considerable concentration of counter ions formed by the ionization of the solvent itself leads to η_{sp}/c *vs.* c curves (Fig. 6), which are characteristic of polyelectrolyte solutions containing small amounts of added counter ions. The addition of water to a 100% sulfuric acid solution of a polyamide results in the formation of a large concentration of counter ions since water reacts nearly completely with solvent sulfuric acid to produce oxonium ions and bisulfate ions. Even as little as 1% water by weight will yield approximately one mole per liter of bisulfate ions, which is more than sufficient to repress completely the polyelectrolyte effect. This accounts for the linear η_{sp}/c *vs.* c curves obtained for polyamide solutions in concentrated (96%) sulfuric acid. Water also represses the self-ionization of the acid to produce sulfur trioxide, and thereby reduces polymer degradation to the point where it may be disregarded (see next section).

Intrinsic Viscosities.—The intrinsic viscosity, $[\eta]$, of the poly-ϵ-caproamides in concentrated sulfuric acid and in *m*-cresol solution (see Table I) were obtained by extrapolation of linear η_{sp}/c *vs.* c (or inherent viscosity *vs.* concentration) graphs to infinite dilution (see Experimental section). The variation of log $[\eta]$ with log $\bar{M}_n$ in each solvent is shown in Fig. 7. Like graphs would be obtained using the viscosity average molecular weight since viscosity and number average molecular weight bear a simple ratio to each other.[3] The data for sulfuric acid check the previous results within the experimental error.[3] The intrinsic viscosities in *m*-cresol are somewhat higher than those observed in concentrated sulfuric acid; however, at higher molecular weights the values in the two solvents approach each other. Degradation in sulfuric acid solution is not responsible for this difference; *e.g.*, the relative viscosities of two representative polymer solutions in concentrated sulfuric acid diminished but 0.3% and 0.2%, respectively, on standing for four days.

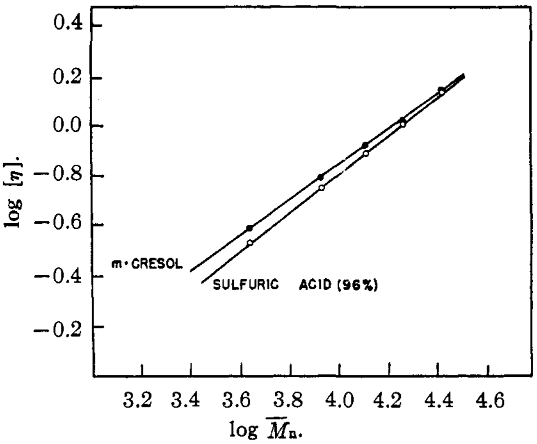

Fig. 7.—Relationships between intrinsic viscosity and number average molecular weight.

The intrinsic viscosity of the polyions in anhydrous formic acid as a function of molecular weight in comparison with tetrachain and octachain polyamides[3] is reported elsewhere.[27]

[27] J. R. Schaefgen and C. F. Trivisonno, forthcoming publication.

AKRON, OHIO RECEIVED DECEMBER 22, 1950

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

The Preparation of the Hydrides of Zinc, Cadmium, Beryllium, Magnesium and Lithium by the Use of Lithium Aluminum Hydride[1]

BY GLENN D. BARBARAS, CLYDE DILLARD, A. E. FINHOLT, THOMAS WARTIK, K. E. WILZBACH AND H. I. SCHLESINGER

The preparation of the hydrides of zinc, cadmium, beryllium and magnesium by the interaction of the corresponding metal alkyls with lithium aluminum hydride in ethyl ether solutions is reported. The use of dimethyl aluminum hydride in place of the lithium salt in some instances is also described. The zinc and cadmium hydrides were obtained in pure condition; from beryllium and magnesium hydrides not all of the solvent could be removed. Indications of the existence of alkyl metal hydrides were observed, and zinc borohydride was prepared for the first time. The new substances are described, but detailed discussion of the reactions is deferred to a later paper.

In their paper on the preparation of lithium aluminum hydride, A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger[2] mentioned that treatment of dimethylzinc with this reagent in ether solution produces zinc hydride, but they gave no details of the procedure nor of the properties of the newly discovered hydride. Investigation of the corresponding reactions of the methyl, or occasionally the ethyl, derivatives of cadmium, of mercury, of magnesium, and of beryllium has shown that in each case, except that of mercury, there is obtained a hitherto unknown hydride of a composition in accordance with the valence of the metal (*i.e.*, MH_2).[3] Lithium hydride is obtained by a similar reaction; its inclusion in this paper is, however, not as a preparative method, but as a part of the larger investigation of the reactions of lithium aluminum hydride with metal alkyls.

The new hydrides are non-volatile white powders. Zinc and cadmium hydrides have been obtained ether-free whereas the hydrides of beryllium and of magnesium retained some of the ether used

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[1] Taken from the reports submitted to the U. S. Navy during the period 1945–1948, and from a thesis submitted by Thomas Wartik to the Department of Chemistry, University of Chicago, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. A summary of the subject matter was presented at the national meeting of the American Chemical Society at San Francisco in March, 1949.

[2] A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, THIS JOURNAL, 69, 1199 (1947).

