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INTRODUCTION OF WATER-SOLUBILIZING GROUPS
INTO SOME ORGANOMETALLIC COMPOUNDS

by

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A Thesis Submitted to the Graduate Faculty
for the Degree of

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INTRODUCTION

Organic compounds of lead have been known and studied for the last ninety years (157). In the course of this time approximately 550 organolead compounds have come to our attention, either through literature references or by work done in these laboratories. Excellent reviews of organolead compounds have appeared in the past (25, 57, 59, 123, 149, 193) and it is not the intention of this review to repeat unnecessarily what has already been discussed in these sources of information. Rather, the aim is to gather additional facts concerning this interesting group of compounds by reviewing the literature up to the end of 1942. At the same time a complete tabulation of the compounds has been made, listing what we believe to be the important references to each compound. In nearly every case, all known literature references to each compound have been included in the tables. In cases where more than common interest has produced a large number of publications on a compound (e.g., tetraethyllead or tetraphenyllead), a few references have been omitted. This omission has occurred only if it was felt that the article did not add to the chemical or physiological knowledge of the compound.

In this review the term organolead compound is taken to mean only those compounds possessing a carbon-lead linkage. Thus diphenyllead diacetate, $(C_6H_5)_2Pb(OOCCH_3)_2$, is included, but lead acetate, $(CH_3COO)_2Pb$, is not included.

R_4Pb COMPOUNDS

General Discussion of R_4Pb Compounds

Compounds of the type R_4Pb, where four similar alkyl or aryl groups are attached to lead, represent the oldest type of organolead compound known. Löwig (157) first produced a compound of this type by the action of ethyl iodide upon lead-sodium alloy. He believed that he had triethyllead; however, Ghira (63), in repeating the work, proved that Löwig had impure tetraethyllead.

The tetralkyllead compounds are colorless and liquid even when the organic group is a fairly long chain. The lowest member of the series known to be a solid is tetratetradecyllead, which melts at 31°. Remarkable stability is exhibited in these symmetrical compounds. They withstand temperatures up to 140°, are little influenced by air or moisture, and are unaffected by dilute acids or alkalies. Tetraethyllead resists the action of cold sulfuric acid of specific gravity 1.4 and this fact is made use of in purifying technical tetraethyllead.

Little difficulty is experienced in vacuum distillation of the straight-chained tetraalkyllead compounds. Tetramethyllead tends to superheat when distilled; this behavior is characteristic of the unpredictable properties of most organometallic compounds containing the methyl group. Unless care is exercised in distilling tetramethyllead, there is danger of decomposition with explosive violence (138).

Secondary alkyl groups impart a lower degree of stability than do primary alkyl groups. The difference in stability between primary and <u>iso</u>

compounds is of the same type but not so marked.

Tetracyclohexyllead is peculiar among the aliphatic lead compounds in that it decomposes before melting. This is probably due to steric factors. As will be noted in the section on R_6Pb_2 compounds, the stable form seems to be hexacyclohexyldilead.

Halogens react with alkyl R_4Pb compounds to give R_3PbX or R_2PbX_2 compounds, depending upon the temperature and concentrations of the reactants. The trialkyllead halides are probably formed first in any case but are quickly converted to the dialkyllead dihalides at higher temperatures and concentrations (102). Cleavage with bromine at -70° yields R_3PbX compounds and, at -25°, R_2PbX_2 compounds. It has been impossible to cleave three alkyl radicals and retain a stable residue. When more than two atom equivalents of halogen are used, the product is always lead halide and the alkyl halide. A method of formation of $RPbX_3$ compounds is mentioned in a later section.

Halogen acids, usually in the gaseous form, also cleave R_4Pb compounds. These reactions are discussed in the section on lead compounds containing two or more different organic radicals.

Bindschadler (14) has shown that cleavage of one alkyl radical from an R_4Pb compound can be accomplished by adding a liquid ammonia solution of a metal to an ether solution of the organolead compound. The product is an R_3PbM compound, never an R_6Pb_2 compound, and it is not isolated but is derivatized by adding an organic halide.

$$R_4Pb + Na \xrightarrow[NH_3]{liq.} R_3PbNa \xrightarrow{R'Br} R_3R'Pb + NaBr$$

Probably because of steric factors, ortho-substituted R_4Pb compounds usually show a higher melting point than the corresponding para-substituted compound. In some cases this difference in melting point amounts to over 100°.

Halogens produce R_3PbX and R_2PbX_2 compounds in the tetraaryllead series just as in the tetraalkyllead series. Here again, it is apparent that the more stable tetra-valency of lead is found with either four organic groups or two organic and two inorganic groups. Addition of more than two atom equivalents of halogen produces only lead halide and the alkyl halide.

The gaseous halogen acids cleave tetraaryllead compounds as do the halogens. This type of cleavage is discussed in greater detail in the section on compounds containing two or more different organic radicals attached to the same lead atom.

Tetraaryllead compounds, like the tetraalkyllead types, have been cleaved to R_3PbM compounds by Bindschadler. The product is never isolated but is derivatized by action of an organic halide.

Makarova and Nesmeyanov (158) obtained a quantitative yield of benzenediazonium nitrate by the action of N_2O_3 and NO on tetraphenyllead.

Schlenk and Holtz (191) obtained impure ethylsodium from the reaction of sodium metal upon tetraethyllead.

R_4Pb compounds containing radioactive lead have been prepared. Tetramethylthorium-D and tetramethylradium-G were reported by Aston (3, 4) and tetraethylradium-D was reported by Calingaert, Beatty, and Hess (27).

Methods of Preparing R_4Pb Compounds

Since the simple tetra-substituted lead compounds are nearly always the starting point in the preparation of other organolead compounds, considerable work has been carried out in perfecting methods of manufacture. The following methods have been used.

Reactions of lead-sodium alloys with organic halides

As stated before, the first organolead compound was prepared by the reaction of ethyl iodide with lead-sodium alloy. This method is also used in the commercial production of tetraethyllead (47), in which case ethyl chloride is the alkyl halide employed. Polis (182) obtained tetraphenyllead by using bromobenzene, in the presence of ethyl acetate as promoter. It has been suggested that the reaction involves reduction (25), and that ethyl acetate, water, etc. promote the reaction by acting as sources of hydrogen. Ghira (63) found that under absolutely anhydrous conditions no reaction occurred between alkyl halides and lead-sodium alloy, but the addition of a little water caused a smooth reaction to take place.

Reaction of sodium, organic halide, and lead chloride

A German patent (62) mentions the preparation of R_4Pb compounds by dropping a mixture of the organic chloride and lead chloride in toluene upon sodium in toluene.

Reaction of metallic lead with alkyl iodides

Cahours (24) mentioned that ethyl iodide attacked metallic lead but no product was isolated. The reaction probably involved the formation of $(C_2H_5)_2PbI_2$, an unstable compound. Calingaert (25) reported that addition of some reagent to take up the halogen caused the reaction to go in good yield. Such agents are powdered aluminum, zinc, or silicon with concentrated sodium hydroxide solutions.

$$Pb + 4C_2H_5I + 2Zn + 8NaOH \longrightarrow Pb(C_2H_5)_4 + 4NaI + 2Zn(ONa)_2 + 4H_2O$$

Reaction of lead chloride with an active organometallic compound

Organozinc compounds. Tetraethyllead has been prepared (19, 55) by adding lead chloride to diethylzinc.

$$2Zn(C_2H_5)_2 + 2PbCl_2 \longrightarrow Pb(C_2H_5)_4 + 2ZnCl_2 + Pb$$

The inflammability of the organozinc compounds has greatly restricted their use in such reactions.

Organolithium compounds. Austin (8) prepared a number of aryllead compounds by the action of aryllithium compounds upon lead chloride. He stated that the action was similar to that when organomagnesium halides are used. The series of reactions is given under organomagnesium halide compounds, below.

Recently (this thesis, p. 108) improved yields were obtained in preparing tetraphenyllead by adding iodobenzene to the reaction mixture:

$$3C_6H_5Li + PbCl_2 + C_6H_5I \longrightarrow (C_6H_5)_4Pb + 2LiCl + LiI$$

Yields based upon the ordinary Grignard reaction (see below) indicated a yield of 160%; based upon the above equation the yield was 80%. Whereas free lead is deposited in the ordinary reaction between lead chloride and an organolithium compound or organomagnesium halide, it is not deposited when an organic iodide is added.

Organomagnesium halides. The first investigators to use the Grignard reagent in preparing an organolead compound were Pfeiffer and Truskier (179) who prepared tetraphenyllead. The reaction product formed from the Grignard reagent and lead chloride must be hydrolized to obtain the organolead compound (119). The exact nature of the product before hydrolysis is not known. A series of reactions like the following is usually given to show the method of formation of lead compounds:

$$12RMgX + 6PbCl_2 \longrightarrow 6R_2Pb + 12Mg(X)Cl$$

$$6R_2Pb \longrightarrow 2R_6Pb_2 + 2Pb$$

$$2R_6Pb_2 \longrightarrow 3R_4Pb + Pb$$

The validity of this mechanism is upheld by the following facts:

(1) The characteristic brown to red coloration associated with R_2Pb compounds is usually noticed in the early stages of preparing R_4Pb compounds.

(2) R_2Pb and R_6Pb_2 compounds can be isolated from the reaction mixtures.

(3) The R_2Pb and R_6Pb_2 compounds are converted to the R_4Pb compounds on the application of heat, in the presence or absence of Grignard reagent.

These reactions may not represent the true course of reaction, however, because the following reaction has been demonstrated:

$$R_3Pb\text{-}PbR_3 + \underline{n}\text{-}C_4H_9Li \longrightarrow R_3PbLi + R_3Pb\text{-}\underline{n}\text{-}C_4H_9$$

A similar reaction with a Grignard reagent has not been observed, but compounds of the type R_3PbMgX have been made (67). The binary system, $Mg + MgX_2 \rightleftarrows 2MgX$, reacts with R_6Pb_2 compounds by adding magnesious halide:

$$R_6Pb_2 + 2\ [\text{-}MgX] \longrightarrow 2R_3PbMgX$$

The following reactions could then take place:

$$R_3PbMgX \longrightarrow R_2Pb + RMgX$$

$$2R_2Pb \longrightarrow R_4Pb + Pb$$

Actually, Gilman and Bailie have been able to carry out a reaction between R_6Pb_2 compounds and the binary system and show that R_4Pb compounds, free lead, and a Grignard reagent were formed.

Reaction of hydrazine sulfate and organolead halides

Hydrazine sulfate has been used to convert triphenyllead chloride and diphenyllead dichloride to tetraphenyllead. An alcoholic mixture of the reactants was heated with sodium carbonate (69).

Electrolytic reduction

Electrolysis of acetone in dilute sulfuric acid, using a lead cathode (188, 202), yielded a red oil that seemed to be composed mainly of diisopropyllead. There were some indications that some tetraisopropyllead might have been present.

Pyrolysis of a plumbonic acid

Lesbre (152) mentioned that pyrolysis of benzylplumbonic acid, $C_6H_5CH_2Pb(OH)_3$, yielded, among other products, some tetrabenzyllead. No further details were given.

Free radicals and metallic lead

Several patents have appeared in which it is claimed that when a hydrocarbon mixture such as gasoline vapor was subjected to thermal decomposition, and the gaseous mixture containing free radicals was brought in contact with lead and quickly cooled, a solution of organolead compounds resulted (207, 208). This is a modification of the Paneth technique on a larger scale.

Physical-Chemical Data

Jones, Evans, Gulwell, and Griffiths (117) have carried out some extensive studies upon some physical properties of alkyllead compounds. These authors found that the boiling points at 10 mm. of straight-chain lead compounds could be calculated by use of the formula:

$$t_{10\ \text{mm.}} + 273.1 = 0.867\ M^{1.037}$$

where M is the molecular weight. The calculated values agreed excellently with experimental values except in the case of tetramethyllead.

