

**HYDRIDES AND BOROHYDRIDES
OF LIGHT ELEMENTS
PROGRESS REPORT NO-XXVIII**

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CONTENTS

	Page
Abstract	vi
I. Explosive Reactions of Aluminum-Hydrogen Compounds	1
II. Further Studies on the Preparation of Sodium Aluminum Hydride. Mechanism of the Reactions Involved	2
III. Preparation of Magnesium Hydride	9
IV. Reaction of Dimethyl Zinc and Dimethyl Mercury With Lithium Borohydride	9
V. Reaction of Lithium Aluminum Hydride With Alkyl Compounds of the Elements	10
VI. Preparation and Polymerization of Borazole	12
VII. Methyl Derivatives of Aminoborine	14
VIII. Miscellaneous Boron-Nitrogen Compounds	15
IX. Work In Progress and Planned	15

ABSTRACT

This report covers the work on hydrides of boron in which there is reported results on sodium aluminum hydride preparation in tetrahydrofuran. A yield of 70% of sodium aluminum hydride of 92% purity was obtained. There is also reported the study on the preparation of borazole and some work on its stability and preliminary steps in the production of other boron-nitrogen-hydrogen compound.

This investigation was sponsored by the Bureau of Aeronautics Project TED No. NRL 3401.

* * *

Since June 30, 1947, the project has lost the services of its most experienced personnel, i.e., of Dr. A. E. Finholt, Geraldine Barbaras and Glen Barbaras. The resignation of Dr. Finholt had been anticipated, and in his place, the part-time service of Dr. G. W. Schaeffer has been secured. The resignations of Mrs. Barbaras (July 31) and of Mr. Barbaras (Aug. 31) came sooner than expected. Furthermore, Mr. Dillard has had to go from a full-time to a half-time basis.

To replace the assistants lost, Mr. A. C. Stewart (full time) and Mr. R. E. Moore (half time) have been appointed and we have a third (full-time) appointment in prospect. Although the new men come to the project with excellent reputations for experimental skill, they are not thoroughly familiar with the techniques required for this investigation. Their training will require some time.

AUTHORIZATION

Progress Report on Contract Number N6ori-20 for the period July 1 to September 30, 1947.*

* The Progress Reports on Contracts Nos. N173s-9058, N173s-9820, N173s-10421 and N6ori-20 are numbered consecutively without regard to change in contract number.

I. Completion of Study of Conditions Under Which Aluminum-Hydrogen Compounds Lead to Explosive Reactions.--Previous reports (F.R.¹⁾ pp 7-8, P.R.¹⁾ XXVII, pp 7-10)

- 1) The abbreviation F.R. refers to the Final Report for the period July 1, 1946 to June 30, 1947; P.R. to the Progress Report indicated by the Roman numeral.
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have described the conditions under which explosions result when solutions of aluminum hydride or of sodium or lithium aluminum hydride in dimethyl ether (and in dimethyl cellosolve) are evaporated. It was shown that in the case of lithium aluminum hydride explosions do not occur with highly purified dimethyl ether, but that they are brought about by the addition of carbon dioxide to such samples. Although this observation, together with others described in the sections referred to, show that carbon dioxide is the probable cause, they did not completely exclude other possibilities.

One of these is that carbon monoxide, either present in dimethyl ether or as a trace impurity or transitorily formed by reduction of carbon dioxide, might play a role. This possibility has now been excluded by experiments of which the following is an example. Carbon monoxide was passed continuously through a solution of 3.3 mmoles of lithium aluminum hydride in 15 cc. of dimethyl ether at -25° C for 15 minutes. Evaporation of the solvent and subsequent heating of the residue were accomplished without explosion or obvious decomposition.

Although the abrupt decomposition, which was observed when dimethyl ether solutions of aluminum hydride were evaporated, was usually not of explosive character, detonation occurred when aluminum chloride was present in the solutions (P.R. XXVII, p. 7 and table on p. 8). Similar explosions have occurred in the preparation of sodium aluminum hydride from aluminum chloride. It was, therefore, important to ascertain whether carbon dioxide plays a role in this reaction also. When aluminum hydride alone was dissolved in dimethyl ether and treated with carbon dioxide under conditions which led to explosive reactions with lithium aluminum hydride, the solvent could be safely evaporated (irrespective of the age of the aluminum hydride used). But when intimate contact between the carbon dioxide and aluminum hydride was achieved by agitating the suspension of the latter in dimethyl ether, violent explosion resulted after the volatile material had been distilled away and the residue had warmed to about 0° C.

The explosions observed when a mixture of aluminum hydride and aluminum chloride in dimethyl ether was evaporated must also be ascribed to the presence of carbon dioxide, as shown by the following experiment. Aluminum hydride (6.09 mmoles) freshly prepared from diethyl ether solution, was mixed with 15.8 mmoles of aluminum chloride, a ratio of the two components which corresponds to that which, according to the table on p. 8 of P.R. XXVII, gave rise to definite explosions when impure dimethyl ether was used. In the present experiment about 18 cc. of pure dimethyl ether was condensed on the mixture, which was then warmed to -25° C. and there maintained for about one hour with occasional stirring. The liquid residue, obtained after removal of the volatile material, slowly turned grey when kept at room temperature for about one-half hour. Thereafter the temperature was raised from 30 to 70° C. during an interval of 20 minutes. At 41° C., some non-condensable material appeared but the pressure had not risen above 12 mm, at the end of this period. Slight further temperature rise then brought about a sudden increase of pressure to 95 mm. and a sudden temperature rise (to over 110° C.). There was, however, no detonation; maintenance of the temperature above

70° C. caused no further gas evolution. The gas evolved contained methane as shown by a vapor tension of 12 mm. at -195° C. These observations indicate that even in the presence of aluminum chloride, truly explosive reactions do not occur unless the dimethyl ether is impure; they also confirm that the stability of aluminum hydride is decreased by aluminum chloride (P.R. XXVI, pp 2-3). The production of methane indicates that the reaction is not merely a sudden decomposition of the hydride but involves interaction of the latter with the ether.

In F.R. p. 8 it was suggested that, in addition to the impurity in the dimethyl ether, an impurity, presumably aluminum hydride, in the lithium aluminum hydride, might also be a factor in the explosions. The special conditions required for the interaction of aluminum hydride with carbon dioxide exclude this possibility. Repetition of the experiments which led to the tentative conclusion that impurity in the lithium compound might have a bearing showed that lithium aluminum hydride does not give rise to explosions with dimethyl ether free from carbon dioxide. The possibility that aluminum hydride is responsible for the inflammability on friction of some samples of aluminum hydride is, however, not excluded.

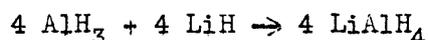
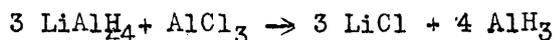
One questionable point still remains. On one occasion the evaporation of a solution of aluminum hydride in dimethyl cellosolve resulted in an unusually violent explosion. It has since been ascertained that the sample of this solvent used for that experiment contained considerable amounts of peroxides and smaller quantities of aldehyde. Since then several experiments on the preparation of sodium aluminum hydride in purified dimethyl cellosolve have been carried out; the products obtained were impure and unquestionably were contaminated with aluminum hydride. No explosions occurred. Nevertheless, should this solvent be used for aluminum hydride, the possibility of explosions should be taken into account.

Finally, it was shown that sodium aluminum hydride, like the corresponding lithium salt, does not cause explosions when its dimethyl ether solution is evaporated in the absence of carbon dioxide, but that explosions do occur if carbon dioxide was previously passed into the solution.

We believe that the experiments herein recorded together with those previously reported, demonstrate that the compounds in question may be safely used in dimethyl ether solutions if the presence of carbon dioxide is excluded. It is, however, also important that the hydrides do not contain considerable quantities of aluminum halides which may give rise to very sudden pressure increases even though they do not cause definite detonations. Attention is again called to the fact that diethyl ether solutions of these substances may also cause explosions if carbon dioxide has been introduced, but the likelihood of the unsuspected presence of the latter in this solvent is very small.

II. Further Studies on the Preparation of Sodium Aluminum Hydride. -- Clarification of the conditions under which evaporation of solutions of aluminum hydride or of the metal aluminum hydrides gives rise to explosions has made it possible to investigate more thoroughly the method of preparation of sodium aluminum hydride and of the corresponding calcium compound. Such an investigation is desirable since, for some of the contemplated work of this project, the sodium salt may be preferable to the lithium salt, and because the preparative method is not yet satisfactory.

