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A Comprehensive Treatment of the Chemistry of the Aliphatic Lead Derivatives

William J. Klug

College of William & Mary - Arts & Sciences

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A COMPREHENSIVE TREATMENT OF THE CHEMISTRY
OF
THE ALIPHATIC LEAD DERIVATIVES

by

William J. Klug, Jr.

SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS
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1932

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INTRODUCTION

The attention of scientists has been brought to the organic lead compounds principally by the discovery of T. Midgley, Jr. and T. A. Boyd (1) that the presence of a small amount of lead tetra-ethyl in gasoline depressed the rate of explosion of the gasoline enough to prevent knocking in internal combustion machines using this fuel. Proper control of the combustion gives a smoother running engine and, hence, greater efficiency of operation. The production and use of this liquid in Ethyl Fluid by the Ethyl Gasoline Corporation have resulted.

The organic derivatives of lead have been studied ever since the middle of the nineteenth century. The purpose of the investigators up to the time of Boyd and Midgley, however, had been merely to produce new compounds and to study these organic compounds in which lead shows such different properties from the lead in inorganic compounds. This is due principally to its difference in valence, for lead has a valence of four in its organic compounds and of two in the majority of its inorganic compounds.

The tetra-alkyl compounds are fairly stable at ordinary

temperatures; but at higher temperatures or in strong light, they decompose slowly, probably through the dialkyl compounds, to lead. The clear liquid above the precipitate is found to be pure tetra-alkyl lead compound. The tetra-alkyl compounds are colorless, heavy liquids miscible with organic solvents in all proportions but immiscible with water.

The salts which the tetra-alkyl compounds form with acids of the general type R_4PbX , where R is any alkyl radical and X any acid radical, are white crystalline substances, soluble in acetone, benzene, and alcohol. All of these salts, especially those which contain a halogen in the acid radical, irritate the mucous membrane and excite excessive sneezing.

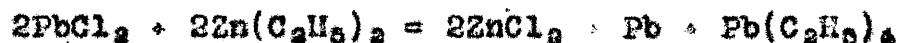
Review of the Literature

C. Lowig, (2) who did considerable work in organo-metallic compounds, was the pioneer in the field of the organic lead compounds. He reported, "I have prepared the compounds which Pb and Sn form with the ethyl group..... They are obtained by interaction of ethyl iodide and sodium alloys." This report came in 1852. A. Cahours (3), in 1853, reported an organic lead compound was formed by heating the metal lead with ethyl iodide. Lowig, who had been working since his first report, published an article (4) giving the method of preparation of an ethyl lead compound and some tri-ethyl lead salts, such as the carbonate, sulphate, and chloride.

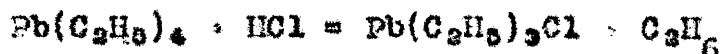
Lowig obtained the carbonate by exposing the liquid he thought to be $\text{Pb}(\text{C}_2\text{H}_5)_3$, but which was actually $\text{Pb}(\text{C}_2\text{H}_5)_4$, to air. From the carbonate, he obtained the sulphate and chloride by the action of dilute sulphuric and hydrochloric acids. He assigned the formula $\text{Pb}(\text{C}_2\text{H}_5)_3$ to the liquid he obtained from his reaction with ethyl iodide and a lead-sodium alloy; because he knew it contained only the elements Pb, C, and H, and also, he had used the ethyl radical in its synthesis. Lowig was working under great difficulties in trying to state and prove the correctness of an organic formula. His work was done long before the time of Cannizzaro, and therefore, the true values of atomic weights and the combining values of the elements were entirely uncertain. His formulae were antiquated. He used HO as the formula for water and 103 for the atomic weight of lead. These difficulties and the difficulties of obtaining a pure substance capable of giving a correct analysis were the causes of his giving the formula $\text{Pb}(\text{C}_2\text{H}_5)_3$ to the substance he had made instead of the formula $\text{Pb}(\text{C}_2\text{H}_5)_4$.

G. B. Buckton (5), in 1859, corrected Lowig's mistake in the formula of the ethyl lead compound and gave it the formula $\text{Pb}(\text{C}_2\text{H}_5)_4$. It is doubtful that his method of determining the formula was really better than Lowig's. He used a better system of atomic weights, probably, and there-

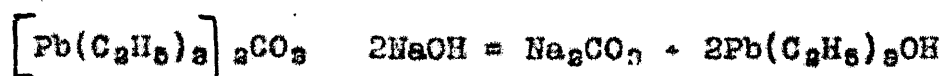
fore, arrived at the proper result. Buckton prepared lead tetra-ethyl by a new method using a double decomposition reaction between lead chloride and zinc diethyl:



Buckton also made triethyl lead salts, but he used the direct action of the acid on the lead tetra-ethyl instead of on the carbonate.



