

Acknowledgment.—The support afforded us by the Naval Research Laboratory in the conduct of this work is gratefully acknowledged. We are especially indebted to Dr. H. I. Schlesinger, Dr. A. E. Finholt and Dr. K. E. Wilzbach for their generous assistance and for making available to us the experience gained in their pioneering work in this field.

Summary

The reduction of aldehydes, ketones, esters,

acid chlorides and acid anhydrides to the corresponding alcohols by lithium aluminum hydride in ether solution is described. Because of the ease and convenience with which these reductions may be carried out, the technique being similar to that employed in Grignard syntheses, and because of the uniformly good yields, it is believed to be a useful synthetic process. It will be particularly valuable for the preparation of unsaturated alcohols, since double bonds are not reduced.

CHICAGO, ILLINOIS

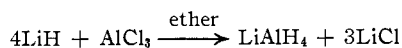
RECEIVED NOVEMBER 27, 1946

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

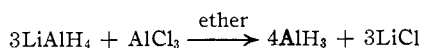
Lithium Aluminum Hydride, Aluminum Hydride and Lithium Gallium Hydride, and Some of their Applications in Organic and Inorganic Chemistry¹

BY A. E. FINHOLT, A. C. BOND, JR.,² AND H. I. SCHLESINGER

When lithium hydride is treated with an ether solution of aluminum chloride under the conditions described in the experimental part of this paper, the new ether soluble compound, lithium aluminum hydride, LiAlH_4 , is formed according to the equation



Addition of further quantities of aluminum chloride yields an ethereal solution of aluminum hydride

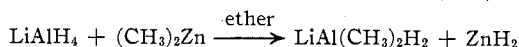
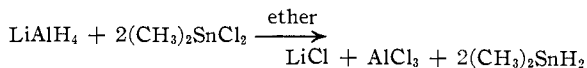
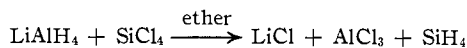


The latter solution is not stable; it soon deposits a white solid in which the atomic ratio of aluminum to hydrogen still is 3:1, but from which the ether cannot be completely removed without loss of hydrogen.³ Lithium aluminum hydride, on the other hand, may be freed from the solvent completely by evaporation of the latter under suitable conditions. Lithium gallium hydride, LiGaH_4 , has been prepared by the method used for the corresponding aluminum compound, but has not yet been studied in detail.⁴

Although we have obtained indirect evidence of the existence of sodium and of calcium aluminum hydrides, lithium aluminum hydride and lithium

gallium hydride are the only compounds containing the AlH_4 and GaH_4 groups as yet isolated.^{5a} Nevertheless, the existence of these two compounds, as well as of aluminum hydride and of digallane,⁵ demonstrates that the questions raised and widely discussed in connection with the nature of the chemical bonds in the hydrides of boron and in the borohydrides, are not problems unique to boron chemistry. These new developments have, therefore, emphasized the importance of these questions and will, we hope, aid in their solution. But the new compounds, especially lithium aluminum hydride, possess not only theoretical interest; their discovery has already led to significant applications in both inorganic and organic chemistry.

Through the use of lithium aluminum hydride, new methods, far simpler than any hitherto available, have been developed for the preparation of hydrides such as silane and stannane and of their partially alkylated derivatives. In addition, its use has led to the preparation of previously unknown hydrides such as those of zinc and of beryllium. The types of reaction by which these results have been achieved are illustrated by the equations



Reactions such as these usually proceed smoothly at room temperature, and in general give excellent yields of products of high purity.⁶

(5a) Since this paper was submitted, sodium and calcium aluminum hydrides have been prepared by us.

(5) E. Wiberg and Th. Johansen, *Die Chemie*, **55**, 38 (1924).

(6) In some, though by no means in all such reactions, lithium hydride may be used in place of lithium aluminum hydride. Even in those cases in which lithium hydride gives the desired product, the reactions are slower and the yields less satisfactory. For some purposes aluminum hydride may be advantageously employed in place of the lithium salt (see page 1202).

