

THE ORGANIC COMPOUNDS OF LEAD

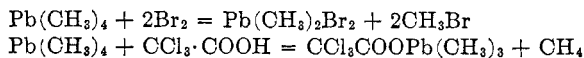
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INTRODUCTION

The chemistry of organo-metallic compounds was studied as early as the middle of the last century, but it has been developed extensively only in more recent years. Scientists have realized how much valuable data could be obtained from a study of compounds in which the metals show properties so different from those of their inorganic salts. For instance, medical science has urged the preparation of compounds in the form of which arsenic and mercury could be used for pharmaceutical purposes.

So many articles and books have been published on the subject that it is reasonable to assume that the reader is familiar with the general chemistry of organo-metallic compounds. The organic compounds of lead resemble in structure, stability and reactions those of tin and silicon. The stable valency of lead in its organic compounds is 4. The tetra alkyl compounds, such as $\text{Pb}(\text{CH}_3)_4$, are colorless heavy liquids, insoluble in water and miscible with organic solvents. They withstand temperatures up to 140°C ., and do not react with dilute acids or alkalis. The action of halogens or strong acids replaces one or two of their organic groups by acid radicals:



The new compounds so obtained, the di and tri alkyl lead salts, are white solids, crystallizable and soluble in water and in organic solvents. Their aqueous solutions give the characteristic reactions of their anions, while the organic lead radicals show properties similar, for the PbAlK_3^+ , to alkaline metals and for the PbAlK_2^{++} to the zinc ion. The aryl compounds are similar in

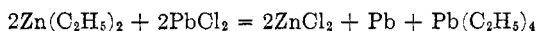
their properties to the alkyl derivatives, but are, in general, more stable and less soluble; the tetra aryl lead compounds are solids instead of liquids.

A few compounds are known corresponding to the types PbR_2 and PbR_3 or Pb_2R_6 . They are unstable and tend to revert to PbR_4 compounds under deposition of metallic lead.

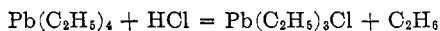
The first reference to organic lead compounds was by Löwig (1) in 1852: "I have prepared the compounds which Pb and Sn form with the ethyl group. . . . They are obtained by interaction of ethyl iodide and sodium alloys." About the same time, Cahours (2) reported that some organic lead compound is formed when metallic lead is heated with ethyl iodide. Lowig (3) then published his complete work, in which he describes the method of preparation of an ethyl lead compound and of triethyl lead salts.

His method consisted in the interaction of lead sodium alloys with ethyl iodide; the product obtained was a heavy liquid, fairly stable, and containing only the elements Pb, C and H. However, he was unable to purify it and assigned to it the formula $Pb(C_2H_5)_3$. Exposed to the air, it went over to a white crystalline compound which proved to be tri ethyl lead carbonate $[Pb(C_2H_5)_3]_2 CO_3$. From this, by the action of acids, he obtained other salts in which the triethyl lead radical acts as a monovalent metal, giving $Pb(C_2H_5)_3Cl$, $[Pb(C_2H_5)_3]_2SO_4$.

In 1859 G. B. Buckton (4) showed that alkyl lead compounds could be prepared by double decomposition between diethyl zinc and lead chloride, according to the reaction:

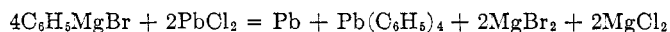


He explained that the product obtained by Löwig was probably impure $Pb(C_2H_5)_4$, and shows that this can be converted into triethyl lead salt by the action of acids:

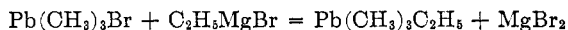


Later, Klippel (5), Frankland and Lawrence (6), Polis (7), Ghira (8) and Werner and Pfeiffer (9) studied the compounds they prepared by the lead sodium or ethyl zinc reactions.

In 1904, an important contribution was made by Pfeiffer and Truskier (10) who showed that tetraphenyl lead could be prepared from a Grignard reagent:



Another new method of preparation was contributed in 1907 by Tafel's discovery (11) that in the electrolytic reduction at a lead cathode of acetone dissolved in sulphuric acid, some di- or tetra-*isopropyl* lead is formed. By direct action of bromine on these products, he obtained tri-*isopropyl* lead bromide, and also a compound of a new type, di-*isopropyl* lead dibromide $\text{Pb}(\text{C}_3\text{H}_7)_2\text{Br}_2$. Not much attention was paid after that to organic lead compounds until 1916, when Grüttner and Krause (12) and later Krause (33) and his co-workers commenced an exhaustive study of alkyl and aryl lead compounds and their derivatives. Their main objective was, at first, to obtain optically active lead compounds, but although they do not report the separation of optically active compounds, their results extend far beyond this. They used Pfeiffer's method to prepare their compounds, and showed that tri-alkyl (or aryl) lead halides, and di-alkyl (aryl) lead di-halides could be made to react with Grignard reagents to give compounds containing different organic radicals (12).



This resulted in the systematic preparation of compounds containing 2, 3 and 4 different organic radicals, and the corresponding salts.

In 1919, Krause prepared a compound containing tri-valent lead, $\text{Pb}(\text{C}_6\text{H}_4\cdot\text{CH}_3)_3$ (13), and in 1922, a divalent organic lead compound, $\text{Pb}(\text{C}_6\text{H}_5)_2$ (14). Finally, an unsaturated alkyl lead compound was isolated by T. Midgley, Jr. (15).

This survey covers the main developments of our knowledge of the chemistry of organic lead compounds. No practical application had been found, nor perhaps thought of, for any of them until the recent discovery of T. Midgley, Jr., and T. A. Boyd, that the presence of a small amount of tetraethyl lead in

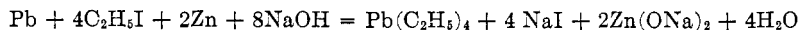
gasoline would prevent detonation in internal combustion engines (16). The preparation of this compound on a large scale has resulted, and its wide use will probably further increase the interest of chemists in the organic compounds of lead.

GENERAL METHODS OF PREPARATION

Unlike other metals, lead does not directly form compounds in which the metal is linked to organic groups and a halogen, as is the case with magnesium, for instance. Such compounds must always be formed indirectly from a compound in which all the valencies of the lead are occupied by hydrocarbon radicals. This accounts perhaps for the fact that most of the methods of preparation of organic lead compounds are different from those used with other metals.

1. *Preparation from organic halides*

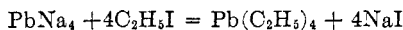
a. Reaction of metallic lead with alkyl iodides. Mention is made by Cahours (2) of the fact that metallic lead is attacked by ethyl iodide, but the amount of product is probably small, as the experimenter was unable to isolate the product, as in the case of mercury and tin. This can probably be accounted for by the fact that the product is not an alkyl lead halide, similar to CH_3HgI , for instance, but a true alkyl compound such as $\text{Pb}(\text{C}_2\text{H}_5)_4$. Indeed, when some reagent is added which will take up the halogen set free, the reaction proceeds smoothly and gives good yields. Suitable reagents for this purpose are, for instance, powdered aluminum, zinc, or silicon with concentrated sodium hydroxide solutions (17). The reaction can probably be written as follows:



Reactions of this type have apparently been studied only in the case of ethyl iodide. They would probably be much less successful with bromides or chlorides, either aliphatic or aromatic.

b. Reactions of lead sodium alloys with organic halides. This method was originated by Löwig (3) as an extension of his method

of preparation of other organo-metallic compounds. In this reaction the organic halide is merely poured onto finely divided lead sodium alloy contained in a flask equipped with a reflux condenser, and the reaction can be written:



the products obtained being tetra-alkyl or aryl lead compounds and sodium halides. Löwig and Klippel (5) used ethyl iodide with lead sodium alloys varying from 16 to 25 per cent Na. They reported a vigorous reaction, and the formation of a compound which they believed to be PbEt_3 or Pb_2Et_6 . In one instance, Löwig amalgamated his lead and sodium with a large excess of mercury. This produced a smooth reaction and gave a good yield of alkyl lead compound, but no mercury compound was formed. Polis (7) used the same reaction on brombenzene, but added a small amount of ethyl acetate to promote the reaction. No satisfactory explanation has been given, however, for the mechanism of the reaction. Ghira (8) states that, if one follows exactly the procedure given by Löwig, no reaction takes place, but that the addition of a small amount of water makes it proceed smoothly, and that, when ethyl iodide is used, the product obtained is $\text{Pb}(\text{C}_2\text{H}_5)_4$ and not $\text{Pb}(\text{C}_2\text{H}_5)_3$.

It seems established, therefore, that no reaction takes place, at least at room temperature, between pure lead sodium alloys and organic halides. The rôle played by the water or the ethyl acetate is not well understood. The remark can be made, however, that zinc plus sodium hydroxide and sodium plus water or an ester are alike in that they both are slow generators of nascent hydrogen, and the process might thus well be considered to be one of reduction.

