[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

# The Reaction of Lithium Aluminum Hydride with Alcohols. Lithium Tri-*t*-butoxyaluminohydride as a New Selective Reducing Agent[1,2]

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Lithium aluminum hydride in ethyl ether solution reacts readily at room temperature with four moles of methyl, ethyl and isopropyl alcohols. Under the same conditions only three moles of *t*-butyl and *t*-amyl alcohol react, thereby forming the new substances, lithium tri-*t*-butoxyaluminohydride and lithium tri-*t*-amyloxyaluminohydride. Reaction with a fourth mole of the tertiary alcohols requires elevated temperatures. Lithium tri-*t*-butoxyaluminohydride exhibits surprising stability—it can be sublimed *in vacuo* at 280° without appreciable decomposition. The compound is a far milder reducing agent than the parent compound. It reduces representative aldehydes, ketones and acid chlorides but fails to react with simple esters and nitriles. The reduction of acid chlorides by equimolar quantities of the reagent can be controlled to provide a convenient synthetic route to aldehydes.

The discovery of the alkali metal borohydrides[4] and the corresponding alkali metal aluminum hydrides[5] provided two groups of reducing agents of vastly different reactivities.[6] As one extreme sodium borohydride reduces readily only aldehyde, ketone and acid chloride groups,[7] whereas lithium aluminum hydride readily attacks practically all reducible groups.

It was previously noted that the reducing capacity of sodium borohydride could be greatly increased by the addition of certain metal salts[8] and by the introduction of alkoxy substituents.[9] The present study was undertaken to examine the effect of alkoxy substituents on the reducing action of lithium aluminum hydride.[10] The preparation of lithium and sodium triethoxyaluminohydride[11] and application of the latter reagent as a reducing agent[12] have been reported recently.

In the latter study the authors prepared the "monomeric α-form" of aluminum ethoxide[13] and treated it with sodium hydride in tetrahydrofuran at 70–90° in an autoclave. In our study the treatment of lithium aluminum hydride with alcohols appeared to offer a convenient route to the trialkoxyaluminohydrides and this procedure was therefore utilized. In the course of the investigation it appeared desirable to learn something of the properties of the lithium tetraalkoxyaluminohydrides. These compounds were therefore prepared and characterized.

## Results

**The Lithium Tetraalkoxyaluminohydrides.**—Lithium tetramethoxyaluminohydride was previously prepared by the reaction of lithium methoxide with aluminum methoxide.[14] Analogous procedures were employed for the preparation of the corresponding ethoxy, isopropoxy and *t*-butoxy derivatives.

$$\mathrm{LiOR} + \mathrm{Al(OR)_3} \longrightarrow \mathrm{LiAl(OR)_4}$$

The products were all white solids. The methoxide melted with some decomposition at 270–276° and the remaining compounds failed to melt below 300°. Above that temperature decomposition was evident. In the case of the tetra-*t*-butoxy derivative, it proved possible to sublime the material at 335° and 1 mm. pressure.

The methoxy and ethoxy derivatives were soluble in methanol and ethanol, respectively, and could be recrystallized from these solvents. The isopropoxy and *t*-butoxy derivatives were insoluble in the corresponding alcohols.

All four products proved to be essentially insoluble in all other solvents examined: benzene, xylene, dioxane, tetrahydrofuran, diethyl ether, acetone, acetonitrile, dimethylformamide, monoglyme (dimethyl ether of ethylene glycol) and diglyme (dimethyl ether of diethyleneglycol). The insolubility of the tetraalkoxy derivatives in tetrahydrofuran and diglyme proved valuable in establishing the synthesis of lithium trimethoxyaluminohydride and lithium tri-*t*-butoxyaluminohydride in these solvents.

**The Reaction of Lithium Aluminum Hydride with Alcohols.**—Treatment of lithium aluminum hydride in ethyl ether solution with four moles of methyl, ethyl or isopropyl alcohol at 25° results in the evolution of four moles of hydrogen and the precipitation of the corresponding lithium tetraalkoxyaluminohydride. However, the addition of four moles of *t*-butyl alcohol results in the formation of only *three* moles of hydrogen. The fourth mole of hydrogen is evolved only on extended treatment at elevated temperatures.