C. Klippel (6), in 1881, continued the work of forming salts. He prepared his salts by the neutralization of the hydroxide, $(\text{C}_2\text{H}_5)_3\text{PbOH}$, with both organic and inorganic acids. By this method, Klippel prepared triethyl lead formate, acetate, butyrate, benzoate, tartrate, oxalate, cyanide, and cyanate. Klippel did not obtain complete determinations for the melting points of these salts. He tried the melting point of the acetate and reported that at 100°C the compound did not melt, but that above that temperature it decomposed explosively. Klippel used Lowig's method of sodium-lead alloy and ethyl iodide to prepare the tetra-ethyl and then obtained the carbonate by exposing the liquid to air. From the carbonate, he made the hydroxide by the action of sodium hydroxide:

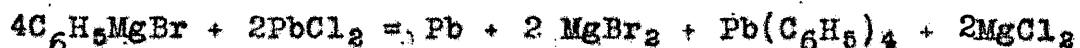


E. Frankland and A. Lawrence (7) used Buckton's method of preparing lead tetra-alkyl compounds in general. Their work was published in 1879.

A. Polis (8), in 1887-8, used Lowig's reaction with brombenzene to make lead tetra-phenyl. He added a small amount of ethyl acetate to speed up the reaction.

A. Ghira (9), in 1894, made a careful study of the mechanism of Lowig's reaction. He found that, if perfectly dry reagents were used, no reaction would take place; but if a small amount of water, alcohol, or ethyl acetate were added, the action would proceed smoothly. He proved conclusively that lead combines with four alkyl groups and, therefore, that Lowig's reaction with ethyl iodide must have given tetra-ethyl instead of triethyl lead.

A big step forward came in 1904 when P. Pfeiffer and P. Truskier (10) applied the Grignard synthesis to the organic lead field. They made tetraphenyl lead by the following:



The application of the Grignard reaction to the formation of both simple and complex tetra-alkyl and aryl compounds became quite extensive later.

J. Tafel (11), in 1907, reported still another method of synthesizing lead tetra-alkyl compounds. He found that

tetra-isopropyl lead was formed when a lead cathode was reduced electrolytically in sulphuric acid solution of acetone. He replaced first one and then two of these isopropyl groups by the action of bromine and made tri-isopropyl lead bromide and di-isopropyl dibromide. This latter compound was not only a new compound but an entirely new type, for two of the alkyl groups around the lead had never before been replaced.

G. Gruttner and E. Krause (12), in 1916, and later Krause and others (13)(14) began an extensive study of both alkyl and aryl compounds and their derivatives. They made compounds which had more than one specific alkyl or aryl radical attached to the central lead. They used Pfeiffer's method to make these compounds and extended the Grignard synthesis to the mixed compounds according to the scheme:



As many as four different radicals were introduced into the tetra-alkyl compound at one time by this method. The original objective of the investigators was to prepare lead compounds which would be optically active. This, they were unable to do, but the amount of research they turned in was tremendous.

G. Calingaert (15), impressed by the amount of work

which had been done on organic lead compounds, and being especially fitted because of his work with T. Midgley, Jr., who later made the discovery of the antiknock properties of the tetra-ethyl, wrote a complete review of the subject which was published in 1925 and covered all available information up to January first of that year. This review was entitled The Organic Compounds of Lead and was written to give a general view of the subject and inspire further research.

O. H. Browne (16) noticed that not many of the organic acid derivatives of the tetra-alkyl compounds had been made. The salts, especially of lead tetra-ethyl, which had been made were the inorganic ones, except those made by Klippel, who had made triethyl lead acetate, formate, butyrate, benzoate, tartrate, oxalate, cyanide, and cyanate. Klippel had not accurately determined the melting points of some of these salts. Browne, in 1926, set about to make the organic salts of lead tetra-ethyl and to study the reactions of the tetra-ethyl in general.

Henry Gilman and others (17)(18)(19)(20), in 1928, 29, and 30, prepared the butyl and isobutyl substitution products of lead tetraphenyl. They studied the value of these compounds for anti-knock purposes. They used the method of the Grignard synthesis, starting with lead tetraphenyl and

going through the successive stages of triphenyl chloride or diphenyl dichloride to butyl, triphenyl lead and dibutyl, diphenyl lead.

Methods of Preparation of the Tetra-alkyl Lead Compounds

Most alkyl metallic compounds are prepared directly from some alkyl metallic halide. The metallic halide is formed spontaneously. Good examples of these spontaneously formed compounds are the magnesium alkyl halides.

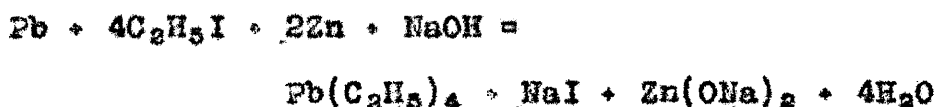
In the case of mercury, methyl mercuric iodide is made to react with either zinc dimethyl, potassium cyanide, potassium hydroxide or aluminum carbide.

