UNCLASSIFIED

AD NUMBER

ADB809156

NEW LIMITATION CHANGE

TO

Approved for public release, distribution unlimited

FROM

DISTRIBUTION AUTHORIZED TO DOD ONLY; ADMINISTRATIVE/OPERATIONAL USE; 03 MAR 1999. OTHER REQUESTS SHALL BE REFERRED THROUGH NAVAL RESEARCH LAB, WASHINGTON, DC 20350.

AUTHORITY

NRL ltr dtd 30 Apr 2002

THIS PAGE IS UNCLASSIFIED

AD# B809156

The U.S. GOVERNMENT

IS ABSOLVED

FROM ANY LITIGATION WHICH MAY ENSUE FROM THE CONTRACTORS INFRINGING ON THE FOREIGN PATENT RIGHTS WHICH MAY BE INVOLVED.

REEL-C
577
A.T.I.
16148

N R L REPORT NO. C-3202

HYDRIDES AND BOROHYDRIDES OF LIGHT ELEMENTS

PROGRESS REPORT NO. XXVIII

DEPARTMENT OF THE NAVY
OFFICE OF NAVAL RESEARCH

NAVAL RESEARCH LABORATORY

WASHINGTON D.C.

NRL REPORT NO. C-3208

HYDRIDES AND BOROHYDRIDES OF LIGHT ELEMENTS

PROGRESS REPORT NO-XXVIII

H. I. Schlesinger, George W. Schaeffer
University of Chicago

Approved by:

Mr. R. R. Miller, Head, Physical and Inorganic Section
Dr. P. Borgstrom, Superintendent, Chemistry Division

Problem No. 32C25-01 December 4, 1947

NAVAL RESEARCH LABORATORY
CAPTAIN H. A. SCHADE USN DIRECTOR
WASHINGTON, D.C.

DISTRIBUTION

BuAer	
Attn: Code PP-51	4
BuOrd	
Attn: Code Re-6	2
Attn: Code Re-24	2
BuShips	
Attn: Code 433	2
AEC	
Attn: R. M. Fry, Library Section TIB	3

		Copy No.
GMC Committee, RDB, Wash., D. C.	A	(1)
CG, AAF, Wash., D. C.,Attn: AC/AS-4, DRE-3, Pentagon	"	(2-5)
CG, AMC, Wright Field, Dayton, Ohio, Attn: TSEON-2	"	(6-30)
CG, Air Univ., Maxwell Field, Ala., Attn: Air Univ. Library	"	(31)
BuAer, Wash., D. C.,Attn: TD-4	"	(32-37)
BuOrd, Wash., D. C.,Attn: Re-9	"	(38-41)
BuShips, Wash., D. C.,Attn: Codes 633, 910A, and 343	"	(42-44)
Ch/GMBranch, Technical Command, Army Chem. Center, Md.	"	(45)
CG, APG, Md., Attn: Ballistic Res. Lab.	"	(46)
CG, Eglin Field, Fla., Attn: First Exp., GM Group	"	(47)
CG, AAS, Fort Bliss, Texas	"	(48)
CO, Frankford Arsenal, Phila., Attn: Fire Control Design Div.	"	(49)
Commander, NAMC, Phila.	"	(50)
CO, NADS, Johnsville, Pa.	"	(51)
CO, ONR, San Francisco	"	(52-53)
CO, SCEL, Bradley Beach, N. J.	"	(54-55)
CO, NAMTC, Pt. Mugu, Calif.	"	(56)
CO, NOTS, Inyokern, Calif.	"	(57)
CO, Alamorgodo Army Air Base, N. M.	"	(58)
Dir., DTMB, Wash., 7, D. C., Attn: Aero. Mechanics Div.	"	(59)
Dir., NACA, Wash., D. C., Attn: Mr. C. H. Helms	"	(60-63)
Dir., NRL, Wash., 20, D. C.	"	(64-66)
Dir., Spec. Devices Center, ONR, Sands Point, L. I., Attn: TID	"	(67)
First Antiaircraft Artillery, GM Btn., White Sands Proving Ground	"	(68)
Head, PG School, U. S. Naval Academy, Annapolis	"	(69)
RDB, Attn: Library	"	(72)
Off. Ch/Ord, Res. and Dev. Div., Rocket Branch, Pentagon	"	(73)
OinC, BOEU, Hydraulics Bldg., Nat'l BuStds., Wash., D. C.	"	(74)
OinC, NOL, NavGun, Wash., D. C., Attn: Dr. R. J. Seeger	"	(75-76)
OinC, Ord. Res. and Dev. Div. Suboffice (Rocket) Ft. Bliss, Texas	"	(77)
CNO, Op-57	"	(78)
Watson Labs., AMC, Eatontown, N. J.	"	(79)
Watson Labs., AMC, Cambridge Field Station, Mass., Attn: Dr. M. O'Day	"	(80)
CG, Army Ground Forces, Ft. Monroe, Va., Attn: Ch/Dev. Sect. GNDEV-9	"	(81)
ONR, c/o Lib. of Congress, Tech. Info. Sect., Attn: J. Heald	"	(82-84)
Ch/Res. and Eng. Div., Off. Ch. Chem. Corps, Army Chem. Center, Md.	"	(85)