The reaction product, lithium tri-*t*-butoxyaluminohydride, is only slightly soluble in ethyl ether, but it is readily soluble in tetrahydrofuran and di-

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(1) Addition Compounds of the Alkali Metal Hydrides. X.

(2) Based upon a thesis submitted by Richard F. McFarlin in January, 1956, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Purdue Research Foundation Fellow, 1953–1955.

(4) H. I. Schlesinger and H. C. Brown, THIS JOURNAL, **62**, 3129 (1940); H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. R. Rapp, *ibid.*, **75**, 199 (1953).

(5) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *ibid.*, **69**, 1199 (1947).

(6) R. F. Nystrom and W. G. Brown, *ibid.*, **69**, 1197, 2548 (1947); **70**, 3738 (1948).

(7) S. W. W. Chaikin and W. G. Brown, *ibid.*, **71**, 122 (1949).

(8) H. C. Brown and B. C. Subba Rao, *ibid.*, **78**, 2582 (1956).

(9) H. C. Brown, E. J. Mead and C. J. Shoaf, *ibid.*, **78**, 3613 (1956).

(10) A preliminary Communication reporting the utility of the reagent lithium tri-*t*-butoxyaluminohydride for the conversion of acid chlorides to aldehydes was published earlier: H. C. Brown and R. F. McFarlin, *ibid.*, **78**, 252 (1956).

(11) O. Schmitz-DuMont and V. Habernickel, *Ber.*, **90**, 1054 (1957).

(12) G. Hesse and R. Schrödel, *Ann.*, **607**, 24 (1957).

(13) H. Adkins, THIS JOURNAL, **44**, 2178 (1922); W. C. Child and H. Adkins, *ibid.*, **45**, 3013 (1923).

(14) H. Meerwein and T. Bersin, *Ann.*, **476**, 113 (1929).

glyme. Accordingly, the reaction with *t*-butyl alcohol was examined in these solvents. Here also the reaction ceases with the evolution of three moles of hydrogen, with the fourth mole being produced only at elevated temperatures. Consequently, the tendency for the reaction to halt with the formation of the tri-*t*-butoxy derivative cannot be attributed to its low solubility in ether.

Treatment of lithium aluminum hydride in ethyl ether with one and two equivalents of *t*-butyl alcohol results in the evolution of one and two molar equivalents of hydrogen, but the solution remains clear. The third equivalent of alcohol results in the precipitation of the tri-*t*-butoxyaluminohydride. Consequently, it appears that lithium di-*t*-butoxyaluminohydride, and, possibly, lithium mono-*t*-butoxyaluminohydride, exist as distinct species.

Lithium tri-*t*-butoxyaluminohydride proved to be surprisingly stable. A sample in diglyme solution, heated to 165° for 5 hr., retained 92% of its active hydrogen. It failed to melt below 400° and exhibited signs of decomposition above that temperature. It could be sublimed at 280° at 2 mm. pressure. Solubilities in a number of solvents were determined (Table I).

TABLE I

SOLUBILITIES OF LITHIUM TRI-*t*-BUTOXYALUMINOHYDRIDE AT 25°

| Solvent | Solubility, g./100 g. solv. | Solvent | Solubility, g./100 g. solv. |
|---|---|---|---|
| Diglyme | 41 | Dibutyl ether | 0.5 |
| Tetrahydrofuran | 36 | Acetonitrile | 0.4 |
| Monoglyme | 4 | *t*-Butyl alcohol | 0 |
| Ethyl ether | 2 | Methylal | 0 |

The reaction of *t*-amyl alcohol with lithium aluminum hydride also was examined briefly. The addition of excess *t*-amyl alcohol to lithium aluminum hydride in ether solution also formed three molar equivalents of hydrogen. In contrast to the corresponding reaction of *t*-butyl alcohol, the ether solution remained clear. However, removal of the ether and excess *t*-amyl alcohol gave a product which was soluble in diglyme and tetrahydrofuran but was only slightly soluble in ethyl ether. When heated in diglyme solution to 80° with *t*-amyl alcohol, the last mole of hydrogen was evolved slowly.

