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THE PREPARATION OF SODIUM AND CALCIUM ALUMINUM HYDRIDES⁽¹⁾

By A. E. FINHOLT, GLEN D. BARBARAS, GERALDINE K. BARBARAS, GRANT URRY, THOMAS WARTIK, and H. I. SCHLESINGER

The George Herbert Jones Laboratory of the University of Chicago
and St. Olaf College

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Abstract—The difficulties encountered in the preparation of sodium and calcium aluminum hydrides and the methods of overcoming them are described, as are some of the properties of these compounds.

SODIUM aluminum hydride was first prepared by the reaction between sodium hydride and aluminum bromide at room temperature in the presence of dimethyl ether as a solvent.⁽²⁾ Although this procedure gave a product of satisfactory purity, it has numerous disadvantages, for which reason publication was deferred. Thus the yield, in terms of aluminum bromide used, approximated only about 60 per cent. Furthermore, it is inconvenient and somewhat hazardous to carry out the reaction, and to filter the reaction product under the high vapour tension of dimethyl ether at room temperature, in the glass vessels available for small-scale laboratory preparations. For large-scale production for which metal apparatus could be employed, the use of aluminum bromide is undesirable because of its cost. The analogous procedure using aluminum chloride gave unsatisfactory yields and impure products.

Calcium aluminum hydride was prepared similarly, i.e., by the reaction of calcium hydride on aluminum bromide in dimethyl ether. The product was an etherate, $Ca(AlH_4)_2 \cdot O(CH_3)_2$. Not only did the procedure have the disadvantages mentioned above, but the etherate obtained was only moderately pure.

Some improvement in the preparation of the calcium salt was achieved by evaporating the dimethyl ether from the reaction mixture before the latter was filtered. The calcium aluminum hydride was then extracted from the residue by tetrahydrofuran and isolated by evaporation of the filtrate. Aluminum chloride instead of the bromide had to be used for this modification of the procedure, since calcium bromide is sufficiently soluble in tetrahydrofuran seriously to contaminate the calcium aluminum hydride. The latter is obtained as a moderately pure etherate of the formula $Ca(AlH_4)_2 \cdot O(CH_2)_4$.⁽³⁾ The corresponding procedure for the sodium salt has not been carried out successfully.

Numerous modifications of the original procedure for the preparation of sodium aluminum hydride have been studied to avoid the use of dimethyl ether, and to make

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⁽¹⁾ A portion of this paper is taken from a thesis presented by GLEN D. BARBARAS to the Department of Chemistry of the University of Chicago in part fulfilment of the requirements for the Ph.D. degree.

⁽²⁾ Final Report for the period July 1, 1946, to June 30, 1947, on contract N6ori-20 (NRL Report No. C3147). The procedure is also described in U.S. patent No. 2,576,311, which deals primarily with the use of metal aluminum hydrides as reducing agents.

⁽³⁾ In this procedure the calcium salt is apparently first produced as a dimethyl etherate. The addition of tetrahydrofuran drives off all of the dimethyl ether. Evidently the tetrahydrofuranate is more stable than the dimethyl etherate. A successful procedure employing tetrahydrofuran as the liquid medium in the preparation of calcium aluminum hydride has been described by W. SCHWAB and K. WINTERSBERGER, *Z. Naturforsch* **8b**, 690 (1953).

possible the substitution of aluminum chloride for the bromide. Most of the modifications involved the use of tetrahydrofuran as the reaction medium, but other solvents were tested. These included diethyl ether, methyl ethyl ether, methyl isopropyl ether, the dimethyl ethers of ethylene glycol, of triethylene glycol, and of tetraethylene glycol, etc. In diethyl, methyl ethyl, and methyl isopropyl ethers, in which the desired sodium salt appears to be insoluble, no reaction was observed; none of the other solvents proved superior to tetrahydrofuran, and most of them had less favorable physical properties (e.g., volatility).

In the course of the investigation it became evident that at least one source of the difficulties encountered was the slowness of the reactions involved. Because of this slowness, cleavage of the solvents occurred and gave rise, not only to decreased yields and purity of the end product, but also to the formation of gelatinous deposits which made filtration difficult and sometimes impossible. Another possible effect of the slowness of the reactions may be that some of the aluminum hydride, formed as an intermediate product, polymerizes and precipitates out of solution.