(1) Presented in abbreviated form before the Symposium on Hydrides and Related Compounds at the Chicago meeting of the American Chemical Society, September 10, 1946.

(2) Present address: University of Michigan, Ann Arbor, Michigan.

(3) O. Stecher and E. Wiberg, *Ber.*, **75**, 2003 (1942), have described the preparation of solid aluminum hydride by a method which does not involve the use of ether, but which is far more cumbersome than the procedure herein described. Their product was also not entirely pure.

(4) The terminology, lithium aluminum hydride and lithium gallium hydride, is not entirely consistent with the name "borohydride" used by Schlesinger and his collaborators for the corresponding boron compounds. Since the latter term is also not entirely satisfactory, and the terminology would not be very euphonious for the aluminum and gallium compounds, we have tentatively decided on the nomenclature herein employed.

Detailed description of the reactions illustrated by the preceding equations, as well as of others dealing with the preparation of hydrogen compounds of elements of the second, fourth and fifth groups of the periodic system, is reserved for forthcoming papers. In the experimental part of this paper, examples of the manner in which the reactions are carried out are chosen from cases involving elements of the third group.

In the field of organic chemistry, lithium aluminum hydride has already proved extraordinarily useful as a reducing agent. One mole of carbon dioxide is quantitatively absorbed at room temperature by an ethereal solution containing two moles of the new compound; among the products of the reaction are lithium and aluminum salts which yield formaldehyde when they are treated with acids, but the course of the reaction has not yet been completely elucidated. Aldehydes, ketones, acid chlorides and esters are reduced to alcohols, nitriles to amines, aromatic nitro compounds to azo compounds. In many cases in which the customary reducing agents require high temperatures or pressures and give poor yields, the new reagent reacts at room temperature and at an easily regulated, convenient rate, and gives almost quantitative yields. Its action is often highly specific. In the reduction of the nitriles so far studied by us, only primary amines were produced. Its usefulness is enhanced by the fact that olefinic double bonds are not attacked, except in special cases, and it is thus possible to accomplish the selective reduction of various functional groups in unsaturated compounds. These reactions have been studied by us only in preliminary fashion on a small scale. They are being investigated by R. Nystrom and W. G. Brown to whose paper we refer the reader for details.⁷

It is of interest to compare the properties of lithium aluminum hydride with those of lithium borohydride. Both compounds are white solids, stable in air at room temperature. Thermal decomposition of lithium borohydride becomes appreciable at from 250 to 275°, and seems to involve an intermediate reversible step in which a compound LiBH_2 is formed.⁸ The decomposition of the aluminum compound becomes noticeable at a considerably lower temperature (125 to 150°), and leads directly to the formation of aluminum, hydrogen and lithium hydride. Both compounds are soluble in diethyl ether; but the solubility of the aluminum compound is from seven to eight times as great as that of the borohydride. The former reacts completely and extremely rapidly when dropped into water; the reaction of the latter is slower and less nearly complete.⁹ Similar differences are observed in the reactions of the two

compounds toward alcohols. Finally, lithium borohydride is inert toward liquid ammonia and toward amines, whereas the aluminum compound reacts with both as described in the experimental part. Insofar as conclusions about relative polarity may be drawn from chemical behavior, lithium aluminum hydride thus seems to be somewhat less polar than lithium borohydride, but much more polar than the borohydrides of aluminum or of beryllium.⁸

The chemical properties of aluminum hydride are similar to those of lithium aluminum hydride, although the instability of the ether solution of the former limits its usefulness. Attention is here called to the possibility that the unstable ether solution of the compound may afford a means of following by molecular weight determinations the course of the polymerization assumed to be responsible for the stable, insoluble solid form of the substance.^{3,10}