**The Reducing Properties of Lithium Tri-*t*-butoxyaluminohydride.**—The failure of lithium tri-*t*-butoxyaluminohydride to react with excess *t*-butyl alcohol at 25° suggested that this reagent should have reducing properties markedly different from those of the parent compound. Accordingly, its behavior at 0° toward molecules containing representative reducible groups was examined. Standard solutions of lithium aluminum hydride in ethyl ether and in diglyme, at 0°, were treated with three molar equivalents of *t*-butyl alcohol, forming the reagent *in situ*. The organic compound under examination was added to the reaction mixture. After 30 minutes at 0°, the reaction mixture was treated with ethanol to convert residual hydridic hydrogen to hydrogen gas. This was collected and measured to provide a measure of the utilization of "hydride" by the organic compound under examination. The results are summarized in Table II.

TABLE II

REDUCING PROPERTIES OF LITHIUM TRI-*t*-BUTOXYALUMINOHYDRIDE AT 0°

| Compound | Utilization of hydride[a] Ethyl ether | Diglyme |
|---|---|---|
| Acetone | 0.93 | 0.99 |
| Acetophenone | | .98 |
| Chloral | .92 | .99 |
| Pinacolone | .73 | .99 |
| Benzaldehyde | .90 | .96 |
| Benzoyl chloride | 1.91 | 1.93 |
| *p*-Nitrobenzoyl chloride | 1.83 | 1.89 |
| Acetonitrile | 0.0 | 0.0 |
| Benzonitrile | .0 | .0 |
| Ethyl benzoate | .0 | .0 |
| Succinic anhydride | 1.95 | |
| Phthalic anhydride | | 1.99 |
| Benzyl chloride | | 0.0 |

[a] Mmoles of hydride per mmole of compound.

Finally, the utility of the trialkoxyaluminohydrides for the conversion of acid chlorides to aldehydes was examined.[10] The products formed by treating one mole of lithium aluminum hydride in ether solution with three moles of methyl, ethyl and isopropyl alcohols were dissolved in diglyme. These solutions then were added to an equivalent of benzoyl chloride in diglyme at 0°. In each case the yield of aldehyde was negligible. On the other hand, lithium tri-*t*-butoxyaluminohydride in diglyme solution converted benzoyl chloride at 0° to benzaldehyde in a yield of 60% (by analysis). Addition of the reducing agent to the acid chloride maintained at approximately −75° increased the yield to 78%. Surprisingly, the use of lithium tri-*t*-amyloxyaluminohydride proved less satisfactory. Under identical conditions this reagent converted benzoyl chloride to the aldehyde in a yield of only 48%. Consequently, we adopted lithium tri-*t*-butoxyaluminohydride as the preferred reagent for this reduction and applied it to the reduction of several representative aromatic and aliphatic acid chlorides.

It was observed that lithium tri-*t*-butoxyaluminohydride in tetrahydrofuran or diglyme solution, added in stoichiometric amount to the acid chloride in the same solvent at −80°, gives the aldehyde in yields of 60 to 80% in the case of aromatic derivatives and 40 to 60% in the case of aliphatic derivatives. In this way *p*-nitrobenzoyl chloride has been reduced to *p*-nitrobenzaldehyde in a yield of 80%, and terphthalyl chloride has been reduced to terphthalyl aldehyde in a yield of 85%.

Typical results are summarized in Table III.

A more extensive study of the applicability of this new aldehyde synthesis has been made by Dr. Subba Rao and will be reported shortly.[15]

## Discussion

Lithium tetramethoxyaluminohydride is soluble in methanol and the corresponding ethyl deriva-

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[15] H. C. Brown and B. C. Subba Rao, THIS JOURNAL, **80**, 5377 (1958).

tive is soluble in ethanol. With these two exceptions we were unable to find any solvent for the tetraalkoxyaluminohydrides. On the other hand, the reaction products formed by the treatment of lithium aluminum hydride with three moles of alcohol were readily soluble in organic solvents, especially in tetrahydrofuran and diglyme.