[3] Magnesium hydride has recently been prepared by E. Wiberg and R. Bauer (*Z. Naturforsch.*, 5b, 396 (1950)) by thermal decomposition of diethylmagnesium. Although their preliminary article contains no analytical data, it seems likely that their method is simpler and may give purer products than ours.

in their preparation. Cadmium hydride is very unstable, undergoing rapid decomposition at about 0°, whereas zinc hydride decomposes only very slowly at room temperature. Beryllium hydride begins to lose hydrogen at a moderate rate at 125° and magnesium hydride is still more stable. In the last two cases the onset of decomposition is obscured by interaction between the retained ether and the hydrogen. Attempts to prepare a hydride of mercury by this method led, even at −80°, to rapid production of mercury and of hydrogen.[4]

Judging from the few observations thus far made, the new hydrides are intermediate in chemical character between aluminum hydride and the hydrides of the strongly electropositive elements of groups IA and IIA. Their insolubility in ether relates them more closely to those of the latter groups; in their relatively low stability all of them, except magnesium, are more like aluminum hydride. It is worthy of mention that zinc and beryllium hydride react with diborane to give the corresponding borohydrides, $Zn(BH_4)_2$ and $Be(BH_4)_2$. The behavior of the others toward diborane was not investigated.[5]

The work herein reported is a part of a broader investigation of the behavior toward lithium aluminum hydride of alkyl derivatives of representative elements of each main group of the periodic system. In a forthcoming paper the behavior of alkyl derivatives of elements of Groups III to VIII, inclusive, will be described. Discussion of the facts herein described is, therefore, deferred to that paper in order that the subject matter may be treated as a whole.

Experimental

Apparatus.—High vacuum techniques were used *throughout*. Modifications of the standard procedures will be described in connection with the experiments which necessitated them.

Preparation and Purification of Materials.—The preparation of many of the reactants is described in some detail because their purity may greatly influence the course of the desired reactions.

Diethyl ether (Mallinckrodt absolute) was further dried by dissolving in it a small amount of lithium aluminum hydride. The ether was removed from the solution by distillation as needed.

Lithium Aluminum Hydride.—A stock solution of this substance in diethyl ether was prepared by the interaction of lithium hydride with an ethereal solution of aluminum chloride. The solution was standardized from time to time. When the solid compound was desired, the ether was removed *in vacuo* at 70°. Purity of the reagent varied from 92 to 98%.

Methyllithium was prepared by the action of the ethereal solution of methyl chloride on metallic lithium.[6] To assure a large, clean surface of the latter, a sample (0.67 g.) was cut under ether into about 150 small pieces. These, together with some of the ether, were transferred out of contact with air or moisture into a nitrogen-filled reaction vessel. After evacuation of the latter, methyl chloride and a fresh sample of ether were introduced. The mixture was stirred for two days at room temperature. The excess of methyl chloride and the ether were removed by evaporation. Fresh ether was then added to obtain a stock solution which was removed from the reaction vessel as needed by use of an all glass syringe. Analysis of the solution by standard methods disclosed a $Li:CH_3$ ratio of 1:0.98.

Dimethylzinc.—Treatment of a large excess of granulated zinc with dimethylmercury[7] in a sealed tube at 120° during 64 hours gave a quantitative yield of dimethylzinc. Its vapor tension was 124 mm. at 0°, as compared with the value, 125 mm., reported by H. W. Thompson and J. W. Linnett.[8]

Dimethylmercury was prepared by the Grignard procedure, and had a vapor tension of 50 mm. at 20.5°, a value in agreement with that reported by the authors just named.[7]

Dimethylcadmium.—Treatment of an ether suspension of cadmium iodide with an ether solution of methylmagnesium bromide gave an 81.5% yield of the desired compound. The latter, separated from ether by fractional condensation in the vacuum line and finally collected in a trap at −63°, exhibited a vapor tension of 8.5 mm. at 0°.[9]

Dimethylberyllium.—The method of H. Gilman and F. Schulze[10] was used. For experiments in which the dimethylberyllium was to react in ether solutions, the latter were obtained exactly as described by these authors. For experiments in which no solvent was employed, the solid dimethylberyllium was obtained by a slight modification of the original procedure. Most of the ether was removed from the solution by passing a stream of nitrogen over it and raising the temperature gradually to 150° as the ether evaporated; the residual ether was removed by continued evaporation of the material in the vacuum system. The solid thus obtained was finally sublimed by use of a free flame into suitable containers maintained at 0° during the process.

The ether solutions, as well as the solid samples, were analyzed by determining either the amount of methane liberated by hydrolysis or the amount of beryllium in an aliquot.

Diethylmagnesium.—A slight excess of magnesium was heated at reflux temperature for some hours with a solution of ethyl bromide in ether. The mixture was allowed to stand overnight and was then treated with about 2.5 moles of dioxane per mole of magnesium, in order to precipitate the diethylmagnesium.[11] The solid, obtained by filtration of the mixture, washing the precipitate with ether, and removing the residual solvent by heating the product at 130° *in vacuo* had a purity of 97.6% as judged by its magnesium content. All of the manipulations were carried out in an atmosphere of nitrogen or *in vacuo*.

Preparation of the Hydrides.—As is true for the preparation of the reagents used, the results in the preparation of the new hydrides may be influenced greatly by the procedures used. The latter are, therefore, described in considerable detail. All reactions were carried out in the absence of air and moisture.

Zinc Hydride.[12]—The most satisfactory method developed by us for the preparation of zinc hydride is the interaction of dimethylzinc with a diethyl ether solution of lithium aluminum hydride according to the equation

$$Zn(CH_3)_2 + 2LiAlH_4 \xrightarrow{\text{ether}} ZnH_2 + 2LiAlH_3CH_3$$

Because it was impossible to remove the ether from the ether-soluble product without decomposing the latter, we

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[4] In one experiment a white precipitate seemed to have formed before the gray color of mercury appeared. The observation could not be duplicated.