It was found that, within the limits of pressures usually encountered in such distillations, the reciprocal of the absolute boiling point was a linear function of the logarithm of the pressure. For tetraethyllead, then, the equation

$$t + 273.1 = 2960/(9.4262 - \log_{10} p)$$

gives the temperature (t) of distillation at any pressure (p).

By assuming that the ratio of the absolute boiling points of two different alkyllead compounds under one pressure is equal to the ratio of the boiling points of the two compounds under another pressure, it is possible to calculate the approximate value of the boiling point of a new compound. This method is of especial interest in calculating the boiling point of a new mixed straight-chain tetraalkyllead compound. The boiling point of the new compound at 10 mm. could be calculated by the first equation above and the values at different pressures for tetraethyllead could be calculated from the second equation. Thus, the approximate boiling point of the unknown at any pressure could be determined mathematically.

Buckler and Norrish (18) found that the vapor pressure of tetraethyllead in the temperature range 0 to 70° could be expressed by the equation $\log_{10} p = 9.428 - 2938/T$.

The ionisation potential of tetraethyllead has been reported as 12.3 v.; that of tetramethyllead (provisional) as 11.5 v. (56).

The molecular volume at zero absolute has been calculated for tetramethyllead, tetraethyllead, tetra-n-propyllead, triethyl-n-propyllead, diethyldi-n-propyllead, tri-n-propylethyllead, triethylmethyllead, and triethyl-n-butyllead (112).

X-ray measurements on tetraphenyllead give the distance between lead and carbon as 2.39 A. (64). Its density is 1.745, and a:b:c was found to be 17.30:17.30:6.454. The elementary cell has four molecules.

Table 1. R_4Pb Compounds

Compound	M.P. or B.P.,* °C.	References
Tetra-*n*-amyl-	170/1	(117)
Tetra-*dl*-amyl-	150/0.5	(117)
Tetra-*o*-anisyl-	148-149	(67)
Tetra-*p*-anisyl-	145-146 (67)	(67, 86)
Tetrabenzyl-	-----	(146, 155)
Tetra-*p*-bromophenyl-	187	(189)
Tetra-*n*-butyl-	157/5 (117)	(43, 117)
Tetracyclohexyl-	dec. 160†	(62, 97, 136)
Tetra-*p*-dimethylaminophenyl-	197-198	(8)
Tetra-*o*-ethoxyphenyl-	219-220	(67)
Tetra-*p*-ethoxyphenyl-	110	(67)
Tetraethyl-	78/10 (117)	(7, 16, 17, 19, 21, 26, 27, 28, 29, 34, 35, 36, 37, 47, 55, 63, 66, 88, 91, 100, 102, 110, 114, 115, 116, 117, 118, 160, 162, 165, 174, 175, 177, 179, 204)
Tetra-2-furyl-	52-53	(85)
Tetra-*n*-heptyl-	-----	(218)

*In all of the tables, the constants given are to be assumed to be melting points unless a / is given. In that case it is a boiling point and 150/10 means 150°C. at 10 mm. pressure.

†In all of the tables, dec. followed by a temperature indicates that decomposition occurs without melting at that temperature, 160 dec. means melting with decomposition at 160°.

Table 1 (concluded)

Compound	M.P. or B.P., °C.	References
Tetra-*n*-hexadecyl-	42	(161)
Tetraisoamyl-	dec. on dist. (106)	(100, 106)
Tetraisobutyl-	-23 (106)	(100, 106, 177)
Tetraisopropyl-	-53.5 (107) 120/14 (107)	(60, 93, 100, 107)
Tetramethyl-	-27.5 (102) 6/10 (117)	(17, 23, 26, 28, 29, 34, 35, 36, 60, 100, 102, 116, 117, 118, 138, 151, 170, 174, 175, 176, 181, 196)
Tetraphenethyl-	------	(146)
Tetraphenyl-	223-225 (8)	(7, 8, 26, 29, 37, 41, 45, 46, 53, 62, 66, 67, 74, 75, 76, 90, 92, 98, 116, 118, 129, 131, 132, 133, 134, 137, 141, 145, 147, 151, 158, 171, 179, 182, 187, 192, 194, 203, 205, 213, 218, 219)
Tetra-*n*-propyl-	126/13 (102)	(29, 100, 102, 177)
Tetra-*n*-tetradecyl-	31	(161)
Tetra-2-thienyl-	152 (142)	(85, 142, 144)
Tetra-*o*-tolyl-	201-202 (5)	(5, 6, 67)
Tetra-*m*-tolyl-	122-123	(67)
Tetra-*p*-tolyl-	240 (141)	(6, 26, 29, 67, 74, 141, 182, 218)
Tetra-*p*-xylyl-	250; dec. 270	(147)

$R_3R'Pb$, $R_2R'_2Pb$, $R_2R'R''Pb$, AND $RR'R''R'''Pb$ COMPOUNDS

General Discussion

Unsymmetrical organolead compounds are ones in which at least two different organic groups are attached to lead by carbon-lead bonds. On the basis of their structures, these compounds may be divided into two different classes. Members of the first class have only organic groups attached to the lead atom; but members of the second class, mixed unsymmetrical organolead compounds, have inorganic groups as well as organic groups attached directly to the lead atom. Unsymmetrical organolead compounds in general were first studied in detail by Grüttner and Krause (101, 103, 104). The method of introducing different organic groups, as developed by these authors, is discussed under the first method of preparing these compounds. All unsymmetrical alkyllead compounds are colorless liquids whose physical-chemical properties may be predicted by using the data that apply to the simple tetraalkyllead compounds.

The unsymmetrical aryllead compounds are white (or slightly off-color) crystalline solids. As with all organolead compounds with mixed substituents, the degree of stability is lower than for the simple R_4Pb compounds. The solubility and reactivity of the unsymmetrical types are greater.

Unsymmetrical alkyl-aryllead compounds are either liquids or solids, depending upon the substituents. In general, those with one aryl group are liquids while those with two or three aryl groups are solids. In cleavage reactions with halogens or hydrogen halides the aryl groups are always cleaved first.

Methods of Preparation

Halogen or hydrogen halide cleavage followed by reaction with an active organometallic compound

When an R_4Pb compound is cleaved with a halogen or hydrogen halide, an R_3PbX or R_2PbX_2 compound is formed (see under these compounds for conditions). Either of these products, upon reaction with an active organometallic compound (R'M), is converted to an unsymmetrical organolead compound. This compound, in turn, may be cleaved to produce further differentiation in the organolead compound. Such a series of reactions is possible because of the gradation in ease of cleavage of different organic groups.

Preferential cleavage, lability, or relative negativity of organometallic compounds has occupied the attention of a number of workers. Extensive work has been done by Kharasch and co-workers (120, 121, 122) on the lability of organomercury compounds. Less extensive tables have been established in the tin series (15, 22). By combining the large number of short series available from organolead cleavage studies, it is possible to obtain a rather extensive relative negativity series of radicals. Comparison of fragments of series obtained by the study of these three different metals indicates that there is little if any difference in the order of cleavage, providing the same method of cleavage is used.

The following series give some idea of the order of cleavage, the most easily cleaved radical appearing first:

α-naphthyl, *p*-xylyl, *p*-tolyl, phenyl, methyl, ethyl, *n*-propyl, isobutyl, isoamyl, cyclohexyl (145).

2-furyl, 2-thienyl, phenyl (85).

(allyl, *β*-styryl), phenyl, 3-butenyl (205).

In generalizing upon cleavage (5) one may say that, in the aromatic series, the heaviest radical is cleaved first. In the primary aliphatic series, the lightest in molecular weight is cleaved first. Aromatic groups are cleaved before aliphatic groups, and aliphatic groups other than primary ones are cleaved before the corresponding primary group. The cyclohexyl radical seems held more firmly than any other. In cases where different radicals have quite similar tendencies to be cleaved that radical is usually cleaved which is present in greatest number.

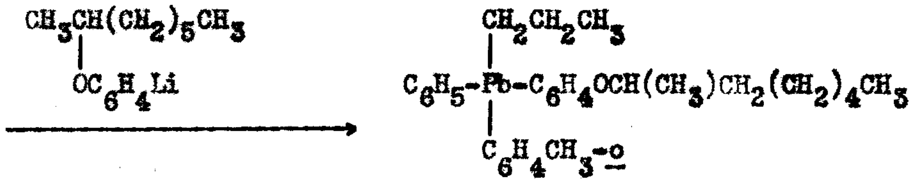
Some rather important exceptions to the generalization that the heaviest aryl radical is cleaved first appear in an article by Gilman and Towne (85). The *α*-furyl and *α*-thienyl radicals are cleaved before the phenyl radical.

An example of an interesting series of reactions making use of this knowledge is taken from Austin (9):

$$(C_6H_5)_4Pb \xrightarrow{HCl} (C_6H_5)_3PbCl \xrightarrow{\underline{n}\text{-}C_3H_7MgBr} (C_6H_5)_3PbCH_2CH_2CH_3$$

$$\xrightarrow{HCl} (C_6H_5)(CH_3CH_2CH_2)PbCl_2 \xrightarrow{\underline{o}\text{-}CH_3C_6H_4MgBr}$$

$$(C_6H_5)(CH_3CH_2CH_2)Pb(\underline{o}\text{-}CH_3C_6H_4)_2 \xrightarrow{HCl} (C_6H_5)(CH_3CH_2CH_2)(\underline{o}\text{-}CH_3C_6H_4)PbCl$$



$$\xrightarrow{\begin{array}{c}CH_3CH(CH_2)_5CH_3\\ |\\ OC_6H_4Li\end{array}} \begin{array}{c}CH_2CH_2CH_3\\ |\\ C_6H_5\text{-}Pb\text{-}C_6H_4OCH(CH_3)CH_2(CH_2)_4CH_3\\ |\\ C_6H_4CH_3\text{-}\underline{o}\end{array}$$

The product contained an asymmetric carbon atom as well as an asymmetric lead atom but it could not be resolved. The publications of Austin and Krause and co-workers have been the sources of most of the information on attempted isolation of optically active organolead compounds. No optically active organolead compound has yet been reported.

The redistribution reaction

The redistribution reaction of Calingaert and co-workers (this reaction is discussed in a separate section) offers the possibility of preparing large quantities of organolead compounds with mixed organic radicals. To date, only lead compounds with up to three different organic substituents have been reported as being prepared by this method. A mixture of tetramethyl-, tetraethyl-, and tetra-n-propyllead yielded, at equilibrium, a product containing the fifteen possible tetravalent lead compounds, in proportions corresponding to a random redistribution of the three different radicals (29).

The disadvantage of such a method of preparation lies in the difficulty of separating the reaction mixture into its components. The reaction has been tried with two or more of the radicals: methyl, ethyl, n-propyl, isopropyl, isobutyl, tert-butyl, phenyl, and p-tolyl, bound to one or more metals including lead, tin, silicon, and mercury (29, 33).

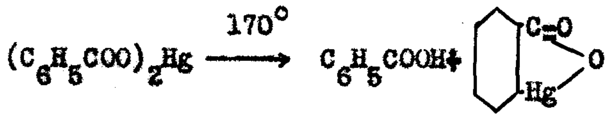
Decarboxylation of organolead salts of organic acids

Kocheshkov and Aleksandrov (126, 127) have reported an interesting method of establishing a carbon-lead linkage. Their method involves decarboxylation of an organolead salt:

$$(C_6H_5)_3PbCl + KO_2CCH_2CO_2C_2H_5 \longrightarrow (C_6H_5)_3PbO_2CCH_2CO_2C_2H_5$$

$$\xrightarrow{\Delta^{\circ}} CO_2 + (C_6H_5)_3PbCH_2CO_2C_2H_5$$

In this connection, it might be well to mention several earlier attempts to obtain a carbon-lead linkage by pyrolysis of a lead salt. Hurd and Austin (114) attempted to prepare such a compound from lead tetrabenzoate. This work was patterned after the known formation of a carbon-mercury bond in the pyrolysis of mercuric benzoate (214):



While benzoic acid was detached, no evidence could be found for an organolead compound in the residue. Vigorous decomposition always took place upon heating the lead tetrabenzoate.