There is no parallel reaction in the lead field for this method of preparation of alkyl mercury compounds. Cahours (3) reports that metallic lead reacts slightly with ethyl iodide, but that he was unable to isolate any ethyl lead iodide. Calingvert (15) explains Cahours' inability to isolate the reaction product by saying that the iodide was not actually formed, but that lead tetra-ethyl itself was formed.

From Organic Halides

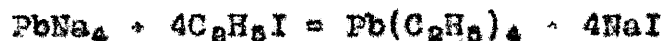
Reactions of Lead with Alkyl Halides. The General Motors Research Corporation has taken out a British patent (21) in which lead is made to react with the alkyl halide

to form the corresponding lead tetra-alkyl compound. A suitable reagent which takes up the halogen as it is set free is added to make a smooth reaction and give good yields. Powdered aluminum, zinc or silicon with concentrated sodium hydroxide solution are given as suitable reagents.



Reactions of Alkyl Halides with Lead-Sodium Alloys.

Lowig's reaction (E) may be written as follows:



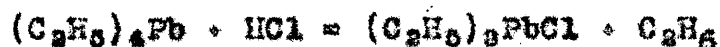
The organic halide is poured on to finely divided lead-sodium alloy contained in a flask. This reaction holds good for any alkyl halide to give the corresponding alkyl lead compound. As Chira (9) explains, a small amount of water or ethyl acetate is necessary to produce a reaction. Calingaert (15) explains this, or rather merely offers the suggestion which might explain this reaction, by saying that sodium plus water generates nascent hydrogen and that the reaction may be one of reduction. This reaction is the one used on a commercial scale for the production of the tetra-ethyl lead used for anti-knock purposes.

From Other Organo-metallic Compounds

By Grignard Synthesis. The reaction with Grignard's reagent may be summed up as follows:



This is a good method to use in the laboratory and in successive stages may easily be applied to the formation of mixed alkyl lead compounds. For example:



By Double Decomposition of Zinc diethyl and Lead

Chloride. Lead chloride and zinc diethyl are slowly mixed together. Tetraethyl lead is formed and metallic lead and zinc chloride precipitate.



Electrolytic Reduction of a Lead Cathode.

J. Tafel (11) noticed that a lead cathode used in electrolyzing acetone dissolved in dilute sulphuric acid was constantly losing weight. On studying this reaction, he found lead di- or tetra-isopropyl was formed. This is not a practical method for making lead tetra-alkyl compounds.

The above methods give all those discovered up to the present time for the formation of lead tetra-alkyl compounds. A list of these compounds which have been made, together with their boiling points under various pressures and their indices of refraction may be found in Calingaert's review in table form (15).

General Methods of the Preparation

Of the Salts of Alkyl Lead Compounds

By Direct Action of Halides on the Tetra-alkyl Lead Compound.

The mono-halides. Gruttner and Krause (12) devised the following method for preparing salts of the type PbR_3X , where X is a halogen and R any alkyl group: Ethyl acetate is cooled to a temperature below $-60^{\circ}C$ by addition of CO_2 snow. The lead tetra-alkyl compound is added and the whole mass stirred vigorously. Chlorine is passed in until free chlorine is seen. The free chlorine is detected by a change in color. After the reaction has taken place, the mixture is heated to $50^{\circ}C$ on a water bath, and the impurities removed by filtration. The ethyl acetate is then evaporated under reduced pressure and the salt crystallized out. After filtering and washing with ether, the salt remains as a pure product. This method may also be adapted to the formation of the monobromides by adding the bromine in ether solution.

The di-halides. The above method of making the mono chlorides and bromides of trialkyl lead may be slightly changed to render it usable for the formation of dichloro and dibromo dialkyl lead compounds. The procedure begins the same as described for the preparation of the monochloride. When the first alkyl group has been replaced at -60°C which is shown by the presence of free chlorine and an accompanying change in color, the temperature of the solution is allowed to rise to -10°C and is kept there by an ice-salt mixture. While the temperature is rising, chlorine is passed in with vigorous stirring. The dichloride precipitates and is washed with ethyl acetate and ether by decantation.

(12)

The aliphatic lead salts, after two alkyl groups have been replaced, are less stable than the trialkyl lead salts. They tend to break down to give inorganic lead salts. The above method is the only known method of forming these salts of the aliphatic series.

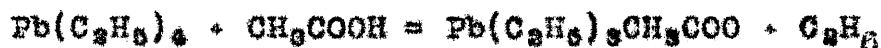
By Direct Action of Acids on the Tetra-alkyl Lead Compound.

G. Renger (22) made the bromide, chloride and the trichloracetate of tetra-ethyl lead by direct action of the acid on the tetra-ethyl lead. He used a ratio of two moles of acid to one mole of the tetra-ethyl. He represented the reaction as follows:



Since Renger used strong acids: HBr, HCl, and CCl_3COOH , he found it only necessary to prime the reaction by slight heating; and once started, the reaction continued.

Browne continued the use of the direct method of acid on lead tetra-ethyl, but he represented the reaction as one in which equimolecular quantities of acid and tetra-ethyl react and the products are the salt and ethane.



