β-fluorines and the fluorosulfate fluorine. The coupling constants (in c.p.s.) were: $J_{SF-\alpha} = 8.1$, $J_{\alpha\beta} = 3.3$.

2-Bromotetrafluoroethyl Fluorosulfate.—Tetrafluoroethylene, diluted 1:3 with nitrogen, was added slowly to red-black bromine(I) fluorosulfate, resulting in a clear solution. After purification by vacuum bulb to bulb distillation a yield of the compound of at least 75% based on bromine fluorosulfate consumption was recovered. Final purification was accomplished by gas chromatography. The principal peaks in the mass spectrum for mass numbers greater than 28 corresponded to the ions: SO_2F^+, $C_2F_4SO_3F^+$, $C_2F_4Br^+$, CF_2Br^+, $CF_2SO_3F^+$, $C_2F_5^+$, CF^+, FCO^+, SOF^+, and $CBrF^+$.

The n.m.r. spectrum of $BrC_2F_4SO_3F$ was very similar to that of $ClC_2F_4SO_3F$, described above. The following shielding and spin–spin coupling values were found: $\delta_{SF} = -49.4$, $\delta_\alpha = 86.1$, $\delta_\beta = 69.4$ (in p.p.m.); $J_{SF-\alpha} = 8.4$, $J_{\alpha\beta} = 3.1$.

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CONTRIBUTION FROM THE ETHYL CORPORATION,
BATON ROUGE, LOUISIANA

Direct Synthesis of Complex Metal Hydrides[1,2]

BY E. C. ASHBY, G. J. BRENDEL, AND H. E. REDMAN

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The direct synthesis of $NaAlH_4$, $LiAlH_4$, $KAlH_4$, and $CsAlH_4$ from the elements has been accomplished. The reaction of the alkali metal, aluminum, and hydrogen proceeds at moderate temperatures and pressures to produce nearly quantitative yields of high purity alkali metal aluminum hydride. The method affords a convenient laboratory as well as commercial route to $NaAlH_4$ and $LiAlH_4$. The effects of temperature, pressure, solvent, and other variables have been determined. A mechanism for the reaction is discussed. The reaction of sodium, aluminum, hydrogen, and olefins to produce compounds of the structure $NaAlR_nH_{4-n}$ also has been accomplished. A promising route to unetherated $LiAlH_4$ has been found. The route involves the metathetical reaction of $NaAlH_4$ and LiCl in diethyl ether. The effects of solvents and temperature on yield of $LiAlH_4$ have been investigated. A convenient method of isolation and purification of $LiAlH_4$ has been developed which produces $LiAlH_4$ in approximately 99% purity.

Introduction

The commercial process in use today for the preparation of $LiAlH_4$ involves the reaction of LiH with $AlCl_3$ in diethyl ether. This is the reaction originally used by Schlesinger and co-workers to prepare the first sample of $LiAlH_4$.[3]

$$4LiH + AlCl_3 \xrightarrow{Et_2O} LiAlH_4 + 3LiCl$$

This reaction proceeds in approximately 85% yield, producing a product of 95% purity when diethyl ether is used as a solvent. Unfortunately, for every four moles of LiH charged in this reaction, three are lost as by-product LiCl. Due to the high cost of lithium metal this fact is not insignificant.

This reaction has been extended to produce $NaAlH_4$ using tetrahydrofuran as a solvent, but in this case the reaction is more difficult. Yields and product purities are lower than for $LiAlH_4$. The failure of sodium hydride to work as well in this reaction is unfortunate, since Finholt has reported[4] the essential equivalency of $LiAlH_4$ and $NaAlH_4$ as reducing agents. The corresponding reaction of MgH_2 with $AlCl_3$ to produce $Mg(AlH_4)_2$ was reported by Wiberg,[5] and the reaction of CaH_2 with $AlCl_3$ was used by the Schlesinger group to prepare $Ca(AlH_4)_2$. Thus, the Schlesinger reaction involving an alkali or alkaline earth hydride and $AlCl_3$ is the only reaction used successfully up to now to prepare complex aluminum hydrides.