The same authors also pyrolyzed lead tetraacetate. Nearly quantitative yields of lead diacetate were obtained.

Towne (205) heated on a water bath the double salt of aniline with lead acetate, $C_6H_5NH_2.Pb(C_2H_3O_2)_2$, and recovered it unchanged.

Table 2. $R_3R'Pb$ Compounds

Compound	M.P. or B.P., °C.	References
Tri-*o*-anisylbenzyl-	80-81	(67)
Tri-*p*-anisyl-2-furyl-	83	(86)
Tri-*o*-anisyltriphenylmethyl-	145-146	(10)
Tricyclohexylbenzyl-	dec. 128	(67)
Tri-*p*-ethoxyphenylbenzyl-	76-77	(67)
Triethylallyl-	86/10 (189)*	(100, 189, 201)
Triethyl-*n*-amyl-	121/15 (104)	(25, 100, 104)
Triethyl-*sec*-amyl-	118/13 (100)	(100, 107)
Triethylbenzyl-	149-150.5/13 with some dec.	(99)
Triethyl-*ε*-bromoamyl-	116.8/13 (104)	(100, 104)
Triethyl-*p*-bromophenyl-	dec.210/3	(189)
Triethyl-3-butenyl-	78/3	(87)
Triethyl-*n*-butyl-	108/13 (84)	(84, 100, 105)
Triethyl-*sec*-butyl-	105-106/14 (84)	(84, 100, 107)
Triethyl-*tert*-butyl-	76/5	(84)
Triethylcarboxymethyl-	137 dec.	(201)
Triethyl-*p*-dimethylaminophenyl-	125/1	(201)

*This compound also exists as a solid dimer which dec. at 115° (201).

Table 2 (continued)

Compound	M.P. or B.P., °C.		References
Triethyl-*β*-hydroxyethyl-	100/2		(201)
Triethylisoamyl-	114.5/13	(101)	(25, 100, 101, 105)
Triethylisobutyl-	102/10	(84)	(84, 100, 101, 105)
Triethylisopropyl-	90/13	(107)	(25, 100, 107)
Triethylmethyl-	70-70.5/16	(101)	(26, 28, 29, 34, 35, 36, 91, 100, 101)
Triethyl-*α*-naphthyl-	176/13		(99)
Triethyl-*n*-octadecyl-	73-74		(185)
Triethylphenyl-	136/13	(99)	(99, 114)
Triethyl-*p*-(N-phthalimide)phenyl-	100/0.0001		(201)
Triethyl-*n*-propyl-	99.5/16	(101)	(29, 100, 101, 105)
Triethyl-*o*-tolyl-	153.5/13		(99)
Triethyl-*p*-tolyl-	154/13		(99)
Triisoamylethyl-	steam dist.	(106)	(100, 106)
Triisoamylisobutyl-	steam dist.	(106)	(100, 106)
Triisoamylmethyl-	steam dist.	(106)	(100, 106)
Triisoamyl-*n*-propyl-	steam dist.	(106)	(100, 106)
Triisobutyl-*n*-butyl-	145-146/10		(42)
Triisobutylethyl-	steam dist.	(106)	(100, 106)
Triisobutylisoamyl-	steam dist.	(106)	(100, 106)

Table 2 (continued)

Compound	M.P. or B.P., °C.	References
Triisobutylmethyl-	121/12 (106) with slow dec.	(100, 106)
Triisobutyl-*n*-propyl-	steam dist. (106)	(100, 106)
Triisopropylmethyl-	-----	(29)
Trimethylbenzyl-	124/13 with dec.	(99)
Trimethyl-*n*-butyl-	64.5/14 (101)	(100, 101)
Trimethyl-*sec*-butyl-	59/13 (31)	(31, 107)
Trimethyl-*tert*-butyl-	5.7;47/13 (31)	(26, 29, 31)
Trimethylethyl-	27/10 (101)	(26, 28, 29, 34, 35, 36, 100, 101, 105)
Trimethylisoamyl-	69-71/12	(101)
Trimethylisobutyl-	58-59/15 (101)	(100, 101)
Trimethylisopropyl-	75/60 (107)	(26, 29, 100, 107)
Trimethylphenyl-	104/13 (99)	(29, 99)
Trimethyl-*n*-propyl-	48-49/16 (101)	(29, 100, 101, 105)
Trimethyl-*o*-tolyl-	117.5-118/13	(99)
Trimethyl-*p*-tolyl-	118-119/13	(99)
Triphenylallyl-	76-77 (6)	(6, 87)
Triphenyl-*o*-aminophenyl-	165-166	(201)
Triphenyl-*p*-aminophenyl-	166-167	(82)

Table 2 (continued)

Compound	M.P. or B.P., °C.		References
Triphenyl-*n*-amyl-	16-17		(9)
Triphenyl-*o*-anisyl-	128-129		(163)
Triphenyl-*p*-anisyl-	152		(86)
Triphenyl-7-(1,2-benzanthryl)-	204-205		(this thesis)
Triphenylbenzohydryl-	122;dec.130		(67)
Triphenylbenzyl-	93;dec.205-210	(146)	(67, 87, 146)
Triphenyl-α-benzyl- α-carbethoxymethyl-	82-84	(126)	(126, 127)
Triphenyl-*p*-bromophenyl-	115	(189)	(75, 189)
Triphenyl-3-butenyl-	84-86		(87)
Triphenyl-*n*-butyl-	47		(83)
Triphenyl-*sec*-butyl-	84		(83)
Triphenyl-*tert*-butyl-	150		(83)
Triphenylcarbethoxymethyl-	59-60	(126)	(126, 127)
Triphenyl-*p*-carbomethoxyphenyl-	125-127		(163)
Triphenylcarboxymethyl-	194		(201)
Triphenyl-*p*-carboxyphenyl	256-258		(163)
Triphenyl-*p*-chlorophenyl-	-----		(75)

Table 2 (continued)

Compound	M.P. or B.P., °C.		References
Triphenylcyclohexyl-	119;dec.160	(147)	(41, 137, 145, 147)
Triphenyl-2-dibenzofuryl-	158.5-159.5		(70)
Triphenyl-3-dibenzofuryl-	125-126		(70)
Triphenyl-4-dibenzofuryl-	99-100		(70)
Triphenyl-$\underline{\beta},\underline{\gamma}$-dihydroxypropyl-	124-125		(6)
Triphenyl-1-[2-dimethylamino-5-(*p*-bromophenylazo)-phenyl]-	-----		(201)
Triphenyl-1-[2-dimethylamino-5-(*p*-carboxyphenylazo)-phenyl]-	-----		(201)
Triphenyl-1-[2-dimethylamino-5-(*p*-chlorophenylazo)-phenyl]-	-----		(201)
Triphenyl-1-[2-dimethylamino-5-(*p*-iodophenylazo)-phenyl]-	-----		(201)
Triphenyl-1-[2-dimethylamino-5-(*p*-nitrophenylazo)-phenyl]-	-----		(201)
Triphenyl-*o*-dimethylaminophenyl-	101-102		(201)
Triphenyl-*p*-dimethylaminophenyl-	124-125		(8)
Triphenylethyl-	42;dec.235	(147)	(37, 53, 145, 147)
Triphenyl-2-furyl-	166-167		(85)
Triphenyl-1-[2-hydroxy-5-(*p*-bromophenylazo)-phenyl]-	-----		(201)
Triphenyl-1-[2-hydroxy-5-(*p*-carboxyphenylazo)-phenyl]-	-----		(201)

Table 2 (continued)

Compound	M.P. or B.P., °C.		References
Triphenyl-1-[2-hydroxy-5-(*p*-chlorophenylazo)-phenyl]-	-----		(201)
Triphenyl-1-[2-hydroxy-3,5-di(*p*-nitrophenylazo)-phenyl]-	-----		(201)
Triphenyl-*p*-(*β*-hydroxyethyl)phenyl-	87-88		(163)
Triphenyl-1-[2-hydroxy-5-(*p*-iodophenylazo)-phenyl]-	-----		(201)
Triphenyl-*o*-hydroxymethylphenyl-	134-136		(163)
Triphenyl-*p*-hydroxymethylphenyl-	98-100		(163)
Triphenyl-1-(2-hydroxy-napthyl)-azophenyl-4-	dec.135		(82)
Triphenyl-*o*-hydroxyphenyl-	217-218		(this thesis)
Triphenylisobutyl-	68-68.5		(83)
Triphenyl-1-[2-methoxy-5-(*p*-nitrophenylazo)-phenyl]-	-----		(201)
Triphenyl-1-[4-methoxy-3-(*p*-nitrophenylazo)-phenyl]-	-----		(201)
Triphenylmethyl-	62-63	(29)	(29, 145)
Triphenyl-*p*-N-methylaminophenyl-	97-98		(201)
Triphenyl-*α*-naphthyl-	131	(87)	(87, 147)
Triphenyl-9-phenanthryl-	169-171		(this thesis)
Triphenylphenethyl-	116-117;dec.205-210		(146)

Table 2 (concluded)

Compound	M.P. or B.P., °C.		References
Triphenylphenetyl-	119-120		(147)
Triphenyl-*p*-phenoxyphenyl-	127		(145)
Triphenyl-*n*-propyl-	69-70		(9)
Triphenyl-2-pyridyl-	210-214		(96)
Triphenyl-*β*-styryl-	107-109		(87)
Triphenyl-2-thienyl-	206-207	(85)	(85, 143, 144)
Triphenyl-*p*-tolyl-	125.5	(147)	(6, 8, 145, 147)
Triphenyltriphenylmethyl-	196-197		(67)
Triphenyl-2,4-xylyl-	111.5-112		(147)
Triphenyl-*p*-xylyl-	104.5	(147)	(145, 147)
Tri-*n*-propylethyl-	118.2/14	(106)	(29, 100, 106)
Tri-*n*-propylisoamyl-	------		(100, 106)
Tri-*n*-propylisobutyl-	------		(100, 106)
Tri-*n*-propylmethyl-	106/13	(106)	(29, 100, 106)
Tri-*o*-tolylphenyl-	161-162		(5)
Tri-*p*-tolylbenzyl-	81-82		(67)

Table 3. $R_2R'_2Pb$ Compounds

Compound	M.P. or B.P., °C.	References
Di-n-amyldi-dl-amyl-	160/1	(117)
Di-n-amyldi-n-butyl-	170/1	(117)
Di-dl-amyldi-n-butyl-	135/0.5	(117)
Di-n-amyldiethyl-	116-118/0.5	(117)
Di-n-amyldi-n-hexyl-	180/0.5	(117)
Di-n-amyldiisoamyl-	160/0.5	(117)
Di-n-amyldiisobutyl-	140/0.5	(117)
Di-n-amyldimethyl-	113/4	(117)
Di-n-amyldi-n-propyl-	150/1	(117)
Di-p-anisyldi-2-furyl-	72-73	(86)
Di-7-(1,2-benzanthryl)diphenyl-	295-296 dec.	(this thesis)
Dibenzyldiphenyl-	dec. 200	(146)
Dibiphenyldiphenyl-	134-135	(205)
Di-p-bromophenyldiphenyl-	123	(189)
Di-n-butyldiethyl-	90/1	(117)
Di-tert-butyldiethyl-	80/10	(189)
Di-n-butyldiisoamyl-	155/0.5	(117)
Di-n-butyldiisobutyl-	135/1	(117)