[5] E. Wiberg and R. Bauer, *Z. Naturforsch*, **5b**, 397 (1950), have recently obtained magnesium borohydride by the interaction of diborane with magnesium hydride, as well as with diethylmagnesium in the presence of diethyl ether. The article does not state whether difficulty was encountered in removing the ether, as we had found when we had used the procedure employing diethylmagnesium. We obtained our best results (about 90% purity) when benzene was used as solvent (see footnote 24 for reference). So far as can be ascertained, from Wiberg and Bauer's preliminary article, their investigation of the reaction is more exhaustive than was ours.

[6] H. Gilman, *Rec. trav. chim.*, **54**, 584 (1935).

[7] E. Frankland and B. F. Duppe, *J. Chem. Soc.*, **17**, 31 (1864).

[8] H. W. Thompson and J. W. Linnett, *Trans. Faraday Soc.*, **32**, 681 (1936).

[9] C. H. Bamford, D. I. Long and D. H. Newitt, *J. Chem. Soc.*, 468 (1946), gave an equation which leads to the value 9.8 mm., but judged by the data of L. H. Long and R. G. W. Norrish (*Trans. Roy. Soc. London*, **A241**, 596 (1949)) the sample used by the former may not have been pure.

[10] H. Gilman and F. Schulze, *J. Chem. Soc.*, 2663 (1927).

[11] W. Schlenk and W. Schlenk, Jr., *Ber.*, **62**, 920 (1929); A. C. Cope, THIS JOURNAL, **57**, 2238 (1935).

[12] Originally described briefly in F. R. 1945–1946, Contract No. 173s-10421, p. 8. The abbreviation F. R. is used for Final Reports to the Navy.

did not determine which of the possible methyl derivatives of lithium aluminum hydride was formed.[13]

A typical preparation was as follows: Dimethylzinc (136 cc., or 6 mmoles) was distilled into a solution of 0.6 g. (15.63 mmoles) of lithium aluminum hydride in 10 g. of diethyl ether. The precipitate, which formed as the mixture was warmed to room temperature, was separated from the residual liquid by filtration, and was washed with several portions of ether. The latter was removed by heating the solid to 50° *in vacuo*. The final product weighed 0.389 g., or 96% of the quantity expected according to the equation. Active hydrogen was determined by hydrolyzing the whole sample with water acidified by dilute nitric acid; zinc in the hydrolysate was determined as the 8-hydroxyquinolate.[14] The results were as shown:

Anal. Calcd. for ZnH_2: Zn, 96.99; H, 3.00. Found: Zn, 93.6; H, 2.96.

Zinc hydride of purity comparable to that just described may also be obtained by the interaction of dimethylzinc with dimethyl aluminum hydride[15] in the absence of a solvent. Products obtained in this way seemed to vary in their stability; furthermore the procedure is less convenient than the preceding one, and need, therefore, not be further described. Use of an ether solution of zinc chloride in place of dimethylzinc gave unsatisfactory results.

The reaction between dimethylzinc and lithium aluminum hydride may be carried out in the absence of ether, but under these conditions does not go to completion. It is of interest that when the volatile material, left after the reaction has apparently ceased, is evaporated and then condensed, non-volatile, solid zinc hydride is found admixed with the liquid condensate. Evidently the initial reaction, under these conditions, produces volatile intermediates, such as dimethyl aluminum hydride or methyl zinc hydride or[16] both. By subsequent reaction of such volatile products with each other (*e.g.*, of methyl zinc hydride with dimethyl aluminum hydride) non-volatile zinc hydride could have been formed. All that could be established was that the liquid portion of the condensate, when hydrolyzed, gave a volume (900 cc.) of gas, closely approaching that obtainable (932 cc.) from an equal quantity of trimethylaluminum; the latter would have resulted from the type of secondary reaction suggested.

Zinc hydride is a white, non-volatile solid not soluble in ether. Although it may be heated to 50° for a short time without appreciable color change, it usually turns gray within one or two days at room temperature, presumably as the result of slight decomposition into its constituent elements. For as yet unknown reasons, the rate of color change varies from sample to sample, as shown by the fact that the specimens prepared from dimethyl aluminum hydride turned gray more rapidly than those prepared from lithium aluminum hydride, although both were of the same degree of purity. When freshly prepared, the hydride reacts very slowly or not at all with air, but samples in which some decomposition has occurred may ignite spontaneously.

The compound reacts fairly slowly with water; to complete the hydrolysis in reasonable time dilute acid had to be added. The only other reaction studied was its behavior toward diborane, which is readily absorbed by an ether suspension of the hydride. In the course of the reaction an almost clear solution is formed. To demonstrate the formation of the new compound, **zinc borohydride**,[17] a small amount of solid was first removed by filtration from the reaction mixture, the clear solution was evaporated to dryness and the solid residue was analyzed for zinc, boron and active hydrogen. The results of the analysis of two samples prepared at different times follow.

Anal. Calcd. for $Zn(BH_4)_2$: Zn, 68.75; B, 22.76; H, 8.42. Found: Zn, 64.75, 70.10, av. 67.42; B, 23.16, 22.37, av. 22.76; H, 8.70, 8.50, av. 8.60.

The results, though not as satisfactory as desirable, leave no doubt that the product is zinc borohydride; it was probably contaminated with small quantities (1–2%) of lithium aluminum hydride.

