definitely at ordinary temperatures. Samples have been stored in sealed capsules for years without discoloration or decomposition.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

New Developments in the Chemistry of Diborane and the Borohydrides. I. General Summary[1]

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The present is the first of a series of papers describing new developments in the methods of preparation and in the chemistry of diborane and of the borohydrides. New and practical methods for the preparation of borohydrides (a) from diborane, and (b) without the use of diborane are discussed. As a result of the availability of borohydrides, prepared without the use of diborane, methods, far more satisfactory than those hitherto known for the preparation of the latter, have been developed. The investigation has led to the preparation of the hitherto unknown borohydrides of sodium, of potassium and of uranium, and some of their derivatives, as well as of a new type of substance, such as sodium trimethoxyborohydride, $NaBH(OCH_3)_3$, formed by the addition of compounds of trivalent boron to alkali metal hydrides. Sodium borohydride, as well as sodium trimethoxyborohydride, are of special interest because of their potential usefulness as reducing agents and sources for the generation of hydrogen; uranium(IV) borohydride and its derivatives are of interest because they are the most volatile compounds of uranium except the hexafluoride. The present paper surveys numerous new observations made and organizes the subject matter in the light of the principle which largely guided the research, namely, the application of the Lewis generalized acid–base concept to the reactions of diborane, of the salt-like hydrides and of the borohydrides. Detailed description of the new preparative methods and data confirming the reaction equations herein presented as well as supporting the composition of new substances are deferred to the remaining papers of the series.

Introduction

Early in 1941 we were asked to undertake the synthesis of new volatile compounds of uranium. We began our search with a study of uranium(IV) and -(VI) complexes derived from 1,3-diketones and related chelating agents. As will be described in a later paper, it soon became evident, from a study of the changes produced in the vapor tensions of the complexes by altering the structure of the diketone, that a vapor tension of 0.1 mm. at a temperature of 130° could probably not be exceeded.

The fact that the borohydrides of aluminum and of beryllium had proved to be the most volatile compounds of these elements[3] suggested that we attempt to prepare a borohydride of uranium. For this purpose, procedures different from those employed previously for the preparation of borohydrides had to be developed, since the earlier methods consisted of the reaction of diborane with a metal alkyl,[3,4] and no alkyls of uranium were known. The desired result was achieved by the interaction of uranium(IV) fluoride with aluminum borohydride.

The resulting uranium(IV) borohydride, $U(BH_4)_4$, as well as the methyl derivatives, $U(BH_4)_3(BH_3CH_3)$ and $U(BH_3CH_3)_4$, actually proved to be the most volatile uranium compounds other than the hexafluoride.[5] Equally interesting are the developments which resulted from our efforts to improve the methods of preparing the starting materials and the intermediates required for the preparation of the uranium borohydrides. As a result of these efforts many new types of reactions were observed and at least partially investigated, hitherto unknown compounds were discovered, and the field of the chemistry of the hydrogen compounds of boron was greatly enlarged.

The urgency of the investigation made it impossible to pursue each new reaction and to characterize each new substance with the utmost thoroughness. Enough data have, however, been obtained to establish beyond reasonable doubt the over-all course of the new reactions and the compositions of the new substances described herein. We, therefore, considered it desirable and appropriate, in spite of certain lacunae, to record our observations in order to make them available to other workers.

Because of the large amount of material to be covered, we have prefaced the papers which describe the experimental and other details of the numerous compounds and reactions involved, by this introductory one, which is essentially a survey, without experimental details, of the papers which are to follow. Furthermore, to coördinate the subject matter, we have organized the presentation according to a central principle which had proved to be an extremely useful guide in the investigation. This theme is the application of the Lewis generalized acid–base concept[6] to the reactions of diborane and of compounds related to it. Although

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(1) Most of the work reported herein constitutes a part of investigations carried out under contracts with the National Defense Research Committee, with the Office of Scientific Research and Development and with the Signal Corps, Ground Signal Agency during the years 1940–1944. They were continued under Navy auspices during 1944–1946. Most of the results were originally described in the final reports on contracts NDC-rc-56, OEM-sr-117 and 368 and N173 s-9058, 9820 and 10,421.