Table 3 (continued)

Compound	M.P. or B.P., °C.		References
Di-*n*-butyldimethyl-	108/10		(117)
Di-*sec*-butyldimethyl-	-----		(31)
Di-*n*-butyldiphenyl-	dec. when heated in vac.		(68)
Di-*sec*-butyldiphenyl-	unstable oil		(68)
Di-*tert*-butyldiphenyl-	177		(68)
Di-*n*-butyldi-*n*-propyl-	120/1		(117)
Di-*p*-chlorophenyldiphenyl-	------		(75)
Dicyclohexyldiphenyl-	178-180 dec.		(97)
Di-*p*-dimethylamino-phenyldiphenyl-	134-135		(8)
Diethyldiisoamyl-	142/13	(103)	(100, 103)
Diethyldiisobutyl-	124/13	(103)	(25, 100, 103)
Diethyldimethyl-	52-53/14	(167)	(26, 28, 29, 34, 35, 36, 100, 103, 167)
Diethyldi-*α*-naphthyl-	116		(147)
Diethyldi-*n*-octadecyl-	58-60		(185)
Diethyldiphenyl-	176/8	(189)	(91, 167, 189)
Diethyldi-*n*-propyl-	99/10	(117)	(26, 29, 100, 103, 117)
Diethyldiisopropyl-	95.5/14	(107)	(100, 107)

Table 3 (concluded)

Compound	M.P. or B.P., °C.		References
Di-2-furyldiphenyl-	118		(85)
Di-2-furyldi-2-thienyl-	117-119		(85)
Diisoamyldimethyl-	122-123/13	(103)	(100, 103)
Diisobutyldimethyl	95.5-96/13	(103)	(26, 29, 100, 103)
Diisobutyldiphenyl-	unstable oil		(68)
Diisopropyldimethyl-	-----		(29)
Dimethyldiphenyl-	151-152/2	(29)	(29, 189)
Dimethyldi-n-propyl-	72/10	(117)	(29, 100, 103, 117)
Di-α-naphthyldiphenyl-	197	(147)	(87, 91, 147)
Di-9-phenanthryldiphenyl-	208-210		(this thesis)
Diphenyldi-2-thienyl-	185		(85)
Diphenyldi-o-tolyl-	134-135		(150)
Diphenyldi-p-tolyl-	121-122	(8)	(8, 74)
Diphenyldi-p-xylyl-	94		(145)

. Table 4. $R_2R'R''Pb$ Compounds

Compound	M.P. or B.P., °C.		References
Diethyl-*sec*-amyl-*n*-propyl-	121/13	(107)	(100, 107)
Diethyl-*n*-butylmethyl-	80/7		(14)
Diethyl-*sec*-butylmethyl-	76-78/16		(14)
Diethyl-*n*-butyl-*n*-propyl-	108/13	(105)	(25, 100, 105)
Diethyl-*sec*-butyl-*n*-propyl-	115.5/14.5	(107)	(100, 107)
Diethylisoamylisobutyl-	131/14	(105)	(100, 105)
Diethylisoamylmethyl-	106/15.5	(105)	(100, 105)
Diethylisoamyl-*n*-propyl-	127.5/15	(105)	(100, 105)
Diethylisobutylmethyl-	87/13	(105)	(100, 105)
Diethylisobutyl-*n*-propyl-	110/13	(105)	(100, 105)
Diethylisopropyl-*n*-propyl-	107/17	(107)	(100, 107)
Diethylmethylphenyl-	98/4		(14)
Diethylmethyl-*n*-propyl-	80.8/15	(105)	(29, 100, 105)
Diisoamylethyl-*n*-propyl-	145.5/13	(105)	(100, 105)
Dimethyl-*sec*-amylethyl-	90/15	(107)	(25, 100, 107)
Dimethyl-*sec*-butylethyl-	74/13	(107)	(25, 100, 107)
Dimethyl-*sec*-butylisoamyl-	115.5/14	(107)	(100, 107)
Dimethylethylisoamyl-	92/14	(105)	(100, 105)
Dimethylethylisobutyl-	74/13	(105)	(100, 105)

Table 4 (concluded)

Compound	M.P. or B.P., °C.		References
Dimethylethyl-*n*-propyl-	65/15	(105)	(25, 29, 100, 105)
Dimethylethylisopropyl-	61.2/15	(107)	(100, 107)
Dimethylisoamyl-*n*-propyl-	105/15	(105)	(100, 105)
Dimethylphenyl-*n*-propyl-	93/3		(14)
Diphenylcyclohexylmethyl-	thick oil		(145)
Di-*n*-propylethylmethyl-	------		(29)
Di-*o*-tolylphenyl-*n*-propyl-	49-50		(9)

Table 5. $RR'R''R'''Pb$ Compounds

Compound	M.P. or B.P., °C.		References
n-Butylethylisoamyl-*n*-propyl-	144/14	(105)	(100, 105)
n-Butylethylmethyl-*n*-propyl-	103/13	(105)	(100, 105)
Ethylisoamylmethyl-*n*-propyl-	115/15	(105)	(100, 105)
p-(*sec*-Octyloxyphenyl)phenyl-*n*-propyl-o-tolyl-	an oil		(9)

R_3PbX, $R_2R'PbX$, $RR'R''PbX$, R_2PbX_2, AND $RR'PbX_2$ COMPOUNDS

General Discussion

In the compounds in which X represents fluorine, chlorine, bromine, or iodine, the presence of the halogen makes the compound a solid. None of the compounds containing fluorine has a melting point; decomposition occurs before the compound melts. Trimethyllead fluoride is mentioned as being "very volatile". Trimethyllead chloride sublimes at 187°. These are the only two alkyl organolead compounds containing halogen attached to lead that show any tendency to distil.

Of the organolead halides, the fluorides and chlorides show the greatest stability. The bromides are relatively stable but the iodides decompose upon standing and, when the compound is at all stable, have a lower melting point than any of the other corresponding halides.

The aryllead salts are more stable than the corresponding alkyllead compounds. In aqueous solution the R_3Pb^+ ions (where the R groups may be different) resemble the alkali metal ions.

There is somewhat less stability in the aliphatic series in the R_2PbX_2 compounds than in the R_3PbX compounds. In the aromatic series, the opposite is the case and here R_2PbX_2 compounds sometimes show amazing stability.

Grüttner and Krause (105) had observed that, unless freshly prepared $R_2R'PbX$ compounds were used in the preparation of $R_2R'R''Pb$ compounds, low yields and impure products resulted. This can now be explained on the basis of the redistribution reaction (p. 78). There is a lead-halogen bond present which acts as a catalyst in this type of reaction. Even at ordinary temperatures, there is some of the reaction of the general type:

$$2\ R_3PbX \rightleftarrows R_4Pb + R_2PbX_2$$

At higher temperatures, irreversible decomposition occurs:

$$R_2PbX_2 \longrightarrow R\text{-}R + PbX_2$$

When there is more than one kind of organic radical it is evident that the aged material would be quite impure.

A few cases of addition compounds of pyridine or ammonia with organolead halides are known. Pfeiffer and Truskier (179) observed compounds with four molecules of pyridine with diphenyllead dichloride and dibromide. These were fairly stable, but diphenyllead dibromide with two molecules of ammonia attached gave up the ammonia upon exposure to the air. Foster, Gruntfest, and Fluck (54) observed ammino compounds formed with triphenyllead chloride but in no case could the amount of ammonia be expressed in small whole numbers.

Physical-Chemical Data

As a part of a program of measurements of the dipole moments of molecules containing metallic atoms with the object of obtaining bond moments and studying their relation to the electronegativities of the bonded elements, the dipole moments of a number of organolead compounds were measured (156, 199, 200). The compounds studied were hexaethyldilead, trimethyllead chloride, triethyllead chloride, diethyllead dichloride, triethyllead bromide, triphenyllead chloride, triphenyllead bromide, and triphenyllead iodide. Some corresponding carbon, silicon, tin, and germanium compounds were included for comparison.

Methods of Preparation

Organolead compounds containing one or two halogens may be prepared in the following manner:

Reaction between halogen or hydrogen halide and an organolead compound

This type of reaction was discussed in the section on lead compounds containing only two or more different organic radicals. It is the method most often used to obtain organolead halides.

Reaction between an acid and an organolead compound, followed by use of a metal halide or hydrogen halide

Polis (182) found that tetraphenyllead could be added to boiling concentrated nitric acid and thus be converted to diphenyllead dinitrate. The two phenyl groups appeared as nitrobenzene in the product. If the diphenyllead dinitrate was dissolved in boiling water and a solution of sodium halide was added, diphenyllead dihalide precipitated in excellent yield:

$$(C_6H_5)_2Pb(NO_3)_2 + 2\ NaI \longrightarrow (C_6H_5)_2PbI_2 + 2\ NaNO_3$$

Tetraethyllead, in chloroform solution, reacted with nitric acid to give diethyllead dinitrate (114). The product was identified by dissolving in methyl alcohol and adding hydrochloric acid. The diethyllead dichloride precipitated and was filtered.

The use of an inorganic acid other than the halogen acids does not lead to good yields of R_3PbX types. For example, R_3PbX compounds may be made from R_3PbNO_3 compounds but nitric acid has a much greater tendency to cleave an R_4Pb compound to an $R_2Pb(NO_3)_2$ compound.

Reaction of diazonium chlorides with lead chlorides

While reactions of the type:

$$(RN_2Cl)_2{\cdot}PbCl_4 \longrightarrow R_3PbCl$$

or

$$RN_2Cl{\cdot}PbCl_2 \longrightarrow R_2PbCl_2$$

are known (130, 172), the yields are only a few per cent. The general procedure for these reactions is to add a powdered metal such as tin, zinc, or copper to a suspension of the diazonium chloride-lead chloride complex, and then heat the mixture.

Makin and Waters (159) were able to prepare R_3SbCl_2 compounds from the diazonium chlorides and antimony powder. The reactants were suspended in acetone or ethyl acetate and the solution kept neutral by adding chalk. When lead powder was substituted for the antimony, only inorganic lead ions were found in the product.

In some earlier work by Sakellarios (190), it had been observed that heating of $(RN_2Cl)_2 \cdot PbCl_4$ complexes without catalysts gave no material with a carbon-lead bond. It might also be mentioned that this same author hydrolyzed the complex $(C_2H_5NH_2 \cdot HCl)_2 \cdot PbCl_4$ and obtained only lead chloride and $C_2H_5NCl_2$.

Controlled reaction of lead chloride with a Grignard reagent

Krause and Schlöttig (145) stated that triphenyllead chloride was produced by adding to phenylmagnesium bromide an amount of lead chloride somewhat in excess of that used to produce tetraphenyllead. The triphenyllead chloride was not isolated as such but was removed by shaking the reaction product with a solution of alkali. The yields were none too good.

Triphenyllead bromide has been found as an occasional by-product in the preparation of tetraphenyllead through the Grignard reaction (194). This compound does not owe its formation to a secondary reaction between tetraphenyllead and magnesium bromide or the binary system ($Mg + MgBr_2$), inasmuch as tetraphenyllead is unaffected by these substances under the conditions of the reaction. The next method might be used in offering a clue to the formation of triphenyllead bromide by assuming a reaction between hexaphenyldilead and magnesium bromide.

Meals (161), in a study of long-chained organometallic compounds, prepared R_3PbCl compounds in over 50% yields by reaction of about one mole equivalent of lead chloride with two mole equivalents of long-chained alkylmagnesium bromide. Attempts to form R_3PbBr compounds by similar reactions using lead bromide were unsuccessful.