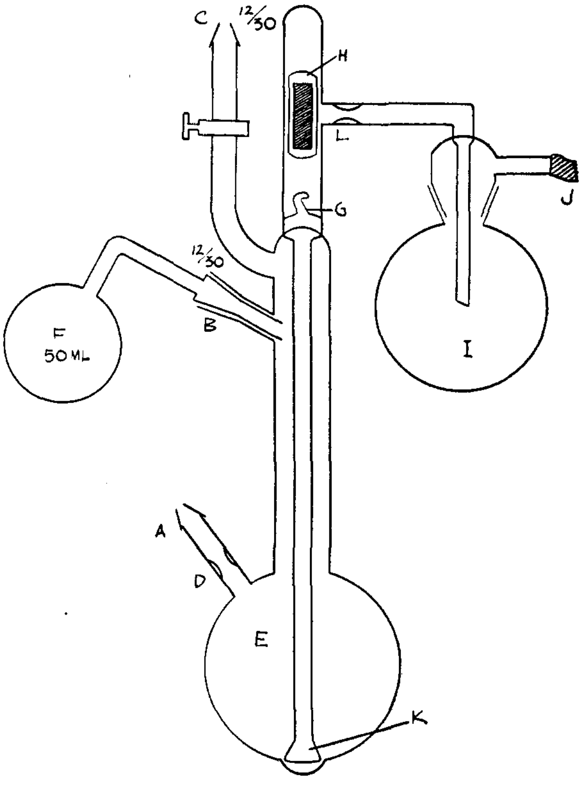

Fig. 1.—Apparatus for preparation of cadmium hydride.

Cadmium Hydride.[18]—Because of the instability of cadmium hydride, the apparatus shown in Fig. 1 was used to permit carrying out all of the operations, necessary in its preparation and identification, at −78.5°, at which temperature it gives no evidence of decomposition. The manipulation of the apparatus in the case of a typical experiment was as follows:

The apparatus, connected to the vacuum line at C, was evacuated and flamed. Dry nitrogen was then admitted, the cap at A was removed, and 25 ml. of an ether solution containing approximately 0.9 g. (24 mmoles) of lithium aluminum hydride was introduced through constriction D by means of an all glass syringe. The cap at A was replaced, bulb E was cooled in a Dry Ice–ether-bath, the system was re-evacuated, and finally sealed off at D.

A weighed quantity of dimethylcadmium (1.916 g. or 13.5 mmoles), together with 20 ml. of dry diethyl ether, was distilled into bulb F, attached directly to the vacuum line for this operation. Dry nitrogen was now admitted and, with nitrogen flowing out of the main apparatus at B, the ground joints at B were united. The contents of F were immediately cooled to −78.5°, and the system was evacuated once more.

Bulb F was now rotated in its ground joint until its contents started dripping into bulb E. A white precipitate formed immediately. Next, the glass divider G was broken with the magnetic hammer H, and dry nitrogen was admitted through C. The other end of the system was evacuated through J. This procedure forced the liquid in the reaction bulb through the sintered disc K into bulb I. When the filtration had been completed, flask I was removed and replaced by a clean vessel, after which the entire system was

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(13) Evidence for the existence of methyl derivatives of lithium aluminum hydride will be presented in a forthcoming paper.

(14) I. Mellan, "Organic Reagents in Inorganic Analysis," Blakiston Co., Philadelphia, Penna., 1941, p. 618.

(15) This compound was prepared by the interaction of trimethylaluminum with lithium aluminum hydride in a sealed tube at 70°. It is also obtained by the interaction of lithium aluminum hydride with trimethylboron. These reactions will be more fully described in a forthcoming paper. See also the reference cited in footnote 12.

(16) Evidence for the existence of such a compound is the observation that zinc hydride dissolves in ether containing a considerable excess of dimethylzinc.

(17) H. I. Schlesinger and A. B. Burg, *Chem. Revs.*, **31**, 36 (1942), mention a compound of empirical formula $ZnBH_6$, which may have been $HZnBH_4$.

(18) First reported in F. R. 1947-1948, on Contract N6ori-20, Task Order X, p. 4.

evacuated and dry ether was distilled into bulb E. The ether was allowed to remain in contact with the solid at Dry Ice temperature for one-half hour, after which time filtration was effected in the manner already described. This process was repeated once more, in order to remove as much of the ether soluble material as possible, thus isolating the cadmium hydride. After constriction L had been sealed off, the residual ether was removed by prolonged evacuation from bulb E (which was still maintained at −78.5°).

Little, if any, hydrogen was liberated while the reaction vessel was allowed to warm slowly in an air-bath, until the temperature reached 2°, at which point the entire sample suddenly decomposed. The gas evolved contained no condensable material, *i.e.*, it consisted wholly of hydrogen. It measured 298 cc. (13.3 mmoles). The metallic material remaining in the reaction flask was dissolved in nitric acid, and cadmium was precipitated from the washings as the anthranilate.[19] The dried cadmium anthranilate weighed 4.974 g., which corresponds to 12.97 mmoles of cadmium. The atomic ratio of cadmium to hydrogen in the compound was thus 0.97:2.00, and the yield, based on the recovery of hydrogen, was 98.6%, or 96.1% if based on the recovery of cadmium.

