Preparation and Properties of Aluminum Hydride

Frank M. Brower, Norman E. Matzek, Paul F. Reigler, Harold W. Rinn, Charles B. Roberts, Donald L. Schmidt,* John A. Snover, and Kazuji Terada

Contribution from The Dow Chemical Company, Midland, Michigan 48640.

Received June 30, 1975

Abstract: Six crystalline phases of nonsolvated aluminum hydride were prepared by desolvation of AlH_3 etherate in the presence of small amounts of $LiAlH_4$. The most stable phase, α-AlH_3, was prepared both from the solid metastable phases and by crystallizing directly from a refluxing diethyl ether-benzene solution. Both the thermal stability and ease of preparation of aluminum hydride phases are highly dependent upon purity.

Aluminum hydride (alane) was first reported as an impure solid[1] and subsequently as amine[2-4] or ether complexes.[5] A convenient synthesis of aluminum trihydride diethyletherate was developed by Finholt, Bond, and Schlesinger.[5] This involves the ethereal reaction of lithium aluminum hydride ($LiAlH_4$) with aluminum chloride and yields an unstable solution because the solvated hydride precipitates.

$$3LiAlH_4 + AlCl_3 \xrightarrow{(C_2H_5)_2O} 4AlH_3\downarrow + 3LiCl\downarrow$$

The ether could not be removed from the complex without decomposition to aluminum and hydrogen. Chizinsky et al.[6,7] reported that nonsolvated aluminum hydride may be prepared by precipitation of the solid unstable hydride etherate from the solution, described by Finholt et al.,[5] by adding pentane or ligroin and then vacuum treatment of the precipitate to remove the diethyl ether. Unfortunately, this procedure as described could not be reproduced consistently; the aluminum hydride was usually obtained as the etherated form, although occasionally partial desolvation was achieved.

Appel and Frankel[8] reported that nonsolvated aluminum hydride may be obtained by bombarding an ultrapure aluminum target with hydrogen ions. Breisacher and Siegel[9] developed a method by which gaseous AlH_3 and its dimer may be studied by time-of-flight mass spectrometry. This involves slowly evaporating aluminum from a hot tungsten filament into hydrogen at low pressure. Both methods produce poorly crystalline material not easily identified by x-ray diffraction.

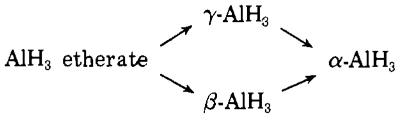
The crystal structure of a stable, crystalline form of nonsolvated aluminum hydride, prepared by us and designated as pattern 1451 (α-AlH_3), was reported by our co-workers Turley and Rinn[10] in 1969. We were unable at that time to report[11] on the preparation of the material used in the x-ray study.

The work reported here concerns the preparation and properties of etherated and nonetherated crystalline forms of aluminum hydride. The AlH_3 described in this paper was initially generated by the ethereal reaction of $AlCl_3$ with $LiAlH_4$.

Results and Discussion

The diethyl etherate, $AlH_3 \cdot 0.3[(C_2H_5)_2O]$,[12] was reported by Finholt et al.[5] to precipitate from solution within 20 min after preparation. The instability was assumed to be due to polymerization of the hydride. Our ebullioscopic measurements indicated the average molecular weight of AlH_3 in freshly prepared solutions of ether varies in a roughly linear relationship from 33 to 48 in solutions ranging from 0.2 to 1.0 M. We obtained no evidence either from ebullioscopic measurements or by light scattering studies that extensive polymerization occurs in solution just before precipitation. Apparently the etherate forms a supersaturated solution and crystallizes rather than polymerizes from solution. The solubility of solid AlH_3 etherate in ether is between 0.20 and 0.22 M at ambient temperature and increases with temperature. It is interesting that after preparation of a supersaturated solution of AlH_3, the time required to reach equilibrium is dependent upon both temperature[12] and concentration. A 0.75 M solution precipitates within 8 min at ambient temperature, but is stable for over 3 h when the preparatory reaction is carried out at −10°. At 25°, a 0.5 M solution of AlH_3 does not precipitate for approximately 90 min, but a 0.67 M solution precipitates within 10 min. The solubility of AlH_3 does not appear to be a function of the method of preparation. We did not observe the solubility differences reported by Ashby et al.[13] when AlH_3 was prepared by the reaction of $LiAlH_4$ with $BeCl_2$, H_2SO_4, or $ZnCl_2$.