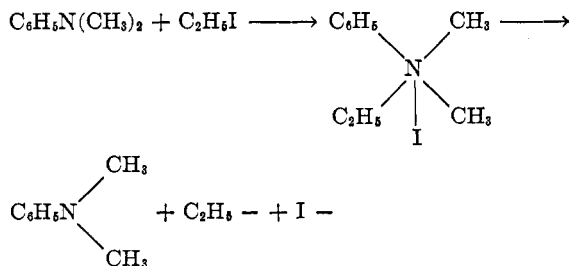
A similar method has been developed by the General Motor Research Corporation for the preparation of organic lead compounds. This method, which is equally suitable for use with alkyl and aryl bromides and chlorides as well as iodides, is used for the preparation of tetraethyl lead on a commercial scale and is somewhat as follows (17):

In a reacting vessel equipped with a suitable stirring device

and a reflux condenser, one molecule of ground lead sodium alloy, PbNa_4 , is poured into four molecules of ethyl bromide to which 0.4 mole of pyridine has been added. Water is then added slowly, under constant stirring. Some hydrogen is evolved, together with butane, the sodium is converted into sodium bromide and most of the ethyl groups go to form tetraethyl lead. Presumably, diethyl lead is formed as an intermediate product, which finally breaks down to metallic lead and tetraethyl lead. The reaction is controlled by the rate of addition of the water and the rate of cooling of the reacting mass. Much heat is evolved in the process and the temperature must be kept around the boiling point of the alkyl halide in order to avoid excessive evaporation losses.

When all the sodium is used up, as indicated by the fact that no reaction takes place on addition of water, enough water is added to render the mass fluid, and it is subjected to a steam distillation. The alkyl halide, if present in excess, distills first, and then the lead tetraethyl, the condensate being tetraethyl lead and water in the ratio 1 to 4 by volume. The product is then washed free from pyridine and filtered or settled to separate a small amount of water kept in suspension.

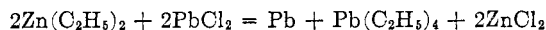
The pyridine, which can be replaced by an amine, triethylamine or dimethylaniline for instance, plays an important, though little understood, part in the mechanism of the reaction. It probably promotes the reactivity of the alkyl halide molecule by the intermediate formation of an addition compound:



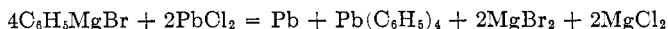
In all cases, the catalyst is recovered unchanged at the end of the reaction.

2. *Preparation by double decomposition with other organo-metallic compounds*

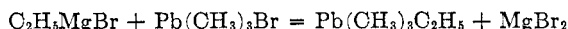
a. *From di-ethyl zinc and lead chloride.* This reaction was originated by Buckton (4) and used later on by Frankland and Lawrence (6). Lead chloride is added slowly to diethyl zinc, and tetraethyl lead is formed, while zinc chloride and metallic lead separate:



b. *From Grignard reagents.*



This reaction was first reported by Pfeiffer and Truskier (10). It presents no difficulty, gives high yields and is probably the best method to use on a laboratory scale. It also lends itself to the preparation of compounds in which the lead is linked to different groups:



Here again, however, the mechanism of the reaction is not fully understood, the equations only summing up the results.

Indeed, according to the above, one would expect the reaction to be complete without the usual hydrolysis of the Grignard complex with water. However, after long interaction, the mixture still reacts vigorously with water, and it is only after the hydrolysis that the final lead compound can be extracted. One must thus admit the formation of an intermediate addition compound, probably containing ether, and which is decomposed by water to give the final products of the reaction.

3. *Electrolytic reduction*

J. Tafel (11) in 1907 reported that a lead cathode used in electrolyzing acetone dissolved in aqueous sulphuric acid was constantly losing weight. He studied the reaction further with G. Renger (19) and found it to be caused by the formation of either di- or tetra-*isopropyl* lead. The yields are far from being quanti-

tative, either on the current or on the acetone used, as many other reduction products are formed at the same time. The method is, however, worth while mentioning, as it illustrates once more the formation of organic lead compounds by a process of reduction.

GENERAL PROPERTIES AND REACTIONS

The important general reactions of organic lead compounds have been suggested in the introduction. They will be studied here somewhat more in detail, under headings indicating the type of reagent considered.

1. *Stability*

In general, the saturated organic lead compounds are quite stable when pure and are little influenced by air, moisture, moderate heating or light. Long exposure to sunlight, however, or heating at a temperature varying with the compounds considered, results in decomposition, with separation of metallic lead.

The tetra alkyl and aryl lead compounds vary in stability with the nature of the organic radicals they contain. In the aliphatic series, the stability decreases with increasing molecular weight; also, secondary alkyl groups give the compounds a much lower stability than the corresponding primary groups. This is probably due to steric hindrance, as the presence of a tertiary carbon atom not directly bound to the lead atom has no effect on stability. Thus, tetra-methyl lead, $\text{Pb}(\text{CH}_3)_4$, is the most stable compound in the alkyl series; tetra-*n*. propyl lead is more stable than tetra-*sec*. propyl lead, whereas the difference between tetra-*n*. and tetra-*isobutyl* lead is much less marked.

In the aryl series, little difference is shown by the various compounds. This is not surprising, for the nature of the Pb-C linkage is hardly affected by further substitutions in the benzene nucleus.

In the few compounds in which the lead is not truly tetravalent, such as $\text{Pb}(\text{C}_6\text{H}_5)_3$, $\text{Pb}_2(\text{C}_2\text{H}_5)_6$, $\text{Pb}(\text{C}_6\text{H}_5)_2$, the stability is much lower. The di-lead hexa alkyl and the di-aryl lead compounds absorb oxygen and are easily decomposed by heat, the former

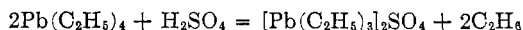
being even slowly decomposed by diffused light into metallic lead and lead tetraethyl.

The organo-plumbic salts are more stable, perhaps, than the saturated alkyl and aryl compounds. They are, in general, not hydrolyzed and some can be recrystallized and melted without decomposition. The compounds of the general type PbR_3X are more stable than the PbR_2X_2 compounds. The latter, in some cases, tend to decompose into hydrocarbons and an inorganic lead salt, as they contain all the elements of the latter with, in addition, the two organic groups.

Compounds in which three of the valencies of lead are satisfied by inorganic radicals, the fourth one alone being a Pb-C linkage, are unknown and, if formed at all, would probably break down instantaneously. This is easily understood when one keeps in mind that lead is respectively di- and tetra-valent in its stable inorganic and organic compounds. For the compounds of tetra-valent lead, the stability will thus decrease with increasing number of inorganic groups.

2. Reaction with acids

The linkage between lead and carbon is stable to dilute acids, but is broken by concentrated strong acids or by weaker acids on heating. For instance, a 1:1 by volume mixture of H_2SO_4 and H_2O does not attack tetraethyl lead at room temperature. On gentle heating the same acid will react to form tri-ethyl lead sulfate and ethane.

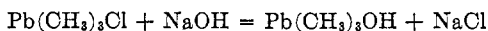


With still stronger acids, such as fuming nitric or 98 per cent sulfuric acid, all organic lead compounds are completely destroyed, the organic matter is partly or completely burnt, and the lead converted quantitatively into nitrate or sulfate.

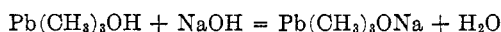
3. Reactions with alkalis

Dilute and even concentrated alkalis are without effect on tetra-alkyl or -aryl lead compounds. The organo-lead salts

react with alkalis as other salts would. The corresponding hydroxides can be obtained by double decomposition:



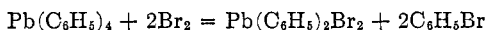
and are soluble in an excess of alkali:



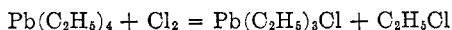
Heating of organic lead compounds with concentrated alkali at high temperatures would probably result in a breaking down of the compound, but no specific data are available on the subject.

4. Action of halogens

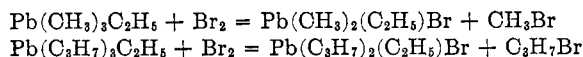
The halogens react readily with the lead compounds containing three or four organic groups. At room temperature and with an excess of halogen, they form di-substituted derivatives:



At lower temperature, it is possible to restrain the reaction to the production of mono-substituted derivatives:

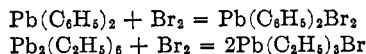


Thus, Grüttner and Krause (20) have constantly used that method to prepare the various derivatives. The action of bromine at -70°C . gives tri-alkyl lead derivatives; at -25°C . the di-substituted compounds. It is also worth mentioning that, in compounds containing different organic radicals, the halogen exerts a very decided selective action, reacting almost invariably with one of the groups of which there is the larger number. Thus:



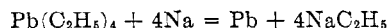
Never does the action of halogen affect another part of the molecule than the Pb-C linkage.

The unsaturated alkyl lead compounds react readily with halogens without elimination of organic halides:



5. Miscellaneous reactions

Metallic sodium reacts with alkyl lead compounds (21) according to the equation:



but the reaction is not quantitative, as when Zn or Hg compounds are used, and no pure NaC_2H_5 is obtained.

No reactions are reported between organic lead compounds and other elements.

Mercury, bismuth, thallium and arsenic halides react somewhat like halogens, converting $\text{Pb}(\text{C}_2\text{H}_5)_4$, for instance, into $\text{Pb}(\text{C}_2\text{H}_5)_3\text{Cl}$ (12) (22).

TETRA ALKYL LEAD COMPOUNDS

An extensive study of these compounds has been made by G. Grüttner, E. Krause and their co-workers.

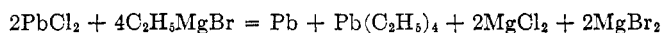
Without exception, all tetra-alkyl lead compounds are colorless liquids, heavier than water, having a rather pleasant odor of fruit. They distill undecomposed under reduced pressure, the lower members of the series even under atmospheric pressure. They form explosive mixtures with air, and burn with a characteristic livid blue flame, giving a heavy yellow smoke of PbO .