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(3) (a) H. I. Schlesinger, R. T. Sanderson and A. B. Burg, THIS JOURNAL, **62**, 3421 (1940); (b) A. B. Burg and H. I. Schlesinger, *ibid.*, **62**, 3425 (1940).

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

(5) Papers X and XI of this series: (a) H. I. Schlesinger and H. C. Brown, *ibid.*, **75**, 219 (1953); (b) H. I. Schlesinger, H. C. Brown, L. Horvitz, A. C. Bond, L. D. Tuck and A. O. Walker, *ibid.*, **75**, 222 (1953).

(6) G. N. Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

this procedure is undoubtedly an over-simplification, it has the advantage of giving unity to what otherwise might become a confusing mass of information.

Nomenclature

At the time they were discovered the term "borohydride" was adopted for compounds containing BH_4 groups or ions and has received general acceptance. With the discovery of related compounds, having formulas such as $Na[BH(OCH_3)_3]$ and $Na[BH(C_2H_5)_3]$, several of which are discussed in the series of which this is the first paper, it became necessary either to expand this type of nomenclature or to adopt a new one.

The first procedure leads to the names sodium trimethoxyborohydride and sodium trimethylborohydride for the compounds the formulas of which are given in the preceding paragraph. A further application of the same kind of name leads to the term sodium tetramethoxyborohydride or lithium tetraethylborohydride for compounds having the formulas, $NaB(OCH_3)_4$ and $LiB(C_2H_5)_4$, respectively.

These last names are obviously illogical since the compounds in question contain no hydrogen. Furthermore, the whole system of nomenclature is not in accord with some general nomenclature rules now under consideration for complex inorganic compounds. Careful consideration was, therefore, given to the desirability of using a different, perhaps more systematic nomenclature in this and the subsequent papers of this series.

We have finally decided to retain the nomenclature based on the name "borohydride." This decision was based on the facts that (1) it is our understanding that international and other committees on nomenclature will soon consider the problem of compounds of this type, and (2) that there is a very considerable difference of opinion about the kind of nomenclature that should be adopted. Under these conditions it seemed thoroughly undesirable to introduce new names now, which might have to be changed again in relatively short time.

Examples of the type of nomenclature we are employing are

$LiBH_4$	lithium borohydride
$Al(BH_4)_3$	aluminum borohydride
$U(BH_4)_4$	uranium(IV) borohydride
$NaBH(OCH_3)_3$	sodium trimethoxyborohydride
$LiBH(CH_3)_3$	lithium trimethylborohydride
$NaBHF_3$	sodium trifluoroborohydride
$U(BH_4)_3(BH_3CH_3)$	B-methyluranium(IV) borohydride
$U(BH_3CH_3)_4$	B,B′,B″,B‴-tetramethyluranium(IV) borohydride

Results and Discussion

For our initial experiments we used diborane prepared by the reaction of hydrogen with boron tribromide in an electrical discharge.[7] Improvements in the process made it possible to prepare this starting material with the speed and in the quantities required. Since still more satisfactory processes for preparing diborane were developed later, we refer the reader to paper II[8] of this series for a description of the improvements in the arc process and turn at once to the preparation of borohydrides by acid–base type reactions.

That diborane behaves as a Lewis acid has been amply demonstrated. We cite only its reactions with trimethylamine to form trimethylamine-borine, $(CH_3)_3N{:}BH_3$,[9a] and with dimethyl ether to form the monoetherate, $(CH_3)_2O{:}BH_3$.[9b] Because the borine fragment, BH_3, appears in the acid–base complexes formed when diborane acts as an acid, we shall frequently write the formula of the latter as $(BH_3)_2$, even though the borine fragment itself has not been isolated.