We observed[14,15] that pure AlH_3 etherate decomposes to the elements if heated under vacuum, but in the presence of excess $LiAlH_4$ the ether can be removed.[16] The use of $LiBH_4$ in combination with $LiAlH_4$ further lowers the temperature at which desolvation occurs. Desolvation cannot be achieved, however, if $LiBH_4$ is used in the absence of $LiAlH_4$. X-Ray powder diffraction studies indicated that the dry etherate phase, mixed with $LiAlH_4$ and $LiBH_4$ in mole ratios of 1:4:1 ($LiAlH_4$-AlH_3-$LiBH_4$) and heated under vacuum to 65°, first changes to a mixture of metastable nonsolvated phases which we designated as β-AlH_3 and γ-AlH_3. Upon further heating, these phases are converted to the more stable α-AlH_3 phase.



It was evident from elemental infrared and x-ray analyses, that γ-AlH_3 phase is nonsolvated and can be prepared in the absence of other phases.[17] If $LiAlH_4$ is removed by ether washing and the pure γ-AlH_3 stored at 25° for 40 days, it will lose hydrogen and change to a mixture of aluminum and α-AlH_3. The AlH_3 phase reported by Chizinsky[6,7] and co-workers had an identical x-ray powder pattern with our γ-AlH_3 phase. It is possible that in the cases where these workers' desolvations were successful, $LiAlH_4$ was inadvertently in larger excesses than reported.

We were unable to prepare a sample that contained only β-AlH_3. Elemental analyses of samples containing as high as 50% β-AlH_3, together with γ- and α-AlH_3, indicated low carbon (0.2–0.5%). Infrared analyses also indicated the absence of ether. It therefore appears that this metastable phase is also nonsolvated.

It is noteworthy that nonsolvated phases of AlH_3 may be obtained directly from an ether solution. Ethereal solutions of AlH_3 containing excess $LiAlH_4$ when heated under pressure to between 70 and 80° yield an essentially nonsolvated AlH_3 phase which we designated as α'-AlH_3.[18] If, during the heating, ether is slowly distilled off sufficiently to yield saturation, mixtures of nonsolvated α- and γ-AlH_3 come out of solution as well-formed crystals.

Repeated attempts to prepare single-phase samples of γ- or α-AlH_3 by this all-ether method were unsuccessful. By using a higher boiling inert diluent, the temperature of the hydride solution was increased, and the pure α phase was prepared. Of the solvents investigated, benzene proved to be the most practical. One method[19] we used required the use of a large excess of benzene and a $LiAlH_4$-AlH_3-$LiBH_4$ mole ratio roughly between 1:8:1 and 1:4:1. The ether is distilled off until the boiling temperature reaches about 76°. At this point, material precipitates which by x-ray analysis was identified as a mixture of AlH_3 etherate and additives $LiAlH_4$ and $LiBH_4$. Within 5-15 min γ and α phases begin to form and after 50 min the material is all α-AlH_3. This batch method produces α-AlH_3 which is apparently formed both by direct crystallization and by conversion of solid crystals of γ phase to the α phase. The α' phase can be prepared either by simply removing the ether more slowly or by not reaching the critical temperature of 76°

Solubility curves for $LiAlH_4$, AlH_3, and $LiBH_4$ in a mole ratio of 1:4:1 in ether-benzene for a batch experiment are shown in Figure 1. The solubilities of the above three hydrides fall off sharply when enough ether is removed to reach a boiling temperature near 76°. Higher mole ratios of 1:2:1 ($LiAlH_4$-AlH_3-$LiBH_4$) do not appreciably change the precipitation temperature but changing the ratio to 1:16:1 decreases the precipitation temperature to about 75°. This procedure is temperature, concentration, and time dependent, and all three variables must be controlled to obtain pure α-AlH_3.