Experimental Part

The Preparation of Lithium Aluminum Hydride. A. Reagents.—Unless the lithium hydride is finer than 100 mesh, its reaction with aluminum chloride occurs very slowly. After weeks of refluxing 20 to 60 mesh hydride with a diethyl ether solution of aluminum chloride, only a slight surface reaction had occurred. The relatively coarse "crystalline lump" hydride, which seems to be the only form now commercially available,¹¹ must be ground before use. The grinding and sifting of the material should be carried out in an atmosphere of dry nitrogen. We have used samples of purity varying from 87 to 94% without significant differences in the results. *The quantities of lithium hydride are stated in the description of the preparative procedures in terms of pure compound.* The aluminum chloride was anhydrous and of reagent quality. Anhydrous diethyl ether of the usual commercial grade proved satisfactory.

B. Apparatus.—Most of the reactions were carried out in three-necked flasks fitted with a mercury-sealed stirrer, a reflux condenser, and a dropping funnel, such as are used for Grignard reactions. Usually an atmosphere of dry, carbon dioxide-free nitrogen was employed both during the reaction and in the filtrations, but these precautions were found not to be absolutely essential. When the reactions were carried out in an evacuated system, the type of apparatus first described by Stock¹² was employed.

C. Procedure.—In a typical preparation, an excess of lithium hydride (23.5 g. or 2.96 moles) was added to a solution of 3.05 g. (0.08 mole) of lithium aluminum hydride in 30 cc. of diethyl ether, and the mixture was stirred for a short time. After the addition of a further quantity of ether (200 cc.), a solution of 71.2 g. (0.534 mole) of aluminum chloride in 300 cc. of ether was introduced at such a rate that boiling of the liquid in the reaction vessel was continuous. The mixture was stirred during this step, and for a short time after the reaction had apparently ceased. The precipitated lithium chloride and the excess of lithium hydride were separated from the solution by passing the latter through a coarse sintered glass disk under nitrogen pressure.

An aliquot (6.049 g.) of the 462.5 g. of combined filtrate and washings was evaporated at atmospheric pressure until a thick sirup had formed. The last of the ether was then removed *in vacuo* at 70°. The resulting solid weighed 0.280 g. and consisted of lithium aluminum hydride of 95.4% purity according to an analysis carried out

(7) R. Nystrom and W. G. Brown, *THIS JOURNAL*, **69**, 1197 (1947).

(8) H. I. Schlesinger and H. C. Brown, *THIS JOURNAL*, **62**, 3434 (1940).

(9) It is to be noted, however, that lithium aluminum hydride may be safely handled, even in very humid air, probably because of the formation of a protective coating of aluminum hydroxide.

(10) H. C. Longuet-Higgins, *J. Chem. Soc.*, 139 (1946).

(11) Maywood Chemical Works, Maywood, N. J.

(12) "Hydrides of Boron and of Silicon," Cornell University Press, Ithaca, N. Y., 1933.

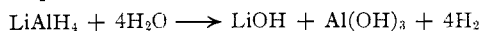
as described later. The quantity of the compound contained in the original solution was, therefore, 20.42 g., of which 3.05 g. had been contained in the original reaction mixture. The net yield thus was 17.37 g. (0.458 mole) or 85.7% of the theoretical. It has been found that allowing the reaction to stand for a longer time before filtration improves the yield and increases the purity of the product (it may become as high as 99% without recrystallization). The bulk of the reaction product was usually not taken to dryness, since most of the reactions to be investigated were carried out in ethereal solutions. For determination of the concentrations of the solutions, measurement of the amount of hydrogen evolved by hydrolysis of an aliquot is adequate.