For the preparation of borohydrides from diborane by an acid–base type reaction, the base to be used is obviously the hydride ion. However, neither sodium hydride nor lithium hydride reacts with diborane in the absence of a liquid medium. But if the latter hydride is suspended in diethyl ether, the reaction proceeds fairly rapidly and almost quantitatively at ordinary temperature with the evolution of considerable heat, to form the monoetherate of lithium borohydride, according to the equation

$$2LiH + (BH_3)_2 + 2(C_2H_5)_2O \longrightarrow 2LiBH_4{\cdot}(C_2H_5)_2O \quad (1)$$

The ether may be removed from the product by heating the latter to from 70 to 100° *in vacuo*.[10]

There are two closely related interpretations which may be tentatively advanced for the effect of the ether. Lithium ion has a marked tendency to undergo solvation; furthermore, lithium borohydride is moderately soluble in diethyl ether. The heat of solvation of the lithium ion by the ether could aid in overcoming the energy barrier of the simple reaction; the solubility of the borohydride in the ether would prevent coating of the lithium hydride with solid borohydride. If these interpretations are accepted, it is easy to understand why sodium hydride does not react in similar fashion, for sodium ions have a muchs maller tendency toward solvation than lithium ions, and sodium borohydride is not soluble in ethyl ether.

Although sodium hydride does not undergo an acid–base type of reaction with diborane, it does so with other boron-containing Lewis acids. Evidence will be presented in papers III and IV of this series[11] to show that boron trifluoride and trialkyl borons add to alkali metal hydrides. Of particular interest in connection with the present discussion is the reaction of sodium hydride with methyl borate.

$$NaH + B(OCH_3)_3 \longrightarrow NaBH(OCH_3)_3 \quad (2)$$

This exothermic reaction proceeds with moderate rapidity and with a great increase in the bulk of the

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(7) (a) H. I. Schlesinger and A. B. Burg, THIS JOURNAL, **53**, 4321 (1931); (b) A. Stock and W. Sutterlein, *Ber.*, **67**, 407 (1934).

(8) H. I. Schlesinger, H. C. Brown, B. Abraham, N. Davidson, A. E. Finholt, R. A. Lad, J. Knight and A. M. Schwartz, THIS JOURNAL, **75**, 191 (1953).

(9) (a) A. B. Burg and H. I. Schlesinger, *ibid.*, **59**, 780 (1937); (b) H. I. Schlesinger and A. B. Burg, *ibid.*, **60**, 290 (1938).

(10) Paper V of this series: H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. R. Rapp, *ibid.*, **75**, 199 (1953).

(11) (a) H. C. Brown, H. I. Schlesinger, I. Sheft and D. M. Ritter, *ibid.*, **75**, 192 (1953); (b) H. I. Schlesinger, H. C. Brown, J. R. Gilbreath and J. J. Katz, *ibid.*, **75**, 195 (1953); (c) see also J. Goubeau and R. Bergmann, *Z. anorg. Chem.*, **263**, 69 (1950), for the reaction of sodium hydride with boron trifluoride.

solid. It may be carried out at reflux temperature in the absence of any liquid medium other than methyl borate itself. Details of the preparation of the new compound, sodium trimethoxyborohydride, $NaBH(OCH_3)_3$, of its physical properties, of its reducing action and other aspects of its chemical behavior are given in paper III of this series.[11a] There the behavior of other alkyl borates toward sodium hydride and toward lithium hydride is also taken up. In the present paper, discussion is limited to the behavior of these alkyl borate-hydride addition products toward other boron-containing Lewis acids and toward thermal decomposition.

The most characteristic property of acids is the displacement of weaker acids from acid-base complexes by stronger acids. From the observed stability of their addition products with dimethyl ether and with trimethylamine, the acid strength of the following boron compounds decreases in the order indicated.[12]

$$F_3B > (H_3B)_2 > (CH_3)_3B > B(OCH_3)_3$$

In accordance with this order, it was found that diborane displaces methyl borate from sodium trimethoxyborohydride.

$$2NaBH(OCH_3)_3 + (BH_3)_2 \longrightarrow 2NaBH_4 + 2B(OCH_3)_3 \quad (3)$$

This reaction, by which sodium borohydride ($NaBH_4$) was prepared for the first time, proceeds so rapidly that it may be used to absorb diborane almost completely from a moderately fast stream of gas, even though the concentration of diborane in the latter is relatively low.[10]