In order to make clear the objectives of the experiments performed during the period covered by this report on the problem under discussion, it is desirable to review some aspects of the previously developed method for the preparation of the corresponding lithium salt. As soon as it had been shown that lithium aluminum hydride reacts rapidly with aluminum chloride to form aluminum hydride and that the latter may be retained in diethyl ether solutions for appreciable periods of time, it became evident that lithium aluminum hydride could not be present in the solutions as long as appreciable amounts of aluminum chloride are present. It may then be assumed that the formation of aluminum hydride by direct interaction of lithium hydride with aluminum chloride is the first step of the reaction and that this step is slow. The aluminum hydride would then react with lithium hydride to form the double hydride; it may, however, be assumed further that this reaction is also relatively slow as long as aluminum chloride is present in the solution. To explain the sudden, violent setting in of the major reaction it may be assumed that after the aluminum chloride is all used up, interaction between the two hydrides is accelerated and develops so much heat that the reaction becomes almost uncontrollable. If, however, preformed lithium aluminum hydride is present in the ether used as solvent, and aluminum chloride is added relatively slowly, aluminum chloride can never be present in excess nor can aluminum hydride ever accumulate. The postulated steps in the reaction would then be: (1) the first of the aluminum chloride is completely and rapidly used by the preformed lithium aluminum hydride to produce aluminum hydride, (2) the latter reacts with lithium hydride to form the double hydride, and this reaction is also rapid because aluminum chloride is not present in excess; the reaction cannot become violent because of the limited amount of aluminum hydride, (3) upon further addition of aluminum chloride these steps repeat themselves; it is to be noted that, according to this scheme of reactions, each addition of aluminum chloride produces 4 moles of lithium aluminum hydride for each 3 momentarily used up:



In the case of the lithium salt, experimental verification of the preceding assumptions did not seem feasible because of the slowness of the initial reaction and because of the unpredictable time interval after which the ultimate violent reaction sets in. In view of the erratic behavior of the corresponding reaction for the preparation of the sodium salt (F. R. pp 5-7, P.R. XXVII pp 1-4), it seemed desirable to investigate more fully the type of reaction mechanism postulated above, and to use the sodium compounds for this purpose since the over-all reactions are slower than is the case with lithium salts. The preliminary reactions discussed in this report were carried out with small quantities in vacuo to avoid the possibility that traces of air or moisture might accelerate the polymerization of the aluminum hydride (P.R. XXVII p 3). Tetrahydrofuran and, occasionally, dimethyl cellosolve were used as solvents because with them higher temperatures could be employed than with the dimethyl ether used as solvent in the original preparations of sodium aluminum hydride. Since the tetrahydrofuran is likely to react with aluminum chloride the latter was first converted to its dimethyl or diethyl etherate which was then dissolved in the tetrahydrofuran.

(a) The first step in this investigation was to demonstrate that aluminum hydride reacts with sodium hydride to form the double hydride (P.R. XXVII pp 3-4).

In the previous experiments just referred to, the aluminum hydride was prepared in the usual way in diethyl ether solution, and therefore contained some of the latter. These experiments have now been repeated with aluminum hydride prepared in either tetrahydrofuran or in dimethyl cellosolve. The solution of the hydride thus obtained was then immediately treated with sodium hydride suspended in the same solvent. The sodium aluminum hydride thus prepared in tetrahydrofuran had a purity of 93% and that prepared in dimethyl cellosolve a purity of 88%. Products of the same range of purity are obtained when the compound is prepared directly from sodium hydride and aluminum bromide without isolation of the intermediate hydride. The products of this range of purity contain only negligible amounts of halide; the H/Al atomic ratio varies from 3.84:1 to 3.95:1 as would be expected if the impurity were aluminum hydride. Two other experiments essentially similar to those just mentioned were carried out in tetrahydrofuran giving products of 88 and 89% purity. The yields were 77% and 79% respectively.

In carrying such reactions out in vacuum systems, it is convenient to introduce the solid reagents (e.g. lithium aluminum hydride and aluminum chloride) into the reaction first, and then to condense the solvent upon the solids at low temperature, whereupon the temperature is allowed to rise to that desired for the reaction. When aluminum hydride was prepared in this way in tetrahydrofuran, about 3/4 hour was required for completion of the reaction; in dimethyl cellosolve the time was about 1 1/2 hours. It was later shown that these time intervals are needed to dissolve the aluminum chloride; the observations, therefore, are not contradictory to the postulate that the formation of aluminum hydride from the double hydride is a relatively rapid reaction.

(b) As is to be expected, aluminum hydride reacts in diethyl ether with lithium hydride to give the double hydride. The purity of the product obtained was 92%, but the yield only 79% which is a low value for this compound. The atomic ratio H/Al was 3.95. The low yield may have been due to the fact that some aluminum hydride was lost by precipitation of the polymer.

(c) It was then shown that aluminum hydride may be used in place of lithium aluminum hydride to initiate and moderate the reaction between lithium hydride and aluminum chloride in diethyl ether. The reaction carried out in this way proceeded smoothly and gave a good yield (84%) of a satisfactory product (92%).

(d) The failure of sodium aluminum hydride materially to affect the course of the reaction between ^{sodium}hydride and aluminum chloride (P.R. XXVI, p 3) as does lithium aluminum hydride in the corresponding preparation of the lithium salt, could be accounted for by slowness of the reaction between aluminum hydride and sodium hydride, especially if the latter reaction were further retarded by an excess of aluminum chloride. Slowness of this reaction could also account for erratic yields and purities of the product, since the slower the conversion of aluminum hydride to the double hydride the greater the likelihood of its conversion to its insoluble, probably polymerized form.

These considerations suggested that the procedure might be improved by adding to a mixture of an excess of sodium hydride and a "seed" of sodium aluminum hydride an amount of aluminum chloride slightly less than required to transform

all of the "seed" to aluminum hydride; and then allowing sufficient time for the aluminum hydride to form fresh sodium aluminum hydride before further addition of aluminum chloride. Such a procedure would prevent the simultaneous presence of aluminum chloride and aluminum hydride in the solution.

Accordingly, a "seed" of 0.01979 g. (3.65 mmoles) of sodium aluminum hydride was dissolved in about 30 cc. of tetrahydrofuran in a flask containing 4 g. (170 m. moles) of sodium hydride. About 30 cc. of a solution containing 2.53 g. (18.96 m. moles) of aluminum chloride was then added from a side arm of the reaction vessel in ever increasing portions, allowing 40 minutes between each addition. As already explained, 3 moles of sodium aluminum hydride reproduce 4 moles of the substance by the postulated series of reactions; consequently, each portion of the chloride added may be $4/3$ greater than the previous one. Thus, in this experiment, the first portion contained about 0.15 g. (1.1 m. mol) or about 10% less than the amount of aluminum chloride necessary to convert all of the original "seed" to fresh lithium aluminum hydride, and 6 additional portions were required. After all of the aluminum chloride had been added, the mixture was stirred overnight and filtered in vacuo. The product obtained was of 92% purity, and the yield approximately 70%.

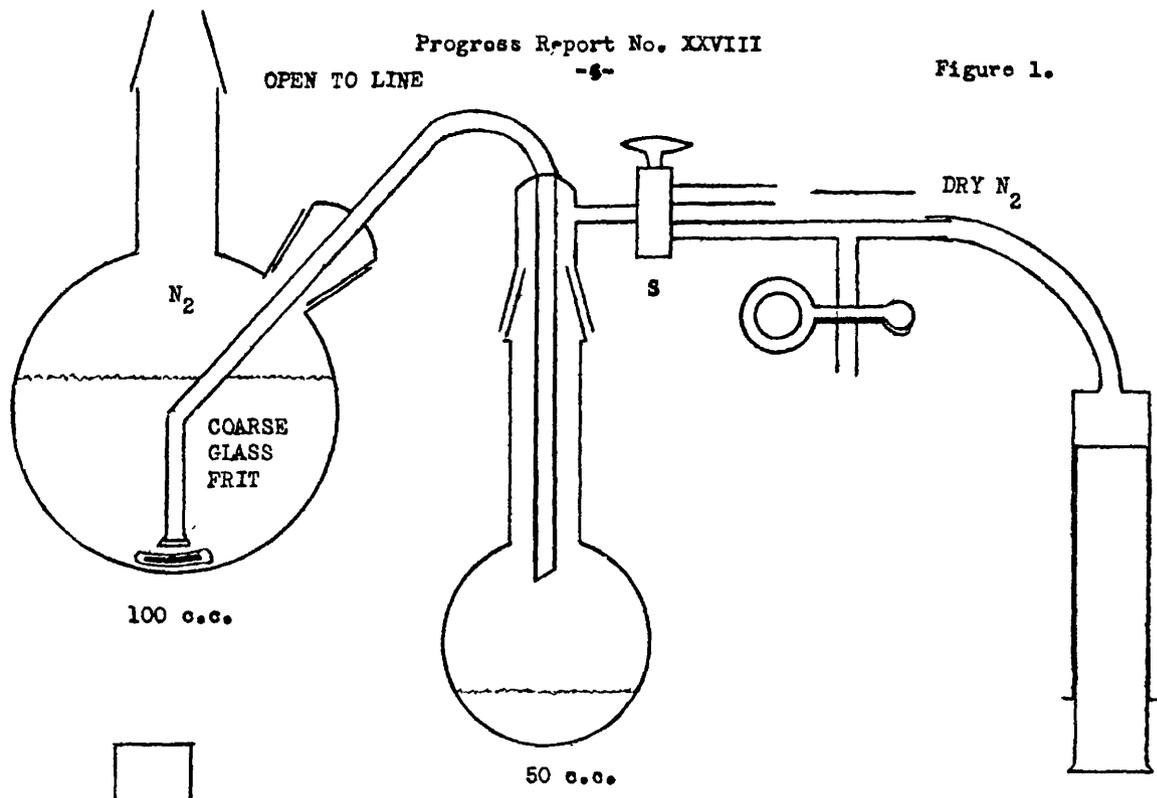
The preceding is the first successful preparation of sodium aluminum hydride from sodium hydride and aluminum chloride in a solvent other than dimethyl ether.