Browne (16) extended this method to the salts of the organic acids such as: propionic, butyric, and valeric acids. For these weaker acids, Browne found it necessary to heat the reaction mixture on a water bath until the evolution of ethane practically stopped. In making triethyl lead chloride, he used a temperature which never exceeded 33°C .

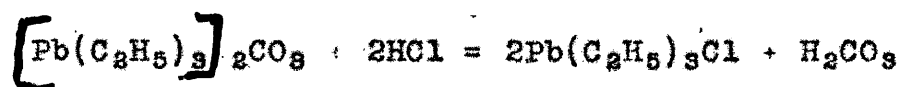
By Neutralization of the Base, PbR_2OH , with the Desired Acids.

Since salts are formed by neutralizing an acid with a base, this is the first method which would suggest itself. The hydroxide has to be made from the tetra-alkyl compound. Klippel (6) and later Browne (16) used this method of preparing triethyl lead salts. Browne found that the hydroxide took up carbon dioxide from the air very rapidly.

For this reason and also, because more steps were necessary to make the salts by the neutralization, he turned to the direct method of acid on lead tetra-ethyl to make the tri-ethyl lead salts. .

From Other Salts by Double Decomposition.

Particularly the inorganic salts of tetra-alkyl compounds are best made by a double decomposition reaction between two suitable salts. Browne used triethyl lead acetate and the sodium or potassium salts of benzoic butyric and hydrocyanic acids in water solutions and obtained triethyl lead benzoate, butyrate, and cyanide as precipitates. This method of making salts is of historical importance because Lowig obtained the first triethyl lead salts by double decomposition from tri-ethyl lead carbonate. The carbonate was obtained spontaneously by leaving lead tetra-ethyl exposed to air.



He used the inorganic acids HCl and H₂SO₄ instead of a salt as the second component of his reaction.

The Trialkyl Lead Hydroxides .

In order to make the trialkyl lead salts by the third method outlined above, it is first necessary to have the trialkyl lead hydroxide. The triethyl lead hydroxide is

a white crystalline substance soluble in organic solvents. It is a strong base, taking up carbon dioxide from the air so readily that it is difficult to keep it in solution. Browne (16) gives a modification of Buckton's method (5) for making triethyl lead hydroxide. The hydroxide may be made by heating the chloride with strong potassium or sodium hydroxide solution and the reaction product crystallized from benzene.

Toxicity of the Organic Lead Compounds

The diseases due to inorganic lead compounds are well known and have been recognized for a long time. Therefore, the treatment and control of this type of poisoning is well developed. Inorganic lead poisoning is met to a great extent in the paint industry where large amounts of lead salts are used. The disease is called "painters' colic" because of this association. The toxicology of organic lead poisoning is not so well developed; because the use of organic lead compounds in industry is only a recent advancement. In order to compare these two types of poisoning, the properties of the compounds, themselves must be considered.

The tetra-alkyl and tetra-aryl lead compounds are heavy, volatile liquids, soluble in fats and oils. Since they have these properties, they may be absorbed by the system either

through the skin by handling, through the lungs, or through the digestive system. They will diffuse rapidly throughout the body by taking advantage of their property of dissolving in fats. Although the salts are not liquids and, hence, not so volatile, nevertheless, small dust particles of the salts may easily be introduced into the respiratory system where their presence is immediately felt by irritation of the mucous membrane. The organic lead compounds continue to spread through the tissues and to keep themselves evenly distributed over the body.

The inorganic lead compounds do not diffuse through the skin and tissues since they are not soluble in fats. Hence, they do not enter the body simply by being handled. They enter the system through the lungs by accumulation of dust particles and through the digestive system. Their solubility is low and, hence, their absorption into the system is not great. These compounds are at once broken up and the lead precipitated as the phosphate and stored in the bones and liver and to a large extent expelled from the system.

Although the differences between organic lead poisoning and inorganic lead poisoning are not so great in the final analysis, these two are not to be confused, especially with regards to some of the early symptoms, treatments of the diseases, and precautions to be taken against them.

From a consideration of the inorganic and organic lead compounds, we realize that the organic compounds could be present in the system to a much greater extent than the inorganic compounds. Many of the symptoms of their poisoning, however, are common to both the organic and inorganic compounds. Calingaert (15), in his review of organic lead compounds wrote, in a section on toxicity, that only two articles (23) had been written on organic lead poisoning. He gave the symptoms held in common by the two kinds of poisoning as: pallor, anemia, stippling of the blood cells, general debility and weakness, constipation, abdominal pain, loss of appetite, and sometimes convulsions.

The symptoms observed in the case of tetra-ethyl lead poisoning, he gave as: headaches, drop of blood pressure, and drop of body temperature. T. Midgley, Jr. (24) also mentioned the symptoms of this poisoning in an article written in 1925 and entitled Tetra-ethyl Lead Poison Hazards. He said that in the order of their appearance, the symptoms were: drop of blood pressure, drop of body temperature, reduced pulse rate, sleeplessness, loss of weight, nausea, and delerium tremens.