Results and Discussion

While studying the behavior of aluminum and hydrogen in the direct synthesis of triethylaluminum, we found that sodium hydride reacted with aluminum and hydrogen in an ether solvent to produce $NaAlH_4$ in quantitative yield.

$$NaH + Al + {}^3/_2H_2 \longrightarrow NaAlH_4$$

Initial experiments involved the reaction of NaH with activated aluminum powder in tetrahydrofuran at 140° and 5000 p.s.i. of hydrogen. Under these conditions $NaAlH_4$ was produced in quantitative yield in 4 hr. Substitution of sodium metal for NaH produced the same results at approximately the same rate. Hence, the direct synthesis of a complex metal hydride, from the elements, was achieved.[1,6,7]

$$Na + Al + 2H_2 \longrightarrow NaAlH_4$$

In contrast to the Schlesinger reaction, the direct synthesis uses only one mole of alkali metal per mole of product instead of four moles. The source of aluminum

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(1) E. C. Ashby, French Patent 1,235,680, granted to Ethyl Corp., May 30, 1960.

(2) Presented at the Southwest–Southeast Regional Meeting of the American Chemical Society, New Orleans, La., December, 1961.

(3) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947).

(4) A. E. Finholt, E. C. Jacobson, A. E. Ogard, and P. Thompson, *ibid.*, **77**, 4163 (1955).

(5) E. Wiberg, *Angew. Chem.*, **65**, 16 (1953).

(6) Clasen later reported the same reaction, but with few details concerning the effect of variables (H. Clasen, *ibid.*, **73**, 322 (1961)).

(7) E. C. Ashby, *Chem. Ind.* (London), 208 (1962).

in the complex metal hydride is aluminum metal rather than $AlCl_3$.

The simplicity of this reaction makes it suitable for the preparation of complex aluminum hydrides both commercially and in the laboratory. For example, to prepare a laboratory sample of $NaAlH_4$ one charges either the alkali metal or its hydride to an autoclave with activated aluminum powder in a solvent such as tetrahydrofuran. The mixture then is subjected to a pressure of 2000 p.s.i. with hydrogen and heated to 150° for several hours. After the absorption of hydrogen is complete the mixture is cooled and the complex aluminum hydride in solution is separated from excess aluminum metal by filtration. White, crystalline $NaAlH_4$ of 98+% purity can be isolated by addition of a hydrocarbon such as toluene to the tetrahydrofuran solution, followed by vacuum distillation of the tetrahydrofuran. The reaction should be run in approximately 2 *M* concentration. With tetrahydrofuran solvent, concentrations above 3 *M* and temperatures above about 165° are not recommended for safety considerations.[8]

The effects of pressure, temperature, catalyst, solvent, and other variables on the rate and conversion of sodium metal to $NaAlH_4$ have been studied. The data show clearly that the rate and conversion of the direct synthesis reaction are functions of all of these variables.

The reaction of an alkali metal hydride with aluminum and hydrogen to form the alkali metal aluminum hydride is an equilibrium reaction.

$$M + {}^1/_2H_2 \longrightarrow MH \qquad (1)$$

$$MH + Al + {}^3/_2H_2 \rightleftharpoons MAlH_4 \qquad (2)$$

In eq. 2 the equilibrium is strongly to the left at the decomposition temperature of the complex aluminum hydride. However, at temperatures somewhat lower than this, high conversions to the complex aluminum hydride can be obtained. In the following discussion the rates are inferred from the time required for the reaction to attain equilibrium. The attainment of equilibrium in all cases was determined by the cessation of hydrogen absorption. The conversions listed, unless otherwise stated, refer to conversions at equilibrium.

The effect of hydrogen pressure on the rate and conversion of sodium to $NaAlH_4$ was determined at 140° in tetrahydrofuran solvent. The data summarized in Table I show that an increase in hydrogen pressure from 1000 to 5000 p.s.i. increases both the rate and the conversion. At pressures below 1000 p.s.i. the rates and conversions decreased appreciably.

TABLE I

EFFECT OF HYDROGEN PRESSURE ON RATE AND CONVERSION

Pressure, p.s.i.	Reaction time, hr.	Conversion of Na to $NaAlH_4$, %
1000	12	90
2000	6	95
5000	3	99

TABLE II

EFFECT OF TEMPERATURE ON RATE AND CONVERSION

Temp., °C.	Reaction time, hr.	Conversion of Na to $NaAlH_4$, %
120	13.5[a]	51
130	11.5[a]	71
140	11.0[a]	80
150	6.0	95
158	7.1	91
165	7.2	90

[a] Incomplete reaction.