A convenient method of studying this crystallization process is by examining samples with a polarizing microscope. The α phase forms crystals with hexagonal or cubic silhouettes. The γ phase appears as bundles of fused needles, and the α' phase appears as small multiple needles growing from single points to form fuzzy balls. The etherated phase precipitates as translucent spheres.

Crystals of α-AlH_3 were grown directly from a refluxing ether-benzene solution by a continuous method. This method consists of first nucleating seed crystals followed by careful addition of a feed or nutrient solution of AlH_3. The seed crystals are nucleated by introducing AlH_3 feed solution into a refluxing (79°) ether-benzene solution of $LiAlH_4$ and $LiBH_4$. The AlH_3 concentration during nucleation of crystals must not exceed 0.005 M to prevent formation of undesirable phases. Microscopic observation appears to indicate that the first seed crystals are often produced by a mechanism similar to the batch method, but subsequent crystals grow directly from solution. Seeding was unsuccessful with α crystals that had been first isolated and then reintroduced into the crystallization media. Apparently because of its reactivity, changes occur at the crystal surface during isolation.

After nucleation in the continuous process, more feed solution is added at a rate to lower and hold the refluxing temperature (increase ether concentration) to between 76 and 77°. Conditions at this point are similar to the steep part of the solubility curve in Figure 1. During the growth process, the solution is supersaturated with respect to the α phase since the metastable etherate and γ phases have higher solubilities than the stable phase. Crystals of α-AlH_3 prepared by this method typically reach a size of between 50 and 100 μ.

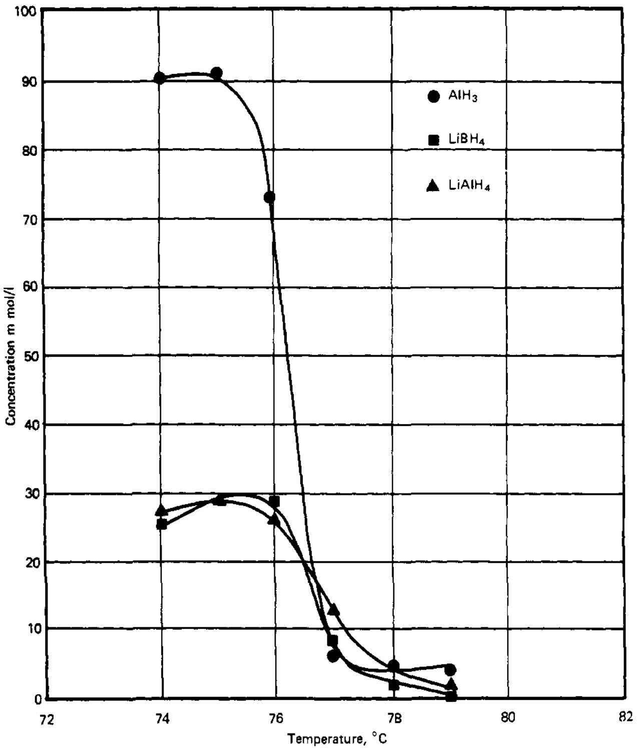


Figure 1. Effect of boiling temperature on the solubility of $LiAlH_4$, AlH_3, and $LiBH_4$ in ether-benzene.

Ebullioscopic studies of AlH_3 and $LiAlH_4$ in ether indicate that there is some association, but the hydrides do not form a single complex with a low whole number ratio of AlH_3 to $LiAlH_4$. This is consistent with the work of Ashby et al.[20] which indicated there are no complexes formed between $LiAlH_4$ and AlH_3 in ether. We obtained no evidence indicating that association takes place between $LiBH_4$ and AlH_3. The latter studies were of little help in explaining the mechanism of $LiAlH_4$ in the desolvation of AlH_3. It is possible that $LiAlH_4$ simply competes with the aluminum-ether oxygen bond at the crystal surface; ether is displaced and the AlH_3 crystal grows by Al-H-Al bond formation. In the nonsolvated solid,[10] each aluminum atom is surrounded by aluminum-hydrogen bridging bonds and is thus stabilized against further interaction with ether.