Of the methods of treatment of organic lead poisoning, Calingaert recommended that of Dr. J. C. Aub (25)(26) of the Harvard School of Public Health. Dr. Aub reasoned that

calcium chloride in intravenous injection would favor the breaking up of the lead compounds and, also, keep a positive calcium balance which would prevent the liberation of lead from the bones. It seems probable that Dr. Aub's method would be applicable to rather advanced cases of poisoning. The method of treatment recommended by T. Midgley, Jr. consisted simply of removal of the patient from exposure to the poison. If the patient already had reached the stage where sleeplessness had developed, he was kept in the open air and given light exercise.

In October 1924, the Standard Oil Company of New Jersey lost nearly forty men who died of acute lead poisoning. This catastrophe prompted an investigation into the safety of distributing Ethyl Gasoline (ratio of one to thirteen hundred of tetra-ethyl to gasoline) to the public. The investigation was carried out by a committee of prominent medical doctors and chemists called the Surgeon Generals' Committee. The findings of this committee were published in a report in Industrial and Engineering Chemistry in 1926 (27). The committee found that, after two years of continuous use of Ethyl Gas in their cars, the drivers showed no absorption of lead. Filling station and garage employees in a similar period showed slight absorption in tests of their feces and blood, but none of them showed any symptoms

of lead poisoning. The conclusion of the Surgeon Generals' Committee was "the regulated manufacture of lead tetra-ethyl and distribution of Ethyl Gasoline are safe as far as can be told."

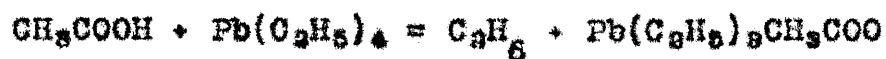
EXPERIMENTAL PART

Statement of the Problem

Calingaert (15) wrote the following equation to represent the formation of a salt by direct action of an acid on a tetra-alkyl compound:



Later, as a method of preparation of a salt, he stated: "One hundred cubic centimeters (0.5 moles) of tetra-ethyl lead are put in a beaker with one mole of the acid in concentrated aqueous solution and the two liquids are stirred vigorously." He was undoubtedly of the opinion that two molecules of the acid reacted with one molecule of the tetra-ethyl. Browne (16) used 10 grams of acid and an equivalent amount of lead tetra-ethyl. He represented the reaction as follows:



One of the objects of this investigation is to verify the method of preparation of the salts and to really find out, if possible, whether one or two molecules of the acid react with one molecule of the tetra-alkyl compound.

Calingaert (15) listed in table form all of the tetra-

alkyl lead compounds and also all of the tri-alkyl lead salts which had been prepared. While many tetra-alkyl compounds have been made with two or three different alkyl groups around the lead atom, no salts have been prepared with different alkyl groups around the lead atom. All of the salts which have been prepared so far are of the type R_3PbX such as triethyl lead acetate.

The main object of this investigation is to attempt to prepare salts of the diethyl methyl lead radical. Browne (29) was of the opinion that, if the tetra-alkyl compound triethyl methyl lead or the compound triethyl propyl lead were made to react with an acid, such as acetic acid, a salt diethyl methyl lead acetate or diethyl propyl lead acetate would be formed. He thought that the lighter group of the compound would always be replaced, but that the methyl group would be an exception to this rule.

The problem may be stated as having three parts: to verify methods of preparation of the trialkyl lead salts by settling disagreements as to the quantities of reactants used; to notice the extent to which the body would be affected while working with the poisonous compounds; and primarily, to extend the chemistry of the organic lead derivatives by preparing mixed salts, especially of the diethyl methyl lead radical.

The Methods and Materials Used

This investigation really divided itself into two closely related parts. First, certain organic salts were made by the action of the acid on lead tetra-ethyl. Their melting points were determined and compared with those found by Browne (16). The percentage of lead of each salt was found by analysis and compared with the theoretical percentage represented by the formula of the particular tri-ethyl lead salt. For each salt made and studied in this way, the corresponding salt for each acid was made by the direct action of the acid on triethyl methyl lead. The melting point and percentage of lead of each of these salts was found as before. These values were compared with the values found for the salts from the tetra-ethyl lead and the percentage of lead was also compared with the theoretical value for the formula of the diethyl methyl lead salt.

Since lead tetra-ethyl was used as a base from which to prepare the triethyl methyl lead, considerable amount of work had to be done each time a fresh quantity of triethyl methyl lead was made. The procedure was to make triethyl lead chloride and then run a Grignard reaction between the triethyl lead chloride, methyl iodide and magnesium. The liquid, triethyl methyl lead, was purified by steam distillation and vacuum distillation. It was identified by its

boiling point under reduced pressure during the vacuum distillation.