TABLE III

REDUCTION OF ACID CHLORIDES TO ALDEHYDES BY LITHIUM TRI-*t*-BUTOXYALUMINOHYDRIDE

| | | Yield of aldehyde | | |
|---|---|---|---|---|
| | | Tetrahydrofuran | Diglyme | |
| Acid chloride | Moles | By analysis | By analysis | By isolation |
| *p*-Nitrobenzoyl | 0.244 | | | 80[a] |
| Benzoyl | .256 | 65 | 78 | 73[b] |
| Terphthalyl | .200 | | | 85[a] |
| *p*-Toluyl | .056 | | 61 | |
| *m*-Chlorobenzoyl | .074 | | 63 | |
| Caproyl | .033 | | 41 | |
| Pivalyl | .033 | 60 | 58 | |

[a] Isolated by precipitation with water. [b] Isolated through the bisulfite addition compound.

Although the insolubility of the tetraalkoxyaluminohydrides was a handicap in the preparation and purification of these substances, it provided a simple proof of the homogeneity of lithium tri-*t*-butoxyaluminohydride with which we were mainly concerned. The reaction of lithium aluminum hydride with three molar equivalents of *t*-butyl alcohol in ether results in the liberation of three molar equivalents of hydrogen. It is evident that the reaction must proceed either to the formation of pure lithium tri-*t*-butoxyaluminohydride or to a mixture of lithium tetraalkoxyaluminohydride and one or more less substituted lithium alkoxyaluminohydrides. However, the reaction product dissolves completely in both tetrahydrofuran and diglyme. Consequently, the tetra-*t*-butoxyaluminohydride cannot be present in the reaction mixture in more than traces. (It was established that lithium tetra-*t*-butoxyaluminohydride does not dissolve in solutions of lithium aluminum hydride in diglyme even at 100°.)

Similarly, lithium tri-*t*-amyloxyaluminohydride dissolves in diglyme readily. However, at 80° it reacts with a fourth mole of *t*-amyl alcohol with the liberation of a mole of hydrogen and the formation of a white, insoluble product. Consequently here also the product must be the simple tri-*t*-amyloxy derivative.

In the case of methyl, ethyl and isopropyl alcohol the reaction with lithium aluminum hydride proceeds readily at 25° with the liberation of all available hydrogen and the formation of the respective tetraalkoxy derivatives.

$$4ROH + LiAlH_4 \longrightarrow LiAl(OR)_4 + 4H_2$$

However, under these conditions only three molecules of the tertiary alcohols react

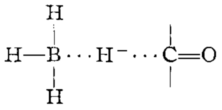
$$3ROH + LiAlH_4 \longrightarrow LiAlH(OR)_3 + 3H_2$$

It is not possible to state at this time to what extent the marked decrease in the rate of the fourth stage in the case of the tertiary alcohols is due to steric factors, the decreased acidity of the tertiary alcohol group, or to the lower reactivity of the remaining hydridic hydrogen in the anion. Probably all influences are involved.

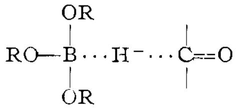
In reductions lithium tri-*t*-butoxyaluminohydride exhibits markedly lower activity than lithium aluminum hydride itself. This decreased activity cannot be due entirely to the large steric requirements of the anion, since a similar decrease in activity has been noted for the related sodium triethoxyaluminohydride.[12,16]

In contrast to this effect of alkoxy substituents in *decreasing* the activity of lithium aluminum hydride is the marked effect of these substituents in *increasing* the reactivity of sodium borohydride.[9] Sodium triisopropoxy- and tri-*t*-butoxyborohydrides are considerably more powerful reducing agents than the parent compound. It is of interest to consider the basis for this marked difference in the effect of alkoxy substituents in the two systems.

Reductions by these complex hydrides presumably proceed through a transfer of hydride ion from the anion to the group undergoing reduction.



$$H_3B\cdots H^-\cdots C{=}O$$

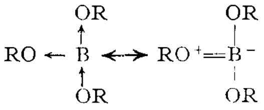


$$(RO)_3B\cdots H^-\cdots C{=}O$$

On this basis, the transfer of hydride ion from the weaker Lewis acid, alkyl borate, should proceed more rapidly than the transfer from the stronger Lewis acid, borane.

Unfortunately, little is known about the relative strengths of aluminum hydride and aluminum alkoxides as Lewis acids. The polymeric nature of the products renders difficult the experimental comparison of their acid strengths. Fortunately, it is possible to rationalize the observed effect on theoretical grounds.