We did not study extensively the preparation of nonsolvated AlH_3 in ethers other than diethyl ether. Crystallization studies, in which aluminum hydride was prepared and heated in di-*n*-propyl ether solutions, indicated that α-AlH_3 could be prepared but was usually present as a mixture with the γ and other phases. By using a 3:4 mole ratio of $LiAlH_4$ to AlH_3, either a nonsolvated or a slightly solvated ζ-AlH_3 phase[21] was prepared by heating at 80°. This phase appears to decompose upon heating rather than convert to the α phase. The x-ray diffraction pattern for the di-*n*-propyl etherate is the same as that for the diethyl etherate except the strongest line is shifted from 12 to 12.5 Å. The ratio of aluminum to di-*n*-propyl ether in this material is 4:1. We were unable to obtain any nonsolvated AlH_3 when either tetrahydrofuran or dioxane was used in the solvent system.

The role of trace impurities in AlH_3 chemistry is significant. Extraneous contaminants present during preparation affect both the thermal stability of the AlH_3 and the phase obtained. Most ether soluble compounds of transition metals cause immediate decomposition. For example, $TiCl_4$ may be used as a catalyst[22] with AlH_3 etherate to generate an aluminum mirror on a substrate. Often nonreproducible results were traced to impurities in the reagents. Using the continuous crystallization method δ-AlH$_3$ and ϵ-AlH$_3$ phases were sometimes formed; presumably these phases resulted from solvent that contained traces of water. We assumed δ- and ϵ-AlH$_3$ were nonsolvated since the infrared spectra and elemental analyses indicated the absence of ether. We were unable to develop a reproducible method for the preparation of pure δ- or ϵ-AlH$_3$. Traces of reactive organic compounds often inhibited the formation of α-AlH$_3$ and led to the formation of α'-AlH$_3$. Other AlH$_3$ phases present to 10–30% were occasionally observed by x-ray powder diffraction. Their presence was assumed to be related to impurities since they were not produced when a different batch of solvent or reagent was used.

The physical properties and stability of the various nonsolvated phases of AlH$_3$ vary considerably.[23] The α phase is the most stable one thus far isolated, and its thermal properties have been measured.[24] Thermal stability increases with increasing crystal size and perfection. Typically, larger crystalline α phase material decomposes between 0.5 and 2.0% after 6 days at 60°. The metastable phases decompose to the elements at rates three to ten times faster than α-AlH$_3$. Reactivity to water is slow with the α phase, faster with γ phase, and violent with α'-AlH$_3$ and AlH$_3$ etherate.

Summary

The unique physical properties and experimental problems inherent in AlH$_3$ chemistry may be responsible for some seemingly contradictory observations published in the literature. Aluminum hydride is unusual because it has at least six nonsolvated crystalline phases which have different physical properties.

The diethyl etherate can be converted without decomposition to a nonsolvated phase only if LiAlH$_4$ is present. During heating, solid AlH$_3$ etherate mixed with LiAlH$_4$ and LiBH$_4$ is converted to the nonsolvated metastable β and γ phases. These metastable phases, upon further heating, are converted to the more stable α phase. The α-AlH$_3$ phase can be crystallized from a diethyl ether and benzene solution by carefully controlling the conditions. Occasionally traces of water apparently cause crystalline δ- and ϵ-AlH$_3$ to form. The nonsolvated phase, α', δ, and ϵ do not appear to convert to α-AlH$_3$ and are much less thermally stable than the α form. A phase that is either nonsolvated or slightly solvated, ζ-AlH$_3$, was prepared from hot di-*n*-propyl ether. This phase does not convert to, and is less thermally stable than α-AlH$_3$. Impurities may act as decomposition catalysts for all phases.