The several preparations and determinations necessary in this investigation were: preparation of triethyl lead chloride, preparation of triethyl methyl lead, preparation of salts by acid on tetra-alkyl compounds, determination of the melting points, and analysis of the salts for Pb. At one time, the supply of methyl iodide in the laboratory ran out; so it was necessary to prepare more before the Grignard reaction could be carried out in the preparation of the triethyl methyl lead.

Triethyl lead chloride. The method used to prepare triethyl lead chloride was that used by Browne (16). Although the method was not original with Browne, he modified and developed it to an exact procedure. It is quoted in full from his article,

"A 600cc beaker is placed in a water bath and provided with a stirrer. In it is placed 275cc of concentrated hydrochloric acid, to which is slowly added 75cc of lead tetra-ethyl from a dropping funnel. The temperature must not be allowed to go above 34°C. A white, butter-like mass is formed. When all of the lead compound has been added, the temperature is maintained between 30° and 33° (no higher). After some time the mass separates into grains of the size and shape of wheat. These are bunches of minute needle crystals. The evolution of ethane is quite rapid. (If the stirrer be stopped the gas will accumulate and lift the product to the surface.) When the grains begin to break up to give a powdery precipitate the reaction

is completed, although ethane will still be coming off to some extent. The chloride is filtered off, washed with water and dried on a porous plate in the dark."

Methyl iodide. The methyl iodide was generally purchased from Phipps and Bird of Richmond, Va.; but the one time that it was necessary to prepare it the directions given by Norris (29) were followed, except that four times the quantities of the reactants, and absolute instead of ordinary methyl alcohol were used.

Triethyl methyl lead. 7.74 grams of Mg and 50cc's of dry ether were placed in a reaction flask equipped with a reflux condenser and a dropping funnel. 50 grams (22cc's) of methyl iodide mixed with 30cc's of dry ether were placed in the dropping funnel. 7.74 grams of magnesium is 10% excess over 95 grams of $Pb(C_2H_5)_3Cl$. 95 grams of lead triethyl chloride was about the yield of product from the above preparation of the salt. 50 grams of methyl iodide figures out to be 10% excess over 7.74 grams of Mg. The methyl iodide was allowed to fall into the reaction flask dropwise, 25cc portions of ether were added from time to time during the reaction. When nearly all the magnesium was dissolved, the flask was heated on a water bath to complete the solution of the magnesium. If perfectly dry reagents are used, the magnesium should dissolve within two hours in a Grignard reaction. The author's experience was that the reaction

took from an hour to an hour and a half.

After all the magnesium had been dissolved, the lead triethyl chloride was added. 95 grams were used and for best results should have been dissolved in ether and added gradually with cooling through the top of the condenser. 95 grams of the salt, however, would take a great amount of ether to effect solution. In order to overcome this difficulty, it was necessary to add the triethyl lead chloride in the dry condition, a little at a time, directly into the reaction flask which was suspended in a freezing mixture of ice and salt. The chloride was stirred in vigorously, and 25cc portions of dry ether used from time to time to wash down the flask. When the chloride was completely dissolved, the Grignard intermediate compound was broken up by adding water from the wash bottle. The cooling and stirring was continued while the water was added. The entire contents of the flask was subjected to a steam distillation and the triethyl methyl lead was separated from the water and ether layers by means of a separatory funnel. The clear, colorless triethyl methyl lead was then distilled in vacuo and the boiling point under certain pressures recorded.

Trialkyl lead salts. The method-Browne (16) recommended was the method used. 11 grams of lead tetra-ethyl or lead triethyl methyl were placed in a small reaction flask along

with a unimolecular amount of the acid. In order to have a 10% excess of the tetra-alkyl compound, the amount of acid was figured on the basis of 10 grams instead of 11 grams of the tetra-alkyl compound. The reaction flask, equipped with a reflux condenser, was heated on a water bath. When the reactants were hot, a few crumbs of silica gel were added as a catalyst and the evolution of ethane began. The heating was continued until the evolution of gas died down. On cooling, the salt crystallized out in a solid mass and was recrystallized from acetone by means of an apparatus described by Browne (16) consisting of an extraction thimble, a large test tube, and a condenser. By this method, salts were made from both tetra-ethyl lead and triethyl methyl lead and the following acids: acetic, propionic, butyric, valeric, and monochloroacetic acid.

One of the phases of the problem was to find out if a unimolecular amount or a bimolecular amount of acid were necessary. The first time the above reaction was carried out a yield of over 50% of the theory figured on the acid was obtained. Since a yield of 50% figured on the acid would have been the maximum yield possible if two molecules of the acid were needed for each molecule of the tetra-alkyl compound. That is the reason the use of unimolecular amounts was continued for all salts. In order to see what the result would be if two moles of acid were used, the

reaction was carried out with twice as much acid as ordinarily used; and the liquid left after the reaction was completed was recovered by distillation. The salt was then purified as much as possible and analyzed for Pb.

Determination of Melting Points

In order to find a thermometer which would be nearly accurate, several thermometers were taken and tested in boiling water and boiling naphthalene. After a fairly accurate thermometer had been chosen, melting points were determined in a sulphuric acid bath, using an ordinary melting point tube fastened on the thermometer and a stirrer operated by lifting and dropping by hand. The temperature was raised as rapidly as was consistent with accurate reading of the thermometer.