The effect of temperature on the rate and conversion of sodium to $NaAlH_4$ was studied briefly. The experiments were carried out in tetrahydrofuran solvent at 2000 p.s.i. of hydrogen, and the reaction temperature was varied between 120 and 165°. Results are summarized in Table II. These data show that an increase in temperature leads to an increased rate of reaction up to temperatures at which the product $NaAlH_4$ is neither thermally decomposing nor cleaving the tetrahydrofuran solvent. The optimum temperature for high conversion under the conditions described is apparently about 150°. Although reaction times and conversions at 158 and 165° appear slightly different from those at 150°; these differences are within the ability to reproduce these experiments. Obviously the reaction rate will increase at temperatures above 165°, but so will the rate of the reverse reaction. Since the decomposition rate of $NaAlH_4$ becomes rapid above about 185°, it is apparent that high temperatures in this range should be avoided unless accompanied by higher pressures. Cleavage of the tetrahydrofuran was not experienced at 165° or below; however, reported[12] explosions which occurred in the 180–200° temperature range indicate rapid solvent cleavage by $NaAlH_4$, NaH, or sodium.

The shift in equilibrium produced by pressure was demonstrated by the reaction of sodium, aluminum, and hydrogen in diglyme at several temperatures and pressures.

$$Na + {}^1/_2H_2 \longrightarrow NaH$$

$$NaH + Al + {}^3/_2H_2 \rightleftharpoons NaAlH_4$$

As illustrated in Table III, at a constant pressure of 1000 p.s.i. an increase in temperature from 140 to 160° greatly lowers the conversion due to an increase in the rate of the reverse reaction. At 2000 p.s.i. the con-

TABLE III

EFFECT OF PRESSURE ON SHIFTING THE EQUILIBRIUM

Pressure, p.s.i.	Temperature, °C.	Conversion of Na to $NaAlH_4$, %
1000	140	97
1000	160	28
1000	180	22
2000	140	99
2000	160	94
2000	180	16
5000	140	99
5000	160	94
5000	180	91
5000	200	59

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(8) *Chem. Eng. News*, **39**, No. 40, 57 (1961).

TABLE IV

EFFECT OF THE SOURCE OF ALUMINUM ON RATE AND CONVERSION

Source of aluminum	Reaction time, hr.	Conversion of Na to $NaAlH_4$, %
Commercial powder	14[a]	54
Activated from $Al(C_2H_5)_3$	6	95
Recycled from direct synthesis	7	93

[a] Incomplete reaction.

version is still high at 160° and the reverse reaction does not become prominent until 180°. As the pressure is increased further to 5000 p.s.i. the conversion at 180° remains high and decomposition does not become appreciable until 2000°. Thus, the temperature at which the reverse reaction becomes appreciable increases with an increase in pressure. The rate of reaction increases with temperature so that the fastest rate of reaction was observed closer to 180° at 5000 p.s.i. However, the rate is not much lower at 150°, so that such high temperatures and pressures are really not necessary. Below 140°, however, the rate falls off appreciably.

Cleavage of the diglyme solvent was observed at 180° or higher. This cleavage was slight when reaction times were short, such as 1 or 2 hr. However, when the reaction was allowed to continue past maximum hydrogen absorption for several hours, cleavage of the diglyme became appreciable.

The rate of reaction of the direct synthesis also depends on the source of aluminum used in the reaction. The rate of reaction observed using commercial aluminum powder is increased substantially if the aluminum powder is first activated. Activation originally was performed by treating aluminum powder with triethylaluminum. It was later found that if an excess of commercial aluminum powder was used in the reaction and recovered, it was activated and could be used in subsequent runs. Hence, no separate step is needed to obtain activated aluminum. The data summarized in Table IV indicate the increased rate experienced with activated aluminum as compared to commercial aluminum powder in the reaction of sodium, aluminum, and hydrogen in diglyme solvent at 140° and 2000 p.s.i. of hydrogen.

It also has been found that under these same conditions an excess of activated aluminum will increase the rate of reaction. For example, if the Al:Na mole ratio is 6:1, the time required for complete reaction is only 2 hr. as compared to 14 hr. when the mole ratio is 1:1. For this reason an approximately 50 mole % excess of aluminum was maintained in all the experiments reported herein.

When the direct synthesis is performed in non-solvating media, a catalyst is desirable in order to obtain the most efficient reaction. Sodium was allowed to react with aluminum and hydrogen at 160° and 5000 p.s.i. in both toluene and hexane to demonstrate this point. This effect is illustrated in Table V. When a catalyst is used with a hydrocarbon solvent, the results are comparable to those in ether solvents with no catalyst.