Because the solid left by the decomposition of the initial reaction product had not been weighed, the experiment just described offers no evidence that the solid consisted entirely of cadmium. In a second experiment, a weighed portion of the solid (0.2148 g.) was analyzed as described above, and was found to consist of 0.209 g. or 97.3% of cadmium. Since the solid was thus shown to be essentially pure cadmium, and the volatile material obtained by decomposition of the initial reaction product was hydrogen, free from condensable matter, the product of the main reaction must have been cadmium hydride without ether of solvation. The instability of the compound precluded more detailed study of its properties. It may be mentioned that the cadmium obtained by decomposition of the hydride is pyrophoric.

Beryllium Hydrides.[20]—Although it did not lead to an ether free product, the most satisfactory method developed by us for the preparation of beryllium hydride consists of the treatment of dimethylberyllium with lithium aluminum hydride in diethyl ether solution. In a typical experiment, a solution of 0.843 g. (21.6 mmoles) of dimethylberyllium in 15 ml. of ether was added dropwise with constant stirring to a solution of 3.77 g. (99 mmoles) of lithium aluminum hydride in 150 ml. of the solvent at room temperature in a previously evacuated vessel. A white solid was formed at once, but stirring was continued for several hours before the mixture was filtered. The solid was washed several times with fresh ether, after which treatment it was dried by evacuation of the reaction vessel.

Samples of the product thus obtained were treated with water *vapor* in the vacuum system. The resulting gas, not condensable at −196°, was collected and measured, as was done with additional gas generated when the residual solid was dissolved in dilute nitric acid. All of the gas collected was then passed over copper oxide at 900°; carbon dioxide, if formed, was separated from water in the vacuum line and measured.

The nitric acid solution was analyzed for beryllium and aluminum by the method of C. L. Parsons and S. K. Barnes.[21] Only in one or two preparations could appreciable amounts of either methyl groups (*i.e.*, carbon dioxide) or aluminum be found in the reaction products. In the cases in which these contaminants were found the atomic ratio of hydrogen to beryllium was far below that expected for beryllium hydride, facts which suggest that in these experiments the reaction had not gone to completion.

Results of analyses of two samples, each of which was free from methyl groups and from aluminum, are as follows: Be, 28.5 and 20.5 mg. (3.17 and 2.28 mmoles); H_2, 140 and 100 cc. (6.25 and 4.46 mmoles).

The ratios H:Be are thus 1.97 and 1.95, respectively. But the weights of these two constituents amount to only 34.8 and 25.1 mg., whereas the weights of the samples were 65.3 and 50.1 mg., respectively. The purity of the two samples was thus only 53.3% and 50%. However, if the contaminant is residual ether, as was made evident by the products of pyrolysis[22] of similar samples, its amounts represent only 0.13 and 0.15 mole of ether per mole of beryllium hydride.

With the objective of obtaining ether-free beryllium hydride, the reaction of dimethylberyllium with the liquid, dimethyl aluminum hydride, in the absence of solvents was studied. Although trimethylaluminum was formed in the reaction, as might be expected from an equation such as

$$2(CH_3)_2AlH + (CH_3)_2Be \longrightarrow 2Al(CH_3)_3 + BeH_2{}^{23}$$

a product free from methyl groups could not be obtained, and in many experiments aluminum was also present in the end-product. The latter difficulty seemed to be due to a tendency of dimethyl aluminum hydride to polymerize or to decompose into a non-volatile, glassy material which, though soluble in dimethyl aluminum hydride, is difficult to remove from the solid reaction products. There was some indication that the presence of methyl groups might be due to an intermediate, reversible reaction represented by the equation

$$(CH_3)_2AlH + (CH_3)_2Be \rightleftarrows CH_3BeH + Al(CH_3)_3$$

Actually, in an experiment in which an excess of dimethylberyllium was used, there was obtained a solid product which yielded 1710 cc. of methane plus hydrogen per gram by hydrolysis, and contained 36.17% of beryllium; the calculated amounts for **methyl beryllium hydride** are 1792 cc. and 36.00%, respectively. The compound was not further studied.

The assumption of a reversible intermediate step suggests the possibility that repeated removal of trimethylaluminum and repeated addition of dimethyl aluminum hydride might not only drive the intermediate reaction to completion, but might also produce pure beryllium hydride. Although this procedure led to increase in the amount of trimethylaluminum found, the solid products obtained invariably contained aluminum as well as methyl groups. The explanation may lie in the production of considerable amounts of the previously mentioned non-volatile, glassy material in the time required to carry out the procedure.

The reaction between dimethyl aluminum hydride and dimethylberyllium was also carried out in isopentane solution with no better results than those obtained in the absence of a solvent. In this connection it is of interest to mention that although dimethylberyllium is not soluble in isopentane, it goes into solution when dimethyl aluminum hydride is added. Since the desired result was not achieved in any of these experiments, the actual manipulations are not described.

Beryllium hydride, as obtained by us, is a white powder, insoluble in ether, toluene and isopentane. When heated at 75–80° for 3 hours *in vacuo*, a sample weighing 0.089 g. generated only 8.5 cc. of hydrogen, an amount so small as to suggest that it may have resulted from the presence of traces of moisture. At 125°, evolution of gas became quite rapid. The volatile material collected contained, besides hydrogen, a condensable fraction which at −112° had a vapor tension of 147 mm. It was presumably a mixture of ether and ethane, such as is usually obtained when diethyl ether containing hydrides are thermally decomposed. No appreciable difference in the temperature at which hydrogen evolution becomes definite was observed in an experiment in which the material was heated in hydrogen at 1.5 atmospheres pressure; in particular, loss of ether without accompanying decomposition did not occur.