Analysis of Salts for Pb

Calingaert (15) recommended precipitation of lead as $PbBr_2$ and weighing in a Gooch crucible. The process, however, involves cooling and the use of CCl_4 and Br_2 . Browne (16) used a method given by Treadwell and Hall (30). The salt was decomposed with nitric acid and the nitric acid replaced by sulphuric acid, directly in a small weighed crucible. The acids and organic matter were driven off by heat, and the $PbSO_4$ weighed in the crucible. Browne's method was tried

first because of its simplicity and the satisfactory results Browne obtained. Considerable care had to be taken to prevent loss both in the decomposition of the salt and the evaporation to dryness. Scott (31) gives a method for determining lead in inorganic compounds and ores. After the ore has been dissolved, the lead is precipitated as the sulphate and the $PbSO_4$ weighed in a Gooch crucible. This method was adapted to the organic lead salts and used in the following manner: From .25 to .35 of a gram of the salt was weighed on a watch glass and brushed into a 250cc beaker. The beaker was washed down with about 10cc's of water from the wash bottle. 3cc's of concentrated nitric acid and 7cc's of concentrated sulphuric acid were added and the beaker, covered with a watch glass, was heated until dense fumes of sulphur trioxide were observed. The precipitate of $PbSO_4$ was collected in a tared and oven-dried Gooch crucible, washed with 10% sulphuric acid followed by 95% ethyl alcohol, and dried in an oven at $110^{\circ}C$. The method has the distinct advantage of being "fool proof" no matter how easily or difficultly the salt decomposes. It is accurate enough to distinguish easily between organic compounds, as the results show.

Results of Experiments

Triethyl lead chloride was prepared by the method quoted above and analyzed for percentage of lead.

Yield 98 grams (77.3% of the theory).

Analysis for Pb

found%	calc'd%
62.32	62.83
62.97	

Lead triethyl methyl, prepared according to the method given, was found to boil at 68°C at a pressure of 11 mm's of mercury. Calingaert (16) gives 69°C at a pressure of 13 mm's of mercury.

Salts from the action of acids on $Pb(C_2H_5)_4$ and $Pb(C_2H_5)_3CH_3$ For comparison, the data obtained from the salts prepared from each acid have been placed together.

From Acetic Acid

$Pb(C_2H_5)_4$	11g used.	$Pb(C_2H_5)_3CH_3$	11g used.
CH_3COOH	1.92g used.	CH_3COOH	1.96g used.
$(C_2H_5)_3PbCH_2COO$	* 6.37g yield.		
(54% of the theory)			

* The 6.37g of salt was obtained after recrystallization from acetone. More care was taken to have a pure salt than to produce a large yield.

Melting point

found 161°

Browne 160.4°

Analysis for Pb

found% 58.98 calc'd%

58.54 58.64

Melting point

found 153°

Analysis for Pb

found% 58.78 calc'd%

59.15 61.06

58.84

From Propionic Acid

$Pb(C_2H_5)_4$ 11g used.

C_2H_5COOH 2.27g used.

Melting point

found 142°

Browne 141°-142°

Analysis for Pb

found% 56.26 calc'd%

56.92 56.40

$Pb(C_2H_5)_2CH_3$ 11g used.

C_2H_5COOH 2.41g used.

Melting point

found 136°

Analysis for Pb

found% 56.48 calc'd%

56.64 58.64

57.03

From Butyric Acid

$Pb(C_2H_5)_4$ 11g used.

C_3H_7COOH 2.73g used.

Melting point

found 109°

Browne 107.9°-108.5°

$Pb(C_2H_5)_2CH_3$ 11g used.

C_3H_7COOH 2.87g used.

Melting point

found 96°

Analysis for Pb

found% 54.46 calc'd%
54.43 54.32

Analysis for Pb

found% 54.32 calc'd%
55.01 56.40

From Valeric Acid

$Pb(C_2H_5)_4$ 11g used.

C_4H_9COOH 3.16g used.

Melting point

found 116°

Browne 115.6°-117°

$Pb(C_2H_5)_2CH_3$ 11g used.

C_4H_9COOH 3.3g used.

Melting point

found 98°

Analysis for Pb

found% 51.25 calc'd%
51.62 52.41

Analysis for Pb

found% 52.03 calc'd%
52.02 54.32

From Monochloroacetic Acid

$Pb(C_2H_5)_4$ 11g used.

$ClCH_2COOH$ 3g used.

Melting point

found 146.5°

Browne 146°-146.5°

$Pb(C_2H_5)CH_3$ 11g used.

$ClCH_2COOH$ 3.06g used

Melting point

found 143.0°

Analysis for Pb

found% 53.50 calc'd%
53.47 53.43

Analysis for Pb

found% 53.95 calc'd%
53.94 55.41

From a bimolecular amount of Acetic Acid

$Pb(C_2H_5)_4$ 21g used.