		Copy No.
AEC, Div. Mil. Applic., Wash., 25, D. C., Attn: Col. D. J. Keirn	B	(1)
BAGR,-ED, NY Nav. Shipyard, Bldg. No. 3, Brooklyn 1, N. Y.	"	(2)
BAGR,-CD, Wright Field, Dayton, Ohio, Attn: Lt. Col. J. A. Gerath	"	(3)
BAGR,-WD, Los Angeles	"	(4)
BuOrd, Wash., 25, D. C., Attn: Re-9	"	(5-8)
CNO, Wash., 25, D. C., Attn: Op-34H, Op34H8, and Op-413	"	(9-11)
CG, AAF, Wash., 25, D. C., Attn: DC/AS, DRD	"	(13)
CG, APG, Md., Attn: Lib. Sect.	"	(15)
CG, AU, Maxwell Field, Attn: Lib. of AAFSSS, Craig Field, Ala.	"	(16)
CG, AU, Maxwell Field, Attn: Lib. for AAFTS, Tyndall Field, Fla.	"	(17)
Comdt., Command and Staff College, Ft. Leavenworth, Kansas	"	(18)
Comdt., Mar. Corps., Wash., D. C., Attn: G-3 (Special Weapons)	"	(19)
Comdt., Armed Forces Staff College, Norfolk 11, Va.	"	(20)
COM NATC, Patuxent River, Md., Attn: Dir. of Tests	"	(21)
CO, NAES, Phila., Attn: Supt. AEL	"	(22)
CO, NAOTS, Chincoteague, Va.	"	(23)
CO, Watertown Arsenal, Mass., Attn: Laboratory	"	(24)
ComOpDevFor, c/o Fleet Post Office, N. Y., N. Y.	"	(25-26)
Dir. Res. and Dev., War Dept. Gen Staff, Pentagon	"	(27)
Dir., Seacoast Service Test Sect. AGF Board No. 1, Ft. Baker, Calif.	"	(28)
Hd. Ord. and Gunnery, USNA, Annapolis	"	(29)
OCO, Ord. Res. and Dev. Serv., Ammunition Branch, Pentagon	"	(30)
OCSigO, Engr. and Tec. Serv., Engr. Div., Pentagon	"	(31)
Off. Sec. of War, Pentagon	"	(32)
[illegible] Radio Co., Cambridge 39, Attn: Dr. H. P. [illegible]	"	(34)
Pres., Army Ground Forces Board No. 1, Ft. Bragg, N. C.	"	(35)
Pres., Army Ground Forces Board No. 4, Ft. Bliss, Texas	"	(36)
Prof. of Ord., U. S. Military Academy, West Point, N. Y.	"	(37)
Sec. Special Board, Comdt. of Marine Corps, Marine Corps School, Quantico	"	(38)
National War College, Wash., D. C., Attn: Library	"	(39)
DCO for APL, JHU, Silver Spring, Md.	C	(1-3)
BAR, Buffalo, for BAC, Niagara Falls, Attn: Mr. R. H. Stanley and Mr. Hamlin	"	(4)
BTL, Murray Hill, N. J., [illegible] W. A. MacNair	"	(5)
Bendix Av. Corp., East Teterboro, N. J., Attn: Dr. H. Selvidge	"	(6)
Boeing Aircraft Corp., Seattle, [illegible]	"	(7)
DCO for C-V Air. Corp., LSL, Daingerfield, Texas. Attn: Mr. Arnold	"	(8)
BAR, Consolidated-Vultee Air. Corp., San Diego, Attn: Mr. [illegible]	"	(9)
BAR for Cornell Aero. Lab., Buffalo, N. Y., [illegible]	"	(10)
BAR for Curtiss Wright Corp., Columbus, Attn: Mr. B. Eaton	"	(11)
BAR for Douglas Aircraft Co., El Segundo, Calif., Attn: Mr. Heinemann	"	(12)
Douglas Air. Co., Santa Monica, Attn: Mr. A. E. Raymond, (Project Rand) and Mr. E. F. Burton	"	(13-14)
INSORD for Eastman Kodak Co., Rochester, N. Y., Attn: Dr. Trotter	"	(15)
Fairchild Eng. and Air. Corp., NEPA Div., Oak Ridge, Attn: Mr. Kalitinsky	"	(16)
RIC-BuAer for Fairchild Eng. and Air. Corp., Farmingdale, Attn: J. A. Slonin	"	(17)
CO, NADS for Franklin Inst. Labs., Phila., Attn: Mr. R. H. McClarren	"	(18)
Gen. Elec. Co., Schenectady, Project HERMES, Attn: Mr. C. K. Bauer	"	(19)
DCO for G. E. Co., Schenectady, Attn: A. L. Ruiz	"	(20)
G. E. Co., Av. Div., Schenectady, Attn: Mr. S. A. Schuler, and Mr. P. Class	"	(21)
BAR for Glenn L. Martin Co., Balt., Attn: Mr. N. M. Voorhies	"	(22)
Glenn L. Martin, Balt., Attn: Mr. W. B. Bergen	"	(23)
INSMAT, Chicago for Globe Corp., Joliet, Ill., Attn: Mr. J. A. Wengle	"	(24)
BAR for Goodyear Aircraft Corp., Akron, Attn: Dr. Carl Arnstein	"	(25)
Goodyear Aircraft, Plant B, Akron, Attn: Mr. A. J. Peterson	"	(26)
BAR for Grumman Air. Engr. Corp., Bethpage, L. I., Attn: Mr. Schwendler	"	(27)
Hughes Aircraft Co., Culver City, Calif., Attn: Mr. D. H. Evans	"	(28)
OinC, Res. and Dev. Serv. Suboffice (Rocket) CIT, Pasadena	"	(29-30)
INSMAT for Kellex Corp., New York, N. Y.	"	(31)
M. W. Kellogg Co., Jersey City, N. J., Attn: Dr. G. H. Messerly	"	(32)

