid and titrated. The result indicated that 50.8 cc of dimethylamine had been formed. Titration for boron in the usual way showed that the amount contained in the nonvolatile residue was equivalent to 25.7 cc of the gaseous element. These data correspond to a ratio for $\text{H}_2:\text{B}:\text{NR}_2\text{H} = 0.98:2.02:4.00$, in good agreement with the ratio 1:2:4 expected

according to the equation:



The yield of the compound was 63% of the theoretical. It was not considered necessary to analyze the solid product of the initial reaction, since it gave every evidence of being dimethylaminohydrochloride contaminated with a trace of a solid which reacted slowly with water to give a reducing solution, but of which too little was obtained for analysis.

(b) The compound $\text{B}_2\text{Cl}_4 \cdot 2\text{NR}_3$.

(b)(1) Melting point, solubility, molecular weight. The compound, prepared and initially described in P.R. XXXVI, p 2, and XXXVII, PP 4-5, has been further studied. Its melting point in an atmosphere of nitrogen is 228°C , but it sinters at 125°C and softens somewhat at 195°C . It is somewhat soluble in diethyl ether and in benzene, and slightly soluble in isopentane. Determination of the molecular weight of the substance by the lowering of the freezing point of benzene gave the following unexpected result:

wt. benzene	18.74 g	t	0.029°C
wt. sample	0.1168 g	Mol wt	1105.

This value is very nearly four times the molecular weight corresponding to the formula $\text{B}_2\text{Cl}_4 \cdot 2\text{NR}_3$ (Theor. mol wt = 279; $4 \times 279 = 1116$). Since the measurement was made at only one concentration it still needs to be demonstrated that the calculated value is real, i.e., that no solid solutions were formed.

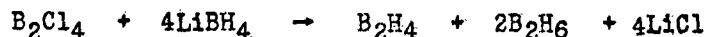
To obtain more information on this point, an attempt was made to determine the molecular weight by measuring the vapor tension lowering of isopentane, but the solubility of the compound in this solvent was found to be too small to promise reliable results. Further work with other solvents, and possibly a measurement of the vapor density of the compound at high temperatures are planned.

(b)(2) Reaction with Lithium Borohydride. The complications encountered in the study of the reaction of the compound $\text{B}_2\text{Cl}_4 \cdot 2\text{NR}_3$ with lithium aluminum hydride (P.R. XXXVII, p 4) led us to replace this reducing agent by the corresponding borohydride. The formation of diborane was anticipated, but it was hoped that this fact would introduce no complications, since diborane does not react with $\text{B}_2\text{Cl}_4 \cdot \text{NR}_3$ at room temperature (P.R. XXXVII, p. 4). The results thus far are disappointing. The only products isolated in a reaction carried out in ether solution at room temperature have been diborane and a volatile solid, the vapor density of which corresponds to that of trimethylamine borine (theory 73, found 72). The identity of the solid as trimethylamine borine was further confirmed by vapor tension measurements, as follows:

t ($^\circ \text{C}$)	v.t. sample	v.t. BH_3NH_3
25.9	0.90	0.80
40.0	2.90	2.54
42.8	13.60	11.9
70.3	20.15	18.7

Evidently there was a somewhat more volatile contaminant, but it could have been only small in amount.

The experiment is to be repeated with the modification that a considerable excess of trimethylamine is to be added. Theoretically, the reaction in question might occur as follows:



The purpose of the excess trimethylamine would be to stabilize the presumably unstable B_2H_4 , by forming an addition compound, possibly $\text{B}_2\text{H}_4 \cdot 2\text{NR}_3$. In that event 6 moles of the amine would be required per mole of B_2Cl_4 , since the diborane would require 4 moles. The compound $\text{B}_2\text{Cl}_4 \cdot 2\text{NR}_3$ obviously does not supply enough if it is assumed that trimethylamine borine is more stable than the hypothetical $\text{B}_2\text{H}_4 \cdot 2\text{NR}_3$. The reaction of lithium aluminum hydride with $\text{B}_2\text{Cl}_4 \cdot 2\text{NR}_3$ will also be reinvestigated since the early experiments (P.R. XXXVII, p 4) may have been vitiated by the presence of a large amount of aluminum hydride in the lithium aluminum hydride used at the time.

(c) Further studies on the decomposition products of tetrachlorodiborane.

Attempts to determine the molecular weight of the red decomposition product obtained by the slow decomposition of tetrachlorodiborane at room temperature were temporarily discontinued when it was found that the red material undergoes further slow decomposition to boron trichloride and the white solid previously described (P.R. XXXII, p 10, December, 1948, and XXXVII, pp 5-6). There is some indication that the decomposition is inhibited by the presence of boron trichloride. Possibly advantage can be taken of this observation, if corroborated, in purifying and studying the compound.

III. The Preparation of Sodium Aluminum Hydride.

As has been previously reported, the only method which has hitherto led to successful preparations of sodium aluminum hydride consisted of the reaction between sodium hydride and aluminum bromide at room temperature in dimethyl ether solution. The reaction mixture was then filtered at room temperature and the ether was evaporated from the filtrate. Not only was the yield not better than 60 or 65%, but the use of aluminum bromide and the relatively high pressures (6-7 atm) at which the reaction and filtrations had to be carried out are objectionable.

Of the very numerous experiments undertaken to avoid these objections, only the last has given decided promise of success. Those which failed are first briefly described, without numerical details.

(a) The reaction of aluminum chloride with sodium hydride in dimethyl ether.
As catalysts both lithium aluminum hydride and sodium aluminum hydride (obtained from aluminum bromide) were tested. When the dimethyl ether solution was filtered, the filtrate still contained chloride ion, even after days of reaction. Evaporation of the dimethyl ether before filtration, and extraction of the residue with tetrahydrofuran (See P.R. XXXII, p 11, December, 1948) gave none of the desired product.