Two additional reactions very closely related to the one just described for converting diborane into sodium borohydride are of interest. The first of these, the reaction of sodium tetramethoxyborohydride, $NaB(OCH_3)_4$, with diborane, is unquestionably another example of the displacement of weaker by stronger acids and obeys the over-all equation[10]

$$3NaB(OCH_3)_4 + 2(BH_3)_2 \longrightarrow 3NaBH_4 + 4B(OCH_3)_3 \quad (4)$$

The reaction is probably best represented by the steps

$$NaB(OCH_3)_4 + {}^1/_2(BH_3)_2 \longrightarrow NaBH_3(OCH_3) + B(OCH_3)_3 \quad (4b)$$

$$NaBH_3(OCH_3) + {}^1/_2(BH_3)_2 \longrightarrow NaBH_4 + BH_2(OCH_3) \quad (4c)$$

$$3BH_2(OCH_3) \longrightarrow (BH_3)_2 + B(OCH_3)_3 \quad (4d)$$

None of the assumed intermediates was isolated, but small amounts of dimethoxyborine, $BH(OCH_3)_2$ were obtained. Its formation by disproportionation of monomethoxyborine, and its further disproportionation into methyl borate and diborane are characteristic properties of alkoxyborines.[13] However, the disproportionation is ordinarily very slow. It is, therefore, likely that in place of step 4(d) monomethoxyborine undergoes further displacement reactions as illustrated by equation 4(f)

$$BH_2(OCH_3) + NaB(OCH_3)_4 \longrightarrow NaBH_2(OCH_3)_2 + B(OCH_3)_3 \text{ etc.} \quad (4f)$$

The second of the reactions mentioned above is that of diborane with sodium methoxide.[10]

$$3NaOCH_3 + 2(BH_3)_2 \longrightarrow 3NaBH_4 + B(OCH_3)_3 \quad (5)$$

We interpret this reaction as consisting of the primary formation of an acid-base complex in which the methoxide ion is the basic substance

$$NaOCH_3 + {}^1/_2(BH_3)_2 \longrightarrow NaBH_3(OCH_3) \quad (6)$$

followed by the reactions represented by equations (4c) and (4d).

Although the three reactions represented by equations (3), (4) and (5) produce sodium borohydride smoothly and fairly rapidly in excellent yields at room temperature, they have the disadvantage of requiring the use of diborane. This difficulty was overcome as a result of the consideration that the methoxide ion of such compounds as sodium trimethoxyborohydride and sodium tetramethoxyborohydride might be displaced by the hydride ion acting as a base stronger than the methoxide ion. Actually the two following reactions are satisfactory methods for preparing sodium borohydride without the use of diborane.[14]

$$3NaH + NaBH(OCH_3)_3 \longrightarrow NaBH_4 + 3NaOCH_3 \quad (7a)$$

$$4NaH + NaB(OCH_3)_4 \longrightarrow NaBH_4 + 4NaOCH_3 \quad (7b)$$

Even simpler methods for the preparation of borohydrides without the use of diborane resulted from an observation, made early in the investigation, namely, that substances formed by the addition of such compounds as boron bromide to lithium hydride undergo disproportionation into compounds containing more hydrogen than the original adduct. We consequently investigated the behavior of the readily prepared sodium trimethoxyborohydride toward heat. The data indicate that it undergoes disproportionation according to the over-all equation

$$4NaBH(OCH_3)_3 \longrightarrow NaBH_4 + 3NaB(OCH_3)_4 \quad (8a)$$

At the temperatures at which this reaction proceeds with appreciable speed, the sodium tetramethoxyborohydride undergoes decomposition into sodium methoxide and methyl borate

$$3NaB(OCH_3)_4 \longrightarrow 3NaOCH_3 + 3B(OCH_3)_3 \quad (8b)$$

It is, however, difficult to drive reactions (8a) and (8b) to completion unless the methyl borate is continuously removed as a gas by evacuation of the reaction vessel. All of these complications are avoided if methyl borate is slowly added to an excess of a well stirred mass of sodium hydride powder at 250°. Under these conditions sodium borohydride is directly formed

$$4NaH + B(OCH_3)_3 \longrightarrow NaBH_4 + 3NaOCH_3 \quad (9)$$

From the reaction mixture the sodium borohydride may be extracted by liquid ammonia or by primary amines, such as isopropylamine, in which the borohydride is very soluble, but in which the methoxide is almost insoluble.[14]

Sodium borohydride, discovered and made readily available for laboratory and industrial

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(12) Quantitative data supporting this order have been obtained by Herbert C. Brown and his students and will be reported soon.