		Copy No.
NORTLO for Chairman, MIT, GMC, Project Meteor Office, Cambridge, Attn: Dr. H. G. Stever	C	(33-34)
BAR for McDonnell Aircraft Corp., St. Louis, Attn: W. P. Montgomery	"	(35)
BAR for NAA, Inc., Los Angeles, Attn: Mr. D. H. Mason	"	(36)
Northrop Aircraft Inc., Hawthorne, Calif.	"	(37)
DCO for P. U. Phys. Dept., Princeton, N. J., Attn: Mr. Harry Ashworth	"	(38)
CO, ONR Branch Office, N. Y. for Princeton U., Attn: Proj. SQUID	"	(39-41)
INSMAT for Radio Corp. of America, Camden, N. J., Attn: Mr. T. T. Eaton	"	(42)
BAR for Radioplane Corp, Van Nuys, Calif., Attn: Mr. Ferris Smith	"	(43)
INSMAT, Boston, for Raytheon Mfgr. Co., Waltham, Attn: Mrs. H. L. Thomas	"	(44)
INSMAT, Brooklyn, for Reeves Instrument Corp., N. Y., N. Y.	"	(45)
Republic Aviation Corp., Farmingdale, L. I., Attn: Dr. Wm. O'Donnell	"	(46)
Ryan Aero. Co., Lindberg Field, San Diego 12, Calif., Attn: Mr. E. A. Sutton	"	(47)
INSMAT, Brooklyn, for Sperry Gyroscope Co, Great Neck, L. I.	"	(49)
BAR U. A. Corp., Stratford, for U. A. Corp, Chance Vought Air. Div., Stratford, Conn., Attn: Mr. P. S. Baker	"	(50)
BAR, U. A. Corp., E. Hartford, for U. A. Corp., Research Dept., E. Hartford, Attn: Mr. J. G. Lee	"	(51)
Univ. of Mich., Aero. Res. Center, Willow Run Airport, Attn: R. F. May and Dr. A. M. Kuethe	"	(52)
BAR, Pasadena for USC, Naval Res. Proj., LA, Attn: Dr. R. T. DeVault	"	(53)
DCO, Univ. of Texas, Defense Res. Lab., Austin, Attn: Dr. C. P. Boner	"	(54)
Lockheed Aircraft Corp., Burbank, Calif., Attn: Mr. H. L. Hibbard	"	(56)
Calif. Inst. of Tech., JPL, Pasadena, Attn: Mr. L. G. Dunn	"	(57)
BAR, Pasadena, for Aerojet Engr. Corp., Azusa, Attn: Mr. K. F. Mundt	DP	(1)
Armour Research Foundation, Chicago, Attn: Mr. W. A. Casler	"	(2)
Arthur D. Little, Inc., Cambridge, Attn: Mr. Helge Holst	"	(3)
Battelle Memorial Institute, Columbus, Attn: Dr. B. D. Thomas	"	(4)
DCO, for Bendix Aviation Corp., N. Hollywood, Attn: R. M. Russell	"	(5)
Bendix Products Div., Bendix Aviation Corp., S. Bend, Ind., Attn: F. C. Mock	"	(6)
CG, AAF, Pentagon, Attn: AC/AS-4, DRE-2E	"	(7)