Experimental Section

General. Operations were performed in the absence of water, oxygen, and other reactive species. All reactions were carried out either in an uncontaminated nitrogen-filled drybox or under an atmosphere of purified nitrogen. Solvents, starting material, and glassware were purified and handled by the methods previously described.[12] Caution was exercised because hydrides may react violently with water or a damp atmosphere. Stabilities of the hydride samples were tested at 60° using the method of Taliani[25] by measuring hydrogen evolution. Dry Fluorolube and Nujol mulls were used to obtain infrared spectra. Light scattering was carried out during the formation and desolvation of aluminum hydride using a Brice-Phoenix light scattering photometer. Ebulliometric molecular weights were obtained using a differential ebulliometer with thermopiles reproducible to ±0.005°. The hydride solutions were filtered immediately after preparation into the test cells, and equilibrium was established within 5–10 min. Boiling point measurements were taken after equilibrium conditions were reached and prior to precipitation. A 1.0 M solution was the maximum concentration of AlH$_3$ that could be used without premature precipitation. Aluminum was analyzed by careful hydrolysis of the sample with dioxane and water and then dissolving it in dilute hydrochloric acid. Aluminum was then chelated with an excess of standardized EDTA in a solution buffered to a pH of 6.5. The excess EDTA was then titrated with a standard ferric iron solution using sodium salicylate as an indicator. The main impurities are B, Cl, Li, and oxygen.

X-Ray diffraction analyses were obtained using Cu Kα radiation with a Debye–Scherrer camera having a 7.16-cm radius. d-Spacings and intensities were read visually using a calibrated intensity strip. The x-ray technique was especially useful in showing the presence of two or more phases in a reaction product and allowed a rough estimate of the relative amounts of each one present. The following paragraph[26] gives d-spacings and intensities for the eight phases discussed.

α-AlH$_3$: (d (Å), I/I_1): 3.226, 100; 2.343, 32; 2.224, 20; 1.967, 4; 1.936, 0.5; 1.831, 10; 1.613, 8; 1.474, 12; 1.414, 8; 1.378, 4; 1.306, 6; 1.284, 3; 1.171, 4; 1.129, 2; 1.112, 1.5; 1.075, 3; 1.051, 2.5; 1.036, 3. **α'-AlH$_3$** (d (Å), I/I_1): 5.6, 100; 3.28, 60; 3.21, 10; 2.79, 60; 2.29, 12; 2.12, 50; 1.855, 3; 1.770, 3; 1.635, 7; 1.610, 8; 1.600, 8; 1.570, 3; 1.540, 2; 1.440, 5; 1.410, 12; 1.395, 5; 1.281, 6; 1.271, 2; 1.144, 5. **β-AlH$_3$** (d (Å), I/I_1): 5.2, 100; 2.71, 36; 2.60, 43; 2.25, 17; 2.06, 14; 1.73, 11; 1.59, 14; 1.52, 14; 1.372, 4; 1.355, 14; 1.300, 5; 1.260, 6; 1.171, 6; 1.125, 2; 1.100, 2; 1.040, 2; 1.032, 4; 1.008, 4. **γ-AlH$_3$** (d (Å), I/I_1): 4.55, 30; 4.33, 63; 3.93, 18; 3.69, 75; 3.48, 50; 3.02, 50; 2.88, 100; 2.68, 25; 2.40, 30; 2.31, 75; 2.26, 25; 2.08, 40; 1.96, 2; 1.85, 5; 1.80, 5; 1.75, 13; 1.73, 8; 1.705, 18; 1.66, 10; 1.61, 4; 1.545, 10; 1.525, 25; 1.51, 3; 1.48, 7; 1.45, 7; 1.438, 8; 1.419, 8; 1.398, 9; 1.361, 4; 1.336, 15. **δ-AlH$_3$** (d (Å), I/I_1): 6.4, 17; 5.75, 7; 4.51, 12; 3.85, 62; 3.58, 100; 3.19, 10; 2.93, 5; 2.87, 10; 2.71, 17; 2.56, 38; 2.45, 7; 2.36, 12; 2.26, 15; 2.14, 15; 2.12, 20; 2.07, 5; 2.04, 7; 2.00, 2; 1.96, 10; 1.79, 5; 1.75, 5; 1.62, 7; 1.59, 7; 1.55, 2; 1.53, 2; 1.51, 4; 1.490, 5; 1.450, 5; 1.440, 2; 1.412, 10. **ϵ-AlH$_3$** (d (Å), I/I_1): 5.3, 13; 4.91, 100; 4.59, 58; 3.84, 12; 3.64, 75; 3.20, 67; 3.01, 62; 2.95, 7; 2.85, 8; 2.79, 67; 2.71, 62; 2.65, 10; 2.58, 75; 2.50, 67; 2.35, 5; 2.29, 12; 2.26, 5; 2.22, 12; 2.18, 40; 2.15, 20; 2.12, 25; 2.10, 25; 2.03, 12; 2.00, 10; 1.96, 33; 1.91, 5; 1.89, 10; 1.85, 8; 1.83, 5; 1.81, 5; 1.78, 12; 1.75, 7; 1.66, 17. **ζ-AlH$_3$** (d (Å), I/I_1): 5.28, 67; 4.60, 53; 3.78, 100; 3.69, 11; 3.45, 11; 3.32, 5; 3.28, 5; 2.88, 87; 2.76, 33; 2.53, 21; 2.46, 33; 2.41, 3; 2.38, 5; 2.33, 40; 2.30, 27; 2.22, 5; 2.15, 5; 2.08, 5; 1.99, 33; 1.95, 8; 1.86, 5; 1.79, 5; 1.75, 3; 1.65, 5; 1.60, 5; 1.58, 3; 1.57, 13; 1.53, 11; 1.50, 8; 1.475, 3; 1.460, 5; 1.440, 8; 1.427, 5; 1.417, 5; 1.409, 3; 1.346, 5; 1.323, 5; 1.277, 5. AlH$_3$ etherate (d (Å), I/I$_1$): 12.0, 100; 4.62, 17; 3.89, 17; 2.88, 17; 2.35, 4; 2.31, 4; 1.54, 3; 1.495, 3; 1.442, 3.