(13) A. B. Burg and H. I. Schlesinger, THIS JOURNAL, **55**, 4020 (1933).

(14) Paper VI of this series: H. I. Schlesinger, H. C. Brown and A. E. Finholt, *ibid.*, **75**, 205 (1953).

purposes by the preceding reactions, is a compound of considerable interest and potential usefulness. It may be heated without decomposition to about 400°; its aqueous solution, if carefully prepared, undergoes but slow decomposition, as is true also of alcoholic solutions; it is soluble in liquid ammonia and in primary amines; it is a strong reducing agent and has many other interesting properties. Details of its preparation and of its physical and chemical behavior are recorded in papers V, VI and IX of this series.[10,14,15]

Various modifications of the reactions thus far mentioned for the preparation of sodium borohydride have been investigated. Thus, methyl borate, when heated under hydrogen pressure with molten sodium produces the borohydride if the mixture is well stirred. The borohydride may also be obtained by heating and grinding together a mixture of sodium hydride and boric oxide

$$4NaH + 2B_2O_3 \longrightarrow NaBH_4 + 3NaBO_2 \quad (10)$$

In place of the methyl esters of boric acid, ethyl and *n*-butyl borates have been used successfully. but without advantages and in some cases with disadvantages. All of these modifications, as well as the results obtained when lithium hydride replaces sodium hydride are discussed in papers III, V and VI of this series.[10,11a,14]

As is evident from the preceding discussion, the Lewis generalized acid–base concept leads to a logical and consistent interpretation of the reactions which have thus far been described. Nevertheless a more detailed examination discloses, as was anticipated, that factors other than relative acid and base strengths are involved. Attention has already been called to the fact that sodium hydride, unlike lithium hydride, does not react with diborane in the presence of ether. It was suggested earlier in this paper that differences in the tendency of the two metal ions toward solvation and differences in the solubilities of the corresponding borohydrides, may account for the differences in the behavior of the two alkali metal hydrides; differences in lattice energies of the solids are probably also involved.

There are a number of similar contrasts. Thus sodium methoxide reacts rapidly and quantitatively with diborane to produce sodium borohydride; the corresponding reaction of lithium methoxide is slow and difficult to carry to completion. Lithium ethoxide, on the other hand, reacts with diborane so rapidly and with the evolution of so much heat that it is necessary to dilute the reactants if larger quantities of them are employed. Another example is the fact that sodium methoxide, prepared by decomposition of sodium tetramethoxyborohydride reacts rapidly with diborane, whereas potassium methoxide, prepared by the action of metallic potassium on methanol, does not react with diborane under comparable conditions. But potassium borohydride is readily prepared by the action of diborane on potassium tetramethoxyborohydride.[10] Finally we cite the fact that sodium hydride reacts relatively slowly with methyl borate even at temperatures as high as 100° to form sodium trimethoxyborohydride, whereas the latter reacts very rapidly with diborane even at room temperature.

In all of the reactions cited in the preceding paragraph, a solid reacts with a gas, or with a liquid solution or with a liquid compound, to form another solid. A clue to a factor which may be responsible for the differences described is suggested by the last of the cases cited. The formation of sodium trimethoxyborohydride from methyl borate and sodium hydride is accompanied by a fivefold increase in the bulk of the solid but when the trimethoxyborohydride reacts with diborane it forms the much more compact sodium borohydride. Similarly the sodium methoxide, which was prepared by decomposition of sodium tetramethoxyborohydride and which reacted rapidly with diborane, was a relatively porous, bulky material, whereas the potassium methoxide prepared from metallic potassium and methanol was relatively compact and did not react with diborane.