(b) Reaction of sodium trimethoxyborohydride with aluminum chloride, as well as the reaction of sodium hydride with aluminum chloride in the presence of aluminum methoxide, proved unsuccessful.

(c) Use of calcium hydride as a catalyst gave only a small amount of calcium aluminum hydride.

(d) The reaction between aluminum chloride and sodium hydride in tetrahydrofuran as a solvent, especially when a seed of lithium aluminum hydride was used as catalyst, appeared to give some of the desired product, but the yield and purity were low. Apparently the low purity was due to the fact that, to obtain adequate reaction, the reaction mixture had to be refluxed for some length of time. It was shown that, under these conditions, interaction of the solvent with the reaction mixture occurred.

(e) The successful experiments were based on the idea that lithium and sodium hydrides do not interact with aluminum chloride per se, but do react with the AlCl_4^- ion. To test this hypothesis we first attempted to obtain this ion in solution by the reaction of ethyl chloride and a diethyl ether solution of aluminum chloride. The product thus obtained was treated with sodium hydride in tetrahydrofuran with no success. Similar failure resulted when the compound NaAlCl_4 was prepared by fusion of the respective simple chlorides, and used in place of aluminum chloride.

Success was apparently achieved in an experiment in which 2.6 g of aluminum chloride, 13.9 g of sodium hydride and 0.0219 g of lithium chloride were stirred for 3 days in tetrahydrofuran. Lithium chloride, rather than sodium salt, was used because the former is known to dissolve in ether solutions of aluminum chloride, presumably to form the desired complex ion, whereas the sodium salt does not do so. After 3 days' stirring of the mixture, followed by filtration and evaporation of the filtrate, there was left a white, crystalline residue which gave 98% of the hydrogen to be expected of NaAlH_4 , showed a ratio of $\text{Al:H} = 1:4.01$, and which therefore is evidently pure sodium aluminum hydride. Repetition of the experiment with the same samples of aluminum chloride and sodium hydride, but without lithium chloride, gave no indication of reaction after 3 days of stirring.

It will be necessary to repeat the experiment to ascertain whether the method gives a satisfactory yield, and to determine the best proportions of reagents and time of reaction. If the further work confirms the results herein described, a more detailed study of the properties of sodium aluminum hydride will be undertaken.

It is interesting to consider the possibility that the interpretation here given for the reaction between hydrides and aluminum halides may explain why the use of lithium aluminum hydride as a catalyst in the reaction between lithium hydride and aluminum chloride is successful. The lithium aluminum hydride reacts rapidly with aluminum chloride in diethyl ether according to the equation:



The lithium chloride thus formed may then react with some of the remaining aluminum chloride to produce a solution of LiAlCl_4 . The latter could be the material which

interacts with lithium hydride, according to the equation



It is obvious that ultimately practically all of the aluminum ion will be used up and that then only a trace of lithium chloride can remain in solution. If, on the other hand, lithium hydride and aluminum chloride are mixed in the absence of lithium aluminum hydride, the initial reaction between the two may be very slow, but will become accelerated by the gradual formation of lithium chloride. Thus the induction period in the interaction of aluminum chloride and sodium hydride, as well as the means of its avoidance, are readily explained.

In the reaction between sodium hydride and aluminum chloride, no such induction period has been observed; instead the reactions are slow throughout. The difference between the lithium and the sodium hydride reaction may, consequently, be due to the difference in the solubilities of lithium and of sodium chloride in ether containing aluminum chloride.

The interpretation of the action of alkali metal hydrides on aluminum halides also offers a possible explanation of why sodium aluminum hydride could be obtained in fair yield in dimethyl ether solution by the interaction of sodium hydride with aluminum bromide but could not be satisfactorily prepared when aluminum chloride was the halide employed. Sodium bromide is presumably more soluble in dimethyl ether than is sodium chloride; consequently the concentration of the aluminum tetrahalogeno ion, assumed to be the active reagent in these reactions, would be the higher if the starting material is aluminum bromide.

IV. The Reaction of Lithium Borohydride with Hydrazine Hydrochloride

As shown in a series of papers by Wiberg (Zeit. anorg. Chemie, 257, 131-37, 1948), by G. W. Schaeffer, (J.A.C.S. 71, 2143 (1949)), by Burg, (2nd Annual Summary Technical Report, Contract N6onr-238-TO-I, 1948), as well as in our own reports (e.g. P.R. XXXI, p 6, Sept. 48, P.R. XXXII, pp 4-6, December 1948, and P.R. XXXIII, p 8, March 49) the reaction of ammonia and amines on diborane, and that of borohydrides with ammonium and amine salts have given interesting results. It was therefore considered worth while to ascertain whether similar reactions, in which ammonia, amines and their salts are replaced by hydrazine and its derivatives, might not lead to new types of interesting compounds.

Preliminary experiments between lithium borohydride and hydrazine dihydrochloride have shown that the expected type of reaction, i.e., the liberation of hydrogen, occurs when the two are allowed to interact in the dry state as well as in diethyl ether. At lower temperatures, a little over one mole of hydrogen was evolved per mole of lithium borohydride used; at higher temperatures the ratio was more nearly 2:1. Details are not given because a complete study of the products has not yet been made.

Such a study is made difficult by the fact that, aside from hydrogen and traces of diborane, all of the products of the reaction are solids. Thus far no solvent has been found which will separate from each other the various solid products undoubtedly present.

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For this reason we are temporarily turning to the--presumably--simpler case of the interaction of anhydrous hydrazine with diborane, work which is as yet not far enough along to be reported in detail. We express our appreciation to the Naval Research Laboratory for the anhydrous hydrazine furnished us for this work.