Microcrystalline γ-AlH$_3$. A 1.0 M diethyl ether solution (100 ml, 0.10 mol) of AlCl$_3$ was added with stirring to a 1.0 M (400 ml, 0.40 mol) solution of LiAlH$_4$. The solution was immediately filtered and the ether removed under vacuum. The dry residue was ground and heated under vacuum at 60° for 4 h. The solid was washed with diethyl ether and dried under vacuum, giving 11.4 g (95%) of the hydride. Anal. Calcd for AlH$_3$: Al, 89.92; H, 10.08. Found: Al, 88.72; H, 9.66. The main impurities are C, B, Cl, and Li; in this example C, 0.28; B, 0.14; Cl, 0.47; and Li, 0.45 were found.

Microcrystalline α-AlH$_3$. The reaction was carried out as described above except after filtration 1.0 M (100 ml, 0.10 mol) LiBH$_4$ was added. After removing solvent, the ground solid was heated at 65° for 6.5 h, washed with ether, and dried under vacuum to give 10.7 g (89%) of colorless product. Anal. Calcd for AlH$_3$: Al, 89.92; H, 10.08. Found: Al, 88.80; H, 9.80.

Batch Crystallization of α-AlH$_3$. An ethereal 1.0 M solution (50 ml, 0.050 mol) of AlCl$_3$ was added with stirring to 0.5 M (400 ml, 0.20 mol) LiAlH$_4$. The solution was immediately filtered and stirred with 2 g of finely ground NaAlH$_4$ for 3–4 min to minimize soluble lithium chloride.[12] After filtration, 1.0 M LiBH$_4$ (50 ml, 0.050 mol) was added and the resulting solution added to 1200 ml of benzene. The solution was heated in a flask equipped with a stirrer and an efficient, packed distillation column (4 × 45 cm). Twenty-five minutes after the solution began to boil, enough ether was fractionally distilled from the solution to give a boiling point of 76° (750 mm). The temperature was then slowly increased to 78° over a period of 80 min. The crystalline solid was collected and washed with ether to give 4.8 g (80%). Anal. Calcd for AlH$_3$: Al, 89.92; H, 10.08. Found: Al, 89.50; H, 9.95. The principal impurities are Li, Cl, B, and carbon; in a typical example C, 0.14; B, <0.15; Cl, <0.1; and Li, 0.17 were found.