In the case of both the alkyl borates and the aluminum alkoxides the electron-withdrawing inductive effect of the alkoxy groups would be expected to increase the acid strengths of the two related derivatives, $(RO)_3B$ and $(RO)_3Al$. However, large resonance contributions in the alkyl borate satisfy the electron deficiency of the boron atom and reverse the anticipated electronic effect of the alkoxy groups.



$$(RO)_3B \longleftrightarrow RO^+{=}B^-(OR)_2$$

Consequently, instead of being strong Lewis acids, alkyl borates are quite weak. Such resonance interactions should be far less important in a second row element, such as aluminum, than in a first row element, such as boron. It would not be unex-

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(16) This conclusion is supported by quantitative comparisons of the reactivity of lithium aluminum hydride and lithium trimethoxyaluminohydride. Unpublished observations of C. J. Shoaf.

pected if the electronic effect of the alkoxyl groups in aluminum derivatives were primarily a reflection of the electron-withdrawing inductive effect of these groups with only minor modifications by the less important resonance interactions. In this way the markedly different effects of alkoxy substituents on the reducing powers of the borohydride and aluminum hydride derivatives is the result of the different capacity of boron and aluminum to participate in resonance interactions involving double-bonded structures with the oxygen atom of the substituent.

Lithium tri-*t*-butoxyaluminohydride is a very mild reducing agent, much closer in these characteristics to sodium borohydride than to lithium aluminum hydride itself. In view of the ready availability of sodium borohydride, the marked selectivity exhibited by lithium tri-*t*-butoxyaluminohydride is probably of more theoretical than practical interest. On the other hand, the ready reduction of acid chlorides to aldehydes by the reagent is of major practical interest. It provides a highly convenient synthetic route for proceeding from the readily available carboxylic acids to the corresponding aldehydes.

## Experimental

**Materials.**—All chemicals were commercial products which were carefully purified by standard methods before use. Special care was given to the drying of the solvents and alcohols, utilizing either lithium aluminum hydride or calcium hydride as drying agents. All apparatus was flamed in a dry atmosphere and allowed to cool in that atmosphere prior to use. Lithium aluminum hydride solutions in ether were prepared and used as clear solutions. The composition of the solutions was established by analysis for hydride (by hydrolysis) and confirmed by analysis for aluminum (with 8-hydroxyquinoline).

**Preparation of Lithium Tetraalkoxyaluminohydrides.**—The following procedure is typical of the preparations proceeding through the reaction of aluminum alkoxide with lithium alkoxide.

Aluminum ethoxide, 128.2 g. (0.79 mole), was melted, poured into a one-l. flask and dissolved in 200 ml. of hot xylene. In another flask 5.5 g. (0.80 mole) of lithium wire was dissolved in refluxing anhydrous ethanol. A minute crystal of phenolphthalein was placed in the aluminum ethoxide and the lithium ethoxide added to the end-point. After standing overnight, the alcohol solution deposited a large mass of white needle-like crystals. A crude yield of 160 g., 95%, was isolated. Beautiful, white, tabular crystals were obtained on recrystallization from a 50-50 ethanol–xylene mixture.

*Anal.* Calcd. for $LiAlC_8H_{20}O_4$: Al. 12.59. Found: Al, 12.56.

Similar procedures were used to prepare the related methyl, isopropyl and *t*-butyl derivatives. In the latter case it was necessary to carry out the reaction at 80°.

The following synthesis illustrates the procedure utilizing lithium aluminum hydride.

In a 500-ml. 3-necked flask fitted with a dropping funnel, stirrer and Dry Ice condenser was placed 100 ml. of a 0.6 *M* solution of lithium aluminum hydride in ethyl ether. Isopropyl alcohol, 50 ml. (0.65 mole), was placed in the dropping funnel and added to the stirred solution. A total of 6.15 l. of hydrogen (25°, 750 mm.) was evolved, 0.24 mole, corresponding exactly to the 0.060 mole of hydride used. The ether and excess alcohol was removed by means of a filter stick, with the last traces removed under vacuum. The product, a white solid, weighed 16.0 g., a yield of 98%.

*Anal.* Calcd. for $LiAlC_{12}H_{28}O_4$: Al, 9.98; C, 53.69; H, 10.44. Found: Al, 10.00; C, 53.10; H, 10.20.