The stability of the compounds towards atmospheric oxygen and other reagents differs greatly with the nature of the Pb-C linkage. When the carbon atom, linked to the lead is primary, the compound is stable in air and little affected by light. With a secondary hydrocarbon group, the compound is slowly attacked by air, giving yellowish white precipitates of tri-alkyl lead oxides or carbonates. No lead compound containing a tertiary hydrocarbon group has been prepared. All the attempts have resulted only in a reduction with deposition of metallic lead. This difference is also indicated by the atomic refraction of the lead atom, the value of which is always exalted when a primary carbon is replaced by a secondary group. Molecular weight determinations made by freezing point lowering of benzene solutions show that all these compounds exist as single molecules.

Methods of preparation

The two older methods of preparation of these compounds, namely, the interaction of lead-sodium alloys with alkyl iodides, and the reaction of lead chloride on diethyl zinc, are not to be recommended. They are expensive and give only low yields.

Pfeiffer's method, the decomposition of a Grignard reagent with lead chloride, is much easier and less expensive to use in the laboratory. The reaction cannot, however, be applied without modification to the preparation of all tetra-alkyl lead compounds. It is possible to prepare organic compounds of tetravalent lead directly from lead dichloride. The reaction takes place according to the equation:



This proceeds quite easily with methyl magnesium chloride, and pure tetramethyl lead can readily be prepared in that way.

When the heavier ethyl magnesium bromide is used, some anomalies are noticeable. After decomposition of the magnesium compound with water, the ether extract is no longer colorless, as was true with tetramethyl lead, but is greenish-yellow and does not contain pure tetraethyl lead. After short exposure to the air, it becomes turbid, and a yellowish-white precipitate separates out, which contains Pb, C and H, and which, upon treatment with acids, gives off CO_2 . This is by all evidence an ethyl lead carbonate. After evaporation of the ether a heavy liquid is left which, distilled in an atmosphere of CO_2 under 20 mm. pressure, decomposes when the bath reaches a temperature of 80°C . Metallic lead separates out, first in the vapor, then in the liquid phase. At a slightly higher temperature, a colorless liquid distills over in a temperature range of a few degrees, while metallic lead is separated and gas given off continually. The distillate still shows, though to a lesser degree, the same instability as the ether solution. If the temperature of the bath is raised to 135°C . a mild explosion takes place in the flask, and a cloud of lead is given off. On repeating the distillation, the same decomposition takes place, though it decreases in intensity, and ceases after three or four distillations. The distillate is then colorless, stable

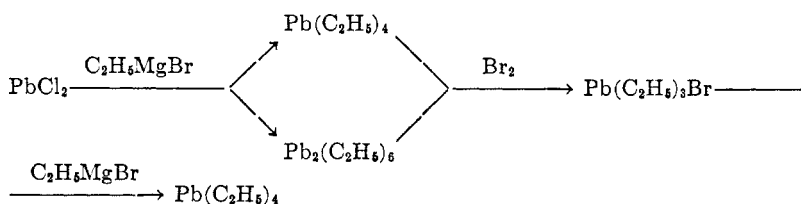
in air, and distills without decomposition under 20 mm. pressure. This proves to be pure lead tetraethyl.

The product obtained from propyl magnesium chloride shows the same properties to an even greater extent.

Such properties cannot be attributed to tetra alkyl lead compounds as these will, when pure, withstand a temperature of 140°C. They recall rather the properties described for unsaturated lead compounds which, as will be seen later, tend to decompose even at room temperature with liberation of metallic lead. Also, the greenish yellow color of the products obtained in this reaction is the same as is shown by $\text{Pb}_2(\text{C}_2\text{H}_5)_6$, or by the crude product obtained by the lead sodium reaction. Such compounds must thus be present in the product of the Grignard reaction, and since their stability increases with increasing molecular weight of the alkyl groups, the method must be modified when it is desired to prepare pure tetra alkyl lead compounds.

Unsaturated alkyl lead compounds add halogen to form di- and tri-alkyl lead halides, in which the lead is tetravalent. A further interaction of these products with a Grignard reagent will then give a tetra alkyl compound, without the loss in yield which is the disadvantage of the distillation method.

This can be represented by the scheme:



Tetramethyl lead. Lead chloride (1.8 mole) is added slowly to an excess of methyl magnesium chloride (4 moles) in absolute ether under constant shaking. The reaction is completed by heating for two hours on a water bath, and the product is then cooled in ice, decomposed with water, but not acidified. The ether extract is dried over calcium chloride and distilled. The product requires no further purification than a distillation; it boils at constant temperature (110°C.) and melts sharply at -27.5°C.

Tetraethyl lead. The impure tetra ethyl lead obtained by the above method decomposes on distillation. A pure product is obtained with much more ease by the following method: The ether extract is converted into triethyl lead bromide (see procedure, page 49), and the latter is made to react with ethyl magnesium bromide. The product is now completely free from unsaturated lead compounds and does not decompose on distillation.

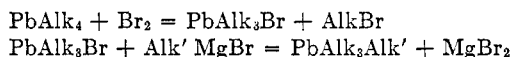
The last method of preparation is general. Thus, *n.* and *isopropyl*, butyl and amyl lead compounds have been prepared in that way.

Technical lead tetraethyl prepared by the General Motors process described above can now be obtained directly from the Eastman Kodak Company. This commercial product can be used in the preparation of many organic lead derivatives. It can be purified easily and with high yields (90 to 95 per cent) by the following method: The technical product is stirred with an equal volume of sulphuric acid, specific gravity 1.40, the temperature being kept below 30°C. This operation is repeated until the acid layer is colorless. The product is then washed with dilute sodium carbonate and distilled water. After drying over CaCl_2 it is fractionated at low pressure in an atmosphere of H_2 or N_2 .

The lead sodium reaction, as described under "General Methods of Preparation" can also be used in the laboratory. It has the advantage of being easier to carry out on a larger scale. However, except for the lower members of the series, the yields are low and the product contains varying amounts of Pb_2Alk_6 compound, from which it is difficult to separate a pure PbAlk_4 . It is nevertheless suitable in the case where it is desired to prepare a trialkyl lead salt without isolating the intermediate alkyl compound in the pure state.

Mixed alkyl compounds. The general method of preparation of organo-metallic compounds reported above gives products in which all the organic radicals are the same. A method has been developed by Grüttner and Krause (12), however, by which it is possible to vary systematically the nature of the organic groups

bound to the metal. They applied it extensively to the preparation of mixed alkyl lead compounds. It is based on the two following typical reactions of tetra-alkyl lead compounds:



By alternate bromination and reaction with a Grignard reagent, it is possible to prepare compounds in which the four valencies of the lead are occupied by 2, 3 or 4 different alkyl groups.

Physical properties of tetra alkyl compounds

The physical properties of all known alkyl lead compounds are reported in table 1. Unless otherwise specified, the compound has been described in Grüttner and Krause's works (24).

It is possible from an inspection of the data given in Table I to draw some conclusions as to the variation of physical properties through the class of tetra alkyl lead compounds.

The *boiling point* of alkyl lead compounds rises with increasing molecular weight. Of two isomers, the more symmetrical one has the higher boiling point. The influence of symmetry is so great that a compound symmetrical in structure and containing n carbon atoms has a higher boiling point than an asymmetrical compound containing $n + 1$ carbon atoms. For compounds differing only in isomerism of the organic radical, the normal compound boils higher than the iso.

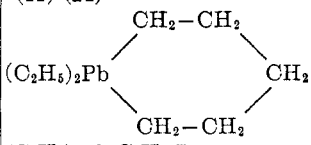
The *specific gravity* decreases with increasing molecular weight. This is the reverse of the case of hydrocarbons, and is simply because the small increase in density due to increase in size of the hydrocarbon radicals is overbalanced by the large decrease consequent to the lowering of the percentage of lead. The effect of distribution of mass is also apparent here, the specific gravity increasing with the symmetry of the molecule.