Preparation of α'-AlH$_3$. This procedure is identical with that described for the above batch crystallization except the ether is fractionated to yield a reaction boiling temperature between 73 and 74°. After 2 h, 4.8 g (76%) of hydride was collected and washed with ether. Anal. Calcd for $AlH_3{\cdot}0.02[(C_2H_5)_2O]$: Al, 85.69; C, 3.05; H, 10.25. Found: Al, 85.83; C, 2.42; H, 9.98. The main impurities are B, Cl, Li, and Na; in a typical example B, 0.12; Cl, 0.27; Li, 0.58; and Na, 0.24 were found.

Continuous Crystallization Method for α-AlH$_3$. This method requires a crystallization flask equipped with a stirrer, addition funnel, and an efficient fractionation column. Samples of the crystallization mixture are withdrawn for inspection by Teflon tubing from the crystallizing flask through a three-way Teflon stopcock into a syringe. The stopcock is then rotated 180°, and the samples are flushed through a glass microscope examining cell and returned through Teflon tubing into the flask. The stopcock is turned to stop the flow while the particles are examined in the viewing cell with a polarizing microscope.

An ethereal AlH_3 solution was prepared by combination of 1.0 M (56 ml, 0.056 mol) $LiAlH_4$, 1.0 M (197 ml, 0.017 mol) $AlCl_3$, and 118 ml of ether followed by filtration. The solution was stirred with 0.5 g of finely ground $NaBH_4$ for 10 min and filtered. After the addition of 130 ml of benzene and 1.0 M (7 ml, 0.007 mol) $LiBH_4$, the resulting feed solution was transferred to an addition funnel.

A crystallization medium containing 500 ml of benzene, 40 ml of ether, 1.0 M (1 ml, 0.001 mol) $LiAlH_4$, and 1.0 M (2 ml, 0.002 mol) $LiBH_4$ was heated to 79°. After 25 min, 20 ml of hydride feed solution had been added, the temperature was 80°, and the first hexagonal-shaped crystals of α-AlH$_3$ appeared. The rate of addition of hydride solution was then increased and the ether fractionally distilled off so that the temperature was maintained between 76.5 and 77°. After the addition was completed (3 h), the reaction was allowed to reflux for 20 min and the crystalline α phase collected. The yield and purity of the sample are comparable to the batch method but the continuous crystallization method produces larger and more symmetrical crystals.

Acknowledgment. We are indebted for the experimental work carried out by W. H. Crawford, A. L. Daniels, E. E. Flagg, L. F. Lamoria, G. H. Mattson, D. Musinski, B. H. Phillips, H. C. Roehrs, J. H. Waibel, and B. L. York. We are grateful to R. A. Nyquist for the interpretation of infrared spectral data and to R. A. Nunemaker for the analysis. We are indebted to J. W. Turley and R. W. Parry for valuable discussions and suggestions. This work was supported by the Air Force Rocket Propulsion Laboratory and Air Flight Test Center, Edwards Air Force Base, Calif., under Contract No. AF-04(611)-7554 and AF-33(616)-6149.