CG, AMC, Wright Field, Attn: TSEPP-4B(2) TSEPP-4A(1) TSEPP-5C(1) TSORE(1) TSEPP-5A(1)	" "	(8-13)
CO, Picatinny Arsenal, Dover, N. J., Attn: Technical Div.	"	(14)
CO, Watertown Arsenal, Watertown, Mass., Attn: Laboratory	"	(15)
BAR for Continental Av. and Engr. Corp., Detroit	"	(16)
Curtiss-Wright Corp., Prop. Div., Caldwell, N. J., Attn: Mr. C. W. Chillson	"	(17)
DCO for Experiment, Inc., Richmond, Va., Attn: Dr. J. W. Mullen, II	"	(18)
BAR, Bethpage, L. I., for Fairchild Air. and Eng. Co., Farmingdale, N. Y.	"	(19)
BAR for Gen. Motors Corp., Allison Div., Indianapolis, Attn: Ronald Hazen	"	(20)
G. M. Giannini and Co., Inc., Pasadena	"	(21)
INSMAT, New York for Hercules Powder Co., Port Ewen, N. Y.		[illegible]
BAR, Pasadena, for Marquardt Aircraft Co., Venice, Attn: Dr. R. E. Marquardt	"	[illegible]
Menasco Mfg. Co., Burbank, Calif., Attn: Robert R. Miller	"	(24)
INSMAT, N.Y. for N. Y. U., Applied Math. Center, N. Y., Attn: Dr. R. Courant	"	(25)
Office of Ch. of Ord., Ord. Res. and Dev. Div., Rocket Br., Pentagon	"	(26)
INSMAT, N. Y. for Polytechnic Inst., of Brooklyn, Attn: Mr. R. P. Harrington	"	(27)
INSMAT, Chicago for Purdue Univ., Attn: Mr. G. S. Meikel	"	(28)
BARR, Dover, for Reaction Motors, Inc., Dover, N. J.	"	(29)
Rensselaer Polytechnic Inst. Troy, Attn: Inst. of Naval Science	"	(30)
Solar Aircraft Co., San Diego, Attn: Dr. M. A. Williamson	"	(31)
INSMAT, N. J. for Standard Oil Co., Esso Lab., Elizabeth, N. J., Attn: W. J. Sweeney	"	(32)
DCO, Charlottesville, for U. of Va., Physics Dept., Attn: Dr. J. W. Beams	"	(33)
INSMAT, Chicago, for U. of Wisconsin, Attn: Dr. J. O. Hirschfelder	"	(34)
BARR, Westinghouse for Westinghouse Electric Co., Essington, [illegible]	"	(35)
BAR, Woodridge, for Wright Aeronautical Corp., Woodridge, N. J.	"	(36)
Supt., Shipbuilding, USN, Quincy, for Bethlehem Steel Corp., Shipbuilding Div., Quincy, Attn: Mr. B. Fox	"	(37)
Ohio State University, Columbus, Attn: Dr. H. L. Johnson	"	(38)
DCO, APL, JHU, for Rocket Propellant Agency, APL, JHU, Attn: Dr. S. Githens	"	(39)