Meals (161) observed that the melting points of R_3PbCl compounds reach a minimum somewhere between tri-n-butyllead chloride (m.p. 109-111°) and tri-n-dodecyllead chloride (m.p. 64-65°), a region in which R_3PbCl compounds have not been investigated. It is interesting to note that in the long-chained alkyllead compounds, mixed melting points do not seem to have much value. A mixture of tetra-n-hexadecyllead and tetra-n-hexadecyltin showed no depression in melting point. A mixture of tri-n-dodecyllead chloride (m.p. 64-65°) and tri-n-tetradecyllead chloride (m.p. 74-75°) melted at 66-67°.

Austin (7) investigated the use of the reaction:

$$R_2PbX_2 + R_2Hg \longrightarrow R_3PbX + RHgX$$

in the synthesis of organolead compounds. Diphenyllead dichloride and diphenylmercury heated in pyridine gave a 21% yield of triphenyllead chloride. The low yield may have been due to the difficulty in isolating triphenyllead chloride as there was a 57% yield of phenylmercuric chloride. When the reaction:

$$(o\text{-}CH_3C_6H_4)_2PbCl_2 + (C_6H_5)_2Hg \longrightarrow (o\text{-}CH_3C_6H_4)_2(C_6H_5)PbCl + C_6H_5HgCl$$

was carried out in an attempt to obtain mixed compounds, phenylmercuric chloride was obtained in a 38% yield, but none of the expected di-o-tolylphenyllead chloride could be isolated from the reaction products. Tetraphenyllead and di-o-tolyllead dihalides did not react when heated in benzene or toluene in an attempt to form mixed aryllead halides.

Reaction of R_4Pb or R_6Pb_2 compounds with some inorganic halides and organic acid halides

Browne and Reid (16) investigated the action of some organic acid halides and inorganic halides upon tetraethyllead. Tetraethyllead reacted readily with acetyl chloride at room temperature on the addition of silica gel. A mixture of equivalent amounts of the two reactants produced triethyllead chloride. Benzoyl chloride reacted also; the only products that could be isolated were lead chloride and benzoic acid.

With phosphorus pentachloride, tetraethyllead in carbon disulfide solution produced a thick syrup from which triethyllead chloride was extracted with petroleum ether. A simple solution of tetraethyllead in carbon disulfide gave a black flocculent precipitate which was insoluble in ether, alcohol, or petroleum ether. It did not melt at 300° but burned readily.

Tetraethyllead and aluminum chloride reacted in organic solvents to give triethyllead chloride as the only material isolated. Silicon tetrachloride likewise gave triethyllead chloride, but titanium tetrachloride was reduced to titanium trichloride with the production of a brown, tarry substance.

Goddard and Goddard (91) observed the action of thallic chloride with several organolead compounds. Thallic chloride and triethylmethyllead yielded triethyllead chloride and thallous chloride. Diethyldiphenyllead yielded diethyllead dichloride and diphenylthallium chloride. Di-α-naphthyldiphenyllead yielded diphenyllead dichloride and di-α-naphtylthallium chloride.

Goddard (89) reacted hexa-m-xylyldilead in benzene with thallic chloride in ether. The solution became warm and a precipitate appeared. After standing a week, crystals of di-m-xylyllead dichloride had formed and the benzene solution contained thallous chloride.

In summarizing the reactions between aliphatic or aromatic organolead compounds and thallic chloride Goddard stated that:

1. Substances of the type R_4Pb give rise to R_2PbX_2 and R_2TlX compounds.
2. Substances of the type R_3PbX and $R_3R'Pb$ (where R' is the radical with lower molecular weight) yield thallous chloride and R_2PbX_2 and R_3PbX, respectively.
3. Substances of the type $R_2R'_2Pb$ produce R'_2PbX_2 and R_2TlX compounds.
4. Substances of the type R_2PbX_2 (where X is bromine or iodine) merely exchange halogen with thallic chloride.

Challenger and Pritchard (38) in tabulating reactions between various organometallic compounds and some inorganic halides stated that tetraphenyllead reacted as follows:

1. With bismuth tribromide at 66° diphenyllead dibromide and diphenylbismuth bromide were formed.
2. With antimony trichloride at 110° diphenyllead dichloride and diphenylantimony chloride were formed.
3. With arsenic trichloride at 110° diphenyllead dichloride and diphenylarsenic chloride were formed.
4. With phosphorus trichloride at 134° there was no action.

Gilman and Bailie (67) found that when benzene-ether solutions of an R_6Pb_2 compound and magnesium iodide were allowed to react, hydrolysis with ammonium chloride gave excellent yields of R_3PbI compound.

The binary system of Gomberg and Bachmann (94) was observed by Gilman and Bailie to undergo two different reactions with R_6Pb_2 compounds. Non-sterically hindered R_6Pb_2 compounds reacted with the binary system to give an R_4Pb compound, lead, and the Grignard reagent. If, however, sterically hindered R_6Pb_2 compounds were used, the product was an R_3PbX compound.

Nesmeyanov and Kocheshkov (171) investigated the action of mercuric chloride upon a number of organometallic compounds including organolead compounds.

Gilman and Apperson (66) reported upon the reactions between some organolead compounds and aluminum chloride, bismuth trichloride, anhydrous ferric chloride, and chloroplatinic acid.

Interchange between R_4Pb and R_2PbX_2 compounds

Austin (7) found that tetraphenyllead and diphenyllead dichloride heated in butyl alcohol gave an 86% yield of triphenyllead chloride. Tetraethyllead and diethyllead dichloride heated in benzene gave a 39% yield of triethyllead chloride. As mentioned in the general discussion of organolead halides, Austin was unable to produce compounds of the $R_2R'PbX$ type by this reaction.

Table 6. R_3PbX Compounds

Compound	M.P., °C.		References
Triamyl- bromide (?)*	------		(124)
Triamyl- chloride (?)	------		(124)
Triamyl- iodide (?)	------		(124)
Tri-*o*-anisyl- iodide	122-123		(67)
Tri-*p*-anisyl- bromide	------		(86)
Tri-*p*-anisyl- chloride	152-153		(86)
Tribenzyl- bromide	dec.150		(146)
Tribenzyl- chloride	unstable		(149)
Tri-*n*-butyl- bromide	------		(43, 167)
Tri-*n*-butyl- chloride	109-111	(180)	(17, 49, 180)
Tri-*sec*-butyl- chloride	dec.130		(188)
Tricyclohexyl- bromide	dec.210		(136)
Tricyclohexyl- chloride	dec.236		(136)
Tricyclohexyl- fluoride	dec.198		(140)
Tricyclohexyl- iodide	91.7	(136)	(41, 67, 136, 137)
Tri-*n*-dodecyl- chloride	64-65		(161)
Tri-*p*-ethoxyphenyl- iodide	99-100		(67)

*In these tables, a ? means no analysis was run, or the analysis was not too close to theoretical, or the compound was never isolated, or it is unclear whether the R group is *n*-, *iso*-, etc.

Table 6 (continued)

Compound	M.P., °C.		References
Triethyl- bromide	103-104	(102)	(26, 29, 34, 67, 102, 156, 157, 200, 202)
Triethyl- chloride	brown 120	(102)	(7, 16, 17, 20, 21, 26, 27, 29, 34, 66, 80, 84, 91, 92, 102, 110, 114, 156, 157, 166, 179, 199, 200, 217)
Triethyl- fluoride	dec.240		(140)
Triethyl- iodide	-----		(24, 157)
Tri-n-hexadecyl- chloride	79-80		(161)
Triisoamyl- bromide	132-133	(106)	(41, 106, 135)
Triisoamyl- fluoride	dec.251		(140)
Triisobutyl- bromide	107-108	(106)	(41, 106, 137)
Triisobutyl- chloride	122dec.		(106)
Triisobutyl- fluoride	dec.230		(140)
Triisobutyl- iodide	unstable		(106)
Triisopropyl- bromide	-----		(93)
Triisopropyl- chloride	-----		(93, 202)
Triisopropyl- iodide	unstable		(202)
Trimesityl- iodide	200-201		(67)
Trimethyl- bromide	133dec.	(102)	(23, 26, 34, 102, 211)
Trimethyl- chloride	sublimes 187	(102)	(17, 23, 26, 29, 34, 102, 156, 192, 200)

Table 6 (concluded)

Compound	M.P., °C.		References
Trimethyl- fluoride	Very volatile		(140)
Trimethyl- iodide	———		(23, 29, 31)
Tri-*n*-octadecyl- chloride	82-83		(161)
Triphenethyl- bromide	91-92		(146)
Triphenyl- bromide	166	(98)	(41, 98, 137, 145, 156, 200)
Triphenyl- chloride	206	(98)	(7, 8, 51, 53, 54, 66, 69, 79, 98, 129, 130, 145, 156, 158, 171, 172, 199, 200)
Triphenyl- fluoride	dec.318	(140)	(41, 137, 140)
Triphenyl- iodide	142	(98)	(51, 53, 67, 98, 141, 156, 200)
Tri-*n*-propyl- bromide	81-82		(180)
Tri-*n*-propyl- chloride	137	(180)	(17, 102, 180)
Tri-*n*-propyl- fluoride	explodes at 235		(41, 137, 140)
Tri-*n*-tetradecyl- chloride	74-75		(161)
Tri-*o*-tolyl- bromide	129-130	(5)	(5, 6)
Tri-*o*-tolyl- chloride	141-142	(6)	(6, 66)
Tri-*m*-tolyl- bromide	146-147		(67)
Tri-*p*-tolyl- chloride	140-141		(6)
Tri-*p*-tolyl- fluoride	dec.280		(140)
Tri-*p*-tolyl- iodide	115	(141)	(67, 141)
Tri-2,5-xylyl- bromide	177		(148)
Tri-*p*-xylyl- chloride	167.5		(141)

Table 7. $R_2R'PbX$ Compounds

Compound	M.P., °C.	References
Di-n-amylmethyl- chloride	dec.121	(117)
Dicyclohexylphenyl- chloride	dec.205	(this thesis)
Diethyl-ε-bromoamyl- bromide	-----	(104)
Diethyl-n-butyl- bromide	not isolated	(105)
Diethylisoamyl- bromide	not isolated	(105)
Diethylisobutyl- bromide	not isolated	(105)
Diethylmethyl- chloride	-----	(34)
Diethyl-n-propyl- bromide	not isolated	(105, 107)
Diisoamylethyl- bromide	not isolated	(105)
Dimethyl-sec-butyl- bromide	not isolated	(107)
Dimethylethyl- bromide	not isolated	(105)
Dimethylethyl- chloride	-----	(26, 34)
Dimethyl-n-propyl- bromide	not isolated	(105)
Diphenyl-n-amyl- chloride	123dec.	(9)
Diphenylbenzyl- bromide	143dec.	(146)
Diphenylbenzyl- chloride	sinters 157	(87)
Diphenyl-3-butenyl- chloride	134-135dec.	(87)
Diphenylcyclohexyl- bromide	135	(145)
Diphenylethyl- bromide	119	(145)

Table 7 (concluded)

Compound	M.P., °C.	References
Diphenylethyl- chloride	dec.146-147	(this thesis)
Diphenylmethyl- bromide	118	(145)
Diphenylphenethyl- bromide	119dec.	(146)
Diphenyl-*n*-propyl- chloride	141dec.	(9)
Diphenyl-2-pyridyl- iodide	137-140	(96)
Diphenyl-2,5-xylyl- bromide	90	(145)
Di-*o*-tolylphenyl- bromide	117-118	(5)
Di-*o*-tolylphenyl- chloride	113-114	(7)

Table 8. RR'R"PbX Compounds

Compound	M.P., °C.	References
Cyclohexylmethylphenyl- bromide	93-94	(145)
Ethylisobutyl-n-propyl- bromide	not isolated	(105)
Isoamylmethyl-n-propyl- chloride	not isolated	(105)
Phenyl-n-propyl-o-tolyl- chloride	103-104	(11)