TABLE V

EFFECT OF A CATALYST IN NON-SOLVATING MEDIA

Solvent	Catalyst	Reaction time, hr.	Conversion of Na to $NaAlH_4$, %
Toluene	None	5	<1
Toluene	$Al(C_2H_5)_3$	2	99
n-Hexane	None	5	<1
n-Hexane	$Al(C_2H_5)_3$	2	99

Several other solvents were investigated in addition to those already mentioned. Table VI summarizes the results obtained with various solvents at 140° and 5000 p.s.i. using triethylaluminum as a catalyst. When triethylaluminum catalyst is used, apparently even a viscous non-polar diluent such as mineral oil will allow successful reaction, although the reaction may be somewhat sluggish. Triethylamine and diethyl ether function quite well although, as in the hydrocarbon solvents, $NaAlH_4$ is not soluble in either.

TABLE VI

SOLVENT EFFECT ON RATE AND CONVERSION

Solvent	Reaction time, hr.	Conversion of Na to $NaAlH_4$, %
Triethylamine	5	99
Trimethylhexane	4	88
Diethyl ether	6	89
Mineral oil	16	49

When triethylaluminum was used as a catalyst, $NaAl(C_2H_5)_2H_2$ was isolated as a hydrocarbon-soluble component in the reaction mixture. It is believed that $NaAl(C_2H_5)_2H_2$ is an intermediate in the catalytic behavior of $Al(C_2H_5)_3$ in the direct synthesis reaction. A solution of this compound in toluene has the same effect on the direct synthesis as starting with $Al(C_2H_5)_3$. It is known that $Al(C_2H_5)_3$ will react with Na or NaH under the conditions of this reaction to produce products which could easily lead to $NaAl(C_2H_5)_2H_2$.

$$4Al(C_2H_5)_3 + 3Na \longrightarrow 3NaAl(C_2H_5)_4 + Al \tag{3}$$

$$NaAl(C_2H_5)_4 + NaAlH_4 \longrightarrow 2NaAl(C_2H_5)_2H_2$$

$$Al(C_2H_5)_3 + NaH \longrightarrow NaAl(C_2H_5)_3H \tag{4}$$

$$2NaAl(C_2H_5)_3H \longrightarrow NaAl(C_2H_5)_2H_2 + NaAl(C_2H_5)_4$$

$$NaAl(C_2H_5)_4 + NaAlH_4 \longrightarrow 2NaAl(C_2H_5)_2H_2$$

Several acid-type catalysts were investigated in addition to $Al(C_2H_5)_3$. Most of these had a pronounced effect on the formation of $NaAlH_4$ in non-complexing media. The catalysts were compared in toluene solvent at 140° and 5000 p.s.i. of hydrogen, conditions which would lead to less than 1% conversion if no catalyst were used. Results are summarized in Table VII.

The detailed mechanistic role of the catalyst in this reaction has not been definitely established. It is well known that in ether solvents such as tetrahydrofuran no catalyst is needed for successful reaction, whereas in hydrocarbons a catalyst is needed for rapid reaction. The effect of tetrahydrofuran as a solvent

TABLE VII

EFFECT OF CATALYST ON CONVERSION

Catalyst	Conversion of Na to $NaAlH_4$, %
$Al(C_2H_5)_3$	93
$Al(CH_3)_3$	70
$B(C_2H_5)_3$	68
$Al(OC_2H_5)_3$	49
$B(C_6H_{13})_3$	41
$Al(C_6H_5)_3$	41

cannot be attributed to its basic character, namely, its available electrons, since reaction in triethylamine goes most efficiently only when a catalyst is used. Nor can the effect of tetrahydrofuran be attributed to its greater solvation properties toward the final complex aluminum hydride, $NaAlH_4$, for $NaAlH_4$ can be produced in toluene, in which it is insoluble, at a comparable rate to that in tetrahydrofuran provided a catalyst is used. Therefore it appears that the catalyst must affect the intermediates formed before the final $MAlH_4$ is formed. $MAlH_4$ compounds are insoluble in non-ether type solvents, including tertiary amines; thus one would expect the intermediates to $MAlH_4$ compounds also to be insoluble. However, in the presence of a catalyst such as $Al(C_2H_5)_3$, reactive intermediates such as $NaAl(C_2H_5)_2H_2$ are formed. Compounds of this type are soluble in hydrocarbons such as toluene and therefore can function catalytically to produce a successful reaction. Thus in tetrahydrofuran a clean aluminum surface is provided by the solubility of the product $NaAlH_4$, whereas in hydrocarbon solvent a fresh aluminum surface is maintained by solubilization of the intermediate to the $MAlH_4$ by means of the $(C_2H_5)_3Al$ catalyst. The differences in the catalytic effect of the different acid catalysts can be explained in terms of acidity, steric requirement, and ease of disproportionation of the reactive intermediates formed in the reaction.