References and Notes

(1) O. Stecher and E. Wiberg, *Ber.*, **75B**, 2003 (1942).
(2) E. Wiberg, H. Graf, and R. Usom, *Z. Anorg. Allg. Chem.*, **227**, 221 (1958).
(3) J. K. Ruff and M. F. Hawthorne, *J. Am. Chem. Soc.* **82**, 2141 (1960).
(4) C. W. Heitsch, C. E. Nordman, and R. W. Parry, *Inorg. Chem.*, **2**, 508 (1963).
(5) A. E. Finholt, A. C. Bond, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947).
(6) G. Chizinsky, G. G. Evans, T. R. P. Gibb, Jr., and M. J. Rice, Jr., *J. Am. Chem. Soc.*, **77**, 3164 (1955).
(7) M. J. Rice, Jr., and G. Chizinsky, "Non-Solvated Aluminum Hydride", Contract ONR-494(04) ASTIA No. 106967, U.S. Office of Naval Research (Aug 1956).
(8) M. Appel and J. P. Frankel, *J. Chem. Phys.*, **42**, 3984 (1965).
(9) P. Breisacher and B. Siegel, *J. Am. Chem. Soc.*, **86**, 5053 (1964).
(10) J. W. Turley and H. W. Rinn, *Inorg. Chem.*, **8**, 18 (1969).
(11) This compound was prepared under Contracts AF-04(611)-7554 and AF-33(616)-6149 and published in reports from 1961 through 1965, but the work was classified until recently. This and other compounds prepared by us were uniquely identified by x-ray powder diffraction and were named following an in-house system of nomenclature for chemically unidentified phases. Because this nomenclature has been used extensively by Dow Chemical and in ref 10 and 12, the following equivalent names are listed to allow easy access to the early literature. α-AlH$_3$ is AlH$_3$-1451, α'-AlH$_3$ is AlH$_3$-1444, β-AlH$_3$ is AlH$_3$-1463, γ-AlH$_3$ is AlH$_3$-1433, δ-AlH$_3$ is AlH$_3$-1717, ϵ-AlH$_3$ is AlH$_3$-1563, ζ-AlH$_3$ is AlH$_3$-1546, and AlH$_3$ etherate is AlH$_3$–1443.
(12) D. L. Schmidt, C. B. Roberts, and P. F. Reigler, *Inorg. Synth.*, **14**, 47 (1973).
(13) E. C. Ashby, J. R. Sanders, P. Claudy, and R. Schwartz, *J. Am. Chem. Soc.*, **95**, 6485 (1973).
(14) F. M. Brower, B. H. Phillips, N. E. Matzek, A. R. Daniels, and D. F. Musinski, U.S. Patent 3 823 226 (1974); *Chem. Abstr.*, **82**, 5719 (1975).
(15) F. M. Brower, N. E. Matzek, and B. H. Phillips, "Aluminum Hydride", Contract AF-33(616)-6149, Special Report No. AR-4S-61, Oct 1961, Defense Documentation Center AD No. 326841.
(16) Workers at Metal Hydrides Incorporated independently observed this behavior.
(17) N. E. Matzek and D. F. Musinski, U.S. Patent 3 819 819 (1974); *Chem. Abstr.*, **81**, 123769 (1974). A detailed treatment of this aspect of AlH$_3$ chemistry will be published.
(18) N. E. Matzek and D. F. Musinski, U.S. Patent 3 883 644 (1975), *Chem. Abstr.*, **83**, 45418 (1975).
(19) D. L. Schmidt and R. W. Diesen, U.S. Patent 3 840 654 (1974); *Chem. Abstr.*, **82**, 5740 (1975).
(20) E. C. Ashby, J. J. Watkins, and H. S. Prasad, *Inorg. Chem.*, **14**, 583 (1975).
(21) We did not carry out sufficient experiments to completely define a process or to determine if ζ-AlH$_3$ is totally nonsolvated.
(22) D. L. Schmidt and R. H. Hellmann, U.S. Patent Re 27 606 (1973); *Chem. Abstr.*, **69**, 69347 (1968).
(23) Several factors relevant to α-AlH$_3$ stability will be discussed in detail in a paper currently in preparation by N. E. Matzek.
(24) G. C. Sinke, L. C. Walker, F. L. Oetting, and D. R. Stull, *J. Chem. Phys.*, **47**, 2759 (1967).
(25) M. Taliani, *Gazz. Chim. Ital.*, **51**, I, 184 (1921).
(26) The x-ray data were compiled by L. R. Ruhberg from data collected by H. W. Rinn. The work was done at the Analytical Laboratories, The Dow Chemical Company, Midland, Mich.