The *index of refraction* decreases with increasing molecular weight. One exception to this rule is that a methyl group gives a lower index than an ethyl group. The index of refraction increasing also with symmetry, the compound with the highest index will be tetraethyl lead. The atomic refraction of lead in

TABLE 1
Physical properties of tetra alkyl lead compounds

LEAD TETRA ALKYL	B.P. 13 MM.	20° d 4°	20 n _D	REFERENCES, REMARKS
Tetramethyl.	110*	1.9952	1.5120	B.P. under 760 mm. M.P. -27.5 (14) (24)
Trimethyl-ethyl.	29	1.8824	1.5154	
Trimethyl- <i>n.</i> propyl.	47	1.7669	1.5095	
Dimethyl-diethyl.	51	1.7906	1.5177	
Trimethyl- <i>n.</i> butyl.	65	1.6777	1.5046	
Trimethyl- <i>isobutyl</i>	57	1.6716	1.5026	
Dimethyl-ethyl- <i>n.</i> propyl.	63	1.6962	1.5118	
Methyl-triethyl.	69	1.7130	1.5183	
Trimethyl- <i>isoamyl</i>	70	1.5241*	1.4926*	d is d $\frac{21.4}{4}$ n is n $\frac{20.3}{D}$
Dimethyl-ethyl- <i>isobutyl</i>	74	1.6240	1.5081	
Dimethyl-di <i>n.</i> propyl.	77	1.6270	1.5086	
Methyl-diethyl- <i>n.</i> propyl.	79	1.6422	1.5150	
Tetraethyl.	82	1.6528	1.5198	(2) (3) (4) (5) (6) (8) (22) (23) (24)
Dimethyl-ethyl- <i>isoamyl</i>	91	1.5595	1.5059	
Methyl-diethyl- <i>isobutyl</i>	87	1.5812	1.5117	
Triethyl- <i>n.</i> propyl.	95	1.5886	1.5168	
Dimethyl-di <i>isobutyl</i>	96	1.5048	1.5024	
Dimethyl- <i>n.</i> propyl- <i>isoamyl</i>	104	1.5047	1.5028	
Methyl-diethyl- <i>isoamyl</i>	103	1.5228	1.5082	
Methyl-ethyl- <i>n.</i> propyl- <i>n.</i> butyl.	103	1.5185	1.5083	
Methyl-tri <i>n.</i> propyl.	106	1.5241	1.5101	
Triethyl- <i>n.</i> butyl.	108	1.5292	1.5123	
Triethyl- <i>isobutyl</i>	106	1.5313	1.5127	
Diethyl-di <i>n.</i> propyl.	105	1.5331	1.5149	
Methyl-ethyl- <i>n.</i> propyl- <i>isoamyl</i>	114	1.4801	1.5068	
Triethyl- <i>n.</i> amyl.	120	1.4823	1.5097	
Triethyl- <i>isoamyl</i>	118	1.4835	1.5099	
Diethyl- <i>n.</i> propyl- <i>n.</i> butyl.	116	1.4817	1.5094	
Diethyl- <i>n.</i> propyl- <i>isobutyl</i>	110	1.4890	1.5115	
Ethyl-tri <i>n.</i> propyl.	117	1.4858	1.5120	
Dimethyl-di <i>isoamyl</i>	122	1.4302	1.5005	
Diethyl- <i>n.</i> propyl- <i>isoamyl</i>	126	1.4411	1.5075	
Diethyl-di <i>isobutyl</i>	118	1.4440	1.5086	
Tetra <i>n.</i> propyl.	126	1.4419	1.5094	
Methyl-tri <i>isobutyl</i>	122	1.3973	1.5030	
Diethyl- <i>isobutyl-isoamyl</i>	130	1.3994	1.5050	

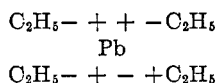
TABLE 1—Continued

LEAD TETRA ALKYLs	B.P. 13 MM.	20° d ₄ ²⁰	20 n _D	REFERENCES, REMARKS
Tripropyl- <i>isobutyl</i>		1.4056	1.5079	
Diethyl-di <i>isoamyl</i>	142	1.3757	1.5041	
Ethyl-propyl- <i>n</i> . butyl- <i>isoamyl</i>	143	1.3730	1.5035	
Ethyl-tri <i>isobutyl</i>		1.3778	1.5064	
Tripropyl- <i>isoamyl</i>		1.3819	1.5051	
Ethyl-propyl-di <i>isoamyl</i> ..	145	1.3552	1.5034	
Propyl-tri <i>isobutyl</i>		1.3501	1.5054	
Methyl-tri <i>isoamyl</i>		1.3153	1.4971	
Tetra <i>isobutyl</i>		1.3241	1.5043	
Ethyl-tri <i>isoamyl</i>		1.2918	1.4981	
Tri <i>isobutyl-isoamyl</i>		1.2981	1.5012	
Propyl-tri <i>isoamyl</i>		1.2756	1.4979	
<i>isoButyl-tri isoamyl</i>		1.2516	1.4960	
Tetra <i>isoamyl</i>		1.2337	1.4947	
Trimethyl- <i>sec</i> . propyl.....	80*	1.7403	1.5095	B.P. under 75 mm.
Dimethyl-ethyl- <i>sec</i> . propyl.	60	1.6962	1.5135	
Dimethyl-ethyl- <i>sec</i> . butyl..	74	1.6342	1.5128	
Dimethyl-ethyl- <i>sec</i> . amyl..	88	1.5669	1.5114	
Triethyl- <i>sec</i> . propyl.....	90	1.5812	1.5181	
Triethyl- <i>sec</i> . butyl.....	104	1.5314	1.5186	
Diethyl-di <i>sec</i> . propyl.....	95	1.5220	1.5159	
Diethyl- <i>n</i> . propyl- <i>sec</i> . propyl.....	104	1.5355	1.5162	
Dimethyl- <i>sec</i> . butyl- <i>iso</i> - amyl.....	112	1.4712	1.5066	
Triethyl- <i>sec</i> . amyl.....	118	1.4921	1.5158	
Diethyl- <i>n</i> . propyl- <i>sec</i> . butyl	114	1.4963	1.5170	
Diethyl- <i>n</i> . propyl- <i>sec</i> . amyl.	121	1.4548	1.5137	
Tetra <i>sec</i> . propyl.....	119	1.4504	1.5223	(11) (24)
Diethyl-cyclopentamethyl- ene.....	111	1.6866	1.5484	
Triethyl- ϵ bromamyl.....	167	1.6851	1.5374	(C ₂ H ₅) ₃ Pb C ₅ H ₁₀ Br
1.5 Di trimethylplumbyl <i>n</i> . pentane.....	166	1.9481	1.5556	(C ₂ H ₅) ₃ PbC ₅ H ₁₀ Pb(C ₂ H ₅) ₃ (25)
Triethyl-allyl.....	92	1.6085	1.5423	(C ₂ H ₅) ₃ PbC ₃ H ₅ (25)
Trimethyl-benzyl.....	124*			Dec. at B.P. (26)
Triethyl-benzyl.....	149*	1.5374*	1.5843*	Dec. at B.P.
				d is d $\frac{23.4}{4}$ n is $\frac{21.4}{D}$ (26)
Tetracyclohexyl.....				(27) (28)

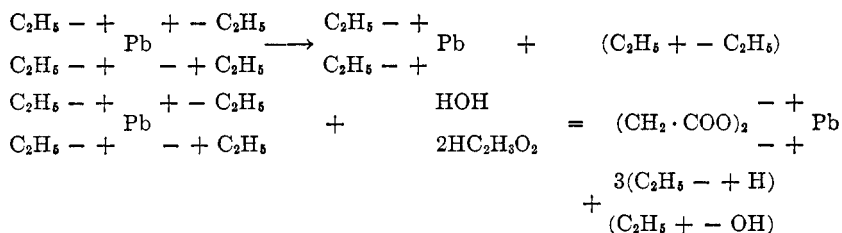
* See Remarks.

the tetra alkyl compounds varies also with the molecular weight, symmetry, and nature of the Pb-C linkages (primary or secondary), being minimum in $\text{Pb}(\text{CH}_3)_4$ ($\text{AR}_D = 17.31$) and maximum in $\text{Pb}(\text{C}_2\text{H}_5)_3\text{C}_3\text{H}_5$ ($\text{AR}_D = 20.12$) (25).

The theory has been proposed (23) that the four Pb-C linkages were not of same value in tetra alkyl lead compounds. According to Werner and Jones, the formula best representing lead tetraethyl would be:



in which three ethyl groups are charged negatively and the fourth positively. Their arguments for the theory are that such a compound easily reverts to compounds of di-valent lead, and that, when decomposed by an acid, it liberates three ethyl groups as hydrocarbons and one as alcohol (or ester):

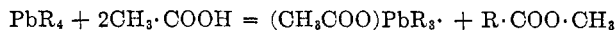


The first reaction never takes place. Quite to the contrary, all evidence points to the fact that the stable valency of lead in its organic compounds is 4: All other compounds revert to that valency whenever possible (see pp. 50-51, and no tetravalent compound goes over to organic compounds of lower valency without the use of strong reducing agents (p. 53).

The only case where tetravalent lead compounds decompose spontaneously into divalent compounds is where two valencies are occupied by inorganic radicals, such as PbR_2Br_2 , for instance. Here, the compound is as much inorganic as organic, and tends to go over to the more stable form, PbBr_2 .

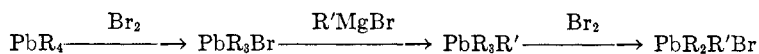
The second reaction is indeed substantiated by experimental evidence:

When lead tetraethyl is decomposed with acetic acid, three ethyl groups are given off as ethane, and the fourth as alcohol (ethyl acetate). However, as will be seen in a later chapter, the replacement of one alkyl group by an acid radical is a very easy reaction:



and the compound so obtained shows properties very different from PbR_4 . This can easily be attributed to the substitution, as is the case, for instance, with methane. The methane molecule is much more resistant to reagents than CH_3OH or CH_3Br , although it has been demonstrated that the four hydrogen atoms occupy positions entirely similar. Thus, the acid first substitutes one of the alkyl group, and in the compound so formed the remaining alkyl groups show a reactivity which is quite different from that of the same groups in a tetra alkyl lead compound.

A decisive argument against the above theory is afforded by the studies of compounds of the type $\text{PbR}_3\text{R}'$. Experience has shown that the following chain of reactions takes place:

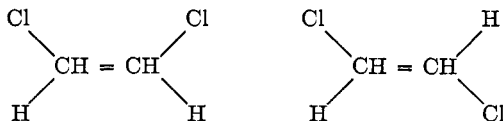


According to Jones and Werner, the bromine will replace the negatively charged alkyl radical in the molecule, and will, in turn, be replaced by the new R' radical, which will thus necessarily become the negative radical. On repeating the bromination on this new compound, the R' radical should thus be displaced. This is in contradiction with experience, which has shown that in all compounds of the type $\text{PbR}_3\text{R}'$ (with only one exception), the halogen displaces one of the three R groups (12).