CONTENTS

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-2820, 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) have described the conditions under which explosions result when solutions of aluminum hydride or of soldium 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

---

[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.

70° C. caused no further gas evolution. The gas evolved contained methane as shown by a vapor tension of 12 mm. at -196° 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 <u>slowly</u>, 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:

$$3\ LiAlH_4 + AlCl_3 \rightarrow 3\ LiCl + 4\ AlH_3$$

$$4\ AlH_3 + 4\ LiH \rightarrow 4\ LiAlH_4$$

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 1½ 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. (3.66 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 93% purity, and the yield approximately 70%.

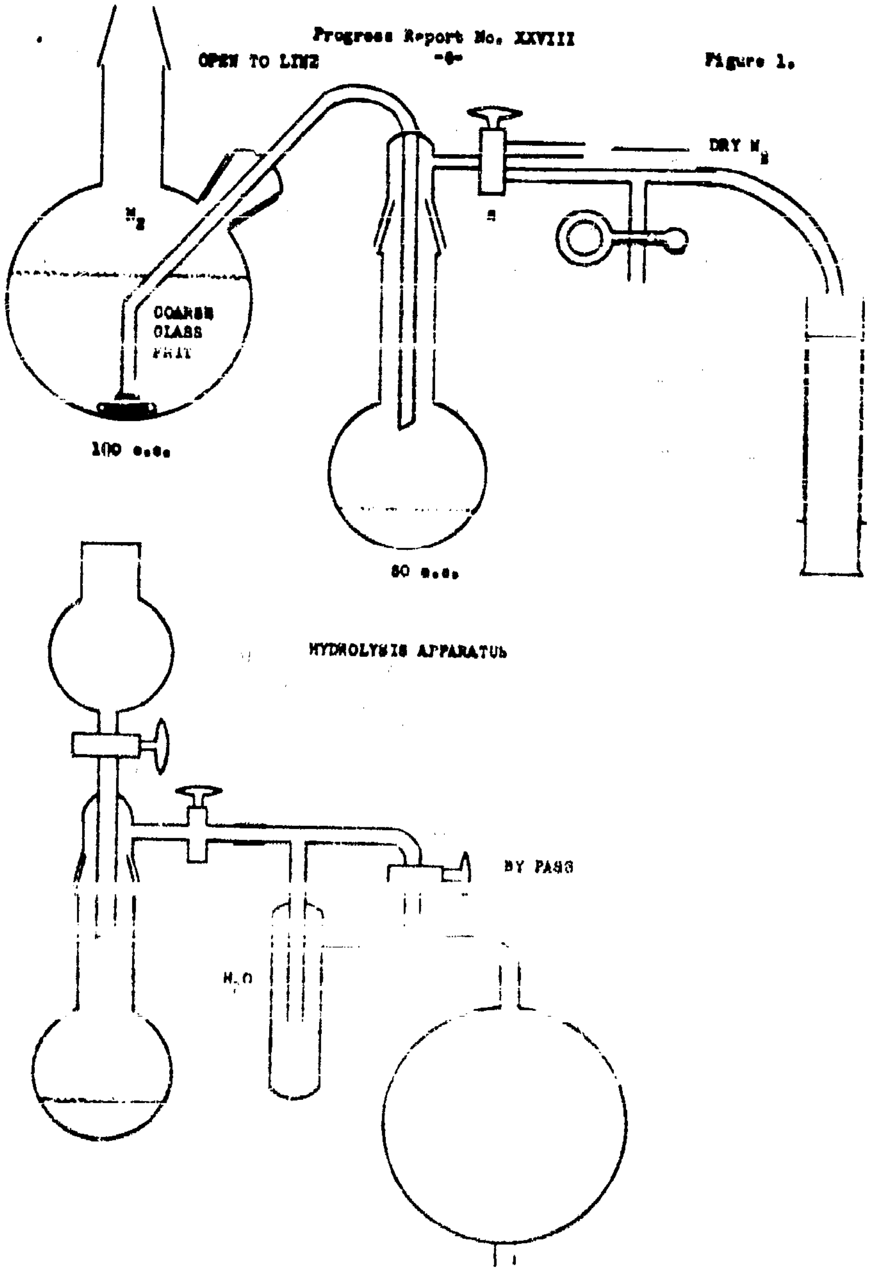
The preceding is the first successful preparation of sodium aluminum hydride from sodium hydride and aluminum chloride in a solvent other than dimethyl ether.

