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Preparation and Properties of Some Alkyllead Hydrides

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Trimethyllead hydride, triethyllead hydride, dimethyllead hydride and diethyllead hydride were prepared by reducing the corresponding chlorides with lithium aluminum hydride in dimethyl ether at −78°. The monohydrides were isolated and characterized. The decomposition of the monohydrides proceeds according to the equation $4\ R_3PbH \rightarrow 2\ H_2 + 3\ PbR_4 + Pb$ and complete decomposition at 0° requires several hours. The alkyllead hydrides react with diazoalkanes in the same manner as other Group IV hydrides. Trimethyllead hydride reacted readily with ethylene to form trimethylethyllead.

Shortly after the reducing properties of lithium aluminum hydride became known Finholt and coworkers[1] attempted to prepare organolead hydrides by reducing organolead halides with this reagent. Some unstable volatile lead compounds were prepared but these were neither isolated nor identified. Since then only a single paper concerning the preparation of an organolead hydride has appeared in the literature. This is a brief paper on the preparation of trimethyllead hydride by Duffy and Holliday.[2] They treated trimethyllead chloride with potassium borohydride in liquid ammonia and obtained a product unstable above −100° which they believe to be trimethyllead hydride.

We have investigated the preparation and properties of several additional alkyllead hydrides. We find that the lithium aluminum hydride route gives excellent results and further that the alkyllead hydrides are much more stable thermally than previously thought.

Experimental

Materials.—Lithium aluminum hydride (95%) and lithium aluminum deuteride (95.5%) from Metal Hydrides, dimethyl ether (Matheson) and anhydrous diethyl ether (Mallinckrodt) were used without purification.

Diazomethane was prepared from N-methyl-N-nitroso-*p*-toluenesulfonamide (Aldrich Chemical Co.) by a standard method.[3] Diazoethane was prepared from nitrosoethyl urethan by the method of Wilds and Meader.[4]

Both trimethyllead chloride and triethyllead chloride were prepared according to the procedure of Calingaert, *et al.*[5]

Anal. Calcd. for Me_3PbCl: Cl, 12.32. Found: Cl, 12.31, 12.34. Calcd. for Et_3PbCl: Cl, 10.14. Found: Cl, 10.69.

Dimethyllead chloride was prepared by a modification of the procedure of Grüttner and Krause,[6] and diethyllead chloride was prepared by the method of Gilman and Robinson.[7]

Anal. Calcd. for Me_2PbCl_2: Cl, 23.01. Found: Cl, 23.28, 23.69. Calcd. for Et_2PbCl_2: Cl, 21.09. Found: Cl, 20.63.

Procedures.—In general the alkyllead hydrides were prepared in this manner: About 2 grams of an organolead chloride was mixed with a slight excess of lithium aluminum hydride in a small reaction tube. This tube was then attached *via* a series of traps to the manifold of a high vacuum system and the system was evacuated. Five to ten ml. of dimethyl ether was condensed (liquid nitrogen) on top of the solid reactants and reaction was initiated by warming to −78°. Reaction is complete in a few minutes at this temperature as evidenced by dissolution of the organolead chloride and the appearance of a black color. A small amount of hydrogen is evolved.

For decomposition studies the hydride under investigation was distilled into a tube equipped with a break-off tip. After sealing the tube the material was decomposed thermally. When decomposition was complete the tube was attached to the vacuum system, opened under vacuum, and the amounts of gases produced during decomposition were determined with a gas buret-Töpler pump system similar to that described by Sanderson.[8] Identification of the gases was accomplished by mass spectrometer analysis. The amounts of lead metal and tetraalkyllead were determined by chemical analyses.

Results

Both trimethyllead hydride and triethyllead hydride were isolated in a fairly pure state. The former compound was obtained consistently in 95% yield while the latter was obtained in 20% yield. The lower yield appears to be due to greater decomposition during distillation because of the less volatile nature of the ethyl compound compared with the methyl. Neither dimethyllead hydride nor diethyllead hydride was isolated as such; however, there is considerable evidence that these compounds exist.

The melting point of trimethyllead hydride was determined by use of the Stock apparatus.[9] While the material did not melt sharply, the melting point is about −106°. At −78° trimethyllead hydride is a colorless liquid. When the material is warmed slowly at the rate of about 0.5° per minute, gas evolution starts at about −30° and even at 0° complete decomposition requires several hours. Upon exposure to the atmosphere the material will detonate.

Triethyllead hydride melts fairly sharply at −145°, and like the methyl analog it is a colorless liquid at −78°. Slow warm-up of this material did not result in gas evolution until a temperature of about −20° was reached. It is somewhat more stable thermally than trimethyllead hydride, and while the material never detonated during our experiments, we would advise that extreme caution be exercised in handling any lead hydrides.