(c) Although the preceding experiment gave the best results yet achieved in solvents other than dimethyl ether, it left undecided whether the rate of addition of aluminum chloride was too rapid to achieve the objective intended, or whether it was slower than necessary. Obviously the maximum possible rate of addition is desirable (1) to prevent loss of aluminum hydride by polymerization and (2) to make the reaction as practical as possible.

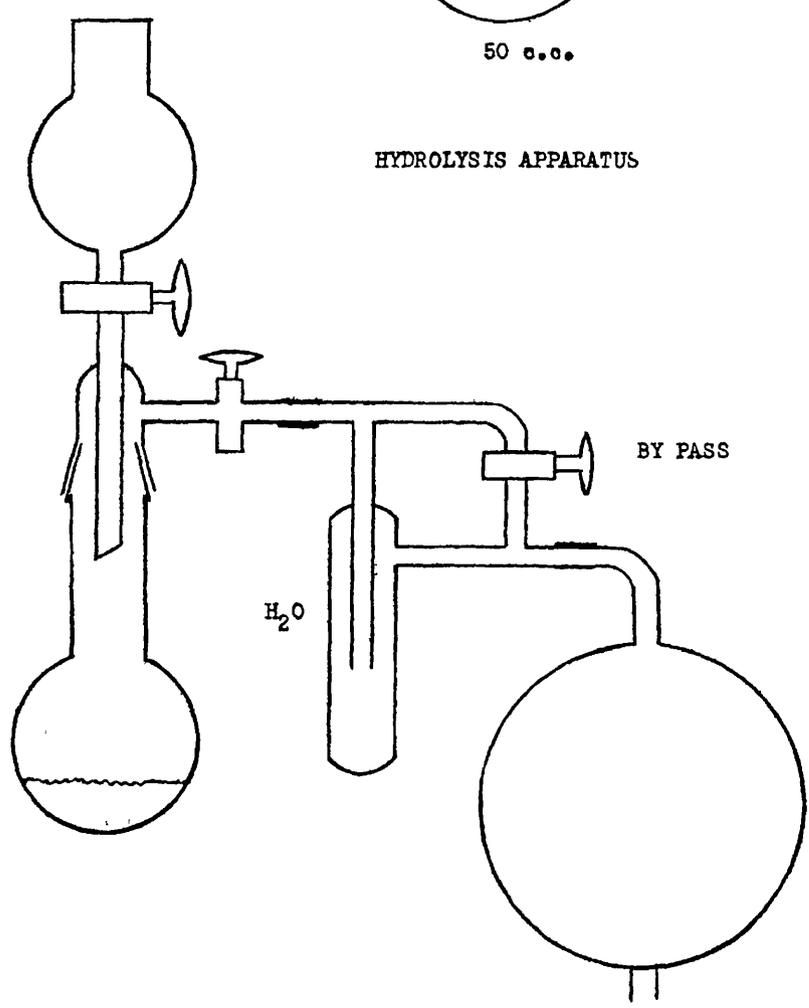
For this reason it seemed desirable to follow the rate of change of the concentrations of the reactants and of the products approximately. Precise rate measurements in this type of reaction are very difficult to carry out because of the many complicating factors, such as the difficulty of filtration, the necessity of exclusion of air and moisture, the possible precipitation of polymerized aluminum hydride during the filtration procedure, and so on. Moreover, precise measurements would probably not repay the effort required, since the rates must be dependant on the state of subdivision of the solid sodium hydride; this factor might, indeed, affect the rate in a single experiment since the finest particles of the hydride would be the first to be used up. Nevertheless the rough experiment has given data which strongly support some phases of the postulated reaction mechanism, and have suggested means of further improving the preparative method.

For the experiment, the assembly of apparatus shown in the upper part of Figure 1 was used. The material in the reaction vessel is stirred by rotating the stirrer in the bottom of the flask by means of a rotating magnet set under the flask. At the desired time, stirring is interrupted, S is opened to the all glass syringe, the plunger is withdrawn somewhat, and a sample of the liquid

Figure 1.



HYDROLYSIS APPARATUS



in the reaction vessel is drawn through the fritted glass filter into the weighed, nitrogen filled flask. By recompressing the syringe, excess of solution may be forced back to the reaction vessel. The sample flask is quickly exchanged for an empty one. The sample is weighed and analyzed for hydrogen, aluminum and halogen. The hydrolysis apparatus, shown in the lower portion of Figure 1, was designed to remove hydrogen halides from the evolved hydrogen; siphoning back is prevented by momentarily opening the by-pass.

In the experiment an excess of sodium hydride was added over a period of three minutes, via a side arm addition flask, to a solution of aluminum bromide diethyletherate in tetrahydrofuran. Unfortunately the sodium hydride used in this experiment was a newly obtained sample, more finely divided than those hitherto used, and the temperature of the mixture rose slightly over room temperature (28°C). As a result, the initial reaction was more rapid during the first few minutes than if no temperature rise had occurred (as was intended). Withdrawal of the first sample required only 1 minute, but as more precipitate formed, filtration became more difficult because of clogging of the filter, until the withdrawal time of the 6th sample was 20 minutes. The final filtration had to be made under nitrogen pressure. These irregularities, of course, cause irregularities in the time measurements, but the effect is relatively small. Some analytical difficulties were also encountered, possibly due to loss of hydrogen bromide; thus in samples 2-4 the quantity of aluminum found is more than equivalent to the sum of the hydrogen and bromine (in molar units.) Likewise the volumetric determination of aluminum proved unreliable in the presence of the solvents used, and will be replaced by gravimetric procedures in future experiments. In spite of these difficulties, inherent and accidental, this preliminary experiment has brought out several significant points.

In samples 1-4 even flame tests failed to reveal the presence of sodium in solution, i.e., no sodium aluminum hydride formed until the bromide had all been completely removed from the solution, as may be seen from the data of the accompanying table. This finding corroborates the assumption that aluminum hydride is the initial product. In the second place, the table shows that between the collection of samples 4 and 5, a rapid decrease in the bromide concentration occurred, together with a large increase in the hydrogen concentration. Also it is striking that samples 5 to 7 show that the hydrogen/aluminum ratio remains close to 3.1 but is slowly rising, indicating slow transformation of aluminum hydride to the sodium salt (Difficulties in the aluminum determination make the results of sample 5 uncertain with respect to the H/Al ratio). This preliminary experiment thus corroborates the assumption that the presence of aluminum halides retards the reaction between the two simple hydrides.

It would not be appropriate to attempt to draw any more definite conclusions from this first experiment. It is to be repeated, if time allows, with aluminum chloride and with changes in technique that should overcome the errors not inherent in the problem (e.g. not due to unevenness of particle size of the sodium hydride). Furthermore, it has suggested modifications in the procedure for preparing sodium aluminum hydride and these are now under investigation.