We plan to report soon on a recent study of the mechanism of the direct synthesis reaction. One significant conclusion which can be drawn from this study is that aluminum hydride, as a distinct species, does not appear to be an intermediate in this reaction. This is contrary to the mechanism proposed by Ziegler for the reaction of aluminum, hydrogen, and ethylene, namely

$$Al + {}^3/_2H_2 \longrightarrow AlH_3$$

$$AlH_3 + 2Al(C_2H_5)_3 \longrightarrow 3(C_2H_5)_2AlH$$

$$(C_2H_5)_2AlH + CH_2{=}CH_2 \longrightarrow Al(C_2H_5)_3$$

The mechanism proposed by Clasen[6] for the direct synthesis of complex metal hydrides also involves the formation of AlH_3 as an intermediate.

We have found that the direct synthesis reaction in the presence of olefin provides a convenient route to complex aluminum alkyls. Sodium aluminum alkyl compounds ($NaAlR_nH_{4-n}$) were readily prepared by the direct reaction of sodium, aluminum, hydrogen, and olefin.

$$Na + Al + 2H_2 + n(RCH{=}CH_2) \longrightarrow NaAl(CH_2R)_nH_{4-n}$$

By conducting the reaction in toluene at 160° and 2000 p.s.i., using $Al(C_2H_5)_3$ as a catalyst, the complex aluminum compounds could be produced in over 80% yield. In one experiment pure $NaAl(C_2H_5)_2H_2$ was isolated in 87% yield by suitably adjusting the hydrogen-to-ethylene ratio. Reaction with excess ethylene produced $NaAl(C_2H_5)_4$ in a high state of purity.

The preparation of $LiAlH_4$ from LiH, Al, and H_2 has been attempted in diethyl ether, tetrahydrofuran, and diglyme. The preparation in diethyl ether is complicated by the fact that $LiAlH_4$ is unstable even at room temperature in the presence of aluminum powder. However, as shown in Table VIII, $LiAlH_4$ was prepared with good conversion in diglyme and in tetrahydrofuran at 120° and 5000 p.s.i. hydrogen in 5 hr.

TABLE VIII

EFFECT OF SOLVENT ON THE FORMATION OF $LiAlH_4$

Solvent	Conversion of LiH to $LiAlH_4$, %
Ether	≈10
Tetrahydrofuran	96
Diglyme	95

$KAlH_4$ was prepared by the direct synthesis in toluene, tetrahydrofuran, and diglyme. $KAlH_4$ is not soluble in toluene and does not have appreciable solubility in tetrahydrofuran. However, $KAlH_4$ is soluble in diglyme and therefore this solvent is ideal for preparing $KAlH_4$, which is easily isolated and purified. Under typical conditions for the direct synthesis, the conversion of potassium to $KAlH_4$ in diglyme solvent is essentially quantitative. Low H/Al ratios in $KAlH_4$ were experienced initially due to cleavage of diglyme by potassium metal. This problem was resolved by running the reaction at lower than the usual temperatures. Although $LiAlH_4$ and $NaAlH_4$ form stable etherates with diglyme, $KAlH_4$ was isolated as the ether-free compound by the toluene precipitation procedure.

$CsAlH_4$ was prepared in toluene solvent in a high state of purity. However, poor results were obtained in diglyme due to the cleavage of diglyme by cesium metal even at room temperature. $CsAlH_4$, however, does not cleave diglyme, so that although this compound was prepared in toluene it was successfully purified by dissolving it in diglyme to separate it from aluminum powder.

We have studied alternate routes to $LiAlH_4$ since the reaction of LiH, Al, and H_2 in diethyl ether solvent does not proceed in high conversion. Although the reaction is quite satisfactory in tetrahydrofuran, it is very difficult to remove the last traces (3–5%) of solvent from the product. In diglyme solvent the reaction proceeds equally as well; however, a strong solvate is formed between $LiAlH_4$ and diglyme.