Presumably the formation of metal aluminum hydrides occurs in steps which may be represented by the overall equations:(4)

$$3MH + AlX_3 \rightarrow 3MX + AlH_3 \qquad (1)$$

$$AlH_3 + MH \rightarrow MAlH_4 \qquad (2)$$

Reaction (1) is slow in the case of sodium hydride; furthermore, aluminum chloride reacts more slowly with either sodium or lithium hydrides than does aluminum bromide.(5) The slowness of the overall reaction:

$$4NaH + AlCl_3 \rightarrow NaAlH_4 + 3NaCl \qquad (3)$$

is, therefore, probably due largely to the slowness of reaction (1), especially when aluminum chloride is the halide used.

Of the numerous modifications of the reaction investigated by us, only two are described here. The first is one of several attempts to accelerate reaction (1);(6) the second is a procedure which avoids step (1) entirely.

The only procedure for accelerating step (1) which appeared at all effective consisted of the addition of small amounts of lithium bromide to mixtures of aluminum chloride, with suspensions of sodium hydride in tetrahydrofuran. This procedure was based on the hypothesis that ions of the type, AlX_4^- (in which X is a halide) react more rapidly with sodium hydride than does aluminum chloride.(7) In the absence of lithium bromide, the reaction produced either no sodium aluminum hydride or only small yields of impure products. The mixtures containing lithium bromide invariably gave moderate amounts of fairly pure sodium aluminum hydride, as is shown in the experimental part.

(4) These equations do not represent mechanisms. Intermediates such as AlX_yH_{3-y} or ions such as $(AlX_xH_{4-x})^-$ are probably involved.

(5) There is some indirect evidence that the presence of aluminum chloride also retards the reactions of aluminum hydride.

(6) Experiments to accelerate the reaction by mechanical means, e.g., by increasing the rate of stirring or continuous grinding of the sodium hydride, were unsuccessful. Ultra-high-speed stirring was not tested.

(7) Both sodium chloride and lithium chloride, like lithium bromide, are soluble in solutions of aluminum chloride in tetrahydrofuran, but lithium bromide is the most soluble, and was used for that reason. The chlorides proved much less, if at all, effective.

The procedure nevertheless proved not to be a satisfactory one. The reactions were still relatively slow, and still led to cleavage of the tetrahydrofuran. The filtration difficulty was again so great that it was impossible in most cases to obtain reliable data about the yields. Attention is furthermore called to the fact that the partial success attending the use of lithium bromide cannot be considered as evidence of the correctness of the hypothesis on which the use was based.

The method which avoids reaction (1) entirely, and which ultimately led to a satisfactory means of preparing sodium aluminum hydride, is based on the sequence of reactions(8)

$$3NaAlH_4 + AlCl_3 \rightarrow 3NaCl + 4AlH_3 \tag{4}$$

$$4AlH_3 + 4NaH \rightarrow 4NaAlH_4 \tag{5}$$

Both of these reactions are rapid when carried out in tetrahydrofuran and with pure materials. Furthermore, the sequence represents a production of sodium aluminum hydride, since from 3 moles of the compound 4 are theoretically obtainable.

In principle this sequence might be achieved by adding to a mixture of an excess of sodium hydride with a small amount of sodium aluminum hydride a quantity of aluminum chloride just enough to convert the sodium aluminum hydride to aluminum hydride. After the latter had then reacted with some of the excess sodium hydride to produce fresh sodium aluminum hydride, a second portion of aluminum chloride, 4/3 as large as the first, could then be added. Because reaction (4) is very rapid, the procedure avoids contact of aluminum chloride with the sodium hydride. Repetition of the steps described could lead to the production of any desired amount of sodium aluminum hydride.

In practice, however, the reaction became slower with each addition of aluminum chloride, and the formation of gummy deposits and the filtration difficulties previously mentioned were again encountered. It seems likely, though not proven, that the cause is the coating of the solid sodium hydride by sodium chloride, which is precipitated in very finely divided form by reaction (4).

Whatever the cause, the difficulty is overcome by physically separating steps (4) and (5), i.e. by treating a solution of sodium hydride free from solid sodium hydride with an equivalent amount of aluminum chloride (or slightly less), and then adding the sodium hydride. It is not necessary to filter the mixture before the addition of the sodium hydride, although it may be desirable to do so if the amount of sodium chloride is large.(9) After the addition of the sodium hydride and completion of the reaction, the mixture is filtered. The filtrate may then be evaporated to isolate the sodium aluminum hydride, or it may be treated with an enlarged amount of aluminum chloride to repeat the cycle of reactions. Yields of 98 per cent of the theoretical, and purity of 95 per cent, may be attained by the procedure, which is described in detail in the experimental part.