(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 maxium 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 dependent 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 fotating 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 tetra hydrofuran. 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 8th 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 ration 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
Sample	Mean time of withdrawal (minutes)	Time of withdrawal (minutes)	Weight of Sample	Al (grams)	Al (mmoles)	Br (grams)	Br (mmoles)	H_2 cc.	H_2 (mmoles, mgs)	Wt of solvent by difference (grams)	Calc Al conc (mmoles) per gram of solvent	$AlBr_3$ conc (mmoles) per gram of solvent
Entire (Initial)	0	—	—		weight of aluminum bromide used = 8.952 = 33.57 moles				—	59.24	0.566	0.566
1	11	1	5.89	.0773	2.85	0.609	7.62	21.6	0.94	5.20	0.548	0.488
2	31	$1\frac{1}{2}$	5.2	.0679	2.52	0.444	5.56	28.6	1.28	4.70	0.537	0.394
3	96 (1^h36^m)	6	6.76	.0904	3.35	0.498	6.24	66.8	2.98	6.17	0.543	0.337
4	216 (3^h36^m)	10	5.25	.0704	2.61	0.279	3.47	82.9	3.70	4.90	0.532	0.236
5	421 (7^h1^m)	16	6.52	(.0724)	(2.68)	absent	—	230.5	8.54	6.44	(0.417)	H/Al ratio (3.19)
6	613 (10^h13^m)	22	5.51	.0632	2.34	absent	—	158.0	7.07	5.45	0.430	3.02
7	1467 (24^h27^m)	*	15.27	.1953	7.23	absent	—	540	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 derivate of lithium aluminum hydride (i.e., $LiAl(CH_3)_2H_2$) 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:

$$LiBH + Zn(CH_3)_2 \rightarrow LiB(CH_3)_2 + ZnH_2$$

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 mercurcy 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.

BEST AVAILABLE COPY

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 derivates 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 (incompleted 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

$$(CH_3)_3B + LiAlH_4 \rightarrow [LiAl(CH_3)_2H_2 + BH_2CH_3] \rightarrow LiBH_3CH_3 + Al(CH_3)_2H$$

$$(CH_3)_3Al + LiAlH_4 \rightarrow LiAlCH_3H_3 + Al(CH_3)_2H$$

$$(CH_3)_3Ga + LiAlH_4 \rightarrow [LiAl(CH_3)_2H_2 + GaH_2(CH_3)] \rightarrow LiGaCH_3H_3 + Al(CH_3)_2H$$

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:

$$LiAlH_4 + 2B_2H_6 \rightarrow LiBH_4 + Al(BH_4)_3$$

Alkyl diboranes, i.e. $(BH_2CH_3)_2$, 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

BEST AVAILABLE COPY

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 $AlMe_2H$*	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 $LiGaMeH_3$ and $LiAlH_4$) 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 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 proceeds according to the following scheme:

(1) $\frac{1}{2}B_2H_6 + NH_3 \rightarrow H_3N{:}BH_3$

(2) $H_3N{:}BH_3 \rightarrow H_2NBH_2 + H_2$

(3) $H_2NBH_2 \rightarrow HNBH + H_2$

(4) $3HNBH \rightarrow 1/3\text{-}B_3N_3H_6$ (Borazole)

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):

(5) $H_3N{:}BX_3 + LiBH_4$ or $LiAlH_4$

(6) $H_2NBX_2 + LiBH_4$ or $LiAlH_4$

(7) $NH_4X + LiBH_4$

---

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

---

[1] Wiberg et al, loc. cit.
[2] Schlesinger, Horvitz, and Burg, J.A.C.S. 58 409 (1936)

BEST AVAILABLE COPY

The reduction of H_2NBCl_2 (68% purity, see below) with $LiAlH_4$ (Reaction 6) has been attempted in diethyl ether, tetrahydrofurane 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 ether[3] and dioxane. In diethyl ether, one mole of 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° C, some borazole is formed, a property characteristic of the diammoniate of diborane[4].

The probable reaction can be expressed by the equation:

$$LiBH_4 + NH_4Cl \rightarrow LiCl + \frac{1}{2}B_2H_6 \cdot 2NH_3 + H_2$$

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° 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.

---

[3] Schaeffer and Anderson, Unpublished work

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

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 ammonia[5] 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 2½ 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	½	0.225	60%
0.376	250	1½	0.0239	64%
0.966	250	4	0.637	66%
0.361	250	6	0.160	44%
0.388	330	½	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.

Naval research laboratory. Report no. C-3208.
Progress report no. XXVIII on hydrides and borohydrides of light elements, by H. I. Schlesinger and George W. Schaeffer. Washington, The Laboratory, 4 December 1947.
15 p 27 cm. UNCLASSIFIED.

Abstract: Report indicates results on sodium aluminum hydride preparation in tetrahydrofuran. Yield of 70% of sodium aluminum hydride of 92% purity was obtained. Also a study of preparation of borazole and some work on its stability.

1. Borohydrides. 2. Chemical compounds - hydr des.
I. Schlesinger, H. I. II. Schaeffer, G. W

Naval research laboratory. Report no. C-3208.
Progress report no. XXVIII on hydrides and borohydrides of light elements, by H. I. Schlesinger and George W. Schaeffer. Washington, The Laboratory, 4 December 1947.
15 p 27 cm. UNCLASSIFIED.

Abstract: Report indicates results on sodium aluminum hydride preparation in tetrahydrofuran. Yield of 70% of sodium aluminum hydride of 92% purity was obtained. Also a study of preparation of borazole and some work on its stability.

1. Borohydrides. 2. Chemical compounds - hydr des.
I. Schlesinger, H. I. II. Schaeffer, G. W

Naval research laboratory. Report no. C-3208.
Progress report no. XXVIII on hydrides and borohydrides of light elements, by H. I. Schlesinger and George W. Schaeffer. Washington, The Laboratory, 4 December 1947.
15 p 27 cm. UNCLASSIFIED.

Abstract: Report indicates results on sodium aluminum hydride preparation in tetrahydrofuran. Yield of 70% of sodium aluminum hydride of 92% purity was obtained. Also a study of preparation of borazole and some work on its stability.

1. Borohydrides. 2. Chemical compounds - hydr des.
I. Schlesinger, H. I. II. Schaeffer, G. W

Naval research laboratory. Report no. C-3208.
Progress report no. XXVIII on hydrides and borohydrides of light elements, by H. I. Schlesinger and George W. Schaeffer. Washington, The Laboratory, 4 December 1947.
15 p 27 cm. UNCLASSIFIED.

Abstract: Report indicates results on sodium aluminum hydride preparation in tetrahydrofuran. Yield of 70% of sodium aluminum hydride of 92% purity was obtained. Also a study of preparation of borazole and some work on its stability.