What appears to be a more attractive route to solid, ether-free $LiAlH_4$, by reaction of $NaAlH_4$ with LiCl, has been demonstrated.[9]

$$NaAlH_4 + LiCl \longrightarrow LiAlH_4 + NaCl$$

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(9) G. C. Robinson, French Patent 1,245,361, granted to Ethyl Corp., September 26, 1960.

The reaction proceeds readily at room temperature in tetrahydrofuran; however, the tetrahydrofuran is rather difficult to remove completely from $LiAlH_4$. Surprisingly, the reaction proceeds just as well in diethyl ether. Since both $NaAlH_4$ and LiCl are quite insoluble in diethyl ether, this is not to be expected. Furthermore, isolation of pure $LiAlH_4$ is quite easy since $LiAlH_4$ is the only soluble component of the reaction mixture and diethyl ether is readily and completely removed from $LiAlH_4$. If a small amount of $LiAlH_4$ is used as an initiator, the reaction proceeds to 95% yield in 3 hr. at room temperature. If $LiAlH_4$ initiator is not used, the conversion can vary, depending on several factors such as purity of starting materials, etc. The $LiAlH_4$ initiator is believed not only to provide a completely anhydrous system, but also to increase the solubility of both LiCl and $NaAlH_4$ in diethyl ether.

An increase in the reaction temperature above room temperature leads to a decrease in $LiAlH_4$ yields, corresponding to the decrease of $LiAlH_4$ stability with temperature. Aluminum powder is known to catalyze the thermal decomposition of $LiAlH_4$. Aluminum powder was present in the crude $NaAlH_4$ (prepared by the direct synthesis in toluene) used to obtain the temperature–yield data summarized in Table IX.

TABLE IX

EFFECT OF TEMPERATURE ON YIELDS OF $LiAlH_4$

Reaction temp., °C.	Yield of $LiAlH_4$, % (3 hr.)
0	74
25	95
50	79
65	70
75	52

When pure $NaAlH_4$ was used in the metathetical reaction with LiCl, thermal decomposition of $LiAlH_4$ at elevated temperatures was far less pronounced. For example, 78% yield of $LiAlH_4$ was obtained at 90° after 4 hr. when purified $NaAlH_4$ was used. The $LiAlH_4$ was isolated by filtration of the NaCl by-product, followed by addition of toluene to the ether filtrate and vacuum removal of the ether content. $LiAlH_4$ was isolated as a white crystalline solid, free of ether and 99% pure.

In summary, we have reported the direct synthesis of complex metal hydrides from the elements. The principal reaction variables were investigated to define the optimum conditions for preparation of various complex metal hydrides. We have defined what appears to be an attractive route to $LiAlH_4$, that is, by the metathetical reaction of $NaAlH_4$ with LiCl. The simplicity and high yields of the direct synthesis should provide low cost complex metal hydrides and thereby open the road for new and widespread applications of these interesting compounds.

Experimental

Materials.—Sodium was obtained from Ethyl Corporation; it was cut and washed in a 1% solution of isopropyl alcohol in benzene. NaH and LiH were obtained from Metal Hydrides, Inc., as a 70% mixture in mineral oil. Aluminum powder, grade MD202, was obtained from Metals Disintegrating Company, Elizabeth, New Jersey. This powder was activated by reaction of 50 g. with 125 ml. of triethylaluminum and hydrogen at 140° and 2000 p.s.i. for 10 hr. The activated aluminum powder which remained after this time was isolated by decantation of the $Al(C_2H_5)_3$–$Al(C_2H_5)_2H$ solution. The powder then was stored under *n*-hexane and measured, when needed, in a nitrogen-filled drybox. The aluminum activation procedure is a modification of that first reported by Redman.[10]

All ether solvents were distilled over $NaAlH_4$ just prior to use. Hydrocarbon solvents were C.P. grade, dried over sodium ribbon.

The triethylaluminum was obtained from Ethyl Corporation.

Equipment.—A 250-ml. Magne–Dash autoclave was used in a high pressure laboratory. The reactor was loaded and unloaded in a nitrogen-filled drybox.