If no sodium aluminum hydride is on hand to start the cycle, it may be prepared from lithium aluminum hydride, which is commercially available. All that is necessary is to substitute lithium aluminum hydride for the corresponding sodium salt in reaction (4) and then to proceed with reaction (5).(10)

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

(9) In terms of the explanation suggested above, one must make the further, reasonable assumption that the sodium chloride coats the hydride only when the chloride is freshly precipitated on the hydride.

(10) The first portion of sodium aluminum hydride may, of course, be made from sodium hydride and aluminum bromide in dimethyl ether, but this procedure is much less convenient.

More important is the fact that lithium aluminum hydride may be readily made from the sodium salt. The advantage of doing so is seen by a comparison of equation (6) with equations (7) and (8):

$$4LiH + AiCl_3 \rightarrow 3LiCl + LiAlH_4 \qquad (6)$$

$$\left\{ \begin{array}{ll} \tfrac{3}{4}NaAlH_4 + \tfrac{1}{4}AlCl_3 \rightarrow \tfrac{3}{4}NaCl + AlH_3 & (7) \\ AlH_3 + LiH \rightarrow LiAlH_4 & (8) \end{array} \right.$$

For the manufacture of $\frac{3}{4}$ mole of sodium aluminum hydride, 3 moles of sodium hydride are required. As shown by equations (7) and (8), for conversion of this $\frac{3}{4}$ mole of sodium aluminum hydride to one mole of lithium aluminum hydride, one mole of lithium hydride is needed. In other words, the preparation of lithium aluminum hydride from the corresponding sodium salt requires 3 moles of sodium hydride plus only 1 mole of lithium hydride per mole of lithium aluminum hydride, whereas in the direct process (equation (6)) 4 moles of the relatively expensive lithium hydride are needed.

The corresponding procedure has been employed for the preparation of calcium aluminum hydride, but, as shown in the experimental part, has not produced as satisfactory results as have been obtained with the sodium salt.

Properties of Sodium Aluminum Hydride

Sodium aluminum hydride reacts much as does the corresponding lithium salt, except that it is not soluble in diethyl ether and that it is somewhat more stable thermally and, in some respects, somewhat less reactive. It is soluble in tetrahydrofuran and in the dimethyl ethers of ethylene glycols. When the dry salt is slowly heated, barely detectable decomposition occurs at temperatures between 145 and 183°C. At the latter temperature the solid begins to melt, but decomposition does not become rapid till about 230–240°C. At these temperatures the decomposition occurs according to the equation:

$$NaAlH_4 \rightarrow NaH + Al + 1.5H_2 \qquad (9)$$

As an example of the reactivity of sodium aluminum hydride, one may cite the fact that it reacts much more slowly than does lithium aluminum hydride with boron trichloride or trifluoride in the presence of diethyl ether to generate diborane. The difference may be largely due to a difference in solubility. Treatment of the sodium salt with liquid ammonia or liquid isopropylamine generates a quantity of hydrogen gas corresponding to complete replacement of the hydrogen of the compound by amine groups, i.e., by NH_2 or $(CH_3)_2CHNH$ groups.

The behavior of sodium aluminum hydride toward organic compounds will be described in a forthcoming paper by A. E. FINHOLT.

EXPERIMENTAL

Materials

Sodium hydride was first obtained from the du Pont Company, later from Metal Hydrides, Inc., from which calcium hydride was also obtained. Lithium hydride was a product of the Maywood Chemical Co.; all of the hydrides were in powdered form of better than 100-mesh fineness. The aluminum halides were commercial samples resublimed *in vacuo*. Dimethyl ether was freed from carbon dioxide by condensing a sample (MATHESON) in a small bulb and pumping on it at −80°C for a short time. Tetrahydrofuran was a technical sample purified by distillation from sodium or sodium hydride, or from lithium aluminum hydride and lithium hydride. The lithium halides were reagent-grade samples dried by heating them *in vacuo*.