We must admit, therefore, that the tetra alkyl lead compounds are symmetrical in structure, the four valencies of the lead atom being identical.

With four valencies of equal value, the tetravalent lead atom could still offer cases of steric isomerism. For instance, if its valencies formed two distinct pairs, there would be a possibility of

existence of cis and trans isomers, as in the case of substituted ethylenes:



Lead compounds of the type $\text{PbA}_2\text{A}'_2$, whatever the method is by which they are prepared, always show the same physical properties (24). It is thus highly probable that there exists no steric isomery and that the four valencies are oriented in the lead atom in directions entirely similar to that of the four valencies of carbon in methane.

TETRA ARYL LEAD COMPOUNDS

Although these compounds have not been studied as extensively as the alkyl compounds, enough information is available on the subject to ascertain the characteristics of the class.

Preparation

The aryl lead compounds can be prepared by either the lead sodium or the Grignard reactions:

1. Five hundred grams of ground Pb-Na alloy (8 per cent Na), 500 grams bromobenzol, and 20 cc. of ethyl acetate are heated under reflux for sixty hours. The product is extracted with hot benzene and purified by recrystallization from the same solvent. The yields are low (20 per cent) on account of the predominance of the formation of diphenyl (7).

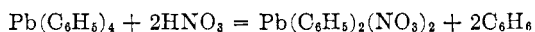
The influence of the ethyl acetate is not explained, but no reaction takes place between alloy and bromide in the absence of a compound from which the sodium will liberate hydrogen.

2. The Grignard reaction can be conducted in a similar way to that described for the alkyl compounds, care being taken to use an excess of Grignard reagent, in order to avoid the contamination of the product by unsaturated lead compounds (10).

All the tetra aryl lead compounds are while solids, crystallizable and of definite melting point. They are insoluble in water,-

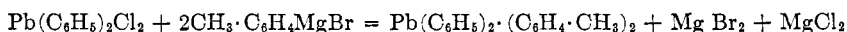
sparingly soluble in most organic solvents, and readily soluble in benzene, carbon bisulphide and chloroform. They are very resistant to heat and atmospheric oxygen. Acids, halogens and the halides of heavy metals convert them into di- and tri-aryl lead salts, but with greater difficulty than the alkyl compounds.

Thus, it is possible to prepare diphenyl lead nitrate, by boiling tetra phenyl lead with concentrated nitric acid (7):



while lead tetraethyl, under the same conditions, is converted completely into lead nitrate.

Mixed aryl compounds. They are prepared, like the mixed alkyl compounds, by the action of aryl lead salts on Grignard reagents:



They also are white crystalline solids. They exhibit, however, a lower stability and a greater reactivity and solubility. It seems that once the high degree of symmetry of the PbAr_4 compounds is reduced, the molecule is at once made more sensitive to outside influences. Thus, the temperatures of decomposition of the compounds are as follows:

PbAr_4	270-300°C.
$\left. \begin{array}{l} \text{AbAr}_2\text{Ar}'_2 \\ \text{PbAr}_3\text{Ar}' \end{array} \right\}$	190-265°C.
PbAlk_4	100-150°C.

They are more readily attacked by bromine than the PbAr_4 compounds, and also react with AgNO_3 in aqueous solution to form organo-silver salts, such as $\text{C}_6\text{H}_5\text{Ag} \cdot \text{AgNO}_3$, which reaction is not shown at all by the PbAr_4 compounds (13).

Mixed alkyl-aryl. These compounds, which are always prepared by Grignard reactions from the corresponding tetra alkyl or aryl compounds, show properties intermediate between those of alkyl and aryl compounds.

The trialkyl aryl compounds are liquids, and can be distilled under reduced pressure. The dialkyl diaryl compounds are

either solids or liquids. The alkyl triaryl compounds are solids, resembling the tetra-aryl compounds in most of their properties.

In general, it can be said that all the compounds in which the four valencies of the lead atom are satisfied by organic radicals are very similar in properties. Their physical properties vary

TABLE 2
Physical properties of tetra aryl and aryl alkyl lead compounds

LEAD TETRA ARYL		M.P.	REFERENCES
Tetraphenyl.....		225	(7) (10) (27)
Tetra <i>p.</i> tolyl.....		240	(7)
Tetra <i>o.</i> xylyl.....		255	(13)
Triphenyl- <i>o.</i> tolyl.....		125	(13)
Triphenyl- <i>m.</i> xylyl.....		112	(13)
Triphenyl- <i>p.</i> xylyl.....		105	(13)
Triphenyl- <i>p.</i> phenetyl.....		120	(13)
Triphenyl- α naphthyl.....		101	(13)
Diphenyl-di α naphthyl.....		197	(13) (22)

ALKYL ARYL LEAD		M.P.	²⁰ d 4	REFERENCES
Diethyl-diphenyl.....			1.6435	(22) (32)
Diethyl-di α naphthyl.....	116			(13)
Diphenyl-dicyclohexyl.....	180			(27)
Triphenyl-ethyl.....	42			(13)
Triphenyl-cyclohexyl.....	119			

ALKYL ARYL LEAD	B. P. 13 MM.	²⁰ d 4	²⁰ n D	REFERENCES
Trimethyl-phenyl.....	104	1.7376	1.5816	(29)
Trimethyl- <i>o.</i> tolyl.....	118	1.7408	1.5793	(29)
Trimethyl- <i>p.</i> tolyl.....	119	1.6826	1.5732	(29)
Triethyl-phenyl.....	136	1.5931	1.5757	(29)
Triethyl- <i>o.</i> tolyl.....	153	1.5853	1.5740	(29)
Triethyl- <i>p.</i> tolyl.....	154	1.5281	1.5686	(29)
Triethyl- α naphthyl.....	176			(29)
	dec.			

with their molecular weight and symmetry. They all show practically the same chemical properties, varying only in intensity with the size and stability of their organic groups.

The influence of the different substitutions on the structure of the lead atom itself is well illustrated by the variation in atomic

refraction of the lead reported above for the alkyl compounds. A similar determination on triphenyl ethyl lead gave $Ar_{H\alpha} = 18.89$, which is close to the value obtained from an alkyl compound containing the same number of C atoms:

$$Pb(i-C_6H_{11})_4, Ar_{H\alpha} = 19.05 \cdot (13)$$

The physical properties of all known aryl and mixed aryl-alkyl compounds are given in table 2.

UNSATURATED LEAD COMPOUNDS

All the compounds studied in the preceding chapter correspond to a tetravalent lead atom. Here and there, however, in their methods of preparation, it has been evident that some compounds are formed corresponding to a different class. The electrolytic reduction of ketones at a lead cathode produces a deep red liquid which, treated with bromine, gives salts corresponding to the formula $PbAlk_2Br_2$ (11). Also, in the action of $PbCl_2$ on Grignard reagents, a red color is first developed which disappears on shaking (29). The same is observed when trialkyl lead salts or alkyl halides dissolved in liquid ammonia are treated with metallic sodium (18). The action of alkyl halides on lead sodium alloys gives a product which is yellow, readily oxidized by air, and separates metallic lead when exposed to light (3). The product obtained in the Grignard reactions have the same yellowish color and instability observed in the lead sodium reactions. From all these observations, it was evident that other organic compounds of lead existed, corresponding to a lower valency of the lead atom. Some of them have finally been isolated and are described below.

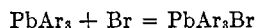
Compounds of the type PbR_3 or Pb_2R_6

a. Aryl compounds. These were first prepared by E. Krause and M. Schmitz (33). They observed that, in the aryl series as in the alkyl series, the amount of unsaturated compounds obtained in the Grignard reaction increased with the molecular weight of the organic radical used. But here, instead of being unstable, non-volatile and not crystallizable, like the correspond-

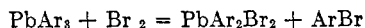
ing alkyl compounds, the aryl compounds were stable solids, which could be recrystallized without decomposition. They proceeded to prepare these compounds in the pure state by the following method:

One-fourth mole of PbCl_2 is added in small portions and with constant shaking to 0.75 mole of the Grignard reagent in 400 cc. of dry ether. The solution turns yellow, then brown, and only a small amount of metallic lead separates out. The solution is heated for 2 hours on a water bath. This converts the divalent compound into trivalent compound, as indicated by the color of the solution, which turns back from brown to yellow. The product is decomposed with water and ammonium chloride, and two-thirds of the ether is distilled off. The remainder of the ether contains only a little of the product with most of the impurities. The mass of the product, mixed with the spongy lead under the aqueous layer, is washed with water and alcohol, and then extracted with hot benzene and recrystallized from the same solvent. The yield is over 50 per cent.

The triaryl lead compounds are greenish yellow solids, stable in air and easily crystallizable from benzene. By the action of sunlight they decompose with separation of metallic lead. By the action of bromine, they first form salts of the type PbAr_3Br , without the formation of aryl bromides:



and with an excess of bromine, they give di-aryl lead di-bromides and an aryl bromide:



They are soluble in benzene, chloroform, pyridine and alcohol. Their molecular weights in solution show, though to a less marked degree, the same anomalies observed with the hexa aryl derivatives of ethane.