1	2	3	4	5	6	7	8	9	10	11	12	13	14
Mean time of withdrawal (minutes)	Time of withdrawal (minutes)	Weight of Al (grams)	Weight of Al (grams)	Al (mmoles)	Br (grams)	Br (mmoles)	H ₂ cc.	H ₂ (mmoles)	H ₂ (mgs)	Wt of solvent by difference (grams)	Calc Al conc (mmoles)	AlBr ₃ conc (mmoles)	Ratio
0	--	--	--	weight of aluminum bromide used = 8.952 = 33.57 moles	--	--	--	--	--	59.24	0.566	0.566	
11	1	5.89	0.0773	2.85	0.609	7.62	21.0	0.94	0.94	5.20	-0.548		0.488
31	1½	5.2	0.0679	2.52	0.444	5.56	28.6	1.28	1.28	4.70	0.537		0.394
96 (1h36m)	6	6.76	0.0904	3.35	0.498	6.24	66.8	2.98	2.98	6.17	0.543		0.337
216 (3h36m)	10	5.25	0.0704	2.61	0.279	3.47	82.9	3.70	3.70	4.90	0.532		0.236
421 (7h1m)	16	6.52	0.0724	2.68	absent	---	230.5	8.54	8.54	6.44	0.417		H/Al ratio (3.19)
613 (10h13m)	22	5.51	0.0632	2.34	absent	---	158.0	7.07	7.07	5.45	0.430		3.02
1467 (24h27m)	*	15.27	0.1953	7.23	absent	---	540	24.1	24.1	14.99**	0.482		3.33

* Filtered under nitrogen pressure

** Calculated on the assumption that 0.06 g of sodium was present

III. Preparation of Magnesium Hydride.--In an extension of the work reported in P.R. XXVI p 5, several attempts have been made to prepare magnesium hydride by the reaction between lithium aluminum hydride and magnesium ethyl in ethyl ether solution.

It has been observed that several factors influence the yield and nature of the products attained. Most important are:

- 1) Purity of reagents. In particular, very pure magnesium ethyl was required (95-98% purity).
- 2) Relative amounts of reactants and order of mixing. The best results were obtained when a small amount of lithium aluminum hydride was added to a large excess of ethyl magnesium.
- 3) The concentrations of the ether solutions of the reactants. Thus when lithium aluminum hydride was added to a concentrated solution of ethyl magnesium (1.9 g. in 25 cc. of ether), a precipitate was obtained which was difficult to filter and from which the last traces of ether could not be removed. On the other hand, a finely divided precipitate, which could be separated from the mother liquor by centrifuging the mixture in an atmosphere of nitrogen, was obtained.

This work was interrupted by serious illness in the family of the assistant to whom it had been assigned. It will be taken up later, but will be deferred to permit work on beryllium hydride in which considerable interest has been expressed by Government projects.

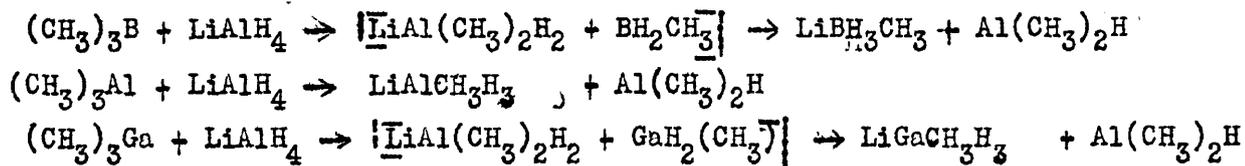
IV. Reaction of Dimethyl Zinc and Dimethyl Mercury with Lithium Borohydride.--Of the methylated lithium borohydrides only the monomethyl derivative has thus far been obtained (P.R. XXVI, p 8) by interaction of trimethylboron on lithium aluminum hydride. Since this procedure did not cause further methylation, it seemed advisable to investigate a reaction analogous to the one by which the dimethyl derivative of lithium aluminum hydride (i.e., $\text{LiAl}(\text{CH}_3)_2\text{H}_2$) was obtained (P.R. XIX, p 2, see also Finholt, Bond and Schlesinger J.A.C.S. 69 1199 (1947)) The desired reaction is represented by the equation:



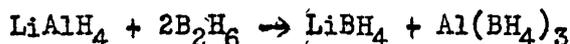
A mixture containing a slight excess of dimethyl zinc over that required by the equation after standing at room temperature for 24 hours, gave no indication that a reaction had occurred, since practically all of the dimethyl zinc could be recovered unchanged. The use of ether did not alter the result, and it therefore, appears that the proposed reaction does not occur under the specified conditions. It is, on that account, unnecessary to give further details.

Similar failure attended the attempt to prepare the desired compound by the interaction of dimethyl mercury in place of dimethyl zinc. Of 7.2 m. moles of the mercury compound, 7.05 m. moles were recovered after three days stirring of the mixture at room temperature.

V. Reactions of Lithium Aluminum Hydride with Alkyl Compounds of the Elements.--
 The work presented under this heading represents the first part of a systematic study of the reactions of lithium aluminum hydride with the alkyl compounds of the elements in the several groups of the periodic system. As is to be anticipated, the alkyl derivatives of the elements to the right of Group IV A behave differently from those elements at the left. Those at the right do not react at all or react by substitution of hydrogen for the element in question, whereas those at the left give hydrides or mixed alkyl hydrides of the elements. Thus the methyl derivative of chlorine, i.e. methyl chloride, yields methane, whereas the alkyl derivative of magnesium produces magnesium hydride (incomplete work not finally demonstrated). In the sixth group, neither ethers (i.e. alkyl oxides) nor diethyl sulfide react with lithium aluminum hydride, and trimethyl amine, if it reacts at all, seems to give only an amminate; the reaction requires further study before a final conclusion is reached. The situation in the third group is more complex as illustrated by the following equations, in which the formulae in brackets represent hypothetical intermediates



That the hypothetical, intermediate substituted lithium aluminum hydride is not the end product in the reaction involving trimethyl boron is not surprising in view of the fact (P.R. XIII p 1) that diborane completely replaces the aluminum of lithium aluminum hydride by boron:



Alkyl diboranes, i.e. $(\text{BH}_2\text{CH}_3)_2$, should behave in similar fashion. That gallium derivatives should behave in analogous fashion is a matter of considerable theoretical interest. The investigation is being extended to the alkyl derivatives of the first group of metals.

Experimental details are given for the reactions of lithium aluminum hydride with (a) methyl chloride (b) diethyl sulfide, and (c) trimethyl gallium

(a) Methyl Chloride and Lithium Aluminum Hydride

Methyl chloride obtained from a storage tank was fractionated on the vacuum line to a vapor tension of 804 mm. at -22.9°C (literature value 801 mm.). A volume of methyl chloride corresponding to 4.03 moles was distilled into a reaction flask containing 6.33 mmoles of lithium aluminum hydride in ether solution. The mixture was allowed to warm to room temperature with stirring, at which point evolution of bubbles and formation of a white precipitate was noticed. Non-condensable gases, which exhibited a vapor tension of approximately 10 mm. at liquid nitrogen temperatures (methane) were removed by the Toepler pump, and the remaining volatile matter was recondensed in the reaction flask. The above process was repeated five times in order to make certain that all of the methyl chloride was brought

into the reaction mixture. At the end of this treatment no more non-condensable gases were observed. Total reaction time (time during which the reaction mixture was at room temperature) was approximately one hour. The amount of methane liberated corresponded to a yield of 103% of the hydrocarbon (4.17 moles).

(b) Diethyl Sulfide and Lithium Aluminum Hydride

To 7.75 moles lithium aluminum hydride in ether solution was added 2.63 moles of diethyl sulfide (V.T.--46.7 mm at 20° C; lit. --48 mm.). When the reaction had been carried out as in the case of methyl chloride, .0478 mmoles (1.07 cc.) of non-condensable gases was found to have been liberated. This may be considered negligible. Fractionation of the volatile matter in the reaction mixture through a -80 bath yielded, after the process had been repeated five times, ether (v.t. -184 mm. at 0° C) and diethyl sulfide (v.t. = 53 mm. at 20° C). No ethane was observed.

(c) Trimethyl Gallium and Lithium Aluminum Hydride

The gallium methyl used in this experiment was prepared from dimethyl zinc and gallium trichloride by a modification of the method described by Kraus and Toonder, Proc. Nat. Acad. 19, 292, 1933. As with the other third group elements, ether was not used as a solvent, since the products of the reaction are likely to form stable etherates which would complicate their isolation. The procedures used were identical with those described earlier in connection with the reaction between trimethyl boron and lithium aluminum hydride (P.R. XXVI, p.6). Dry lithium aluminum hydride (2.99 mmoles) was allowed to stand in contact with 1.35 ^{mmoles} gaseous trimethyl gallium (v.t. at 0° C - 65.9; lit. -66). Fractionation of the volatile contents of the reaction bulb yielded .05 cc. of a volatile impurity and a viscous, sparingly volatile liquid which was shown by the vapor tension measurements below to be aluminum dimethyl hydride.

T	Vapor Pressure AlMe ₂ H*	Vapor Pressure Observed
35.8° C	3.6	3.7
54.6	11.7	12.0
67.2	22.9	23.5

* (P.R. XXVI, p 10)

The material which remained behind in the reaction bulb (probably a mixture of LiGaMe₃ and LiAlH₄) turned greyish on standing and liberated non-condensable gases slowly. This might be expected in view of the fact that lithium gallium hydride itself is much less stable than lithium borohydride.