These observations suggest that in reactions like those under discussion, in which a solid reacts with a gas or a liquid to form a second solid, reaction is favored by a decrease in the volume occupied by the solids. Obviously additional data are necessary to confirm the suggestion. Data on the appropriate physical properties of lithium methoxide and ethoxide, and of the corresponding sodium salts should be obtained and the reactions of diborane with sodium methoxide prepared by the reaction of sodium with methanol, as well as its reaction with potassium methoxide prepared by decomposition of potassium tetramethoxyborohydride, should be studied. Because of the urgency of other aspects of the investigation herein reported these studies were not made.

Once methods had been developed for avoiding the use of diborane in the preparation of borohydrides, it became evident that the preparation of diborane could be made far simpler than is possible either by the original method of Stock[16] or by the electrical discharge process.[7] Since the borohydrides may be considered to be acid–base complexes of the basic hydride ion and the borine fragment, it should be possible to displace the latter, and thus prepare diborane, by the treatment of a borohydride, or a derivative thereof, with an acid stronger than diborane. As was pointed out earlier, boron fluoride is such an acidic substance.[17] Actually the use of the latter in the form of its diethyl etherate leads to highly efficient procedures for the generation of diborane by any one of the reactions represented by the equations[11b,18]

$$3NaBH_4 + 4(C_2H_5)_2O{:}BF_3 \longrightarrow 3NaBF_4 + 2B_2H_6 + 4(C_2H_5)_2O \quad (11)$$

$$3LiBH_4 + (C_2H_5)_2O{:}BF_3 \longrightarrow 3LiF + 2B_2H_6 + (C_2H_5)_2O \quad (12)$$

$$6NaBH(OCH_3)_3 + 8(C_2H_5)_2O{:}BF_3 \longrightarrow 6NaBF_4 + B_2H_6 + 8(C_2H_5)_2O + 6B(OCH_3)_3 \quad (13)$$

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[15] H. I. Schlesinger, H. C. Brown, A. E. Finholt, J. R. Gilbreath, H. R. Hoekstra and E. K. Hyde, THIS JOURNAL, **75**, 215 (1953).

[16] A. Stock and C. Massenez, *Ber.*, **45**, 3539 (1912).

[17] Obviously there are other acidic substances, such as hydrogen chloride or boron trichloride, which might be used, especially in ethereal solutions in place of boron fluoride. Likewise the dimethyl etherate of boron fluoride has been used in place of the ethyl etherate in special cases.

[18] If an excess of the etherate is used, lithium borofluoride rather than the fluoride may be obtained in reaction (12).

Presumably the first step in these reactions is the displacement of borine (which immediately dimerizes to diborane) and the formation of compounds of the type $M[HBF_3]$, in which M represents sodium or lithium. The end result could then be attained by disproportionation of the intermediate, as occurs at higher temperatures in the case of sodium trimethoxyborohydride (equation 8a).[19]

Closely related to the preceding reactions is that of boron trifluoride diethyl etherate toward lithium hydride in the presence of excess ether. Diborane is generated according to the equation[20]

$$6LiH + 8(C_2H_5)_2O:BF_3 \longrightarrow B_2H_6 + 6LiBF_4 + 8(C_2H_5)_2O \quad (14)$$

Evidence is presented in the fourth paper of this series[11b] that in the reaction of lithium hydride with the etherate, intermediates like those postulated for the reactions of borohydrides with the etherate are involved.

Four reagents, lithium or sodium borohydrides, sodium trimethoxyborohydride and lithium hydride, have thus been shown to react readily with boron fluoride etherate to produce diborane. Which of the four is to be used depends upon the quantity of diborane desired and on the availability of the reagent. For larger quantities, the use of finely divided lithium hydride is most economical. For small scale production lithium borohydride is probably the most convenient because of its solubility in ether.[21]

The alkali metal borohydrides, aside from their use in the preparation of diborane by acid-base type reactions, are valuable for carrying out metathetic reactions leading to the formation of other borohydrides. Particularly interesting from the point of view of the original objective of this investigation is the formation of the volatile aluminum borohydride by mere heating of aluminum halides with lithium or sodium borohydrides at moderate temperatures.[22]

$$AlCl_3 + 3MBH_4 \longrightarrow Al(BH_4)_3\uparrow + 3MCl\ (M = Li\ or\ Na) \quad (15)$$