Benzene solutions of concentrations higher than 0.01 mole of Pb_2Ar_6 per 1000 grams contain only the Pb_2Ar_6 compound. At lower concentrations the compounds dissociate into free PbAr_3 radicals. the degree of dissociation apparently decreasing with

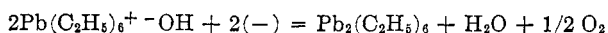
increasing molecular weight. The figures on the subject are not too reliable, as they are calculated from observed very small freezing-point lowerings, varying between 0.01 and 0.05°C. They are, however, corroborated by the reactivity and stability. One would expect, as is the fact, a compound like $\text{Pb}_2(p\text{-C}_6\text{H}_4\text{-CH}_3)_6$ to be more stable than $\text{Pb}_2(\text{C}_6\text{H}_5)_6$, which dissociates more readily.

b. Alkyl compounds. Only one alkyl compound of this type has been prepared, $\text{Pb}_2(\text{C}_2\text{H}_5)_6$. It was obtained (15) by electrol-

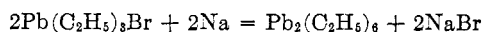
TABLE 3
Physical properties of triaryl lead compounds

TRI ARYL LEAD	DEC. AT °C	CONC. MOLES $\text{Pb}_2\text{Ar}_6/1000$ GRAMS C_6H_6	PER CENT DISSOC. IN PbAr_6	REFERENCES
Triphenyl.....	155	{ 0.008 0.001	{ 19 98	(14)
Tri- <i>o.</i> tolyl.....	240			(14)
Tri- <i>p.</i> tolyl.....	193	{ 0.008 0.001	{ 5 95	(14)
Tri- <i>p.</i> xylyl.....	220	{ 0.008 0.0015	{ 10 100	(13)
Tri-cyclohexyl.....	195			(28)

ysis of a solution of triethyl lead hydroxide in aqueous NaOH:



Another method consists in the treatment with metallic sodium of a solution of $\text{Pb}(\text{C}_2\text{H}_5)_3\text{Br}$ in liquid ammonia (18).



The yields are low in the first reaction and nearly quantitative in the second. Both methods are quite different from those used by Krause in the preparation of aryl compounds. They have apparently not been applied to the preparation of other alkyl or aryl compounds, but there is every reason to believe that they could be used with equal success.

Triethyl lead or di-lead hexaethyl is a greenish yellow liquid of specific gravity 1.94. It can be steam-distilled without much decomposition and boils around 100°C. under 2 mm., but cannot be distilled directly. It is miscible with organic solvents and does not freeze at -80°C. It absorbs oxygen from the air, depositing a brownish yellow solid, and is decomposed by light into $\text{Pb}(\text{C}_2\text{H}_5)_4$ and Pb. It was not obtained as pure as the aryl compounds, as it could not be crystallized or distilled without decomposition.

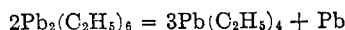
Molecular weight determinations in benzene solutions show the following percentage dissociation:

MOLES $\text{Pb}_2(\text{C}_2\text{H}_5)_6$ PER 1000 GRAMS BENZENE	DISSOCIATION INTO $\text{Pb}(\text{C}_2\text{H}_5)_2$
	<i>per cent</i>
0.006	30
0.003	100

These figures, although sensible of the same inaccuracy as those reported in table 3 for the aryl compounds, indicate a higher dissociation, corroborated again by the greater instability of the compound.

The action of bromine gives only $\text{Pb}(\text{C}_2\text{H}_5)_3\text{Br}$ and $\text{Pb}(\text{C}_2\text{H}_5)_2\text{Br}_2$, and no reaction could be performed which would break a Pb-C linkage in preference to the Pb-Pb bond.

Furthermore, $\text{Pb}_2(\text{C}_2\text{H}_5)_6$ shows to an even greater degree than $\text{Pb}_2(\text{C}_6\text{H}_5)_6$ a tendency to go over to the more stable compound of tetravalent lead:



Indeed, when exposed to light, $\text{Pb}_2(\text{C}_2\text{H}_5)_6$ goes over slowly to $\text{Pb}(\text{C}_2\text{H}_5)_4$ with deposition of lead and without evolution of gas. At high temperatures, however (140°C.), it explodes violently.

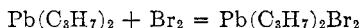
The properties reported here for $\text{Pb}_2(\text{C}_2\text{H}_5)_6$ seem sufficient to prove that the unsaturated lead compounds present in the products of either the lead-sodium or the Grignard reaction belong to the same type: They are all greenish yellow liquids, show the same instability in air, and can be distilled with only partial

decomposition when they are mixed with enough of the tetra-compound to lower their boiling point below the temperature at which they decompose.

That they do not belong to the PbA_2 type will be made evident from the study of these compounds in the following section.

Compounds of the type PbA_2

The existence of these compounds was already suspected by early experimenters. Tafel obtained by electrolytic reduction a dark red oil, highly unstable, absorbing oxygen and CO_2 to give colorless compounds, and adding bromine directly. He wrote the last reaction as follows:



but was unable to isolate his red dialkyl compound in the pure state on account of its instability (11).

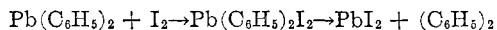
Pfeiffer reported that they were formed in the Grignard reaction, but decomposed at once, as was shown by the immediate disappearance of the red coloration (29).

Di-aryl lead compounds.

E. Krause and M. Schmitz were the only ones to prepare divalent organic lead compounds in a pure state (14).

The Grignard reagent solution of 0.2 mole of C_6H_5MgBr is cooled with ice and salt and stirred vigorously. One-tenth mole of $PbCl_2$ is added slowly in a current of nitrogen, care being taken to keep the temperature below $2^\circ C$. The product is treated with ice water and extracted with benzene. It is separated from some triphenyl lead by fractional crystallization and finally precipitated with alcohol, all operations being under nitrogen (yield 15 per cent).

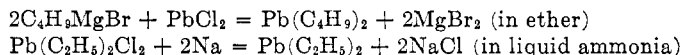
Lead diphenyl is a blood-red amorphous solid, very soluble in benzol, less in ether, insoluble in alcohol and water. It is oxidized to colorless compounds by atmospheric oxygen and decomposes at about $100^\circ C$. in air. Iodine converts it into lead iodide, with intermediate formation of diphenyl lead iodide:



At comparatively high concentration (0.008 mole PbAr_2), it shows no molecular association.

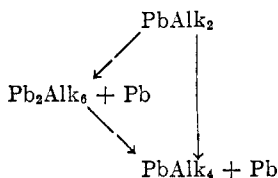
Di-p. tolyl lead was prepared in the same manner and shows similar properties to those of diphenyl lead.

Di-alkyl lead compounds. As was said above, evidence of the formation of di-alkyl lead compounds is obtained in various reactions but they were never isolated. Attempts were made in the author's laboratory to carry on the following reactions:



but no dialkyl lead compound could be isolated in either case.

The red coloration observed there as in the Grignard reaction is, however, an indication of their formation, and since Pb_2Alk_6 compounds are present in the final products of some reactions, the complete mechanism of the reaction must involve either or both of the following series:



The decomposition of the dialkyl compound is always rapid; that of the dilead hexa alkyl decreases with increasing molecular weight, the tetra alkyl compound being, however, the more stable form in all cases.

ORGANIC LEAD SALTS

Under the heading of organic lead salts are included all the compounds in which one or more of the valencies of the lead are satisfied by inorganic or acid radicals, such as Cl , OH , SO_4 and CH_3COO .

These compounds differ greatly from the preceding ones, resembling to a certain extent the similar compounds of mercury.

They are, as a rule, white crystalline solids, somewhat soluble in water and in liquid ammonia as well as in organic solvents. Their aqueous solutions are ionized and show the typical reactions of their acidic ions. Their metal ions, PbR_3^+ or PbR_2^{++} , show properties which differ somewhat with the nature of the substituents. In general, the PbR_3^+ ions resemble the alkaline metals; their hydroxides are strong bases, which precipitate the heavy metals from their solutions and displace ammonia from its salts. The PbR_2^{++} ions resemble Zn^{++} ; their chloride solutions have a strong acidic reaction, their hydroxides are soluble in both acid and alkali, and their sulfides are precipitated by H_2S as white flocks, soluble in acetic acid and ammonia.

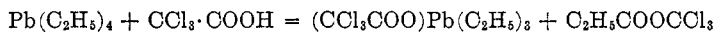
As would be expected, the properties of the organic lead salts in organic solvents are greatly influenced by the nature of the substituents. In the aliphatic series, the solubility increases with increasing molecular weight; in the aromatic series not enough data are available from which to draw definite conclusions. The PbR_3X compounds are soluble in ethyl and methyl alcohol, in benzene and in chloroform. The PbR_2X_2 salts are, at best, only slightly soluble in the above solvents and are more soluble in aniline, dimethyl aniline and pyridine.

The decrease in solubility in organic solvents is usually accompanied by an increase in solubility in water.

Only a few of the organic lead salts show definite melting points as most of them decompose before melting, partly from oxidation and partly by the release of their organic groups. The influence of the acid groups on the stability is also greatly marked, the fluorides and the chlorides showing the greatest stability. No addition compounds are reported for PbR_3X salts. Some addition compounds of PbR_2X_2 salts with pyridine and ammonia have been prepared by Möller and Pfeiffer (29). They were obtained by recrystallizing the salts from pyridine, or by passing dry ammonia gas over them. They are stable, but lose their pyridine or ammonia when exposed to air. They are insoluble in water and in organic solvents.