Boron-Nitrogen Compounds

As explained in our last conference with the representatives of the Navy, we have decided to include the study of boron-nitrogen-hydrogen compounds in the investigation. The present report represents the initial steps in this phase of the work.

VI. Borazole and its derivatives.--Borazole ($B_3N_3H_6$) is probably the most interesting compound in the nitrogen containing group. It is closely related to benzene in its structure and physical properties.¹ Hitherto, the most satisfactory

1. Wiberg and Bolz, Ber. 73 209 (1940)

preparation of borazole has consisted of heating diborane and ammonia at about 300° C for a short period. Yields are low (about 35 to 40%), the procedure is time consuming, and the method cannot be readily adapted to large scale preparations. We are investigating what seem more promising methods of preparation.

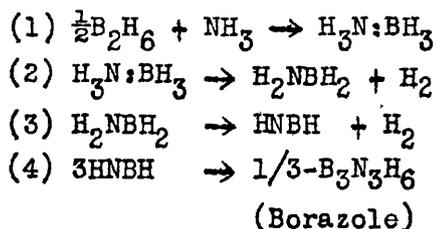
(1) Preparation of Borazole

It has been postulated^{1,2} that the reaction between diborane and ammonia

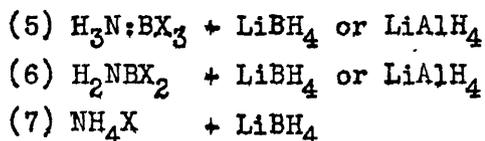
1. Wiberg et al., loc. cit.,

2. Schlesinger, Horvitz, and Burg, J.A.C.S., 58 409 (1936)

proceeds according to the following scheme:



If this postulated mechanism is correct, any reaction which would give compounds 1 or 2 should ultimately produce borazole, and might possibly avoid complicating side reactions and improve the yield. The following reactions are being considered (X = F, Cl Br):



The reduction of H_2NBCl_2 (66% purity, see below) with $LiAlH_4$ (Reaction 6) has been attempted in diethyl ether, tetrahydrofuran and dioxane. In all cases, a vigorous reaction occurs and large amounts of hydrogen and some volatile products, inseparable from the solvent, are produced. An effort is being made to find a more suitable solvent.

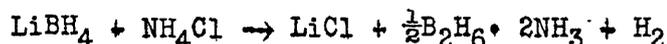
The reaction between ammonium chloride and lithium borohydride has been studied in diethyl ether³ and dioxane. In diethyl ether, one mole of

. Schaeffer and Anderson, Unpublished work

hydrogen for each mole of borohydride, a non-volatile, ether-insoluble substance with the empirical formula BNH_6 , and lithium chloride are formed. If the non-volatile products are heated to $300^\circ C$, some borazole is formed, a property characteristic of the diammoniate of diborane⁴.

. Schlesinger and Burg, J.A.C.S. 60 290 (1938)

The probable reaction can be expressed by the equation:



In dioxane, a preliminary experiment indicates a similar reaction,

(2) The polymerization of Borazole

While borazole is rather stable, it has been noted that there is a slow decomposition to give a white glassy solid and one mole of H_2 per mole of borazole used. In one experiment, a tube which originally contained 121 cc of borazole and had been allowed to stand at room temperature for three years was opened and found to contain 125 cc of H_2 or 1.03 moles per mole of borazole used. Hydrolysis of the solid polymer by heating it with 20% HCl at $120^\circ C$ for several hours suggests that there are still two boron to hydrogen bonds in the polymer, although entirely satisfactory data have as yet not been obtained. From these data it seems probable that the polymerization occurs through the formation of a boron to nitrogen bond between the borazole nuclei. Because the rate of polymerization increases as the ratio of the volume of vapor to the volume of the liquid in the reaction tube decreases, it is probable that the reaction occurs in the liquid phase. There is some indication that the rate is increased by ultraviolet radiation. Investigation of the rate of formation of the polymer and the condition under which polymerization occurs is in progress.

VII. Methyl derivatives of aminoborine.--Because the parent compound, $H_2N:BH_2$ does not seem to be stable we are attempting to prepare as many as possible of its stable derivatives. Study of the whole series should give us considerable information about the character of the boron to nitrogen bond.

(a) N-dimethylaminoborine ($H_2BN(CH_3)_2$)

N-dimethylaminoborine can be prepared by the reaction of equimolar quantities of lithium borohydride and dimethyl ammonium chloride in diethyl ether at room temperature. The reaction is best carried out by the addition of a concentrated ether solution of lithium borohydride to the dimethyl ammonium chloride. During the first part of the reaction, it is necessary to cool the reaction flask. After the addition of the borohydride is complete, the reaction mixture is refluxed for 30 minutes. The ether solution containing the product is separated from the precipitated lithium chloride by filtration, and the ether is then removed from the slightly volatile product (vapor pressure at 25° , - 8 mm; m.p. 74° C) by distillation. The yields are about 50% in small scale runs, in which the greatest losses appear to be mechanical; they are close to 100% on runs carried out in the vacuum apparatus

Because the procedure makes N-dimethylaminoborine available in quantity, we are attempting to prepare $(CH_3)_2BN(CH_3)_2$ and $(CH_3)HBN(CH_3)_2$ by direct methylation of $H_2BN(CH_3)_2$ with trimethylboron. Preliminary experiments show that a reaction takes place to form a clear liquid which slowly evolves hydrogen at room temperature. Identification of other products is at yet incomplete.

(b) B-dimethylaminoborine, $(CH_3)_2BNH_2$

B-dimethylaminoborine has been prepared by the reaction of tetramethyldiborane and ammonia⁵ and by the thermal decomposition of ammonia-trimethylboron.

5. Schlesinger, Ritter and Burg, J.A.C.S. 60 1296 (1938)

The latter method is more convenient because the preparation of the unstable tetramethyldiborane is avoided.

In a typical preparation 9.85 cc. of ammonia-trimethylboron, $H_3N:B(CH_3)_3$ was heated in a sealed tube (vol. 24.3 cc.) for $2\frac{1}{2}$ hours at 400° C. The tube was opened, methane (v.p. = 12 m. at -196°) removed, and the condensable material transferred to the fractionation system of the vacuum apparatus. Fractionation through a -80° and a -112° bath gave 0.91 cc of a substance of low volatility, probably B-trimethylborazole and 6.95 cc of nearly pure B-dimethylaminoborine (Mol. wt. obs. 55.2, calc. 56.8). Yield: 70.5%.

B-dimethylaminoborine adds one mole of hydrogen chloride. This reaction and the physical properties of the compound are being studied. It is noteworthy that trimethylboron, which is a weaker acid than hydrogen chloride, does not add to B-dimethylaminoborine. This fact suggests that the boron-nitrogen bond has considerable double bond character.

VIII. Miscellaneous boron-nitrogen compounds.--The impure BCl_2NH_2 used in the experiments reported above was prepared by the thermal decomposition of BCl_3NH_3 . BCl_3NH_3 , heated to temperatures between 200 and 300 degrees gives off hydrogen chloride, and forms a white solid which may contain BCl_2NH_2 . The solid is not volatile enough to be readily handled in a vacuum. Consequently, pure BCl_2NH_2 has not been isolated from the reaction products, but the impure material has been used in the experiments mentioned in the preceding paragraph. Investigation of the reaction to determine optimum conditions is summarized in the following table. Yields are calculated on the basis of hydrogen chloride released and on the assumption that the residue is a mixture of BCl_3NH_3 and BCl_2NH_2 . This assumption needs further verification.

M moles BCl_3	Temp	Hours	m.e. HCl	Yield
0.455	100	15	0.098	21%
0.377	250	$\frac{1}{2}$	0.225	60%
0.376	250	$1\frac{1}{2}$	0.0239	64%
0.966	250	4	0.637	66%
0.361	250	6	0.160	44%
0.388	330	$\frac{1}{2}$	0.207	56%

IX. Work in progress or planned for the near future.--Since this is the first report of the present fiscal year, a brief outline of the work planned for the coming months is presented with the understanding that it is subject to alteration depending on the promise of success in each specific topic as it develops.

- A. Continuation of experiments directed toward the preparation of hydrides of beryllium and of magnesium hydrides.
- B. Reactions of lithium aluminum hydride with ethereal solutions of halides of other metals, e.g. cobaltous chloride.
- C. Continuation of the investigation of the reaction of lithium aluminum hydrides with metal alkyls, to ascertain whether new types of compounds of special interest to the project can be obtained.
- D. Improvement in the method for preparing sodium aluminum hydride.
- E. Preparation of aluminum borohydride from sodium aluminum hydride. Thus far, the prospects do not look favorable, but success is not yet excluded.
- F. Experiments directed toward the preparation of B_2Cl_4 with the objective of ascertaining whether this compound can be hydrogenated and then converted to B_4H_{10} or B_5H_9 . The ultimate objective is to gain further insight into the mechanism of the formation of the latter. This work will not be undertaken until the most experienced members of the staff have completed present assignments, since it will probably prove difficult. We realize that the chances of success are limited, but nevertheless shall devote some time to the experiments since success, if attained, might prove very valuable in the B_5H_9 problem.
- G. Further work on boron-nitrogen compounds along the lines already outlined in this report.