The results of decomposition studies are summarized in Table I, from which it is seen readily that both trimethyllead hydride and triethyllead hydride decompose according to the equation

$$4R_3PbH \longrightarrow 2H_2 + 3PbR_4 + Pb$$

In several experiments with the deuterides (from lithium aluminum deuteride), it was established that D_2 and RD are formed instead of HD and

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[1] A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. I. Schlesinger, THIS JOURNAL, **69**, 2692 (1947).

[2] R. Duffy and A. K. Holliday, *Proc. Chem Soc.*, 124 (1959).

[3] T. J. DeBoer and H. J. Backer, *Org. Syntheses*, **36**, 16 (1956).

[4] A. L. Wilds and A. L. Meader, Jr., *J. Org. Chem.*, **13**, 763 (1948).

[5] G. Calingaert, F. J. Dykstra and H. Shapiro, THIS JOURNAL, **67**, 190 (1945).

[6] G. Grüttner and E. Krause, *Ber.*, **49**, 1415 (1916).

[7] H. Gilman and J. D. Robinson, THIS JOURNAL, **52**, 1975 (1930).

[8] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 72.

[9] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p. 183.

RH. The first step of decomposition appears to be the homolytic fission of the lead–hydrogen bond. Measurements on the rate of hydrogen evolution from trimethyllead hydride at 0° indicated that first order kinetics are obeyed. Half-life values of 65 and 95 minutes were obtained in the two runs made, during both of which the decomposition was followed for at least four half-life periods.

TABLE I

DECOMPOSITION PRODUCTS OF TRIALKYLLEAD HYDRIDES

Hydride	Decomposition products, mmole H_2	RH	Pb	PbR_4	Pb_2R_6
Me_3PbH	1.39	0.04	0.73	2.12	0.0
Me_3PbH	2.82	.00	1.40	4.09	.0
Et_3PbH	1.65	.20	0.90	2.82	.1
Et_3PbH	0.99	.03	.45	1.41	.0
Et_3PbH	0.85	.02	.43	1.18	.0

With triethyllead hydride the first order plot was linear for the first half-life (250 minutes), but after that the line curved downward. This was not investigated further, and the data are presented here only for comparison with the methyl compound.

Since diazoalkanes are known to react readily with derivatives of germane and stannane,[10,11] their reactions with lead hydrides were attempted. The reactions were run in a sealed tube at temperatures of −80° to room temperature using diethyl ether as solvent. Analysis was by gas chromatography. The results are shown in Table II.

TABLE II

REACTIONS OF ALKYLLEAD HYDRIDES WITH DIAZOALKANES

Hydride	Diazoalkane	Reaction products, weight % Me_4-Pb	Me_3-PbEt	Me_2-$PbEt_2$	Me-$PbEt_3$	Et_4Pb
Me_3PbH	$C_2H_4N_2$	89	11			
Me_2PbH_2	$C_2H_4N_2$	83	12	5		
Et_3PbH	CH_2N_2				31	69
Et_2PbH_2	CH_2N_2			2	1	97

The R_4Pb compounds result from the thermal decomposition of the starting hydrides. No attempt to improve yields was made after reaction was proved possible. The presence of the unsymmetrical alkyllead compounds in the product from the dialkyllead hydrides can be explained by assuming the presence of the trialkyllead hydride, formed by disproportionation. This type of disproportionation has been demonstrated for alkyl lead halides, giving trialkyllead chloride, lead chloride and alkyl chloride.[12]

Lastly we studied the reaction of ethylene with trimethyllead hydride. We found that ethylene adds in diglyme at 0° and 500 p.s.i.g. to give trimethylethyllead in 92% yield. Identification was by gas chromatography.

Discussion

Our results show that derivatives of plumbane are less stable than derivatives of other Group IV hydrides. The reaction with ethylene indicates that derivatives of plumbane are more reactive toward olefins than stannanes.[13] This is a continuation of the trend that reactivity of Group IV hydrides toward olefins increases as one goes from silicon to lead.

The stability of trimethyllead hydride and the mode of decomposition as determined in this work do not agree entirely with the results reported by Duffy and Holliday.[2] In attempting to repeat this preparation of trimethyllead hydride, we were able to obtain a material which was apparently a volatile lead hydride. This material decomposed to form a red liquid as reported by Duffy and Holliday. However, with material prepared by our method we found no evidence of such a decomposition product. The stability, as reported above, is much greater than that of the material prepared by the previous investigators. We found the lithium aluminum hydride route to be more convenient and less complicated.

The reactivity of the lead–hydrogen bonds with olefins has provided a means of preparing many unique alkyllead compounds.

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