Salts of the type PbR₃X

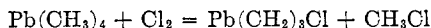
Preparation. a. Salts of strong acids. The organic lead salts of strong acids can be prepared by direct action of the acid on the tetra alkyl or aryl lead compound:



One hundred cubic centimeters (0.5 mole) of tetraethyl lead are put in a beaker with 1 mole of the acid in concentrated aqueous solution, and the two liquids are stirred vigorously. If no reaction has taken place after a few minutes, a slight heating by means of hot water will generally suffice to prime it. The reaction is exothermic, and once it is started, it may be necessary to cool the vessel to avoid complete decomposition. The product, a white solid, is separated from the remaining liquid by pressing and is recrystallized from a suitable solvent.

This procedure gives satisfactory results with CCl_3COOH , HBr , HCl (19).

b. Halogen salts. These can be prepared by direct action at low temperature of the halogens, care being taken to avoid an excess of the latter (20):

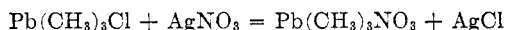


In a 3-liter beaker, CO_2 snow is added to 500 grams of ethyl acetate until it covers the liquid completely. One hundred grams of lead tetramethyl are added, and the mass is kept stirred vigorously. A slow current of chlorine, about 2 bubbles a second, is then passed through the solution by means of a wide tube, until free chlorine becomes visible. This end-point can be detected after a little practice by the change in color. The temperature must be kept below -60°C . by continued addition of CO_2 snow. After completion of the reaction the temperature is allowed to rise, the mixture is heated to 50°C . on a water bath, and the impurities mechanically entrained, together with some dichloride formed by excessive chlorination, are removed by filtration. The solution is concentrated in vacuo, the salt crystallizes out, in well-formed needles which require only to be washed with

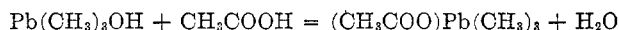
ether to give a pure product. The yield is practically quantitative and only traces of PbCl_2 are formed.

The above method is general for the preparation of monochlorides and bromides, the bromine being added as a solution in ether.

c. General methods. The salts of the weaker acids are prepared indirectly from the preceding ones, either by double decomposition when one of the products is insoluble:



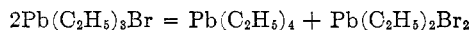
or by saturation of the base by an acid:



The base itself can be readily obtained by the action of strong alkalis on the halogen salts (3) (15) (30).

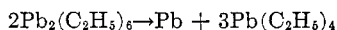
Properties. To summarize, it might be said that, in aqueous solution, the PbR_3^+ ions resemble the alkaline metal ions, the solid salts decrease in stability with increasing molecular weight in the aliphatic series, and that the aryl salts are more stable than the corresponding alkyl compounds. With the same R groups, the stability depends on the anion, some of which are listed here in order of decreasing stability: OH-F-Cl-Br-I—

Trialkyl lead salts are not volatile enough to be distilled with steam, but when heated for a few hours in the presence of water, they undergo the following reaction (18):



A quantitative yield of the tetra-alkyl compound is formed, while the di-alkyl salt partly loses its organic groups.

This reaction, compared with the similar spontaneous rearrangement of tri-alkyl compounds into tetra-alkyls (18):



illustrates the remarkable symmetry of the tetra-alkyl compounds to which all other forms tend to revert.

All available data on PbR_3 salts are given with references in table 4.

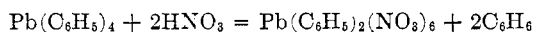
TABLE 4
Salts of the type PbR_3X

NAME OF LEAD SALT	MELTING POINT	DECOM- POSES	REFERENCE
Trimethyl fluoride.....		305	(30)
Trimethyl chloride.....	187 subl.		(2) (20)
Trimethyl bromide.....	133 dec.		(2) (20)
Trimethyl iodide.....			(2)
Triethyl fluoride.....		240	(30)
Triethyl chloride.....		170	(2) (3) (4) (5) (10) (20) (22)
Triethyl bromide.....	104		(3) (11)
Triethyl iodide.....			(2) (3)
Triethyl hydroxide.....		190	(2) (3) (4) (5) (15) (30)
Other ethyl salts (nitrate, sulphate, carbonate, phosphate, formate, acetate, butyrate, benzoate).....			(3) (4) (5)
Tri <i>n.</i> propyl fluoride.....		235	(30)
Tri <i>n.</i> propyl chloride.....	137		(20) (31)
Tri <i>n.</i> propyl bromide.....	87		(31)
Tri <i>n.</i> propyl hydroxide.....		140	(30) (31)
Tri <i>n.</i> propyl {sulfate acetate}.....			(31)
Tri <i>isopropyl</i> chloride.....		170-190	(11)
Tri <i>isopropyl</i> iodide.....			(11)
Tri <i>n.</i> butyl chloride.....	111		(31)
Tri <i>n.</i> butyl {hydroxide bromide}.....			(31)
Tri <i>isobutyl</i> fluoride.....		230	(30)
Tri <i>isobutyl</i> chloride.....	122 dec.		(24)
Tri <i>isobutyl</i> bromide.....	100 dec.		(24)
Tri <i>isobutyl</i> iodide.....			(24)
Tri <i>isobutyl</i> hydroxide.....		115	(30)
Tri- <i>sec.</i> butyl chloride.....	130 dec.		(19)
Tri <i>isoamyl</i> fluoride.....		251	(30)
Tri <i>isoamyl</i> bromide.....	132		(24)
Tri <i>isoamyl</i> hydroxide.....			(3) (30)
Tri <i>isoamyl</i> {sulphate iodide}.....			(3)
Tri cyclohexyl fluoride.....		198	(30)
Tri cyclohexyl chloride.....	226		(28)
Tri cyclohexyl bromide.....		210	(28)
Tri cyclohexyl iodide.....	92-125		(28) (30)
Tri cyclohexyl hydroxide.....			(28) (30)
Diethyl- ϵ brom amyl bromide.....			(24)
Triphenyl fluoride.....		318	(30)
Triphenyl chloride.....	206		(26)
Triphenyl bromide.....	166		(26)
Triphenyl iodide.....	139		(14) (26)
Triphenyl oxide.....			(26) (30)
Triphenyl sulfide.....			(26)
Tri <i>p.</i> tolyl fluoride.....		280	(30)
Tri <i>p.</i> tolyl hydroxide.....			(30)
Tri <i>p.</i> tolyl iodide.....	115		(14) (30)
Tri <i>p.</i> xylyl chloride.....	167	195	(14)
Tri <i>p.</i> xylyl bromide.....	177		(13)

Salts of the type PbR₂X₂

Preparation. a. By acids. Some of these salts can be prepared by direct action of the acid:

Thus, on treating lead tetraphenyl with concentrated boiling nitric acid, diphenyl lead nitrate is obtained (7):



This reaction is successful when working with the very stable $\text{Pb}(\text{C}_6\text{H}_5)_4$ nucleus. With almost any other compound, especially with the alkyl lead compounds, such a drastic treatment would result in a complete destruction of the organic molecule, leaving lead nitrate. The method gave good results with organic acids of medium strength (propionic, valerianic, trichloroacetic, oxalic, *p*-nitrobenzoic) but failed to give any results with weaker acids (22).

b. Halogen salts. The dichlorides and dibromides can be prepared by direct reaction on the tetra alkyl (aryl) compounds. The beginning of the procedure is the same as described above for the preparation of the monochloride. As soon as the coloration due to the presence of free chlorine in the solution becomes perceptible, the addition of CO_2 snow is stopped, and more chlorine is passed through the solution with vigorous stirring. The dichloride formed precipitates. When the temperature reaches -10°C ., it is kept there by using an ice-salt mixture. The solution is then decanted, and contains no lead compounds. The precipitate is washed by decantation with ethyl acetate, and finally with ether. The yields are quantitative (20).

c. General method. All salts can be prepared by neutralizing the corresponding base with acid. The base itself is readily obtained by decomposing the dihalides with alkalis (20).

Properties. In the aliphatic series, the PbR_2X_2 salts are somewhat less stable than the PbR_3X . They show a tendency to lose their organic constituents to leave an inorganic lead salt, this tendency increasing with increasing molecular weight. In the aromatic series, they are much more stable, as some of them will not even decompose on boiling with concentrated acids.

They are soluble in water, in which they have an acid reaction, only sparingly soluble in alcohol and ether, and more readily in carbon tetrachloride, benzene, chloroform, aniline, dimethylaniline and pyridine.

Some addition compounds have been prepared of diphenyl lead salts with pyridine and ammonia. The pyridine salts, prepared by recrystallizing the salts from that solvent, correspond to the formula $PbR_2X_2 \cdot 4Py$. They are insoluble in other solvents and lose their pyridine on standing. The ammonia salts, of the type $PbR_2X_2 \cdot 2NH_3$, are obtained by passing NH_3 gas over the salt. They decompose readily when the ammonia gas is replaced by air (31).