The ether-containing compound does not react, or reacts only very slowly, with dry air at room temperature. Even with oxygen at atmospheric pressure no change in pressure was observed during four hours at room temperature. On the other hand, its reaction with water or with methanol is so vigorous, even at −196°, that the white powder is scattered through the vacuum system, and that thermal decomposition occurs, as shown by the blackening of the residual

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(19) I. Mellan, ref. 14, p. 297. A small amount of gelatinous precipitate, probably aluminum hydroxide, was noticed on neutralization of the solution. This was removed by filtration and the analysis was continued in the usual manner.

(20) Originally briefly described in F. R. 1947–1948 on Contract N6ori-20, Task Order X.

(21) As reported in J. W. Mellor and H. V. Thompson, "Treatise on Quantitative Inorganic Analysis," Griffin and Co., New York, N. Y., 2nd Edition, 1938, p. 403.

(22) Diethyl ether, ethane and ethylene, in addition to hydrogen.

(23) Polymerization of the aluminum compounds need not be considered.

solid. It is for this reason that the initial hydrolysis was effected by water vapor. The fact that acid had to be employed to complete the hydrolysis is probably due to coating of the sample with beryllium hydroxide.

Like zinc hydride, beryllium hydride reacts with diborane to produce beryllium borohydride.[24] Owing to the presence of ether, which forms a non-volatile complex with the borohydride, the quantity of volatile reaction product was less than that expected for complete reaction.

Magnesium Hydride.[25]—Although all of the procedures described in connection with the preparation of zinc hydride and beryllium hydride were investigated, the only one which led to satisfactory results was the treatment of diethylmagnesium with lithium aluminum hydride in diethyl ether solution.

Even when that procedure is used, the purity and possibly the nature of the product depend on the proportions of the reactants, the order of their addition and the concentration of the solutions. Thus, when an ether solution of diethylmagnesium is added to a large excess of an ether solution of lithium aluminum hydride, no precipitate results, and the solution remains clear, even though enough ether is evaporated to produce a saturated solution of the lithium salt. Addition of benzene (which causes neither the lithium salt nor the magnesium alkyl to precipitate) to the mixture causes the deposition of a solid which contains magnesium, aluminum and hydrogen in the atomic ratios 0.96:1.00:5.05, but which is not free from residual ether. The composition might indicate a compound of the formula $HMgAlH_4$, but the material may also be a mixture of magnesium and aluminum hydrides.

When the order of addition of the reacting solutions is reversed, a precipitate forms and then redissolves. The final solution on long standing deposits a gelatinous precipitate containing a higher percentage of aluminum than that of the material precipitated by benzene.

Only if an ether solution of lithium aluminum hydride is added to an excess of an ethereal solution of diethylmagnesium of high purity is a product of low aluminum content obtained. Thus an ether solution containing 0.296 g. (approximately 7.8 mmoles) of the lithium salt was added drop by drop with constant stirring to a solution of 2.25 g. of diethylmagnesium (approximately 27 mmoles) in 50 ml. of ether. After a short period of additional stirring, the mixture was filtered *in vacuo* and the solid was twice washed with fresh ether. The latter was then removed by evacuating the flask and gradually raising the temperature to 70°, at which level it was maintained for one hour. The product was a very fine white powder with a slightly gray tinge.

For hydrolysis of the product, as a first step in its analysis, water was carefully admitted to the reaction vessel in such a way that only its vapor came into contact with the solid hydride during the early stages of the reaction. The hydrogen evolved was separated in the vacuum line from water vapor, and from a fraction condensable at −80°. The quantity of the latter corresponded to a volume of only 22.5 cc. of gas at S.P.T. and had a vapor tension at −112° of 191 mm. Since the amount proved to be too small for effective fractionation, this fraction was considered to consist of ethane (−112° tension, 174.5 mm.) contaminated with a little ethylene (−112° tension, 455 mm.). The amount is recorded in the summary of analytical results as "ethyl groups."

In the hydrolysate, aluminum was first precipitated as the 8-hydroxyquinolate from an ammonium acetate buffered solution. The resulting filtrate was heated to 60°, made alkaline with ammonium hydroxide, and treated while hot with an excess of the quinolate. The mixture was allowed to stand for several hours to precipitate magnesium.[26]

The following analytical results are given for the product obtained in the experiment just described and in another which differed only in more thorough washing of the initial precipitate and in the treatment of the latter with a second, smaller portion of lithium aluminum hydride. Mg, 0.2555 and 0.3306 g. (10.5 and 13.6 mmoles, resp.); Al, 0.0040 and 0.0290 g. (0.15 and 1.07 mmoles, resp.); H_2, 457 and 620.5 cc.[27] (20.3 and 27.7 mmoles, resp.); ethyl groups 22.5 and 11.06 cc. (1.0 and 0.49 mmoles, resp.). In the experiments, the ratios Mg:H are 1.00:1.93 and 1.00:2.04, respectively. Per mole of magnesium hydride, the first sample contained 0.10 mole of aluminum and 0.095 mole of ethyl radical, while for the second sample the quantities were 0.08 and 0.045 mole, respectively. The sum of the weights of the magnesium, hydrogen, aluminum and ethyl radical amount to only 86% of the total weight (0.357 g.) of the first sample and 89% of the total weight (0.449 g.) of the second. The amount of ether retained is thus assumed to be 14% and 11%, respectively, or about 0.06 and 0.05 mole of ether per mole of magnesium hydride. In terms of the actual amount of magnesium hydride contained in the two products, the purity thus averaged about 75%.