[Reprinted from the Journal of the American Chemical Society 69, 1197 (1947)]

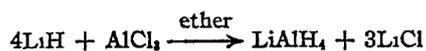
Lithium Aluminum Hydride, Aluminum
Hydride and Lithium Gallium Hydride,
and Some of their Applications in
Organic and Inorganic Chemistry

By A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger

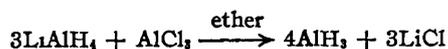
[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

Lithium Aluminum Hydride, Aluminum Hydride and Lithium Gallium Hydride, and Some of their Applications in Organic and Inorganic Chemistry¹BY A. E. FINHOLT, A. C. BOND, JR.,² AND H. I. SCHLESINGER

When lithium hydride is treated with an ether solution of aluminum chloride under the conditions described in the experimental part of this paper, the new ether soluble compound, lithium aluminum hydride, LiAlH_4 , is formed according to the equation



Addition of further quantities of aluminum chloride yields an ethereal solution of aluminum hydride



The latter solution is not stable, it soon deposits a white solid in which the atomic ratio of aluminum to hydrogen still is 3:1, but from which the ether cannot be completely removed without loss of hydrogen.³ Lithium aluminum hydride, on the other hand, may be freed from the solvent completely by evaporation of the latter under suitable conditions. Lithium gallium hydride, LiGaH_4 , has been prepared by the method used for the corresponding aluminum compound, but has not yet been studied in detail.

Although we have obtained indirect evidence of the existence of sodium and of calcium aluminum hydrides, lithium aluminum hydride and lithium

(1) Presented in abbreviated form before the Symposium on Hydrides and Related Compounds at the Chicago meeting of the American Chemical Society, September 10, 1946

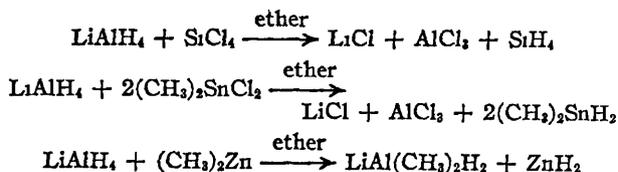
(2) Present address University of Michigan, Ann Arbor, Michigan

(3) O Stecher and E Wiberg, *Ber.*, **75**, 2003 (1942), have described the preparation of solid aluminum hydride by a method which does not involve the use of ether, but which is far more cumbersome than the procedure herein described. Their product was also not entirely pure

(4) The terminology, lithium aluminum hydride and lithium gallium hydride, is not entirely consistent with the name "borohydride" used by Schlesinger and his collaborators for the corresponding boron compounds. Since the latter term is also not entirely satisfactory, and the terminology would not be very euphonious for the aluminum and gallium compounds, we have tentatively decided on the nomenclature herein employed.

gallium hydride are the only compounds containing the AlH_4 and GaH_4 groups as yet isolated.^{5a} Nevertheless, the existence of these two compounds, as well as of aluminum hydride and of digallane,⁵ demonstrates that the questions raised and widely discussed in connection with the nature of the chemical bonds in the hydrides of boron and in the borohydrides, are not problems unique to boron chemistry. These new developments have, therefore, emphasized the importance of these questions and will, we hope, aid in their solution. But the new compounds, especially lithium aluminum hydride, possess not only theoretical interest; their discovery has already led to significant applications in both inorganic and organic chemistry.

Through the use of lithium aluminum hydride, new methods, far simpler than any hitherto available, have been developed for the preparation of hydrides such as silane and stannane and of their partially alkylated derivatives. In addition, its use has led to the preparation of previously unknown hydrides such as those of zinc and of beryllium. The types of reaction by which these results have been achieved are illustrated by the equations



Reactions such as these usually proceed smoothly at room temperature, and in general give excellent yields of products of high purity.⁶

(5a) Since this paper was submitted, sodium and calcium aluminum hydrides have been prepared by us

(5) E Wiberg and Th Johannsen, *Die Chemie*, **55**, 38 (1924)

(6) In some, though by no means in all such reactions, lithium hydride may be used in place of lithium aluminum hydride. Even in those cases in which lithium hydride gives the desired product, the reactions are slower and the yields less satisfactory. For some purposes aluminum hydride may be advantageously employed in place of the lithium salt (see page 1202).

Detailed description of the reactions illustrated by the preceding equations, as well as of others dealing with the preparation of hydrogen compounds of elements of the second, fourth and fifth groups of the periodic system, is reserved for forthcoming papers. In the experimental part of this paper, examples of the manner in which the reactions are carried out are chosen from cases involving elements of the third group.

In the field of organic chemistry, lithium aluminum hydride has already proved extraordinarily useful as a reducing agent. One mole of carbon dioxide is quantitatively absorbed at room temperature by an ethereal solution containing two moles of the new compound; among the products of the reaction are lithium and aluminum salts which yield formaldehyde when they are treated with acids, but the course of the reaction has not yet been completely elucidated. Aldehydes, ketones, acid chlorides and esters are reduced to alcohols, nitriles to amines, aromatic nitro compounds to azo compounds. In many cases in which the customary reducing agents require high temperatures or pressures and give poor yields, the new reagent reacts at room temperature and at an easily regulated, convenient rate, and gives almost quantitative yields. Its action is often highly specific. In the reduction of the nitriles so far studied by us, only primary amines were produced. Its usefulness is enhanced by the fact that olefinic double bonds are not attacked, except in special cases, and it is thus possible to accomplish the selective reduction of various functional groups in unsaturated compounds. These reactions have been studied by us only in preliminary fashion on a small scale. They are being investigated by R. Nystrom and W. G. Brown to whose paper we refer the reader for details.⁷

It is of interest to compare the properties of lithium aluminum hydride with those of lithium borohydride. Both compounds are white solids, stable in air at room temperature. Thermal decomposition of lithium borohydride becomes appreciable at from 250 to 275°, and seems to involve an intermediate reversible step in which a compound LiBH_2 is formed.⁸ The decomposition of the aluminum compound becomes noticeable at a considerably lower temperature (125 to 150°), and leads directly to the formation of aluminum, hydrogen and lithium hydride. Both compounds are soluble in diethyl ether, but the solubility of the aluminum compound is from seven to eight times as great as that of the borohydride. The former reacts completely and extremely rapidly when dropped into water; the reaction of the latter is slower and less nearly complete.⁹ Similar differences are observed in the reactions of the two

(7) R. Nystrom and W. G. Brown, *THIS JOURNAL*, **69**, 1197 (1947)

(8) H. I. Schlesinger and H. C. Brown, *THIS JOURNAL*, **62**, 3434 (1940)

(9) It is to be noted, however, that lithium aluminum hydride may be safely handled, even in very humid air, probably because of the formation of a protective coating of aluminum hydroxide

compounds toward alcohols. Finally, lithium borohydride is inert toward liquid ammonia and toward amines, whereas the aluminum compound reacts with both as described in the experimental part. Insofar as conclusions about relative polarity may be drawn from chemical behavior, lithium aluminum hydride thus seems to be somewhat less polar than lithium borohydride, but much more polar than the borohydrides of aluminum or of beryllium.⁸

The chemical properties of aluminum hydride are similar to those of lithium aluminum hydride, although the instability of the ether solution of the former limits its usefulness. Attention is here called to the possibility that the unstable ether solution of the compound may afford a means of following by molecular weight determinations the course of the polymerization assumed to be responsible for the stable, insoluble solid form of the substance.^{3,10}

Experimental Part

The Preparation of Lithium Aluminum Hydride A. **Reagents**—Unless the lithium hydride is finer than 100 mesh, its reaction with aluminum chloride occurs very slowly. After weeks of refluxing 20 to 60 mesh hydride with a diethyl ether solution of aluminum chloride, only a slight surface reaction had occurred. The relatively coarse "crystalline lump" hydride, which seems to be the only form now commercially available,¹¹ must be ground before use. The grinding and sifting of the material should be carried out in an atmosphere of dry nitrogen. We have used samples of purity varying from 87 to 94% without significant differences in the results. The quantities of lithium hydride are stated in the description of the preparative procedures in terms of pure compound. The aluminum chloride was anhydrous and of reagent quality. Anhydrous diethyl ether of the usual commercial grade proved satisfactory.