Preparation of Sodium Aluminum Hydride in Dimethyl Ether

A typical preparation of sodium aluminum hydride from sodium hydride and aluminum bromide in dimethyl ether was as follows. After the apparatus (Fig. 1) had been evacuated and filled with nitrogen, 4.470 g (16.75 mmoles) of molten aluminum bromide was poured into the reaction bulb, *B*, from a container having a long spout. The apparatus was re-evacuated to remove any hydrogen bromide formed during the transfer, and was refilled with nitrogen. Sodium hydride (3.34 g or 139.5 mmoles) was then introduced into *B*. A constriction was then made at *A* to facilitate later sealing of the apparatus. Bulb *B* was cooled with a −196°C bath and evacuated to permit the condensation of an amount of dimethyl ether equal to about 15–20 ml of liquid. It is important that the ether be freed from all but small amounts of carbon dioxide, as described above, since the presence of the latter may give rise to explosions when the reaction product is evaporated.(11)

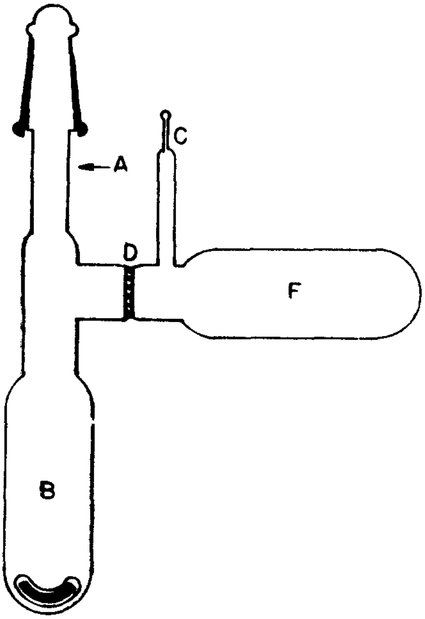

Fig. 1.

When the reaction bulb was warmed to −25°C rapid reaction occurred, presumably due to the formation of an etherate of aluminum bromide. Any hydrogen generated was removed with *B* at −196°C, whereupon the apparatus was sealed at *A*. It was then warmed to room temperature and there maintained for about three hours with magnetic stirring. The resulting mixture was filtered through the fritted disk, *D*, into bulb *F*, from which the ether was then recondensed in *B*. After another repetition of this step, the apparatus was connected to the vacuum system through a tube opener and break-off side arm *C*.

Evaporation of the solvent left a white powder weighing 0.54 g, a yield of about 60 per cent based on the aluminum bromide used.(12) Analyses by the usual methods gave the values: Na, 42.1 and 41.8 per cent; Al, 49.2 and 49.1 per cent; H_2, 7.5 per cent; theory for $NaAlH_4$: 42.6, 49.9, and 7.5 per cent, respectively.

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(11) GERALDINE BARBARAS, GLEN D. BARBARAS, A. E. FINHOLT, and H. I. SCHLESINGER, *J. Amer. Chem. Soc.* **70**, 877 (1948).

(12) In spite of the fact that only 60 per cent of the aluminum was recovered as sodium aluminum hydride there was no bromine left in the solution or in the final product.

Preparation of Calcium Aluminum Hydride

(a) A preparation involving 2.64 g of aluminum bromide and3.02 g of calcium hydride (85 per cent pure) was carried out in about 25 ml of dimethyl ether, using the apparatus and techniques as for the preparation of sodium aluminum hydride. The product weighed 243.4 mg. It contained 87.3 mg (3.23 mmoles) of aluminum, 58.2 mg (1.45 mmoles) of calcium, and 6.7 mg (0.084 mmole) of bromine, and generated 282 cc (12.6 mmoles) of hydrogen. Assuming that the bromine was present as unchanged aluminum bromide, the aluminum so bound amounted to 0.028 mmole, leaving 3.23 — 0.028 or 3.20 mmoles of aluminum as calcium aluminum hydride. Furthermore, the sum of the calcium, aluminum, bromine, and hydrogen (atomic) was only 164.3 mg, whereas the weight of sample was 243.4 mg. Assuming that the discrepancy is due to retained dimethyl ether, the quantity of the latter was 79.1 g, or 1.71 mmoles. On the assumption made above about the source of the bromine, 0.03 mmole of the ether would have been bound to the aluminum bromide, leaving 1.71 $-$ 0.03 $=$ 1.68 mmoles present in the calcium aluminum hydride. The ratio of constituents in the latter then is $Ca : Al : H : (CH_3)_2O = 1.46 : 3.20 : 12.6 : 1.68 = 0.9 : 2.0 : 7.9 : 1.05$ mmoles, thus corresponding satisfactorily to the formula $Ca(AlH_4)_2 \cdot O(CH_3)_2$. A somewhat purer sample was obtained as described in paragraph (b).