The addition of the small amount of previously prepared lithium aluminum hydride to the reaction mixture prevents a phenomenon which otherwise may be very troublesome. Without this addition, an initial reaction usually manifests itself by a slight rise in temperature, but soon either ceases entirely or becomes too slow to be appreciable. After an induction period, which may last for only a few minutes or may persist for hours, the reaction again sets in, this time with such vigor that it can usually not be controlled by cooling of the mixture. In the presence of a small initial quantity of lithium aluminum hydride, the reaction sets in at once at a rate controlled by the rate of addition of aluminum chloride. To obtain lithium aluminum hydride for this purpose when none is available from previous preparations, two procedures are illustrated by the following examples:

1. A small quantity of aluminum chloride (2.7 g.) was mixed with a 6-fold excess of lithium hydride (4 g.) under dry nitrogen in a small round bottom flask, which was then attached through a standard ground glass joint to a vacuum system, and evacuated. About 15 cc. of ether was condensed on the reaction mixture at liquid nitrogen temperature. The reaction, which began as the flask was warmed slowly, was allowed to proceed vigorously, but was kept under control by cooling the flask with liquid nitrogen from time to time. The reaction was usually completed in about five minutes. Filtration of the resulting mixture and removal of the solvent from the filtrate as previously described yielded a sample of lithium aluminum hydride adequate for initiation of the reaction of larger batches.

2. Solid lithium hydride (7.0 g.) was mixed with solid anhydrous aluminum chloride (15.96 g.) in a 500 cc. flask previously flushed with dry nitrogen. Subsequent addition of 150 cc. of dioxane caused the temperature to rise to 50°. The mixture was refluxed for one-half hour, after which it was cooled, diluted with 135 cc. of diethyl ether, and refluxed again for another three hours. The resulting mixture was filtered. The solid obtained from the filtrate by the procedure used in the preceding examples seemed to contain only about 30% of lithium aluminum hydride, but nevertheless served to initiate the desired reaction.

Analysis of Lithium Aluminum Hydride.—Analysis of the compound was achieved by its hydrolysis according to the equation

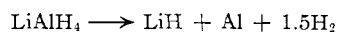


If lithium aluminum hydride is treated with any but very large amounts of water, the resulting reaction is so vigorous that the solid may become heated to incandescence with a resultant loss of hydrogen by thermal decomposition. This difficulty was avoided by mixing the sample with anhydrous dioxane, and then adding the water drop by drop. In the resulting solution, aluminum was determined as the oxide, and lithium as the sulfate. Results of a typical analysis are as follows: sample, 0.3824 g.; found: Li, 0.0691 g., Al, 0.2689 g., H₂, 884.0 cc.¹³; calcd. for LiAlH₄: Li, 0.0699 g., Al, 0.2719 g., H₂, 903.7 cc. The atomic ratios thus are represented by the formula $\text{Li}_{1.00}\text{Al}_{1.00}\text{H}_{3.86}$, and the total weights found correspond to

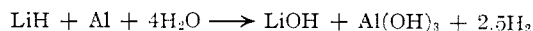
(13) Volumes of substances measured in the gaseous state are referred to standard conditions.

98.7% of the weight of the sample. The impurity probably was residual ether.

For confirmation of the analysis, pyrolysis was employed. The compound decomposes according to the equation



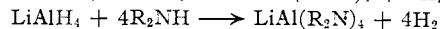
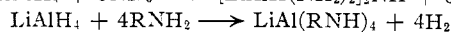
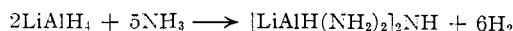
The residue gives additional hydrogen on treatment with water



Although the compound decomposes fairly rapidly at 150° the temperature of the sample was gradually raised to 220° to assure complete decomposition. The following data were obtained: sample, 0.2462 g.; hydrogen from pyrolysis 218 cc., calcd., 218 cc.; hydrogen from hydrolysis of residue 364 cc., calcd., 363 cc.

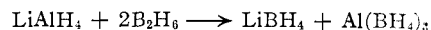
Solubility of Lithium Aluminum Hydride. Its Reactions with Amines and Ammonia.—The solubilities of lithium aluminum hydride in grams per 100 g. of various ethers at 25° are as follows: diethyl ether, 25–30, tetrahydrofuran 13, dibutyl ether 2, dioxane 0.1. Because of the difficulty of handling the extremely viscous solutions obtained in the first two of these solvents, the data are of only approximate character.