B. **Apparatus**.—Most of the reactions were carried out in three-necked flasks fitted with a mercury-sealed stirrer, a reflux condenser, and a dropping funnel, such as are used for Grignard reactions. Usually an atmosphere of dry, carbon dioxide-free nitrogen was employed both during the reaction and in the filtrations, but these precautions were found not to be absolutely essential. When the reactions were carried out in an evacuated system, the type of apparatus first described by Stock¹² was employed.

C. **Procedure**—In a typical preparation, an excess of lithium hydride (23.5 g. or 2.96 moles) was added to a solution of 3.05 g. (0.08 mole) of lithium aluminum hydride in 30 cc. of diethyl ether, and the mixture was stirred for a short time. After the addition of a further quantity of ether (200 cc.), a solution of 71.2 g. (0.534 mole) of aluminum chloride in 300 cc. of ether was introduced at such a rate that boiling of the liquid in the reaction vessel was continuous. The mixture was stirred during this step, and for a short time after the reaction had apparently ceased. The precipitated lithium chloride and the excess of lithium hydride were separated from the solution by passing the latter through a coarse sintered glass disk under nitrogen pressure.

An aliquot (6.049 g.) of the 462.5 g. of combined filtrate and washings was evaporated at atmospheric pressure until a thick sirup had formed. The last of the ether was then removed *in vacuo* at 70°. The resulting solid weighed 0.280 g. and consisted of lithium aluminum hydride of 95.4% purity according to an analysis carried out

(10) H. C. Longuet-Higgins, *J. Chem. Soc.*, 139 (1946)

(11) Maywood Chemical Works, Maywood, N. J.

(12) "Hydrides of Boron and of Silicon," Cornell University Press, Ithaca, N. Y., 1923.

as described later. The quantity of the compound contained in the original solution was, therefore, 20.42 g, of which 3.05 g had been contained in the original reaction mixture. The net yield thus was 17.37 g (0.458 mole) or 85.7% of the theoretical. It has been found that allowing the reaction to stand for a longer time before filtration improves the yield and increases the purity of the product (it may become as high as 99% without recrystallization). The bulk of the reaction product was usually not taken to dryness, since most of the reactions to be investigated were carried out in ethereal solutions. For determination of the concentrations of the solutions, measurement of the amount of hydrogen evolved by hydrolysis of an aliquot is adequate.

The addition of the small amount of previously prepared lithium aluminum hydride to the reaction mixture prevents a phenomenon which otherwise may be very troublesome. Without this addition, an initial reaction usually manifests itself by a slight rise in temperature, but soon either ceases entirely or becomes too slow to be appreciable. After an induction period, which may last for only a few minutes or may persist for hours, the reaction again sets in, this time with such vigor that it can usually not be controlled by cooling of the mixture. In the presence of a small initial quantity of lithium aluminum hydride, the reaction sets in at once at a rate controlled by the rate of addition of aluminum chloride. To obtain lithium aluminum hydride for this purpose when none is available from previous preparations, two procedures are illustrated by the following examples.

1. A small quantity of aluminum chloride (2.7 g) was mixed with a 6-fold excess of lithium hydride (4 g) under dry nitrogen in a small round bottom flask, which was then attached through a standard ground glass joint to a vacuum system, and evacuated. About 15 cc of ether was condensed on the reaction mixture at liquid nitrogen temperature. The reaction, which began as the flask was warmed slowly, was allowed to proceed vigorously, but was kept under control by cooling the flask with liquid nitrogen from time to time. The reaction was usually completed in about five minutes. Filtration of the resulting mixture and removal of the solvent from the filtrate as previously described yielded a sample of lithium aluminum hydride adequate for initiation of the reaction of larger batches.

2. Solid lithium hydride (7.0 g) was mixed with solid anhydrous aluminum chloride (15.96 g.) in a 500 cc. flask previously flushed with dry nitrogen. Subsequent addition of 150 cc. of dioxane caused the temperature to rise to 50°. The mixture was refluxed for one-half hour, after which it was cooled, diluted with 135 cc. of diethyl ether, and refluxed again for another three hours. The resulting mixture was filtered. The solid obtained from the filtrate by the procedure used in the preceding examples seemed to contain only about 30% of lithium aluminum hydride, but nevertheless served to initiate the desired reaction.

Analysis of Lithium Aluminum Hydride—Analysis of the compound was achieved by its hydrolysis according to the equation



If lithium aluminum hydride is treated with any but very large amounts of water, the resulting reaction is so vigorous that the solid may become heated to incandescence with a resultant loss of hydrogen by thermal decomposition. This difficulty was avoided by mixing the sample with anhydrous dioxane, and then adding the water drop by drop. In the resulting solution, aluminum was determined as the oxide, and lithium as the sulfate. Results of a typical analysis are as follows: sample, 0.3824 g; found: Li, 0.0691 g, Al, 0.2689 g, H₂, 884.0 cc¹³; calcd. for LiAlH₄: Li, 0.0699 g, Al, 0.2719 g, H₂, 903.7 cc. The atomic ratios thus are represented by the formula $\text{Li}_{1.00}\text{Al}_{1.00}\text{H}_{3.96}$, and the total weights found correspond to

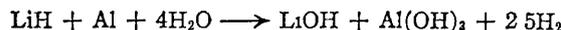
(13) Volumes of substances measured in the gaseous state are referred to standard conditions.

98.7% of the weight of the sample. The impurity probably was residual ether.

For confirmation of the analysis, pyrolysis was employed. The compound decomposes according to the equation



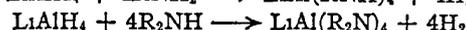
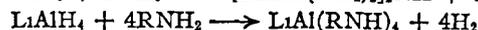
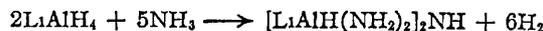
The residue gives additional hydrogen on treatment with water



Although the compound decomposes fairly rapidly at 150° the temperature of the sample was gradually raised to 220° to assure complete decomposition. The following data were obtained: sample, 0.2462 g, hydrogen from pyrolysis 218 cc, calcd., 218 cc, hydrogen from hydrolysis of residue 364 cc, calcd., 363 cc.

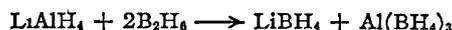
Solubility of Lithium Aluminum Hydride—**Its Reactions with Amines and Ammonia**—The solubilities of lithium aluminum hydride in grams per 100 g. of various ethers at 25° are as follows: diethyl ether, 25–30; tetrahydrofuran 13; dibutyl ether 2; dioxane 0.1. Because of the difficulty of handling the extremely viscous solutions obtained in the first two of these solvents, the data are of only approximate character.

Ammonia and primary and secondary amines, some of which are excellent solvents for borohydrides, react with lithium aluminum hydride to give a quantity of hydrogen which is from 93 to 99% of that calculated according to equations



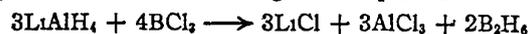
Since the postulated equations need further verification by analysis of the solid products, details concerning the reactions are not recorded herein, it is evident, however, that they result in the formation of hitherto unknown types of compounds.

Reaction of Lithium Aluminum Hydride with Diborane—An excess of diborane was continuously circulated over 0.955 g (25.2 mmoles) of lithium aluminum hydride in a vacuum system which contained a U-tube maintained at -80° to remove the aluminum borohydride formed by the reaction. The reaction vessel was heated at 70° for three and a quarter hours and then at 90° for three and three-quarter hours. The amount of diborane absorbed (1030 cc, or 46.0 mmoles) and the quantity of gaseous aluminum borohydride collected (505 cc, or 22.5 mmoles) correspond to the values calculated according to the equation



if it is assumed that the reaction had gone about 90% to completion. This assumption was corroborated by the fact that the solid product weighed 0.585 g, whereas the value calculated on the basis of the same assumption is 0.592 g.

The Reaction of Lithium Aluminum Hydride with Boron Chloride—As an example of the preparation of inorganic hydrides through the use of lithium aluminum hydride, we have chosen its reaction with boron chloride to produce diborane according to the equation

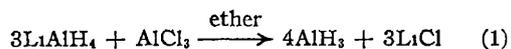


A solution of 0.277 g (7.3 mmoles) of lithium aluminum hydride in 5 cc. of anhydrous diethyl ether, contained in a vessel attached to a vacuum line, was frozen at liquid nitrogen temperature. An excess of tensimetrically pure boron chloride (1.279 g, or 10.91 mmoles) was then distilled into the evacuated vessel. A vigorous reaction, probably the formation of boron chloride etherate, occurred as soon as the material had melted; after the completion of this reaction, the mixture gradually was warmed to room temperature and thoroughly stirred. The material volatile at room temperature was passed through a -112° bath, the uncondensed portion consisted of 4.83 mmoles of pure diborane, a yield of 99.4%. The correctness of

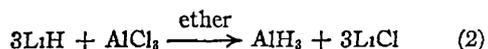
the equation was further confirmed by the addition of aluminum chloride to the residue to liberate the excess of boron trichloride from the ether. The amount of boron trichloride thus recovered showed that 9.7 mmoles, or 99% of the theoretical, had reacted.