(b) An experiment involving 3.916 g of aluminum chloride, 6.624 g of calcium hydride, and 70 ml of dimethyl ether was carried out as described above, except that the apparatus was opened and the dimethyl ether was distilled away before the reaction mixture was filtered. The fact that eight days of vigorous stirring was required before any noticeable change had occurred (e.g., change in volume of the solid) illustrates the fact that aluminum chloride reacts more slowly than aluminum bromide, the reaction of which was complete in less than two days.

After removal of the dimethyl ether, about 70 ml of tetrahydrofuran was condensed into the reaction vessel, the resulting mixture shaken and then filtered through the fritted disk. Evaporation of the solvent left behind a white powder. A 0.0826-g sample of the latter contained 0.0035 g of hydrogen (generated by hydrolysis), 0.0173 g of calcium, and 0.0240 g of aluminum, a total of 0.0448 g. If the 0.0378 g unaccounted for is assumed to have been retained tetrahydrofuran, the atomic (and molecular) ratios $Ca : Al : H : O(CH_2)_4$ are $1 : 2.07 : 8.14 : 1.2$ moles. The result is in satisfactory agreement with the formula $Ca(AlH_4)_2 \cdot [O(CH_2)_4]$, especially if one takes into consideration the fact that the solid was not heated to drive off mechanically retained solvent.

The best yield obtained in several similar experiments was 63.5 per cent, but the results were erratic, probably because it is difficult to extract all of the desired product from the residue left after evaporation of the dimethyl ether. It was noted that addition of a little preformed calcium aluminum hydride to the mixture of calcium hydride and aluminum chloride appeared to accelerate the reaction somewhat.

Reaction of Sodium Hydride with Aluminum Chloride in the Presence of Lithium Bromide and Tetrahydrofuran

Eight experiments were carried out to study the effect of lithium bromide on the reaction between aluminum chloride and sodium hydride in tetrahydrofuran. In all of these a large excess of sodium hydride (from nine- to fifteen-fold the theoretical amount) was used. The amount of lithium bromide was varied from 0.015 to 0.045 mole per mole of aluminum chloride. In each case the reaction mixture was stirred at room temperature under an atmosphere of nitrogen until a small sample of the solution, withdrawn from the reaction vessel, was free from halide. The time required for attaining this condition varied from three to six days. The reaction mixture was then filtered, the filtrate was evaporated to dryness, and the resulting solid was hydrolyzed to determine the amount of hydrogen generated per gram.(13) Judged by this criterion the purity of the products obtained varied from 80 to 85 per cent. Because of the difficulty of filtration (as mentioned in the earlier discussion of this reaction) the yield could be determined in only four of the eight experiments: in these it varied from about 55 to 65 per cent. Such moderately good results were not obtained by this type of procedure without the use of lithium bromide.

(13) The ratio of hydrogen to aluminum was also determined, but the results were considered unreliable, since in a number of cases the ratio exceeded the theoretical value 4. This observation was apparently the result of the precipitation, during hydrolysis, of a white, aluminum-containing but active hydrogen-free solid which could be completely redissolved in acid only with great difficulty.

No relation between the amount of lithium bromide and yield or purity was detected; probably because the smallest amount employed was sufficient to produce the maximum effect. For this reason it seemed unnecessary to report the details of the eight experiments involved.

Preparation of Sodium Aluminum Hydride by Successive Additions of Aluminum Chloride to Sodium Hydride

Increasing portions of a solution of 19 mmoles of aluminum chloride in 30 ml of tetrahydrofuran were added at room temperature to a mixture of 3.65 mmoles of sodium aluminum hydride with 170 mmoles of sodium hydride (a large excess). The first portion of solution contained about 1.1 mmole of aluminum chloride, i.e., about 10 per cent less than required to react with all of the initial sodium aluminum hydride. Each of the six succeeding portions was about 33 per cent larger than the preceding one. Between each of the additions the mixtures were stirred for about forty minutes to allow the aluminum hydride formed to react with sodium hydride.