The aluminum borohydride thus obtained was employed in the preparation of uranium(IV) borohydride by slightly heating a mixture of the reactants of the equation[5]

$$2Al(BH_4)_3 + UF_4 \longrightarrow U(BH_4)_4\uparrow + AlF_2(BH_4) \quad (16)$$

Other metathetic reactions are represented by the equations[22]

$$NaBH_4 + LiCl \xrightarrow[\text{amine}]{\text{isopropyl}} LiBH_4 + NaCl\downarrow \quad (17)$$

$$Al(BH_4)_3 + 3LiC_2H_5 \xrightarrow{\text{benzene}} 3LiBH_4\downarrow + Al(C_2H_5)_3 \quad (18)$$

$$2LiBH_4 + BeBr_2 \longrightarrow Be(BH_4)_2\uparrow + 2LiBr \quad (19)$$

Reaction (17) is at present probably the most convenient method for preparing lithium borohydride, since the corresponding sodium salt is commercially available. Other primary amines, as well as liquid ammonia, may replace isopropylamine as a solvent. Reactions (16) and (19) are carried out in the absence of solvents. Attention is called to the preparation of borohydrides of titanium, zirconium, hafnium and thorium by similar metathetic reactions.[23]

In the preceding discussion, which has emphasized the ideas and principles which guided the investigation, no experimental data have been given to support the numerous reactions and to verify the composition of the new substances involved. Such data, additional discussion of matters dealt with too briefly herein, and directions for carrying out the reactions and preparations discussed in this survey are presented in the following papers II to XI of this series. Paper VIII of the series describes a convenient procedure for preparing the methyl borate required for several of the reactions studied.[24]

Acknowledgments.—The urgency and nature of the investigation made it necessary to shift individual investigators from one phase of the project to another as particular problems became of immediate importance. Under these circumstances it is impossible to give each member of our research group specific credit for his full contributions to the complete investigation. We have, therefore, adopted the policy of indicating in the papers which follow, those members who were mainly concerned with each study in question. In this paper we wish to acknowledge, in addition to that of the collaborators already mentioned, the help and coöperation of: H. Russell, Jr., P. A. Schulze, R. P. Straetz, W. H. Urry and F. Vaslow.

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(19) In view of the observation of J. Goubeau and R. Bergmann (ref. 11c) that the compound, $NaBHF_3$, may be formed at 200° from sodium hydride and boron trifluoride and that it is stable at this temperature, the intermediate $M(HBF_3)$ probably first reacts with additional boron trifluoride to produce MBF_4 and a second intermediate HBF_2. The latter, like all compounds of this type, would disproportionate and dimerize to produce diborane and regenerate boron fluoride. It is also possible that the compound HBF_2 undergoes a series of displacement reactions of the type: $BHF_2 + NaBH_4 \rightarrow NaBH_2F_2 + {}^1/_2(BH_3)_2$, etc.

(20) Although the main course of the reaction under the conditions used by us was that given by equation (14), there was definite indication that under other conditions the reaction may proceed to yield lithium fluoride instead of borofluoride

$$6LiH + 2(C_2H_5)_2O:BF_3 \longrightarrow B_2H_6 + 6LiF + 2(C_2H_5)_2O$$

(21) Diborane may also be prepared by the reaction of the etherates of boron fluoride or chloride on lithium aluminum hydride [A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, THIS JOURNAL, **69**, 1199 (1947)]. It is at present more readily available than lithium borohydride.

(22) Paper VII of this series: H. I. Schlesinger, H. C. Brown and E. K. Hyde, *ibid.*, **75**, 209 (1953).

(23) H. R. Hoekstra and J. J. Katz, *ibid.*, **71**, 2489 (1949).

(24) H. I. Schlesinger, H. C. Brown, D. L. Mayfield and J. R. Gilbreath, *ibid.*, **75**, 213 (1953).