Ammonia and primary and secondary amines, some of which are excellent solvents for borohydrides, react with lithium aluminum hydride to give a quantity of hydrogen which is from 93 to 99% of that calculated according to equations



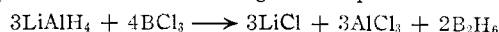
Since the postulated equations need further verification by analysis of the solid products, details concerning the reactions are not recorded herein; it is evident, however, that they result in the formation of hitherto unknown types of compounds.

Reaction of Lithium Aluminum Hydride with Diborane.—An excess of diborane was continuously circulated over 0.955 g. (25.2 mmoles.) of lithium aluminum hydride in a vacuum system which contained a U-tube maintained at –80° to remove the aluminum borohydride formed by the reaction. The reaction vessel was heated at 70° for three and a quarter hours and then at 90° for three and three-quarter hours. The amount of diborane absorbed (1030 cc., or 46.0 mmoles.) and the quantity of gaseous aluminum borohydride collected (505 cc., or 22.5 mmoles.) correspond to the values calculated according to the equation



if it is assumed that the reaction had gone about 90% to completion. This assumption was corroborated by the fact that the solid product weighed 0.585 g., whereas the value calculated on the basis of the same assumption is 0.592 g.

The Reaction of Lithium Aluminum Hydride with Boron Chloride.—As an example of the preparation of inorganic hydrides through the use of lithium aluminum hydride, we have chosen its reaction with boron chloride to produce diborane according to the equation

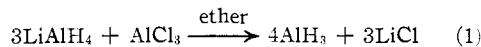


A solution of 0.277 g. (7.3 mmoles.) of lithium aluminum hydride in 5 cc. of anhydrous diethyl ether, contained in a vessel attached to a vacuum line, was frozen at liquid nitrogen temperature. An excess of tensimetrically pure boron chloride (1.279 g. or 10.91 mmoles.) was then distilled into the evacuated vessel. A vigorous reaction, probably the formation of boron chloride etherate, occurred as soon as the material had melted; after the completion of this reaction, the mixture gradually was warmed to room temperature and thoroughly stirred. The material volatile at room temperature was passed through a –112° bath; the uncondensed portion consisted of 4.83 mmoles. of pure diborane, a yield of 99.4%. The correctness of

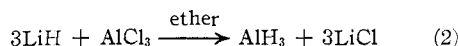
the equation was further confirmed by the addition of aluminum chloride to the residue to liberate the excess of boron trichloride from the ether. The amount of boron trichloride thus recovered showed that 9.7 mmoles., or 99% of the theoretical, had reacted.

This procedure illustrates the speed and high yields obtainable in reactions of this type. For the preparation of larger quantities, it is often desirable to moderate the initial reaction by dissolving the inorganic chloride in ether before adding it to the lithium aluminum hydride solution.

Preparation of Aluminum Hydride.—Aluminum hydride was prepared both by the reaction



and by the reaction



Although the latter seems simpler, the former is preferred, especially when lithium aluminum hydride is available, since it is more rapid and proceeds more smoothly.

Reaction (1).—A solution containing 0.546 g. (14.4 mmoles.) of lithium aluminum hydride in 9.1 g. of diethyl ether was diluted with 15 g. of additional solvent, and treated with 0.629 g. (4.72 mmoles.) of anhydrous aluminum chloride in a flask previously flushed with nitrogen.¹⁴ The lithium chloride precipitated during the course of the vigorous, but rapidly subsiding, reaction was removed by filtration, and the ether was evaporated from the filtrate through a vacuum line. The resulting white solid was slowly heated to about 96°, at which temperature heating was discontinued because slight evolution of hydrogen and discoloration of the solid were observed. The ether content of the solid products is discussed in the next section.