The Reaction of Lithium Aluminum Hydride with Methyllithium.—Immediately upon mixing an ether solution of methyllithium with one of lithium aluminum hydride a white microcrystalline precipitate was formed. To avoid contamination of this precipitate with the solids which are produced slowly whenever either of the reagents is brought into contact with fresh glass surfaces, a special piece of apparatus shown in Fig. 2 was employed. The apparatus was evacuated through ground joint A while B was capped. After filling the apparatus with nitrogen an ethyl ether solution of lithium aluminum hydride was admitted to bulb A through its side arm by means of an all glass syringe. Contamination by air and moisture was reduced to a minimum by a continuous flow of nitrogen. In like manner, there was introduced into bulb B an ether solution of methyllithium in such an amount that the lithium aluminum hydride would be present in excess when the solutions were mixed. Both solutions were then cooled with liquid nitrogen, and the apparatus, after evacuation, was sealed at constrictions A and B.

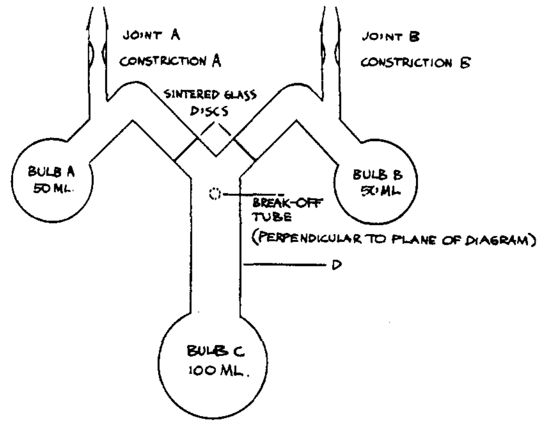

Fig. 2.—Apparatus for reaction of lithiummethyl with lithium aluminum hydride.

After standing at room temperature for 24 hours, the apparatus was tilted so as to allow the lithium aluminum hydride to flow into bulb C through the sintered disc; thereafter it was tilted in the opposite direction to admit the methyl lithium solution through the other disc. A white crystalline solid precipitated at once. The last traces of solution were washed out of bulbs A and B by causing ether vapor to condense in them, and passing the resulting solutions into bulb C.

To separate the solid reaction product from the solution, the apparatus was tilted so that the liquid flowed through the disc into bulb B when the latter was cooled with an ice-bath. The reaction product formed a cake on the disc and was washed repeatedly by condensing ether vapor in bulb C and causing the liquid to flow into B.

After completion of these operations, the apparatus was evacuated through the break-off tube, and the dried cake of reaction product was shaken down into C. The tube was

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(24) This compound has been described by A. Burg and H. I. Schlesinger, THIS JOURNAL, **62**, 3425 (1940).

(25) Originally reported in F. R. 1946–1947 on Contract NRL No. 3147, p. 8, and F. R. 1947–1948 on Contract N6ori-20, Task Order X, p. 9. The preparation of magnesium borohydride, mentioned in note 5, is found in F. R. 1944-5, p. 11, on Contracts N173s-9058 and 9820.

(26) See, for example, I. Mellan, ref. 14, pp. 242, 440. Occasionally, the tartrate procedure was used (R. Berg, *Z. anal. Chem.*, **71**, 23, 369 (1927)).

(27) Hydrolysis proceeded so rapidly that a small amount of hydrogen was lost. No correction was applied.

opened at D; the bulb was quickly introduced into the dry-box where a sample of its contents was removed for analysis.

From 0.0531 g. of the solid, hydrolysis generated 126 cc. (5.63 mmoles) of hydrogen; the lithium content proved to be 0.0382 g. (5.50 mmoles). The ratio (1/1.02) of hydrogen generated to the lithium content is thus in excellent agreement with the equation

$$LiH + H_2O \longrightarrow LiOH + H_2$$

The total quantities of hydrogen and of lithium were, however, only about 88% of those expected of 0.0531 g. of lithium hydride. The nature of the impurity was not ascertained.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

The Addition of Boron Trifluoride, Sulfur Trioxide and Sulfur Dioxide to Trimethylphosphine Oxide

BY ANTON B. BURG AND WILLIAM E. MCKEE[1]

Trimethylphosphine oxide reacts with boron trifluoride to form the vacuum-stable new compound $(CH_3)_3POBF_3$ (m.p. 149°, water-soluble, with reversible removal of BF_3 by the water). With sulfur trioxide, the less stable $(CH_3)_3POSO_3$ is formed; unlike $(C_2H_5)_3NOSO_3$ this is readily alcoholized, to form $(CH_3)_3POHOSO_3C_2H_5$ (m.p. 87°). Pressure–composition isotherms indicate a weak interaction between $(CH_3)_3PO$ and SO_2, whereas $(CH_3)_3NOSO_2$ is very firmly bonded. It appears that the oxygen atom in $(CH_3)_3PO$ is somewhat weaker as an electron donor than the oxygen atom in a trialkylamine oxide—a comparison bearing upon the question of the P–O bond order in $(CH_3)_3PO$.

Introduction

Trimethylphosphine oxide, $(CH_3)_3PO$, is formally similar to trimethylamine oxide, $(CH_3)_3NO$, which has been shown to form very stable compounds by addition to electron-acceptor substances.[2–5] Hence it is of interest to try the preparation of similar addition compounds of $(CH_3)_3PO$, in order to make a general comparison of the electron-donor powers of oxygen in these oxides. As a step toward this comparison, we have studied the behavior of BF_3, SO_3 and SO_2 with $(CH_3)_3PO$.