Table 9. R_2PbX_2 Compounds

Compound	M.P., °C.	References
Di-*m*-aminophenyl- dichloride	------	(192)
Di-*n*-amyl- dibromide	sinters 89	(117)
Di-*n*-amyl- dichloride	dec.123-125	(117)
Di-*dl*-amyl- dichloride	sinters 67	(117)
Di-*p*-anisyl- dichloride	------	(86)
Di-*p*-anisyl- diiodide	122-123	(67)
Di-*n*-butyl- dibromide	sinters 110 (117)	(43, 117)
Di-*sec*-butyl- dibromide	------	(188)
Di-*n*-butyl- dichloride	dec.180 (117)	(49, 117)
Dicyclohexyl- dibromide	dec.142 (136)	(97, 136)
Dicyclohexyl- dichloride	dec.180	(97)
Dicyclohexyl- diiodide	unstable (136)	(97, 136)
Diethyl- dibromide	------	(102, 167, 202)
Diethyl- dichloride	------	(7, 80, 91, 102, 114, 156, 167, 199, 217)
Diethyl- diiodide	------	(102)
Diisoamyl- dibromide	sinters 93	(106)
Diisoamyl- dichloride	dec.107	(106)
Diisobutyl- dibromide	dec.102	(106)
Diisobutyl- dichloride	dec.100	(106)
Diisopropyl- dibromide	------	(107, 202)
Diisopropyl- dichloride	unstable	(202)

Table 9 (concluded)

Compound	M.P., °C.	References
Diisopropyl- diiodide (?)	------	(202)
Dimethyl- dibromide	unstable	(102)
Dimethyl- dichloride	*	(102, 192)
Dimethyl- diiodide	unstable	(102)
Di-*m*-nitrophenyl- dibromide	------	(128)
Di-*m*-nitrophenyl- dichloride	sublimes 250	(this thesis)
Di-*m*-nitrophenyl- diiodide	dec.135	(this thesis)
Di-3-pentyl- dibromide	------	(188)
Diphenyl- dibromide	------	(41, 138, 146, 180, 182, 183, 194, 219)
Diphenyl- dichloride	dec.284 (219)	(7, 66, 67, 69, 79, 90, 91, 129, 130, 158, 171, 172, 180, 183, 194, 200, 213, 219)
Diphenyl- difluoride	not melted at 300	(194)
Diphenyl- diiodide	101-103 (183)	(183, 194, 219)
Di-*n*-propyl- dichloride	dec.228	(102)
Di-2-thienyl- dichloride	dec.202	(85)
Di-*o*-tolyl- dibromide	150-151	(5)
Di-*o*-tolyl- dichloride	178-179 (6)	(6, 7)
Di-*p*-tolyl- dibromide	------	(184)
Di-*p*-tolyl- dichloride	------	(6, 7, 184)
Di-*m*-xylyl- dichloride	------	(89)
Di-*p*-xylyl- dibromide	120dec.	(148)

*Sinters slightly around 155° and then there is no change to 230°. (102)

Table 10. RR'PbX_2 Compounds

Compound	M.P., °C.	References
3-Butenylethyl- dichloride	-----	(87)
3-Butenylphenyl- dichloride	unstable	(87)
ε-Chloroamylethyl- dichloride	dec.120	(104)
Ethylisoamyl- dichloride	dec.128	(105)
Ethylisobutyl- dibromide	unstable	(105)
Ethylmethyl- dichloride	unstable	(105)
Ethylmethyl- diiodide	-----	(105)
Isoamylisobutyl- dibromide	dec.95	(106)
Isoamyl-*n*-propyl- dichloride	unstable	(105)
Isobutyl-*n*-propyl- dibromide	remarkably stable	(105)
Isobutyl-*n*-propyl- dichloride	very stable	(106)
Phenyl-*n*-propyl- dichloride	dec.266	(9)
Phenyl-*o*-tolyl- dibromide	116-117	(5)

R_2Pb COMPOUNDS

The so-called divalent organolead compounds are characterized by their highly colored solutions and by their great instability. The deep brown to red solutions that develop in the early stages of the reaction between lead chloride and alkyl Grignard reagents have been attributed to the formation of divalent lead compounds (102). Only diphenyllead and di-*p*-tolyllead have been isolated (141) in small yields by the reaction of lead chloride and the corresponding Grignard reagent. Rigorous control of the reaction and a high degree of manipulative skill were required to prevent the products from decomposing. The diaryllead compounds were blood-red amorphous powders, quite unstable in the air or light but in their absence the compounds could be kept for a period of a week. Iodine reacted with them readily to form the diaryllead diodides, and alcoholic silver nitrate was instantly reduced. In benzene solution the compounds were found to be in the monomolecular form.

Diphenyllead, when heated in a capillary tube, decomposed around 100°, turned yellow at 120°, melted above 200°, and turned black at 260°.

The only other known method for preparing divalent organolead compounds is by electrolytic reduction of a ketone using a lead cathode in a sulfuric acid bath. Tafel (202) prepared diisopropyllead in this manner but isolated his product as the dihalide derivative.

Calingaert (25) attempted to prepare dialkyllead compounds from dialkyllead dihalides by the action of sodium in liquid ammonia. It has been observed in these laboratories that there was a transitory brown to red coloration of the ammonia solution when the ammonia-soluble metal was first added to a diaryllead dihalide. This coloration quickly disappeared as more metal was added and the hexaaryldilead was isolated from the reaction.

Krause and Reissaus (141) added a benzene solution of iodine to a blood red solution of diphenyllead in benzene and observed an immediate disappearance of the red color. They stated that diphenyllead diiodide was formed and that this soon decomposed with formation of lead iodide.

These same authors observed the following changes when diphenyllead was heated in a melting point tube: the sample turned pale and decomposed at about 100°, the decomposition product turned yellow at 120°, and melted above 200°. No black color had appeared at 260°. These observations do not lend support to the series of equations given to explain the formation of R_4Pb compounds (see under R_4Pb compounds). Hexaphenyldilead was formed from diphenyllead by gently refluxing an ether-benzene solution of diphenyllead and phenylmagnesium bromide.

Table 11. R_2Pb Compounds

Compound	Comments	References
Di-sec-butyl-	no anal. but derivatized	(188)
Diisopropyl-	-----	(50, 93, 202)
Di-3-pentyl-	no anal. but derivatized	(188)
Diphenyl-	dec. around 100 (141)	(141, 167)
Di-p-tolyl-	-----	(141)

R_6Pb_2 COMPOUNDS

General Discussion

A great discrepancy appears in the literature dealing with the degree of dissociation of the R_6Pb_2 compounds into organolead "radicals":

$$R_6Pb_2 \rightleftarrows 2\ R_3Pb$$

The wide divergence in the amount of dissociation as reported by various authors may be attributed to the different methods of measurement. Molecular weight measurements by Krause and Reissaus (141) and Foster, Dix, and Gruntfest (53) indicated that hexaphenyldilead was appreciably dissociated in dilute benzene solution. The assumption was that the dissociation product was triphenyllead. While there was a steady rise in molecular weight with increase in concentration, no mass action constant could be calculated from the data.

As triphenyllead would possess an odd number of electrons, Preckel and Selwood (186) undertook to determine the degree of dissociation through magnetic susceptibility measurements. Magnetic measurements set the upper limits of dissociation at 0.1% in the solid and 1.4% in a benzene solution within the temperature range of 30 to 80° and the concentration range of 0.02265 M to 0.01547 M.

Under these circumstances it was deemed advisable to investigate these divergences further. Krause (136) found that molecular weight measurements of hexacyclohexyldilead in freezing benzene indicated 47% dissociation. Morris and Selwood (169) found by magnetic susceptibility measurements that hexacyclohexyldilead was practically completely associated in benzene at 90°. Unfortunately the degree of accuracy of magnetic susceptibility measurements is not of a very high order, but a degree of dissociation such as that found in freezing benzene would have been very apparent. These last authors suggested that a clue to the low molecular weights found by Krause, Foster, and others might possibly be found in the reactions undergone by hexaarylethanes. Although no evidence yet exists for comparison, it is not improbable that a compound such as hexaphenyldilead might slowly decompose to several fragments of relatively low molecular weight, especially at moderately elevated temperatures.

An explanation for the fact that free radicals are not found may be that the atomic radius of the metal atom is much greater than that of carbon. The covalent radius of lead is at least twice that of carbon, hence the effect of three phenyl groups is only that of protuberances on the surface of the lead. With carbon, the action of the phenyl radicals is more that of a tightly fitting envelope. As a result, the chance of an effective collision leading to the formation of a dimer is much greater in the case of lead than in the case of carbon radicals.

Electron diffraction measurements upon hexamethyldilead (197) have indicated that the main bond distances in the molecule are 2.88±0.03 A. for Pb-Pb and 2.25±0.06 A. for Pb-C.

Austin (5) added bromine, with stirring, to a chloroform solution of hexa-o-tolyldilead until the bromine color no longer disappeared. The solution was filtered to remove lead bromide and was then evaporated. Recrystallization from alcohol yielded di-o-tolyllead dibromide. When 40% hydrobromic acid was shaken with a chloroform solution of hexa-o-tolyldilead, a clear solution resulted. This solution on evaporation yielded a mixture of tri-o-tolyllead bromide and di-o-tolyllead dibromide.

Krause and Reissaus (141) observed that cooled benzene solutions of hexaphenyldilead and iodine, when mixed, precipitated lead iodide. If, however, a benzene solution of hexaphenyldilead was shaken with a mixture of one part of iodine in alcohol solution and two parts of water, triphenyllead iodide was produced without decomposition. Similar results were obtained with hexa-p-tolyldilead except that the iodination product did not decompose as readily as in the case of the phenyl compound.

Gilman and Bailie (67) found that ice cold chloroform solutions of iodine and hexa-p-(or -o-)methoxyphenyldilead gave about 50% yields of the R_3PbI compound together with some lead iodide and the R_2PbI_2 compound. Seemingly, the combined effect of lower temperature and more stable organic radical prevented complete decomposition to lead iodide.

When a slow stream of dry hydrogen chloride gas was bubbled into a solution of hexaphenyldilead in chloroform cooled to 0°, a white solid started to precipitate immediately. After three minutes, this solid was filtered and found to consist of 82.6% of lead chloride and 16.5% of diphenyllead dichloride.

All of the aryl R_6Pb_2 compounds are yellow crystalline bodies, the color being more intense in the compounds containing heavier aryl groups. Hexaphenyldilead has just a trace of yellow color in the solid state but it forms yellow solutions which deepen somewhat on heating and become lighter again on cooling.

Methods of Preparation

While the R_6Pb_2 compounds possess a much greater stability than the R_2Pb compounds, it has only been within comparatively recent times that the pure compounds have been prepared and studied. The following methods of preparation have been reported.

Reaction of an alkyl iodide with sodium-lead alloy

The action of an alkyl iodide upon sodium-lead alloy gave a product containing some R_6Pb_2 compound, but consisting mainly of R_4Pb.

Controlled reaction of lead chloride with an active organometallic compound

If the final period of reflux (see under R_4Pb compounds) was omitted, fairly good yields of the R_6Pb_2 compound were obtained from the reaction of lead chloride and a Grignard reagent (8, 19, 31, 89, 141, 148). In the case of a few organic radicals, careful control of the reaction is not necessary. Krause (136) was unable to prepare tetracyclohexyllead from lead chloride and cyclohexylmagnesium bromide. Even prolonged heating of the reaction mixture failed to convert the hexacyclohexyldilead to tetracyclohexyllead.

Hexamesityldilead (67) is another compound that seemingly fails to decompose to an R_4Pb compound.

Electrolysis of an R_3PbOH compound

In the electrolysis of an R_3PbOH compound in alcoholic solution, using lead electrodes, gas was evolved at the anode and an R_6Pb_2 compound was formed at the cathode (166).