After all of the aluminum chloride had thus been added, the mixture was subjected to filtration. Even though nitrogen pressure was used, only about one-half of the liquid could be forced through the filter plate. Consequently the total yield could not be determined. Evaporation of the filtrate obtained left a solid which consisted of sodium aluminum hydride of 92 per cent purity, as judged by the amount of hydrogen generated by hydrolysis.

Preparation of Sodium Aluminum Hydride by the "Cyclic Process"

(a) To a solution of 1.44 g (26.7 mmoles) of sodium aluminum hydride, dissolved in 52 g of tetrahydrofuran, 1.19 g (8.91 mmoles) of aluminum chloride was added. The white precipitate, formed immediately, was removed by filtration, and 3.0 g (125 mmoles) of sodium hydride was added to the solution. After fifteen minutes of agitation the mixture became warm, and remained so for another fifteen minutes. After four hours of stirring the mixture was filtered. All manipulations were carried out under an atmosphere of nitrogen.

The 52 g of filtrate was divided into several portions. From an 11.8-g portion most of the tetrahydrofuran was removed at room temperature *in vacuo*. Hydrolysis of the residue generated 718 cc (S.T.P.) of hydrogen. Sodium was determined in the hydrolysate by use of the flame attachment of a Beckman Model DU Quartz spectrometer.(14) The amount of sodium found in the aliquot was 182 mg (7.91 mmoles), corresponding to an atomic H/Na ratio of 4.05. The amount of hydrogen generated corresponded to a total of 35.43 mmoles of sodium aluminum hydride. Theoretically the initial 26.7 mmoles of the latter should have produced 35.6 mmoles by the procedure used: the yield was, therefore, 99 per cent.

From another portion of the final solution, the solvent was removed by evaporation. The residue was heated for forty-five minutes under nitrogen at 110°C. The purity, as determined by hydrolysis and measurement of the hydrogen generated, was only 87 per cent. Whether the impurity was retained tetrahydrofuran or a product of decomposition of the latter was not ascertained.

(b) A preparation was carried out with very nearly the same quantities of reactants and in the same manner as was the preceding one, except that the sodium chloride precipitated in the first step was not removed by filtration before addition of the sodium hydride. The amount of hydrogen generated by hydrolysis showed that from 27.2 mmoles of sodium aluminum hydride 35.1 mmoles had been obtained, a yield of 96.6 per cent. The H/Na ratio was 4.06. The sodium aluminum hydride was not isolated from the solution.

It was also shown that aluminum chloride may be replaced by aluminum bromide. Since no advantage results therefrom, the experimental data are not further reported herein.

Preparation of Lithium Aluminum Hydride from Sodium Aluminum Hydride

To demonstrate the feasibility of preparing lithium aluminum hydride from the corresponding sodium salt, a tetrahydrofuran solution of aluminum hydride was prepared from sodium aluminum hydride by the addition of aluminum chloride. To a portion of this solution, containing 1.80 g (60.0 mmoles) of the solute in 64 g of the solvent, an excess of powdered lithium hydride (of about 90 per cent purity) was added. The mixture, which became warm almost immediately, was stirred for several hours and then filtered.

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(14) P. T. GILBERT, JR., R. C. HAWES, and A. O. BECKMAN, *Anal. Chem.* **22**, 772 (1950).

The solvent was removed from an aliquot of the filtrate by heating it for an hour *in vacuo* at 80°C. The amount of hydrogen generated by hydrolysis of the residue indicated that the total amount of lithium aluminum hydride obtained was 61 mmoles, in other words, was 100 per cent of the expected 60 mmoles, within the limit of accuracy of the analysis. However, the solid was only about 86 per cent pure, since 0.433-g sample generated only 882 instead of the 1020 cc of hydrogen by hydrolysis. The impurity in this case also was probably retained tetrahydrofuran or a product of decomposition of the latter.

Preparation of Sodium Aluminum Hydride from Lithium Aluminum Hydride

This application of the method under discussion would be used only to start the "cyclical" procedure when sodium aluminum hydride is not available. Furthermore, it is in all respects analogous to the preceding case, and gives equally good results. For this reason the example chosen is one which also illustrates that the same solvent need not be used for both steps of the procedure.