Analysis of the product was carried out essentially as for lithium aluminum hydride, except that aluminum was determined as the 8-hydroxyquinolate.¹⁵ The product yielded 1165 cc. (52.0 mmoles.) of hydrogen and contained 0.4693 g. (17.4 mmoles.) of aluminum, corresponding to an atomic ratio of $\text{Al}_{1.00}\text{H}_{2.99}$, and a yield of 92% based on the aluminum chloride used.

Reaction (2).—The apparatus and procedures were essentially those used for the preparation of lithium aluminum hydride. The ratio of lithium hydride (5.90 g. or 0.743 mole) to aluminum chloride (33.0 g. or 0.248 mole) was as nearly as possible that demanded by the equation, and a large total amount of ether (440 cc.) was used to avoid precipitation of aluminum hydride before the lithium chloride had been removed. A small amount (0.3 g.) of lithium aluminum hydride was added to initiate the reaction. The mixture was stirred for one hour after the addition of the aluminum chloride, and was then filtered.

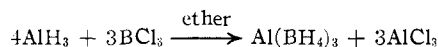
Analysis was carried out as in (1). The results showed the solution to have contained 0.621 mole of active hydrogen and 0.212 mole of aluminum, a ratio of 2.93:1 and a yield of 85%.

Composition and Solubility of "Solid Aluminum Hydride."—The composition of the solid obtained from diethyl ether solutions of aluminum hydride, either by spontaneous precipitation or by evaporation of the solvent, is variable. The ratio of hydrogen to aluminum is always 3:1 within experimental error, but the weight of these constituents is always less than the total weight of the sample. The difference in these weights was assumed to represent the ether content of the material analyzed. The longer the product is kept in a continuously evacuated vessel, and the higher the temperature at which the ether is removed, the lower is the content of the latter in the

residue. Thus a sample, obtained by spontaneous precipitation and subsequent removal of the mother liquor by several washings with ether, was evacuated at room temperature for one hour; it then had a composition corresponding to 2.26 moles of the hydride to one of ether. Another sample was evacuated at the same temperature for twenty hours, and then had an aluminum hydride-ether ratio of 3:1. When the evacuation was carried out at 80°, the ratio became 4.85:1. At still higher temperatures additional ether was removed, but decomposition of the hydride also set in. Although the data obtained by complete pyrolysis were not conclusive, and are, therefore, not included, they indicated that ether is the only impurity in the aluminum hydride, as was assumed in obtaining the preceding ratios.

In spite of the fact that spontaneous precipitation occurs even in dilute solutions, the solids obtained by evaporation of an ether solution may again be at least partially redissolved. In one case the ether was removed from a freshly prepared solution, and the resulting solid was gradually warmed to 80°, at which temperature it was maintained for one-half hour. After stirring a 0.2-g. sample of this product with ether at room temperature, 0.1 g. was found to have dissolved in 40–50 cc. of the solvent. Evaporation of this solution produced a material of which only a part could again be dissolved. The transformation of the soluble to the insoluble form is thus a progressive change; the magnitude of the soluble fraction will depend on the temperature and other conditions according to which the solid is prepared.

Reaction of Aluminum Hydride with Boron Chloride.—Aluminum hydride, like lithium aluminum hydride, reacts with boron chloride to form diborane. Since the latter reacts further with aluminum hydride to give aluminum borohydride,³ appropriate choice of the proportions of the reagents leads, as shown by the following experiment, to the reaction



At the melting point of a mixture containing 1.350 g. (11.52 mmoles.) of boron trichloride, 0.459 g. (15.3 mmoles.) of aluminum hydride and 33 cc. of diethyl ether, a vigorous reaction occurred. Two liquid layers were first formed, but at about 0° the mixture became homogeneous.