Chemical reduction

Chemical reduction has been demonstrated by Goldach (93). When acetone in sulfuric acid was treated with a lead-sodium alloy, hexaisopropyldilead was formed.

Electrolytic reduction

In the electrolytic reduction of ketones in sulfuric acid (see under the section on R_2Pb compounds) considerable amounts of hexaalkyldilead are also formed. This is indicated by the isolation of R_3PbX as well as R_2PbX_2 compounds when the highly colored product is treated with halogens.

Liquid ammonia reactions

Perhaps the most satisfactory method of preparing the largest number of R_6Pb_2 compounds is by the elimination of halogen from R_3PbX compounds by use of liquid ammonia-soluble metals in liquid ammonia (67):

$$2\ (C_6H_5)_3PbI + 2\ Na \longrightarrow (C_6H_5)_6Pb_2 + 2\ NaI$$

If triphenyllead chloride is used in place of the iodide in the preparation of hexaphenyldilead, the reaction does not proceed so smoothly. This is evidently due to the lower solubility of the chloride in liquid ammonia (53). If tetrasodium nonaplumbide, Na_4Pb_9, is used in place of sodium, the yield of R_6Pb_2 compound is much improved. Evidently the tetrasodium nonaplumbide is a much weaker reducing agent than sodium and permits the reduction to proceed without cleavage of phenyl groups from lead:

$$9\ PbCl_2 + 22\ Na \longrightarrow Na_4Pb_9 + 18\ NaCl$$

$$Na_4Pb_9 + 4\ (C_6H_5)_3PbCl \longrightarrow 2\ (C_6H_5)_6Pb_2 + 4\ NaCl + 9\ Pb$$

Table 12. R_6Pb_2 Compounds

Compounds	Comments	References
Hexaamyldi- (?)	-----	(124)
Hexa-*o*-anisyldi-	dark 198	(67)
Hexa-*p*-anisyldi-	138-140; dec. 198-200 (67)	(67, 86)
Hexabutyldi- (?)	not isolated	(43)
Hexacyclohexyldi-	dec.196 (67)	(41, 67, 136, 137, 169)
Hexa-*o*-ethoxyphenyldi-	170-171dec.	(67)
Hexa-*p*-ethoxyphenyldi-	178-179dec.	(67)
Hexaethyldi-	dec.100/2 (166)	(19, 31, 67, 110, 124, 157, 166)
Hexaisopropyldi-	-----	(93)
Hexamesityldi-	melts above 325	(67)
Hexamethyldi-	37-38;dec.238 (31)	(31, 110, 197)
Hexa-*α*-naphthyldi-	darkens 255; melts 268-269	(67)
Hexaphenethyldi-	-----	(146)
Hexaphenyldi-	dec.155 (141)	(41, 53, 66, 67, 74, 137, 141, 145, 156, 186)
Hexa-*o*-tolyldi-	dec.240 (141)	(5, 6, 66, 67, 141)
Hexa-*m*-tolyldi-	109;dec.116-117	(67)
Hexa-*p*-tolyldi-	dec.193 (141)	(6, 67, 74, 141)
Hexa-*m*-xylyldi-	233.5dec.	(89)
Hexa-*p*-xylyldi-	167.5;dec.195 (141)	(141, 147, 192)

UNCLASSIFIED ORGANOLEAD COMPOUNDS

Those organolead compounds that do not conform with any of the classifications previously given are grouped in Table 13.

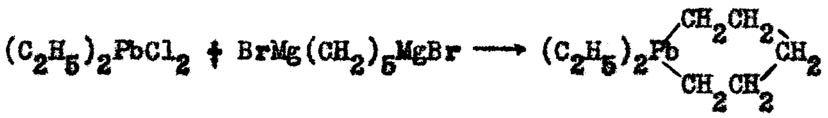
The only known organolead compounds containing three halogens and only one carbon-lead linkage have been prepared by Lesbre (153, 154). They were prepared in a manner analogous to that used in preparing tin compounds of the same type:

$$PbCl_2 + CsCl \longrightarrow CsPbCl_3 \xrightarrow{RI} RPbI_3$$

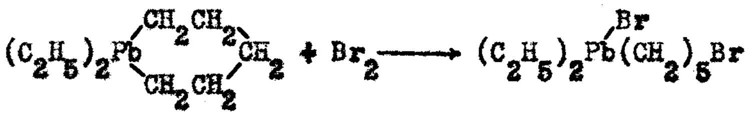
The actual mechanism of formation is not clear. Only one $RPbCl_3$ compound, methyllead trichloride, has been mentioned (154). This same reference also speaks of $RPbBr_3$ compounds but makes no mention of any specific compound. The alkyllead triiodides are said to have a characteristic odor resembling foliage. All of the trihalides are unstable and easily hydrolyzed to the plumbonic acid:

$$RPbX_3 + 3H_2O \longrightarrow RPb(OH)_3 + 3HX$$

The interesting heterocyclic organolead compound, diethylcyclopentamethylenelead, was prepared (104) by the reaction of the di-Grignard reagent of *α,ε*-dibromopentane with diethyllead dichloride. It has a ketone-like odor.



Addition of bromine to an ether solution of this compound at -75° opened the ring. When this product, diethyl-ε-bromoamyllead bromide, was treated with a Grignard reagent the bromine attached to lead was replaced.



$$+ C_2H_5MgBr \longrightarrow (C_2H_5)_3Pb(CH_2)_5Br$$

The triethyl-ε-bromoamyllead was converted to a Grignard reagent by reaction with magnesium. This is the only known case of an organolead compound also being a Grignard reagent.

Trimethyl(trimethylpentamethylenetin)lead was prepared (109) from trimethyllead bromide and the Grignard reagent formed by the action of magnesium upon trimethyl-ε-bromoamyltin.

α,β-Di-triphenylleadsuccinic acid (this thesis, p.111) was prepared by the reaction of hexaphenyldilead with maleic anhydride.

Table 13. Unclassified Organolead Compounds

Compound	Comments	References
n-Butyl- triiodide (?)	------	(153)
Ethyl- triiodide (?)	------	(153)
n-Propyl- triiodide (?)	------	(153)
Diethylcyclopentamethylene-	111/13 (104)	(100, 104)
Diethyl- bromochloride (?)	------	(149)
Diisobutyl- bromochloride	dec.110	(106)
α,β-Di-triphenyllleadsuccinic acid	------	(this thesis)
Di(trimethyl)pentamethylenedi-	166.5/14 (109)	(100, 109)
Triethyl(pentamethylenemagnesium bromide)-	not isolated	(104)
Trimethyl(*p*-triethyl-phenylenesilicon)-	191/17	(108)
Trimethyl(trimethyl-pentamethylenetin)-	162/17.5	(109)
Lead carbide (lead acetylide)	------	(168)
p,p'-Biphenylenedi[5-azo-2-hydroxyphenyltriphenyl-]	------	(201)
p-Phenylenedi(triphenyl-)	285-288'	(163)

R_3PbY, $(R_3Pb)_2Y$, R_2PbY_2, AND $RR'PbY_2$ COMPOUNDS

In these compounds, in which Y represents either an organic or inorganic salt radical, the C-Y linkage is of a C-O, C-S, C-N, or C-metal type. Strictly speaking the C-halogen linkage should also be included in this section, but this type was discussed separately because of the large number of such compounds. The linkages discussed in this section are formed either by action of an acid (16) upon a compound of the general type R_4Pb:

$$(C_2H_5)_4Pb + CH_3COOH \longrightarrow (C_2H_5)_3PbOOCCH_3 + C_2H_6$$

$$(C_2H_5)_4Pb + HNO_3 \xrightarrow[CHCl_3]{boiling} (C_2H_5)_2Pb(NO_3)_2 + 2C_2H_6$$

or by reaction of such products with other materials:

$$(C_2H_5)_3PbOOCCH_3 + KCN \longrightarrow (C_2H_5)_3PbCN + CH_3COOK$$

The first reaction is sometimes catalyzed with silica gel (16). The second reaction is often carried out with an organolead halide:

$$(C_2H_5)_3PbCl + NaOH \longrightarrow (C_2H_5)_3PbOH + NaCl$$

$$(C_6H_5)_2PbBr_2 + 2NaOH \longrightarrow (C_6H_5)_2PbO + 2NaBr + H_2O$$

A few compounds are prepared in liquid ammonia in the following manner:

$$(C_6H_5)_3PbBr + 2Li \longrightarrow (C_6H_5)_3PbLi + LiBr$$

Variations may be made in some of the above reactions by using an R_6Pb_2 compound in place of an R_4Pb or R_3PbX (or R_3PbY) compound:

$$(C_6H_5)_6Pb_2 + 2Ca \longrightarrow (C_6H_5)_3PbCaCaPb(C_6H_5)_3$$

In general, the compounds containing salt radicals exhibit more of the properties of the salt portion than of the organolead portion of the molecule. A greater number of the compounds of these types are water-soluble than is the case in any other group. Their aqueous solutions are ionized and show the typical reactions of their acidic ions. The hydroxides are strong bases which precipitate the heavy metals from their solutions. The alkyllead hydroxides must not be allowed to stay in contact with the air as they are converted to the carbonates by the carbon dioxide in the air.

Table 14. R_3PbY* Compounds

Compound	M.P. or B.P., °C.	References
Tri-n-butyl- hydroxide	dec. 115	(180)
Tricyclohexyl- hydroxide	-----	(136)
Tri-n-dodecyl- acetate	59	(161)
Tri-n-dodecyl- nitrate	44-45	(161)
Triethyl- acetate	160.4 dec. (16)	(16, 124)
Triethyl- acid oxalate	not melted at 200	(1)
Triethyl- acid succinate	304 dec.	(1)
Triethyl- acid tartrate	-----	(124)
Triethyl- p-aminobenzoate	84-86 (77)	(71, 77)
Triethyl- benzoate	127 (16)	(16, 124)
Triethyl- bromoacetate	121	(16)
Triethyl- butylmercaptide	82-83/0.5	(1)
Triethyl- butyrate	107.9-108.5 (16)	(16, 124)
Triethyl- caproate	94.7-95.8	(16)
Triethyl- caprylate	85-87.5	(16)
Triethyl- chloroacetate	146-146.5	(16)
Triethyl- cresolate (?)	———	(206)
Triethyl- cyanide	194 (16)	(16, 124)

*In this table Y represents a monovalent salt radical.