The synthesis of the methyl and ethyl derivatives proceeded similarly. In the case of the reaction with *t*-butyl alcohol, the reaction at room temperature stops after the addition of the third molar equivalent of alcohol. The reaction can be completed at elevated temperatures, as illustrated by the following synthesis.

*t*-Butyl alcohol, 100 ml., was placed in a 300-ml. 3-necked flask equipped with a water condenser and a solids-introduction vessel. The condenser was connected through a Dry Ice trap to a flowmeter. Freshly prepared lithium tri-*t*-butoxyaluminohydride, 9.47 g. (37.2 mmoles), was weighed into the solids-introduction vessel and added slowly to the refluxing alcohol. Hydrogen was evolved (36.9 mmoles) over a period of several hours. When evolution ceased, the excess alcohol was removed by distillation, the last traces being removed under vacuum at 100°. The weight of material in the flask, 21.1 g., corresponded to the theoretical yield.

The reaction product was heated to 335° at 1 mm. in a tube furnace. Over a period of several hours, a considerable portion had sublimed.

*Anal.* Calcd. for $LiAlC_{16}H_{36}O_4$: Al, 8.26; C, 58.88; H, 11.12. Found: Al, 8.24; C, 58.62; H, 10.90.

**Reaction of Lithium Aluminum Hydride with Alcohols.**—The following experiments are typical of those carried out with methyl, ethyl, isopropyl, *t*-butyl and *t*-amyl alcohol. Careful drying of all equipment and careful attention to detail was necessary to achieve reproducible, quantitative results.

The reactions were carried out in 300-ml. flasks fitted with a stirrer, pressure equilized dropping funnel and a Dry Ice condenser. Hydrogen evolved was passed through the condenser to a gas meter.

To the flask was added 205 ml. (52.5 mmoles) of a clear solution of lithium aluminum hydride in ether. *t*-Butyl alcohol, 15.6 g. (0.210 mole), was added in four equal portions (52.5 mmoles each). The solution remained clear after the addition of the first and second molar equivalents. The hydrogen evolved at each stage corresponded quantitatively to the alcohol added. The third molar equivalent of *t*-butyl alcohol resulted in the formation of a white precipitate and the evolution of a third molar equivalent of hydride. No hydrogen was evolved during the addition of the fourth mole.

A total of 156 mmoles of hydrogen was evolved (theoretical, 156.5 for the reaction

$$LiAlH_4 + 3(CH_3)_3COH \longrightarrow 3H_2 + Li[(CH_3)_3O]_3AlH)$$

The addition of methanol to the reaction mixture resulted in the immediate evolution of the fourth mole of hydrogen, 51 mmoles.

A solution of lithium tri-*t*-butoxyaluminohydride, 44 mmoles, in 50 ml. of diglyme was treated with excess *t*-butyl alcohol, 10 ml. (105 mmoles). The solution remained clear, with no hydrogen being evolved. On raising the temperature to 80°, hydrogen was slowly but steadily evolved over a period of hours, as a white precipitate formed in the solution. A total of 43.2 mmoles of hydrogen was collected.

Similarly, 100 ml. of lithium aluminum hydride (28.0 mmoles) in ether was treated with 16 g. of *t*-amyl alcohol (180 mmoles). There was obtained 85.0 mmoles of hydrogen, 76% of the total available. The addition of water to the clear ethereal solution liberated an additional 28.0 mmoles of hydrogen.

In diglyme also excess *t*-amyl alcohol failed to react with lithium tri-*t*-amyloxyaluminohydride at 25°, but at 80° the fourth equivalent of hydrogen was evolved slowly.

**Preparation of Lithium Tri-*t*-butoxyaluminohydride.**—A 2-l. flask, fitted with a stirrer, pressure-equalized dropping funnel and Dry Ice condenser, was flamed and flushed with dry nitrogen. An ether solution, 600 ml., of lithium aluminum hydride (0.32 mole) was placed in the flask and 74 g. (1.00 mole) of *t*-butyl alcohol was added dropwise to the stirred solution. A bulky white solid now filled the flask. Most of the ether was removed by decantation, with the last portions of ether and excess *t*-butyl alcohol removed under vacuum. The product weighed 81.0 g., an essentially quantitative yield.

A weighed sample of product was analyzed for active hydride by treatment with water and measurement of the hydrogen evolved. The solution was analyzed for aluminum gravimetrically with 8-hydroxyquinoline.