The data available on the salts of this type are too scant and too incoördinate to be put in a comprehensive table. For the sake of completeness, a list is given below of all the salts which have been reported, together with the corresponding references:

Salts of the type PbR_2X_2

Dimethyl (20)
Diethyl (11) (20) (31)
Di *n.* propyl (20)
Di *isopropyl* (11)
Di *sec.* butyl (19)
Di *isobutyl* (24)
Di *isoamyl* (24)
Di diethylmethyl (11)
Di cyclohexyl (27) (28)
Methyl ethyl (24)
Ethyl *isobutyl* (24)
Ethyl *isoamyl* (24)
n. propyl *isobutyl* (24)
n. propyl *isoamyl* (24)
isobutyl isoamyl (24)
Ethyl- ϵ bromamyl (24)
Diphenyl (7) (9) (10) (14) (22) (31)
di *p.* tolyl (7)
di *p.* xylyl (13)

METHODS OF ANALYSIS

Organic lead compounds are easy to characterize as such, if it is not desired to identify them. Heated in a test tube they decompose to leave a residue of metallic lead, lead oxide or a lead salt, according to the compound investigated. Boiled with a mixture of hydrochloric and nitric acid, they dissolve entirely and give a solution which precipitates PbSO_4 by addition of sulphuric acid. When it is desired to detect a compound in dilute solution, the addition of bromine gives a PbR_2Br_2 salt or PbBr_2 , according to the conditions and the nature of the compound. Either salt will precipitate as a white powder, in which the presence of lead can be ascertained easily. It is not recommended to attempt to concentrate the solutions of alkyl lead compounds before testing as they are volatile enough to distill with the solvent. A better procedure consists in adding an excess of bromine first, and concentrating afterwards if no precipitate is apparent.

With a solution of $\text{Pb}(\text{C}_2\text{H}_5)_4$ in kerosene, it was found that a concentration as low as 0.0005 N is easily detected in that manner.

Quantitative determination of lead

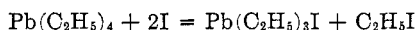
According to Treadwell (32) this is made by treating with an excess sulphuric acid and weighing the lead as sulfate. Polis (7) dissolved the non-volatile aryl lead compounds in concentrated sulfuric acid, and oxidized them to PbSO_4 with a permanganate solution. For volatile compounds, a Carius combustion can be made (12).

A better and easier method, applying equally well to all compounds, is as follows (12):

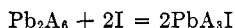
The weighed sample, to which is added 10 times its amount of carbon tetrachloride, is cooled with ice and decomposed by the addition of a large excess of a 10 per cent solution of bromine in CCl_4 . The mixture is then heated on a water bath until nearly dry. The precipitate, PbBr_2 , is boiled for a few minutes with absolute alcohol, cooled and filtered through a Gooch crucible, and washed with a small amount of ice-cold absolute alcohol.

To titrate the amount of tetra alkyl or aryl lead available in a concentrated preparation, the following method is quite accurate and rapid:

Dissolve 1 cc. or 1 gram in 50 cc. of benzol, add aqueous iodine solution in KI in slight excess, shake for a minute or two and then titrate the excess of iodine with standard sodium thiosulfate. The reaction takes place according to the equation:



(Private communication from Dr. Graham Edgar.) This method will, however, not differentiate between PbA_4 and Pb_2A_6 compounds, both using two atoms of iodine:



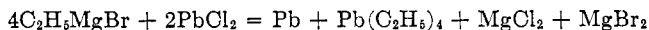
USES

The first investigators of the field of organic lead compounds had apparently no other purpose than to study the properties of new compounds. The determination of the atomic refraction of the lead, and the preparation of optically active lead compounds were the main incentives to the preparation of scores of compounds.

Working in quite a different field, while they were studying the characteristics of explosions in internal combustion engines, the engineers of the General Motors Research Corporation found that the presence of small amounts of organic lead compounds would prevent detonation or, in other words, remove the objectionable "knock" familiar to all motorists (16). This resulted in the development of the industrial preparation of tetraethyl lead. The product called "ethyl gas" is a commercial grade of gasoline to which is added 3 cc. of tetraethyl lead per gallon, plus a certain amount of an organic bromide, the rôle of which is to convert the lead into PbBr_2 when the fuel is burnt.

According to recent newspaper reports, the use of organic lead compounds as a war gas was investigated during the late war by the Chemical Warfare Service, but was reported as "not quite poisonous enough."

Two other uses of lead tetraethyl can be mentioned. The first is based on the reaction:



Half of the lead being converted into alkyl compounds while the other half is recovered as metal, it was suggested that this reaction might show a selectivity between lead and its isotope, Radium D. By repeating the reaction a sufficient number of times, it should thus be possible to separate completely the two isotopes. The experimenters successively announced positive and negative results (33), and in the light of the figures available at present, it is still doubtful whether the separation afforded in this way is noticeable.

The second is suggested in a patent (34) which relates to the use of tetraethyl lead in a process of coating iron with metallic lead. It was impossible to find out to what extent the process is being used, but it is interesting in that it is probably the first time that the use of an organo-metallic compound was mentioned in connection with a metallurgical process.

The possibility of uses for organic lead compounds is far from being exhausted. It has been shown that alkyl and aryl lead salts exhibit properties both of metallic salts and of organic compounds. It should be possible by varying the nature of the organic groups to prepare organo-lead ions occupying any desired position in the electromotive series, either coinciding with or intermediate to that of true metals. The use of such radicals may prove to be of value in analytical chemistry. That field has probably not been investigated at all. Metallic cations can be precipitated from their solutions by organic reagents, as is Ni^{++} by dimethyl glyoxime. It is possible that the use of the new organo-metallic ions would effect the separation of anions difficultly separable by the present methods, and perhaps give methods of precipitating some anions of which all known salts are soluble. Furthermore, the compounds so formed could probably be extracted with organic solvents, thus offering another almost entirely new tool in analytical chemistry. Finally, the high atomic weight of lead and the ease with which its compounds

are converted into heavy and insoluble $PbSO_4$ or $PbBr_2$ molecules makes its use of unusual attraction in analytical work.

TOXICITY

Organic lead compounds are more dangerous than the inorganic lead salts on account of their volatility and of the ease with which they penetrate through organic tissues. The odor of alkyl lead compounds is not unpleasant, and therefore does not warn against the danger of breathing them. The salts, especially the more volatile ones such as the tri-alkyl lead halides, are irritating, producing sneezing and tears.

The toxicology of organic lead compounds is almost nonexistent compared with the development of our knowledge of the diseases due to inorganic lead poisoning. Only two papers seem to have been Published on the subject (35). However, some useful information can be derived from the available data. The usual early symptoms of lead intoxication common to organic and inorganic lead poisoning are: Pallor, anemia, stippling of the blood cells, general debility and weakness, constipation, abdominal pain, loss of appetite, and sometimes convulsions. The symptoms observed in cases of tetraethyl lead intoxication differ inasmuch as they show striking mental excitement with appearance of: Sleeplessness, nightmares, hallucinations, headaches, drop of blood pressure and body temperature.

The difference between the two diseases comes from the wide difference between the rate of absorption of the compounds by the organism and of the rate at which the latter is able to react against them.

Inorganic lead compounds are practically not absorbed through the skin, they penetrate mostly through the lungs and the digestive system. Their rate of absorption is thus controlled primarily by their solubility, which is low. At the low concentrations attained, they are at once precipitated in the blood stream as tri-lead phosphate. This is then stored up in the tissues, mostly in the bones and liver, and to a lesser extent in the nerves and the intestines. The characteristic signs of lead intoxication may then not be evident until a relatively large amount of lead

stored up by the organism is suddenly released by a change in the economy of the system (35).

Organic lead compounds, on the other hand, penetrate through the skin and tissues with great rapidity and diffuse probably throughout the organism because of their solubility in fat. The amount of lead which can be present at one time is thus much greater than in the case of inorganic lead. Moreover, the organic compounds are much more resistant to the methods of protection of the organism.

Alkyl or aryl lead salts when submitted to the same reagents as inorganic salts will react much more slowly, if at all, their metallic ion having properties quite different from those of the lead ion. Tetra alkyl or aryl lead compounds will not be reacted upon at all by the precipitating reagents until they are either decomposed by acids or oxidized.

The choice of antidotes for organic lead poisoning should thus be guided by the above characteristics of the compounds. The intravenous injection of sodium thiosulfate has been used in certain cases, on the grounds that this produces lead sulfite, which is extremely insoluble. It seems much more recommendable that in acute cases an antidote be given, which would promote the decomposition of the stable organic compounds. Calcium chloride in intravenous injection probably affords the most promising method of treatment: it is known to increase the acidity of the blood stream, thereby favoring the conversion of the organic lead compounds into inorganic lead salts, which can then readily be precipitated by the phosphates present in the blood (private communication from Dr. J. C. Aub, Harvard School of Public Health.) The calcium chloride has the further advantage of producing a positive calcium balance, thereby preventing the liberation of calcium and lead from the bones, as would be the result of the acidosis in the absence of calcium (36).

Although the organic lead compounds are extremely poisonous, once absorbed, it has been shown by several laboratories that they can be manipulated continuously without danger, providing suitable precautions are taken.

The main points to observe are: To use hoods, preferably with

suction pipes at the level of the table; never to allow the organic lead compounds to come in contact with the skin; to wash with bromine water the utensils which have contained organic lead compounds, and also the walls and shelves in the laboratory, or any corner in which the heavy vapor or dust of the compounds are liable to have settled. Rubber gloves should be used to protect the skin from contact with organic lead compounds. However, since the compounds are readily absorbed by rubber, the gloves should be discarded as soon as they become impregnated.

The aim of this survey is to cover all the information available to date (January 1, 1925) on the chemistry of organic lead compounds. The author hopes that his presentation of the subject will be of some assistance to the reader interested in this particular field of organic chemistry, and that further research may be inspired by it.

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