General Procedure for Preparing a Metal Aluminum Hydride by the Direct Synthesis.—Approximately 0.25 mole of an alkali metal or its hydride is put into a 250-ml. Magne-Dash autoclave. To this is added 125 ml. of solvent and 0.38 mole of activated aluminum powder. At this point 2 ml. of triethylaluminum catalyst is added if a hydrocarbon solvent is used. If an ether solvent is used the catalyst is not necessary for efficient reaction. The reaction is then run at 150° and 2000 p.s.i. for several hours (the exact reaction time depends on the exact system; however, 24 hr. is sufficient for any system). The reaction mixture then is allowed to cool and is filtered through a glass frit of medium porosity. If the complex metal hydride product is soluble and appears in the filtrate, it can be analyzed by conventional methods for alkali metal, aluminum, and hydrogen. The residue is the excess aluminum used in the reaction. If the product is insoluble in the reaction diluent, then the filtrate can be discarded. The precipitated product can be separated from the aluminum powder by solubilization of the product in another solvent (usually tetrahydrofuran). By addition of toluene to the product solution, followed by vacuum distillation and filtration, one obtains a white crystalline product which is the alkali metal aluminum hydride. Yields are usually above 90% and product purity is usually above 97%.

Sodium Aluminum Hydride.—To 125 ml. of freshly distilled tetrahydrofuran was added 6 g. (0.26 mole) of sodium and 10 g. (0.37 mole) of activated aluminum powder. The resulting mixture was allowed to react at 150° and 2000 p.s.i. of hydrogen. The reaction was complete in 6 hr. as evidenced by the termination of pressure drop. The mixture was cooled and filtered. The resulting solution contained: Na, 5.61 g.; Al, 6.67 g.; H, 1015 mmoles. The Na:Al:H ratio was 1.0:1.0:4.1 and the analysis shown represents a 93.4% yield. To the tetrahydrofuran solution was added 100 ml. of toluene. The resulting solution was subjected to vacuum distillation until a copious white solid precipitated. The solid was filtered, washed with 50 ml. of diethyl ether, and dried.

Anal. Calcd. for $NaAlH_4$: Na, 42.6; Al, 50.0; H, 74.0 mmoles/g. Found: Na, 42.2; Al, 50.0; H, 72.4 mmoles/g.

Cesium Aluminum Hydride.—Activated aluminum powder (12 g., 0.45 mole) together with 6.05 g. (0.045 mole) of cesium metal, 1.0 ml. of $Al(C_2H_5)_3$, and 100 ml. of toluene, was pressurized in an autoclave with 4000 p.s.i. hydrogen and heated to 150° for 13 hr. Judged by the pressure drop, reaction was complete within 1 hr. The resulting mixture was filtered and the solids were washed with toluene. $CsAlH_4$ then was separated from the excess aluminum powder by extraction with 100 ml. of diglyme. The product solution was filtered, and finely-divided white $CsAlH_4$ then was precipitated by slowly adding 250 ml. of toluene to the agitated colorless filtrate. The product was isolated by filtration, washed with toluene, and dried *in vacuo* at room temperature, yielding 5.1 g. (81% of theory).

Anal. Calcd. for $CsAlH_4$: Cs, 81.08; Al, 16.45; H, 24.4 mmoles/g. Found: Cs, 80.9; Al, 16.4; H, 23.4 mmoles/g.

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[10] H. E. Redman, U. S. Patent 2,885,314 (1959).

If reaction is incomplete, and metallic cesium remains with the excess aluminum, treatment with diglyme will lead to orange-brown soluble cleavage products which finally form a diglyme-insoluble material as an impurity in the CsAlH$_4$.

Sodium Aluminum Tetraethyl.—To 6 g. (0.26 mole) of sodium was added 7 g. (0.26 mole) of activated aluminum powder in 125 ml. of toluene. To this mixture was added 2 ml. of triethylaluminum catalyst. The resulting mixture was allowed to react for 16 hr. at 160° and 2000 p.s.i. pressure of hydrogen and ethylene. Filtration of the reaction mass, followed by washing with hexane, yielded 23.06 g. of solids. The toluene filtrate was diluted to 500 ml. with hexane to precipitate additional solid product weighing 10.32 g. The yield of sodium aluminum tetraethyl was 77.5%.

Anal. Calcd. for NaAl(C$_2$H$_5$)$_4$: Na, 13.8; Al, 16.3; ethane evolved on hydrolysis, 24.08 mmoles/g. Found (fraction 1): Na, 14.6; Al, 16.2; ethane evolved, 23.8 mmoles/g.; (fraction 2): Na, 14.7; Al, 16.9; ethane evolved, 25.3 mmoles/g.

NaAl(C$_2$H$_5$)$_2$H$_2$.—This reaction was run exactly as described for the preparation of sodium aluminum tetraethyl except that the amount of ethylene added was controlled. The yield as solid product obtained in two fractions was 87%.