The uncombined ether, together with traces of diborane, was removed from the reaction product, which was then treated with 1.20 g. (9.0 mmoles.) of aluminum chloride to free the aluminum borohydride from its etherate. After the mixture had been stirred for twenty minutes, the volatile material was removed by gradual heating of the reaction vessel to 70°, and was then fractionated in the vacuum system. This treatment resulted in the isolation of 9.18 cc. (0.41 mmoles.) of diborane, and 75.9 cc. (3.39 mmoles.) of pure gaseous aluminum borohydride. The yield of the latter was thus 88.3% of that demanded by the equation, and the total recovery of boron and of hydrogen was 96% of that used. Diborane was probably formed in a reaction between aluminum borohydride and traces of hydrogen chloride contained as an impurity in the aluminum chloride.

Preparation and Analysis of Lithium Gallium Hydride, LiGaH_4 .—Anhydrous gallium chloride, 0.59 g. (3.35 mmoles.), was sublimed *in vacuo* into a reaction vessel which was attached to a vacuum line, and was fitted through a ground glass joint to a bent side tube containing lithium hydride. About 5 cc. of anhydrous diethyl ether was condensed by means of liquid nitrogen into the reaction vessel, which was then slowly warmed until the chloride had dissolved. The solution was cooled to –80°, and lithium hydride was added in about 4-fold excess (0.47 g. or 59 mmoles.) by slowly tilting the side tube. After the initial, moderately vigorous reaction had subsided, the mixture was gradually warmed to room temperature, and was then filtered through a sintered glass disk. The ether was removed from the filtrate by evacuation for twenty hours at room temperature.

(14) To avoid contamination of the desired product with the lithium salt, the excess of the latter was kept at a minimum. It is essential, on the other hand, to avoid an excess of aluminum chloride, since it causes lithium chloride to dissolve in ether.

(15) Lundell and Knowles, *Bur. Standards J. Research* **3**, 92 (1929).

After hydrolysis of the resulting white solid, and measurement of the hydrogen evolved, gallium was precipitated from the solution as the 8-hydroxyquinolate. The 0.2250 g. of product yielded 233.4 cc. (10.42 mmoles.) of hydrogen and contained 0.178 g. (2.56 mmoles.) of gallium. These data correspond to an atomic ratio of 4.07:1.00, a purity of 93% and a yield of 76%. The low yield was probably due in large part to incomplete washing of the lithium chloride, and the low purity to inadequate removal of ether from the product. The fact that the compound turns gray; *i. e.*, begins to decompose in a comparatively short time even at room temperature, necessitated the defects in procedure. Complete pyrolysis of the compound leads to the formation of metallic gallium and, presumably, lithium hydride and hydrogen.

Acknowledgment.—It gives us pleasure to acknowledge the cooperation of Dr. Kenneth Wilzbach, who carried out many of the reactions of lithium aluminum hydride. We desire also to acknowledge the financial support and continued interest of the Naval Research Laboratory in this investigation.

Summary

1. The preparation and some of the properties of the new compounds, lithium aluminum hydride, LiAlH_4 , and of lithium gallium hydride, LiGaH_4 , have been described. Included is a new, simple

procedure for preparing an ether solution of aluminum hydride, $(\text{AlH}_3)_x$, as well as an insoluble, probably polymerized, ether-containing solid form of the latter.

2. The interaction of lithium aluminum hydride with halides or alkyls of elements of the second, third, fourth and fifth groups of the periodic system constitutes a convenient procedure for preparing hydrogen compounds of these elements in pure form and in good yield. As a specific example, a new method for preparing diborane has been described in detail.

3. Aluminum hydride behaves in many respects like lithium aluminum hydride, except for the greater solubility of the latter in ether and the consequent greater convenience of its reactions. As an example of the usefulness of aluminum hydride, the development of a new method for preparing aluminum borohydride is described.

4. Attention is called to the usefulness of lithium aluminum hydride in the reduction of organic compounds. The smoothness of such reactions, as well as their specificity in certain cases, has been emphasized.