This procedure illustrates the speed and high yields obtainable in reactions of this type. For the preparation of larger quantities, it is often desirable to moderate the initial reaction by dissolving the inorganic chloride in ether before adding it to the lithium aluminum hydride solution.

Preparation of Aluminum Hydride—Aluminum hydride was prepared both by the reaction



and by the reaction



Although the latter seems simpler, the former is preferred, especially when lithium aluminum hydride is available, since it is more rapid and proceeds more smoothly.

Reaction (1)—A solution containing 0.546 g (14.4 mmoles) of lithium aluminum hydride in 9.1 g of diethyl ether was diluted with 15 g of additional solvent, and treated with 0.629 g (4.72 mmoles) of anhydrous aluminum chloride in a flask previously flushed with nitrogen.¹⁴ The lithium chloride precipitated during the course of the vigorous, but rapidly subsiding, reaction was removed by filtration, and the ether was evaporated from the filtrate through a vacuum line. The resulting white solid was slowly heated to about 96°, at which temperature heating was discontinued because slight evolution of hydrogen and discoloration of the solid were observed. The ether content of the solid products is discussed in the next section.

Analysis of the product was carried out essentially as for lithium aluminum hydride, except that aluminum was determined as the 8-hydroxyquinolate.¹⁵ The product yielded 1165 cc (52.0 mmoles) of hydrogen and contained 0.4693 g (17.4 mmoles) of aluminum, corresponding to an atomic ratio of $\text{Al}_{1.00}\text{H}_{2.99}$, and a yield of 92% based on the aluminum chloride used.

Reaction (2)—The apparatus and procedures were essentially those used for the preparation of lithium aluminum hydride. The ratio of lithium hydride (5.90 g or 0.743 mole) to aluminum chloride (33.0 g or 0.248 mole) was as nearly as possible that demanded by the equation, and a large total amount of ether (440 cc) was used to avoid precipitation of aluminum hydride before the lithium chloride had been removed. A small amount (0.3 g) of lithium aluminum hydride was added to initiate the reaction. The mixture was stirred for one hour after the addition of the aluminum chloride, and was then filtered.

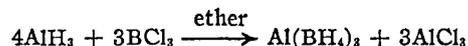
Analysis was carried out as in (1). The results showed the solution to have contained 0.621 mole of active hydrogen and 0.212 mole of aluminum, a ratio of 2.93:1 and a yield of 85%.

Composition and Solubility of "Solid Aluminum Hydride"—The composition of the solid obtained from diethyl ether solutions of aluminum hydride, either by spontaneous precipitation or by evaporation of the solvent, is variable. The ratio of hydrogen to aluminum is always 3:1 within experimental error, but the weight of these constituents is always less than the total weight of the sample. The difference in these weights was assumed to represent the ether content of the material analyzed. The longer the product is kept in a continuously evacuated vessel, and the higher the temperature at which the ether is removed, the lower is the content of the latter in the

residue. Thus a sample, obtained by spontaneous precipitation and subsequent removal of the mother liquor by several washings with ether, was evacuated at room temperature for one hour, it then had a composition corresponding to 2.26 moles of the hydride to one of ether. Another sample was evacuated at the same temperature for twenty hours, and then had an aluminum hydride-ether ratio of 3:1. When the evacuation was carried out at 80°, the ratio became 4.85:1. At still higher temperatures additional ether was removed, but decomposition of the hydride also set in. Although the data obtained by complete pyrolysis were not conclusive, and are, therefore, not included, they indicated that ether is the only impurity in the aluminum hydride, as was assumed in obtaining the preceding ratios.

In spite of the fact that spontaneous precipitation occurs even in dilute solutions, the solids obtained by evaporation of an ether solution may again be at least partially redissolved. In one case the ether was removed from a freshly prepared solution, and the resulting solid was gradually warmed to 80°, at which temperature it was maintained for one-half hour. After stirring a 0.2-g sample of this product with ether at room temperature, 0.1 g was found to have dissolved in 40–50 cc of the solvent. Evaporation of this solution produced a material of which only a part could again be dissolved. The transformation of the soluble to the insoluble form is thus a progressive change, the magnitude of the soluble fraction will depend on the temperature and other conditions according to which the solid is prepared.

Reaction of Aluminum Hydride with Boron Chloride—Aluminum hydride, like lithium aluminum hydride, reacts with boron chloride to form diborane. Since the latter reacts further with aluminum hydride to give aluminum borohydride,³ appropriate choice of the proportions of the reagents leads, as shown by the following experiment, to the reaction



At the melting point of a mixture containing 1.350 g (11.52 mmoles) of boron trichloride, 0.459 g (15.3 mmoles) of aluminum hydride and 33 cc of diethyl ether, a vigorous reaction occurred. Two liquid layers were first formed, but at about 0° the mixture became homogeneous.

The uncombined ether, together with traces of diborane, was removed from the reaction product, which was then treated with 1.20 g (9.0 mmoles) of aluminum chloride to free the aluminum borohydride from its etherate. After the mixture had been stirred for twenty minutes, the volatile material was removed by gradual heating of the reaction vessel to 70°, and was then fractionated in the vacuum system. This treatment resulted in the isolation of 9.18 cc (0.41 mmoles) of diborane, and 75.9 cc (3.39 mmoles) of pure gaseous aluminum borohydride. The yield of the latter was thus 88.3% of that demanded by the equation, and the total recovery of boron and of hydrogen was 96% of that used. Diborane was probably formed in a reaction between aluminum borohydride and traces of hydrogen chloride contained as an impurity in the aluminum chloride.

Preparation and Analysis of Lithium Gallium Hydride, LiGaH_4 —Anhydrous gallium chloride, 0.59 g (3.35 mmoles), was sublimed *in vacuo* into a reaction vessel which was attached to a vacuum line, and was fitted through a ground glass joint to a bent side tube containing lithium hydride. About 5 cc of anhydrous diethyl ether was condensed by means of liquid nitrogen into the reaction vessel, which was then slowly warmed until the chloride had dissolved. The solution was cooled to -80° , and lithium hydride was added in about 4-fold excess (0.47 g or 5.9 mmoles) by slowly tilting the side tube. After the initial, moderately vigorous reaction had subsided, the mixture was gradually warmed to room temperature, and was then filtered through a sintered glass disk. The ether was removed from the filtrate by evacuation for twenty hours at room temperature.

(14) To avoid contamination of the desired product with the lithium salt, the excess of the latter was kept at a minimum. It is essential, on the other hand, to avoid an excess of aluminum chloride, since it causes lithium chloride to dissolve in ether.

(15) Lundell and Knowles, *Bur Standards J Research* 3, 92 (1929).

After hydrolysis of the resulting white solid, and measurement of the hydrogen evolved, gallium was precipitated from the solution as the 8-hydroxyquinolate. The 0.2250 g of product yielded 233.4 cc (10.42 mmoles) of hydrogen and contained 0.178 g (2.56 mmoles) of gallium. These data correspond to an atomic ratio of 4.07:1.00, a purity of 93% and a yield of 76%. The low yield was probably due in large part to incomplete washing of the lithium chloride, and the low purity to inadequate removal of ether from the product. The fact that the compound turns gray, *i. e.*, begins to decompose in a comparatively short time even at room temperature, necessitated the defects in procedure. Complete pyrolysis of the compound leads to the formation of metallic gallium and, presumably, lithium hydride and hydrogen.

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Summary

1. The preparation and some of the properties of the new compounds, lithium aluminum hydride, LiAlH_4 , and of lithium gallium hydride, LiGaH_4 , have been described. Included is a new, simple

procedure for preparing an ether solution of aluminum hydride, $(\text{AlH}_3)_x$, as well as an insoluble, probably polymerized, ether-containing solid form of the latter.

2. The interaction of lithium aluminum hydride with halides or alkyls of elements of the second, third, fourth and fifth groups of the periodic system constitutes a convenient procedure for preparing hydrogen compounds of these elements in pure form and in good yield. As a specific example, a new method for preparing diborane has been described in detail.

3. Aluminum hydride behaves in many respects like lithium aluminum hydride, except for the greater solubility of the latter in ether and the consequent greater convenience of its reactions. As an example of the usefulness of aluminum hydride, the development of a new method for preparing aluminum borohydride is described.

4. Attention is called to the usefulness of lithium aluminum hydride in the reduction of organic compounds. The smoothness of such reactions, as well as their specificity in certain cases, has been emphasized.

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