CH_3COOH 4g used.

Melting point

found 196°

Brown 200°

Analysis for Pb

found% 64.56, 64.62

calc'd% for $\text{Pb}(\text{CH}_3\text{COO})_2$

63.70

4.93g of a liquid was obtained by distillation which contained a large percentage of ethyl acetate.

Effects of Compounds of Health of Experimenter.

The organic lead compounds were handled for one college year of nine months. During the first semester, ten hours a week were spent in the laboratory; and during the second semester, fourteen hours a week were passed working with the compounds. Over the whole period, the body temperature of the experimenter was taken about twice a week. The temperature was always taken on awakening in the morning and invariably was 97.3°F . This temperature, although low, was normal for the experimenter. The blood pressure was never anything but normal during the whole time. The only effects on the body which could be attributed to the lead compounds were headaches which persisted only a few hours. These headaches were experienced whenever the vapors of the liquids or dust particles of the solids were inhaled to any extent. Most extensive inhalation of the vapors and dust particles took place during the steam distillation of the triethyl methyl

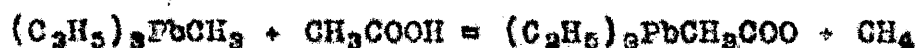
lead and the recrystallization and grinding of the salts.

Discussion and Conclusions

When triethyl lead acetate was first prepared from unimolecular amounts of acetic acid and lead tetra-ethyl, a yield of 54% was obtained. The 54% was not based on the crude salt but on a salt which had been recrystallized with the aim of producing a pure salt rather than to obtain a high yield. If two molecules of acid react with one of the tetra-ethyl, the results could not have shown more than a 50% yield. The fact that more than 50% was obtained proves conclusively that the reaction is one in which one molecule of acid reacts with one molecule of the tetra-alkyl compound. When two molecular equivalents of acetic acid were used, the lead compound was decomposed all the way to the lead acetate. Browne (16) had a similar experience in attempting to produce diethyl lead diacetate by using a bimolecular amount of acid. The melting point did not check with Browne's because the salt was not in the pure state. A suitable organic solvent could not be found from which to recrystallize.

The salts from the action of acids on lead triethyl

methyl were made with the object of making new compounds, namely, salts of the diethyl methyl lead radical. When the melting points of these salts showed different melting points from the triethyl lead salts, it was immediately supposed that the aim had been accomplished. Analysis of the salts, however, proved the salts were those of the triethyl lead radical and not of the diethyl methyl lead radical. The analyses agree well enough with the theoretical percentage of lead for the triethyl salts to prove indisputably the salts to be triethyl lead salts rather than diethyl methyl lead salts. The methyl group must have come off as methane according to the scheme:



The salts from tetra-ethyl lead and triethyl methyl lead were made under the same conditions and recrystallized in the same manner. If the reaction with the triethyl methyl lead were exactly as represented above, one would expect the melting point of the product to agree with the melting point of the salt made from the tetra-ethyl lead. The fact that these melting points did not agree suggests that the reaction did not go entirely as above but that a small amount of diethyl methyl lead salt was produced. If a small amount of the diethyl methyl lead salt were present, it would influence

the melting points considerably but its effect would not be noticeable in the analyses. If the product were a mixture of the two salts, it would be nearly impossible to remove all traces of one salt and leave a pure product because of the similarity of the two salts. Whatever the impurity was that caused the difference in melting points in every case, it was almost impossible to remove it because repeated recrystallizations and new preparations gave melting points which corresponded closely to the original.

The health of the experimenter showed that with reasonable precautions, an investigation of this type could be carried out without any real danger. However, considerable discomfort is experienced whenever there is the least slackness in precautions or the slightest accident. It is recommended that the work be not prolonged over several months unless interposed by recess periods.

SUMMARY

The literature for the entire field of aliphatic lead derivatives has been reviewed, and the chemistry of tetra-alkyl compounds and trialkyl salts has been discussed. A method of analysis for the organic lead salts has been modified and improved.

The reactions between lead tetra-ethyl and lead tri-ethyl methyl and certain organic acids have been carried out with the following conclusions:

1. The reactions are unimolecular reactions, one mole of tetra-alkyl compound reacting with one mole of acid.

2. In the case of lead tetra-ethyl, one ethyl group is replaced giving off ethane; while in the case of lead triethyl methyl, the methyl group is replaced giving off methane. Both substances give the same salts, namely, tri-ethyl lead salts.

3. With proper precautions the poisonous organic lead compounds may be handled without danger.

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BIOGRAPHY

William James Klug, Jr. was born in Glen Rock, New Jersey, March 8, 1910. He received his early education in the public schools of Ridgewood, New Jersey, and graduated from Ridgewood High School, June 1927. He entered St. John's College of Annapolis, Maryland in the fall of 1927, where he received the degree of Bachelor of Arts, June 1931. Since September 1931, he has studied at the College of William and Mary in Virginia.