1. Bor ydrides. 2. Chemical compounds - hydr des.
I. Schl inger, H. I. II. Schaeffer, G. W

TSDIN FORM 80 (13 MAR 47)

Schlesinger, H. Schaeffer, G. AUTHOR(S)	DIVISION: Fuels and Lubricants (12) SECTION: Solid Propellants (6) CROSS REFERENCES: Metal - Preparation (49831.7); Boron compounds (18025)	P-12-6-4
		ATI- 16148
		ORIG. AGENCY NUMBER [illegible]-3[illegible]08
		REVISION U

AMER. TITLE: Hydrides and borohydrides of light elements

FORG'N. TITLE:

ORIGINATING AGENCY: Office of Naval Research, Naval Research Lab., Washington, D.C.

TRANSLATION:

COUNTRY	LANGUAGE	FORG'N.CLASS	U. S.CLASS.	DATE	PAGES	ILLUS.	FEATURES
U.S.	Eng.		Unclass.	Dec'47	22	3	table, diagrs

ABSTRACT

Experimental work on boron hydrides is described which resulted in the development of a method of preparing 92% pure sodium aluminum hydride in 70% yields of theory. In addition, report is given of the status of work at present devoted to the study of the stability and methods of preparing borazole and a number of other boron-nitrogen-hydrogen compounds.

AD-B809 156

251950

TECHNICAL INDEX WRIGHT FIELD, OHIO, USAAF

WF-O-21 MAR 47 30M

Naval Research Laboratory
Technical Library
Research Reports Section

DATE: April 30, 2002

FROM: Mary Templeman, Code 5227

TO: **Code 6180 Dr. Murday**

CC: Tina Smallwood, Code 1221.1 fx 6/7/02

SUBJ: Review of NRL Reports

Dear Sir/Madam:

1. Please review NRL Report 2964and 3208 for:

☑ Possible Distribution Statement
☐ Possible Change in Classification

Thank you,

Mary Templeman

Mary Templeman
(202)767-3425
maryt@library.nrl.navy.mil

The subject report can be:

☑ Changed to Distribution A (Unlimited)
☐ Changed to Classification ____ ____
☐ Other:

James Murday 5/8/2002
Signature Date

Page: 1 Document Name: untitled

-- 1 OF 1
-- 1 - AD NUMBER: B809156
-- 2 - FIELDS AND GROUPS: 7/2
-- 3 - ENTRY CLASSIFICATION: UNCLASSIFIED
-- 5 - CORPORATE AUTHOR: NAVAL RESEARCH LAB WASHINGTON DC
-- 6 - UNCLASSIFIED TITLE: HYDRIDES AND BOROHYDRIDES OF LIGHT ELEMENTS
-- 8 - TITLE CLASSIFICATION: UNCLASSIFIED
--10 - PERSONAL AUTHORS: SCHLESINGER, H.; SCHAEFFER, G.
--11 - REPORT DATE: DEC 1947
--12 - PAGINATION: 22P MEDIA COST: $ 7.00 PRICE CODE: AA
--14 - REPORT NUMBER: C-3208
--18 - MONITOR ACRONYM: XD
--19 - MONITOR SERIES: XD
--20 - REPORT CLASSIFICATION: UNCLASSIFIED
--22 - LIMITATIONS (ALPHA): DISTRIBUTION AUTHORIZED TO DOD ONLY;
-- ADMINISTRATIVE/OPERATIONAL USE; 03 MAR 1999. OTHER REQUESTS SHALL
-- BE REFERRED THROUGH DEFENSE TECHNICAL INFORMATION CENTER, DTIC-BCS,
-- 8725 JOHN J KINGMAN RD., FT. BELVOIR, VA 22060-6218
--23 - DESCRIPTORS: *BORON HYDRIDES, SOLID PROPELLANTS.
--24 - DESCRIPTOR CLASSIFICATION: UNCLASSIFIED
--25 - IDENTIFIERS: ATI-16148
--26 - IDENTIFIER CLASSIFICATION: UNCLASSIFIED
--29 - INITIAL INVENTORY: 1

-
--33 - LIMITATION CODES: 4
--35 - SOURCE CODE: 251950
--36 - ITEM LOCATION: DTIC
--40 - GEOPOLITICAL CODE: 1101
--41 - TYPE CODE: N
--43 - IAC DOCUMENT TYPE:
--50 - CITATION CREATION DATE: 22 JAN 1998

APPROVED FOR PUBLIC
RELEASE - DISTRIBUTION
UNLIMITED