To a solution of 4.87 g (122 mmoles) of lithium aluminum hydride in 159 g of diethyl ether, 5.39 g (40.3 mmoles) of aluminum chloride were added. After removal of the precipitated lithium chloride by filtration, the solvent was evaporated from a portion of the filtrate to give a solid etherate which was shown to contain 1.70 g (56.6 mmoles) of aluminum hydride. The latter was dissolved in 60 g of tetrahydrofuran. After addition of 1.82 g (75.8 mmoles) of sodium hydride to the resulting solution, the mixture was stirred for four hours.

The solvent was evaporated at room temperature *in vacuo* from a 14.05-g portion of the 62 g of filtrate. The resulting solid, which was not entirely free from tetrahydrofuran, generated 1130 cc (50.2 mmoles) of hydrogen, indicating a yield of 98 per cent. The H : Na ratio in the solid was shown to be 4.00. In another similar experiment, in which the residual solvent was removed at 150°C *in vacuo*, the purity of the product was 95 per cent.

The Reaction of Calcium Hydride with Aluminum Hydride

The statement in the introductory section that the two-step procedure had proved less successful for the preparation of calcium aluminum hydride than of the sodium salt, is based on experiments in which a tetrahydrofuran solution of aluminum hydride (prepared by the action of an equivalent amount of aluminum chloride on a solution of sodium aluminum hydride) was treated with an excess of calcium hydride. The best yield of calcium aluminum hydride was only 20 per cent of the theoretical. For this reason it seems unnecessary to present details of the experiments.

Composition of Sodium Aluminum Hydride

The temperature of a 0.2650-g sample of sodium aluminum hydride (prepared in dimethyl ether solution) was raised to between 230 and 240°C during a period of two hours. Care was taken that in removing the hydrogen by means of a Toepler pump, the pressure in the heated zone did not fall below 2 mm, since at 240°C the dissociation pressure of sodium hydride is 0.06 mm. The amount of hydrogen recovered by this pyrolysis was 158.9 cc (S.T.P.), or 98.4 per cent of that corresponding to equation (8). Treatment of the residue with water and acid produced 262.9 cc more of hydrogen, which is 97.9 per cent of that corresponding to the equation:

$$NaH + Al + 4HCl \rightarrow NaCl + AlCl_3 + 2.5H_2 \qquad (8)$$

Reaction of Sodium Aluminum Hydride with Ammonia and with Isopropylamine

When sodium aluminum hydride is treated with sufficient ammonia or isopropylamine to assure the presence of liquid reactant, an amount of hydrogen corresponding to equations (9) and (10) is evolved.(15)

$$NaAlH_4 + 4NH_3 \rightarrow NaAl(NH_2)_4 + 4H_2 \qquad (9)$$

$$NaAlH_4 + 4(CH_3)_2CHNH_2 \rightarrow NaAl[(CH_3)_2CNH]_4 + 4H_2 \qquad (10)$$

Thus a 0.1843-g sample of sodium aluminum hydride of 94.2 per cent purity at −33°C evolved 278.4 cc (S.T.P.) of hydrogen; at room temperature another 5.2 cc was obtained, thus bringing the total to 98.4 per cent of that demanded by equation (9). The total amount of ammonia consumed was

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(15) When lithium aluminum hydride is treated with gaseous ammonia the reaction appears to take a somewhat different course (ref. 4), but the lithium salt behaves with liquid ammonia as does the sodium salt.

283.2 cc (gas at S.T.P.) or 98.3 per cent of the theory. Similarly a 0.3926-g sample of the sodium salt (95.3 per cent purity) consumed 620 cc of isopropyl amine (reported as a gas at S.T.P.) and generated 621 cc of hydrogen. These quantities are 99.6 and 99.7 per cent respectively of the requirements of equation (10).(16)

ACKNOWLEDGEMENTS

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(16) A solid having the composition $NaAl(NH_2)_4$ was obtained by F. W. BERGSTROM (*J. Amer. Chem. Soc.* **45**, 2788 [1923]) but differs from ours in that it melts at 90°C with evolution of one mole of ammonia, whereas our product could be heated without melting to 95°C. At this temperature ammonia was evolved. The evolution became very slow after 4.5 hours, by which time about one mole of ammonia had been generated. But loss of ammonia did not cease. By raising the temperature slowly to 295°C, another mole of ammonia could be driven off. The product obtained appeared to be inhomogeneous, and was not further investigated.