*Anal.* Calcd. for $LiAlHC_{12}H_{27}O_3$: Al, 10.61; $H^-$, 0.394. Found: Al, 10.58; $H^-$, 0.385.

The lithium tri-*t*-butoxyaluminohydride deposited large tabular crystals from a supersaturated solution in diglyme, but the salt could not be freed from the solvent. The compound could be sublimed at elevated temperatures, 280° at 1 mm., without appreciable decomposition.

**Preparation of Lithium Tri-*t*-amyloxyaluminohydride.**—The procedure was essentially identical with that above except that the calculated quantity of *t*-amyl alcohol, not an excess, was added to the lithium aluminum hydride in ether. Since the product is soluble in ether, the solvent was removed by distillation, the last traces being removed under vacuum.

The product, a white solid, decomposed in the range of 280–285°. It was highly soluble in tetrahydrofuran and diglyme, giving solutions which were 1.4 and 1.5 *M* in the reagent, respectively. However, the solid could not be recovered readily from these solvents; residual solvent adhered to the product even at 100° under vacuum. Only by washing the pasty material several times with anhydrous ethyl ether could a white solid product be obtained. A sample was hydrolyzed and the ratio of aluminum and active hydrogen determined: Al:H = 1.00:0.97.

**Reduction of Representative Compounds.**—The procedure utilized for examining the reducing capacity of lithium tri-*t*-butoxyaluminohydride in diglyme toward representative compounds is as follows. One molar solutions of the compounds were prepared by dissolving 0.500 mole of each compound in diglyme in a 500-ml. volumetric flask. An aliquot of the solution, 25.0 ml. (25.0 mmoles), was transferred into a flat-bottomed flask containing a magnetic stirring bar, and the flask was immersed in an ice-bath. To the flask was added 35.0 ml. of lithium tri-*t*-butoxyaluminohydride (representing approximately 31.5 mmoles of hydride), and the mixture was stirred under an atmosphere of dry nitrogen for 30 min. In another flask a blank determination was carried out by adding 35.0 ml. of the reducing agent to 25.0 ml. of diglyme, also in a flask cooled to 0°. From the difference in the hydrogen yield, the extent of the reaction was calculated. For example, hydrolysis of the reaction mixture containing benzonitrile liberated 31.2 mmoles of hydrogen, whereas the blank liberated 31.5 mmoles. Obviously, no significant reaction had occurred.

In the experiments in ether[17] the insolubility of the reagent made it necessary to prepare it *in situ* by adding the theoretical quantity of *t*-butyl alcohol to a standard solution of lithium aluminum hydride in ether. The volatility of the solvent also created difficulties in the precise measurement of the hydrogen evolved. Consequently, the experimental results for this system exhibit considerably lower precision.

The results are summarized in Table II.

**Reduction of Acid Chlorides to Aldehydes.**—The following conversion of *p*-nitrobenzoyl chloride to *p*-nitrobenzaldehyde is representative.

Dry *t*-butyl alcohol, 60 g. (0.80 mole), was added with stirring to 500 ml. of a 0.5 *M* solution of lithium aluminum hydride in ether. The white precipitate was allowed to settle, the ether decanted and the solid dissolved in 200 ml. of diglyme. The solution was added over a period of 1 hr. to 45.3 g. (0.244 mole) of *p*-nitrobenzoyl chloride (recrystallized from hexane, m.p. 74–75°) in 100 ml. of diglyme maintained at approximately −75° by a Dry Ice bath. The mixture was permitted to warm to room temperature over a period of approximately 1 hr. and poured onto crushed ice. The mixture was filtered and the solid pressed dry and extracted several times with 95% ethanol. Evaporation of the solvent yielded the crude product, m.p. 103–104°, 29.4 g., a yield of 80%. After recrystallization from aqueous ethanol, the pure aldehyde was obtained in the form of light tan crystals, m.p. 104–105°, 25.4 g., a yield of 69%.

Yields realized in other cases are summarized in Table III. Yields realized in the application of this reaction to numerous other acid chlorides will be reported shortly.[15]

LAFAYETTE, INDIANA

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[17] R. F. McFarlin, M.S. Thesis, Purdue University, 1953.