CHICAGO, ILLINOIS

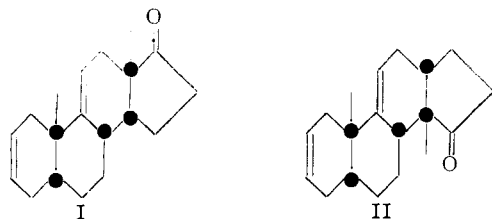
RECEIVED DECEMBER 19, 1946

[CONTRIBUTION FROM THE BUREAU OF ANIMAL INDUSTRY, AGRICULTURAL RESEARCH ADMINISTRATION, UNITED STATES DEPARTMENT OF AGRICULTURE]

The Synthesis of Condensed Ring Compounds. XVIII.¹ Dimethylsteradienones

BY ADAM M. GADDIS AND LEWIS W. BUTZ

The mixture of hydrocarbons containing 10-methyl-1-vinyl-1,7[?]-naphthitadiene which was described in the preceding paper¹ and an excess of 1-methylcyclopenten-5-one were allowed to react at 200°. The preparation and analysis of a semicarbazone showed that the products contained a ketone, $\text{C}_{19}\text{H}_{26}\text{O}$. Since the same mixture of hydrocarbons with *p*-benzoquinone at 50° gave a *D*-homosteroid,¹ it is probable that the new compound is a dimethylsteradienone, I, II, or an isomer with other positions of the $\text{C}=\text{C}$ bonds. The configurations shown are the most likely for the reasons discussed before.¹ Not enough material has been prepared for a proof of structure. The work is being reported at this stage because it has to be interrupted.



(1) For preceding paper see *THIS JOURNAL*, **69**, 1165 (1947). This work was supported by an allotment from the Special Research Fund (Bankhead-Jones Act of June 29, 1935). Not subject to copyright.

Experimental

1-Methylcyclopenten-5-one.—1-Methylcyclopentene, *b. p.* 75–79°, was prepared from cyclopentanone. To a mixture of 8.2 g. of 1-methylcyclopentene, 10.2 g. of ethyl nitrite, and 8 ml. of acetic acid, cooled in an ice-salt-bath, 9.8 ml. of concentrated hydrochloric acid was added slowly with shaking. Filtration through a cooled apparatus and washing the crystals three times with cold methanol gave 7.5 g. of nearly white 1-methylcyclopentene nitroschloride, *m. p.* 82–85°. A mixture of 9.5 g. of nitroschloride, 22 ml. of dry acetone, and 5.5 ml. of pyridine dried over barium hydroxide was warmed to about 30° to completely dissolve the nitroschloride. The solution was heated cautiously on a steam-bath, as the beginning of reaction may be violent. Separation of the solid pyridine oxime hydrochloride, $\text{C}_6\text{H}_9\text{N}\cdot\text{C}_5\text{H}_9\text{NO}\cdot\text{HCl}$, occurred in a few minutes. Cooling, filtration, and washing with small volumes of acetone gave 8.5 g., pure enough for conversion to 1-methylcyclopenten-5-one. For analysis, some of the salt was washed with ether, dissolved in methanol, and reprecipitated with ether; *m. p.* 156–159° *cor.* (dec.).

*Anal.*³ Calcd. for $\text{C}_{11}\text{H}_{16}\text{N}_2\text{OCl}$: C, 58.3; H, 6.7; N, 12.4; Cl, 15.6. Found: C, 58.5; H, 6.7; N, 12.3; Cl, 15.4. Careful concentration of the mother liquor from the salt gave 1.76 g. of 1-methylcyclopenten-5-one oxime, *m. p.* 125–127°. About 1 g. more of the oxime was obtained by removing all of the solvent and subliming the residue. Yield of oxime and salt (calcd. as oxime) was 88.2%. This is essentially the procedure used by Wallach⁴ for the decomposition of limonene nitroschloride. We

(2) By Dr. Eleanore W. J. Butz.

(3) By Arlington Laboratories, Fairfax, Virginia.

(4) Wallach, *Ann.*, **414**, 257 (1918).