Anal. Calcd. for NaAl(C$_2$H$_5$)$_2$H$_2$: Na, 20.9; Al, 24.6; gas evolved on hydrolysis, 36.4 mmoles/g. Found (fraction 1): Na, 20.3; Al, 24.5; gas evolved, 35.3 mmoles/g.; (fraction 2): Na, 21.9; Al, 24.9; gas evolved, 37.3 mmoles/g.

Preparation of LiAlH$_4$ from NaAlH$_4$ and LiCl.—About 13 g. of commercial LiCl (Foote Mineral, 99±%; dried *in vacuo* at 100–120°) was charged to a 250-ml. Magne-Dash autoclave with an equimolar amount or slight excess (up to 4%) of crude NaAlH$_4$ (prepared by the direct synthesis in toluene), 0.5 mole % LiAlH$_4$ as reaction initiator, and 100 ml. of diethyl ether (distilled over LiAlH$_4$). After a 3-hr. reaction at a temperature preferably near room temperature (see Table IX), the resulting product solution of LiAlH$_4$ in ether was filtered and the solids were washed with fresh ether. Filtration difficulties were eliminated by using Celite as filter aid. Crystalline LiAlH was recovered from the solution in diethyl ether as follows: dry toluene (about 5 ml./g. of LiAlH$_4$) was added to the solution, and ether then was distilled from the mixture *in vacuo* (40–50° at 400–150 mm.). Crystalline LiAlH$_4$ precipitated during this procedure and finally a slurry in toluene was obtained.[11] The product then was separated by filtration and dried *in vacuo* at room temperature. The purity of the products (96–99%) was determined by elemental analysis (hydride content measured by gas evolution upon hydrolysis). The impurities consisted of 0.4–0.6% Na and 0.1% Cl.

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[11] The LiAlH$_4$ recovery is virtually quantitative, if the ether is sufficiently removed.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
ST. OLAF COLLEGE, NORTHFIELD, MINNESOTA

Complex Aluminum Hydrides Containing Nitrogen, Phosphorus, and Arsenic

BY A. E. FINHOLT, C. HELLING, V. IMHOF, L. NIELSEN, AND E. JACOBSON

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Ammonia, phosphine, and arsine react with aluminum hydrides to evolve hydrogen and form a variety of complex hydrides. Under the proper conditions, definite compounds LiAl(NH$_2$)$_4$, NaAl(NH$_2$)$_4$, and LiAl(PH$_2$)$_4$ were prepared. The new compound LiAl(PH$_2$)$_4$ reacts with ethyl iodide to form ethylphosphine in high yield but reactions with silicon halogen compounds were less straightforward.

Introduction

Reactions between hydrides of the fifth group elements and lithium aluminum hydride have been reported by a number of investigators. Most of these reactions have been carried out in ethyl ether with the stoichiometry somewhat obscure. The equation for the reaction between the hydride and ammonia has been reported[1] as

$$2LiAlH_4 + 5NH_3 \longrightarrow [LiAlH(NH_2)_2]_2NH + 6H_2 \quad (1)$$

More work has been done with alkylated compounds. With primary amines one hydrogen is replaced rapidly

$$LiAlH_4 + 4RNH_2 \longrightarrow LiAl(RNH)_4 + 4H_2 \quad (2)$$

but eventually the second hydrogen does react.[2] Similar equations have been proposed for secondary amines and primary and secondary phosphines.[3,4]

In the present work the stoichiometry of the reactions of ammonia, phosphine, and arsine with aluminum hydrides has been further studied. The course of the reaction can be controlled and definite products containing nitrogen and phosphorus have been isolated.

Results and Discussion

Under the proper conditions alkali metal aluminum hydrides reacted with ammonia, phosphine, and arsine according to the equation

$$MAlH_4 + 4EH_3 \longrightarrow MAl(EH_2)_4 + 4H_2 \quad (3)$$

Products of the composition MAl(EH$_2$)$_4$ were prepared from ammonia and phosphine with lithium or sodium aluminum hydride. Arsine also reacted in the same manner but no attempt was made to isolate a complex aluminum dihydrogen arsenide product. On hydrolysis these aluminum compounds released the fifth group hydrides quantitatively according to the stoichiometry

$$MAl(EH_2)_4 + 4HOH \longrightarrow 4EH_3 + MAl(OH)_4 \quad (4)$$

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