One might expect $(CH_3)_3PO$ to be a far weaker electron-donor than $(CH_3)_3NO$, since the latter has a strictly single-bonded oxygen atom, with a considerable negative formal charge, whereas the PO bond could have chiefly double-bond character through the use of hybridized 3d orbitals on the phosphorus atom. However, the well-known base-strengthening effect of the methyl group would tend to induce electron density toward oxygen, increasing the donor powers. A fuller discussion of oxygen in such situations appears elsewhere.[6] The present results indicate that $(CH_3)_3PO$ is a fairly strong electron donor, but evidently weaker than $(CH_3)_3NO$.

Experimental Part

Preparation of $(CH_3)_3PO$.—The method of Pickard and Kenyon[7] was modified for convenience: a solution of 0.167 mole of $POCl_3$ in 200 ml. of ether was added slowly to 0.50 mole of CH_3MgCl in one liter of ether, well stirred and cooled by ice–salt. The ether was evaporated off and the powdery residue was treated first with water and then with 500 ml. of a hot solution of Na_2CO_3 (slightly over 1 molar), to precipitate magnesium. After filtration, the solution was evaporated to a thick sirup, with occasional removal of solid NaCl. Finally the $(CH_3)_3PO$ was extracted by hot chloroform and purified by vacuum sublimation; yield 52%, based on CH_3MgCl; m.p. 137.5–138.5°.

The Compound $(CH_3)_3POBF_3$.—The addition of BF_3 to $(CH_3)_3PO$ was done first by leading a stream of BF_3 into a solution of 272 mg. of $(CH_3)_3PO$ in 5 ml. of $CHCl_3$. Most of the precipitate was collected on a sintered glass filter-stick and weighed as 295 mg. (68% recovery). After purification by sublimation in high vacuum, it melted in the range 148–150° (reproducible after heating at 215°). Titration of boric acid, after hydrolysis in boiling water and removal of fluoride as CaF_2,[3] gave 4.87% B (calcd. 4.77). Micro-combustion[8] gave 22.60% C (calcd. 22.53) and H as 5.67% (calcd. 5.67), confirming the formula $(CH_3)_3POBF_3$.

The compound $(CH_3)_3POBF_3$ was established also by synthesis without a solvent. Two glass U-tubes were sealed together in series and a 1:4 mixture of BF_3 and N_2 was passed over a weighed sample of $(CH_3)_3PO$, contained in the U-tube nearest to the gas inlet. After 45 minutes (room temperature) the gain in the weight of the system indicated completion of the addition reaction, but for certainty the gas stream was continued at 110°, with the second U-tube serving to catch any sublimate. The weight-gain was 216.5 mg. per 292.7 mg. of $(CH_3)_3PO$, or 1.003 BF_3 per $(CH_3)_3PO$. The entire product sublimed cleanly *in vacuo* and melted at 148–150°, demonstrating a quantitative synthesis.

Behavior of $(CH_3)_3POBF_3$ **toward Water.**—Although weight-stable in the open air, $(CH_3)_3POBF_3$ dissolves in water (very slowly unless pulverized), and lowers the freezing point nearly three times as far as expected from the formula weight. Thus 94.9 mg. of this complex, in 10.5 ml. of water, lowered the f.p. by 0.31°, or 2.9 times the expected 0.106°; also, 238.2 mg. in 10.2 ml. gave a lowering of 0.66°, or 2.44 times the expected 0.271°. Such results could be understood in terms of the equation $(CH_3)_3POBF_3 + 2H_2O \rightleftarrows (CH_3)_3PO + H_3O^+ + HOBF_3^-$, the reversibility of which would explain the higher average molecular weight in the more concentrated solution. This reversibility was further indicated by an 80% recovery of $(CH_3)_3POBF_3$ (m.p. 149–150°), obtained by evaporating the solution *in vacuo* and subliming the residue *in vacuo*.

This reversal of the hydrolytic decomposition was fully confirmed by the preparation of $(CH_3)_3POBF_3$ from an aqueous solution of $(CH_3)_3PO$. A 660-mg. sample of this oxide was dissolved in 5 ml. of water and treated with 1.5 ml. of $(C_2H_5)_2OBF_3$, diluted by 3 ml. of ether. After shaking to extract the BF_3 from the ether, the volatile solvents were evaporated off *in vacuo* and the residue was sublimed at pressures below 0.1 mm. (bath temperature 140°); yield

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[1] Most of the details of this work are to be found in the M.S. thesis of William Edgar McKee, University of Southern California Libraries, 1950 (available on microfilm).

[2] A. B. Burg, THIS JOURNAL, **65**, 1692 (1943).

[3] A. B. Burg and J. H. Bickerton, *ibid.*, **67**, 2261 (1945).

[4] W. K. Godfrey, M.S. Thesis, University of Southern California Libraries, 1948.

[5] H. Z. Lecher and W. B. Hardy, THIS JOURNAL, **70**, 3789 (1948).

[6] C. M. Phillips, J. S. Hunter and L. E. Sutton, *J. Chem. Soc.*, 146 (1945).

[7] R. H. Pickard and J. Kenyon, *ibid.*, **89**, 262 (1906).

[8] This analysis was done by Dr. A. Elek, of Elek Microchemical Laboratories, Los Angeles, Calif.