Table 14 (continued)

Compound	M.P. or B.P., °C.	References
Triethyl- dibromoacetate	98.6-101.8	(16)
Triethyl- dichloroacetate	113.5-114.5	(16)
Triethyl- ethoxide	18	(1)
Triethyl- ethyl thioglycolate	94-96/0.5	(1)
Triethyl- ferricyanide (?)	------	(16)
Triethyl- ferrocyanide (?)	------	(16)
Triethyl- formate	------	(124)
Triethyl- furoate	153-154 (77)	(71, 77)
Triethyl- furylacrylate	119-121 (77)	(71, 77)
Triethyl- heptoate	90-90.8	(16)
Triethyl- heptylmercaptide	114-115/0.5	(1)
Triethyl- hydroxide	------	(16, 20, 110, 124, 140, 166)
Triethyl- isobutyrate	119.4-121.8	(16)
Triethyl- isovalerate	119.4-119.8	(16)
Triethyl- methyl thiosalicylate	91-93/0.008	(1)
Triethyl- monophosphate	not melted at 250 (77)	(17, 71, 77, 124)
Triethyl- nitrate	------	(114, 157)
Triethyl- pelargonate (?)	88-90	(16)
Triethyl- phenoxide	75/0.5 (1)	(1, 206)
Triethyl- phenylacetate	101-106 (77)	(71, 77)

Table 14 (continued)

Compound	M.P. or B.P., °C.		References
Triethyl- phenylmercaptide	111-113/0.5		(1)
Triethyl- N-phthalimide	126-128		(1)
Triethyl- propionate	141-142		(16)
Triethyl- saccharide	142-143		(1)
Triethyl- salicylate	83-91	(77)	(71, 77)
Triethyl- thioacetate	42-43		(1)
Triethyl- thiocyanate	------		(124)
Triethyl- thiosalicylate	97-99		(77)
Triethyl- trichloroacetate	135.5-138.6		(16)
Triethyl- _p_-toluenesulfonate	167-168	(77)	(71, 77)
Triethyl- valerate	115.6-117		(16)
Triisoamyl- hydroxide	an oil	(140)	(106, 140)
Triisobutyl- hydroxide	dec. 115		(140)
Trimethyl- hydroxide	------		(110, 140)
Tri-_m_-nitrophenyl- nitrate	------		(this thesis)
Triphenyl- acetate	206-207	(6)	(6, 8)
Triphenyl- acid maleate	------		(this thesis)
Triphenyl- ammonium (?)	------		(53)
Triphenyl- ethyl benzylmalonate	131-132	(126)	(126, 127)
Triphenyl- ethyl malonate	159-160	(126)	(126, 127)

Table 14 (concluded)

Compound	M.P. or B.P., °C.	References
Triphenyl- hydroxide	-----	(6, 98, 140, 145)
Triphenyl- hyponitrite	222-224 dec.	(1)
Triphenyl- laurate	91	(52)
Triphenyl- myristate	102-103	(52)
Triphenyl- nitrate	dec. 220-225	(this thesis)
Triphenyl- palmitate	110	(52)
Triphenyl- -sodium (?)[†]	-----	(53, 67)
Triphenyl- stearate	112	(52)
Tri-*n*-propyl- acetate	116	(180)
Tri-*n*-propyl- hydroxide	dec.140 (140)	(140, 180)
Tri-*p*-tolyl- acetate	161-162*	(6)
Tri-*p*-tolyl- hydroxide	-----	(140)

[†] Compounds containing a lead-metal linkage are represented in these tables by this single entry. None of this type has been isolated as such and analyzed. Metals linked to carbon include Li, Na, K, Rb, Mg, Ca, Sr and Ba. Representative references to the subject include 10, 14, 53, 67, and this thesis.

*When recrystallized from pet. ether. Heating at 140° in a vacuum for three hours caused it to melt at 158-159°.

Table 15. $(R_3Pb)_2Y$* Compounds

Compound	References
Di-tri-n-amyl- oxide	(124)
Di-tri-n-amyl- sulfate	(124)
Di-triethyl- carbonate	(16, 157)
Di-triethyl- chromate (?)	(16)
Di-triethyl- oxalate.H_2O	(124)
Di-triethyl- oxide	(124, 157)
Di-triethyl- pyrocatecholate (?)	(206)
Di-triethyl- resorcinolate (?)	(206)
Di-triethyl- sulfate	(21, 157)
Di-triethyl- sulfide (?)	(124)
Di-triphenyl- maleate	(this thesis)
Di-triphenyl- oxide	(6, 98)
Di-triphenyl- sulfide	(98)
Di-tripropyl- sulfate	(180)

*In this table Y represents a divalent salt radical, each valence of which is attached to a separate lead.

Table 16. R_2PbY_2* Compounds

Compound	M.P., °C.	References
Di-*m*-aminophenyl- dihydroxide	-----	(192)
Di-*n*-amyl- dihydroxide	not isolated	(117)
Di-*n*-amyl- dinitrate.$2H_2O$	sinters 96-98 also anhyd.	(117)
Di-*n*-amyl- sulfate	sinters 177	(117)
Di-*p*-anisyl- diacetate	-----	(86)
Di-*n*-butyl- dihydroxide	-----	(117)
Di-*n*-butyl- dinitrate.$2H_2O$	sinters 116-117; anhyd.123-125	(117)
Dicyclohexyl- sulfide	dec. 100	(97)
Diethyl- dibenzoate	165-167	(1)
Diethyl- dinitrate	-----	(114)
Diethyl- oxide	-----	(157)
Diisopropyl- chromate (?)	-----	(202)
Diisopropyl- dinitrate	-----	(202)
Diisopropyl- oxide	not isolated	(93, 202)
Diisopropyl- sulfide (?)	-----	(202)
Dimethyl- chromate	-----	(102)
Dimethyl- oxide	-----	(102, 192)
Dimethyl- sulfide	-----	(102)

*In this table Y_2 represents either two monovalent salt radicals or a single divalent salt radical, attached to a single lead.

Table 16 (continued)

Compound	M.P., °C.	References
Di-*m*-nitrophenyl- diacetate	------	(this thesis)
Di-*m*-nitrophenyl- dinitrate	------	(40, 213)
Di-*m*-nitrophenyl- oxide	------	(192)
Diphenyl- basic cyanide	------	(183, 219)
Diphenyl- basic nitrate	------	(182)
Diphenyl- chromate	------	(183)
Diphenyl- diacetate	195 (183)	(134, 183)
Diphenyl- dibenzoate	231-232	(135)
Diphenyl- dibutyrate	132-134	(135)
Diphenyl- dicaproate	oil	(135)
Diphenyl- dicyanide	dec.245-255	(219)
Diphenyl- diformate.H_2O	dec.200 (183)	(134, 183)
Diphenyl- di-*α*-hydroxybutyrate	198-200dec.	(135)
Diphenyl- diiodate	stable to 300	(90)
Diphenyl- diisovalerate	166-168	(135)
Diphenyl- dilactate	212-215dec.	(135)
Diphenyl- dinitrate.$2H_2O$	------	(17, 40, 180, 183, 194, 219)
Diphenyl- di-*p*-nitrobenzoate	256dec.	(90)
Diphenyl- dipropionate	170-172 (135)	(17, 90, 135)
Diphenyl- dithiocyanide	------	(183)

Table 16 (concluded)

Compound	M.P., °C.	References
Diphenyl- di-trichloroacetate	sinters 170-175; dec.210	(90)
Diphenyl- divalerate	168-170	(90)
Diphenyl- oxalate.$3H_2O$	dec.293-294	(90)
Diphenyl- oxide	-----	(172, 183, 219)
Diphenyl- sulfide	dec.80-90	(183)
Di-n-propyl- dinitrate.$2H_2O$	87-89	(117)
Di-o-tolyl- dinitrate	not isolated	(5)
Di-p-tolyl- basic nitrate	explodes when heated	(184)
Di-p-tolyl- chromate	-----	(184)
Di-p-tolyl- diacetate.$2H_2O$	183.5	(184)
Di-p-tolyl- diformate	dec.233	(184)
Di-p-tolyl- dinitrate	not isolated	(184)
Di-p-tolyl- sulfide	98dec.	(184)

Table 17. $RR'PbY_2$ Compounds

Compound	References
Ethylmethyl- chromate	(105)
Ethylmethyl- sulfide	(105)
Isoamylpropyl- sulfide (?)	(105)
Isobutylpropyl- sulfide (?)	(105)
Phenyl-*o*-tolyl- dinitrate.$2H_2O$	(5)

UNCLASSIFIED ORGANOLEAD SALTS

Organolead salts whose structure is such that they cannot be placed in any of the other tables of salts are placed in Table 18.

Application of the Meyer reaction (164) to lead has given $RPb(OH)_3$ compounds (152, 155). The reactions were carried out at 5°. The compounds commenced to decompose in moist air at 35°. Heated in a sealed tube, they decomposed to give lead oxide, the alcohol, and water:

$$RPb(OH)_3 \longrightarrow PbO + ROH + H_2O$$

The behavior of benzylplumbonic acid was exceptional in that some tetrabenzyllead (155) was formed along with the above decomposition products.

The inner anhydride of diethyl-o-carboxyphenyllead hydroxide is discussed under Introduction of Water-Solubilizing Groups into Organolead Compounds (p. 85).

Table 18. Unclassified Organolead Salts

Compound	M.P.	References
Allylplumbonic acid (?)	------	(152)
Benzylplumbonic acid (?)	------	(152)
n-Butylplumbonic acid (?)	------	(152)
Ethylplumbonic acid (?)	------	(152)
Isopropylplumbonic acid (?)	------	(152)
Methylplumbonic acid (?)	------	(152)
n-Propylplumbonic acid (?)	------	(152)
Diphenyl- basic carbonate	------	(183)
Tri-diphenyl- diphosphate	------	(183)
Inner anhydride of diethyl-o-carboxyphenyllead hydroxide	208-209	(1)

THE REDISTRIBUTION REACTION

While metathetical reactions of the type

$$AY + BZ \rightleftharpoons AZ + BY$$

are common in inorganic chemistry, there have been few recognized cases of this type of reaction in organic chemistry. The usual example given is that of esterification of organic acids.

There are several references in the literature of organolead chemistry of migration of organic radicals from one molecule to another. A good example of this is found in a paper by Austin (7) wherein he reports of disproportionation occurring when samples of R_4Pb and R_2PbCl_2 were refluxed in solution. With tetraphenyllead and diphenyllead dichloride, triphenyllead chloride was obtained in good yield. With tetraethyllead and diethyllead dichloride, Austin isolated triethyllead chloride. He failed to realize the potentialities of the reaction relative to the use of two or more different organic groups in the same reaction.

Calingaert and co-workers (see ref. 65, Chap. 24 for a general discussion; or 26, 27, 28, 29, 32, 33, 34, 35, 36 for individual references) were the first to recognize the nature of the interchange process and to give it the name of "random redistribution". They showed that there were a number of liquid-phase equilibria of the above general type, free of side reactions (such as the formation of AA, YY, etc.). These reactions proved distinctive in that while the compounds involved might be wholly covalent, no ionizing solvent was required, although a catalyst was needed; and the interchange was strictly at random. The amounts of products could be calculated in advance from the law of probability.

$$8(CH_3)_4Pb + 8(C_2H_5)_4Pb \longrightarrow (CH_3)_4Pb + 4(CH_3)_3C_2H_5Pb + 6(CH_3)_2(C_2H_5)_2Pb + 4CH_3(C_2H_5)_3Pb + (C_2H_5)_4Pb$$

Temperature had no effect upon the equilibrium composition and the amount of energy of each kind of bond involved had no directive influence.

There are cases of interchange in bismuth and zinc compounds (39, 139) without the use of a catalyst but, in general, the presence of a metal-halogen bond is necessary. This bond may be supplied in one of the reactants, such as R_3PbX, or it may be supplied in the form of an inorganic salt, such as aluminum chloride.

The temperature has a marked effect on the reaction velocity. The actual temperature used depends upon the lowest boiling point of any of the products or reactants but in general the temperature is kept at 60-80° for four or five hours.

There is no need of using an inert solvent, but hexane or decalin is usually added to provide an inert atmosphere and to promote agitation of the mixture.

Except in the case of compounds having relatively unstable carbon-lead linkages (e.g., triethyl-tert-butyllead) the redistribution reaction takes place without any precipitation of free lead, decomposition, or evolution of gas.

PYROLYSIS OF ORGANOLEAD COMPOUNDS TO GIVE FREE RADICALS

The transformation of a compound into another substance, or substances, through the agency of heat alone is called pyrolysis. The term pyrolysis must not be confused with thermal decomposition. While it is true that decomposition often enters into pyrolysis, the term pyrolysis itself is much broader. Decomposition implies the formation of two or more simpler substances. Pyrolysis includes, besides the breaking down of molecules, the joining of two or more molecules or the formation of new compounds by rearrangement.

Zechmeister and Csabay (219) noted some decomposition in the sublimation of organolead compounds. Tetraphenyllead at a pressure of 15-20 mm. was heated in a fractionation bulb with an outside temperature of 240°. It distilled unchanged, nearly quantitatively. Energetic heating at 270° gave metallic lead, some unchanged material, and a good yield of biphenyl. Diphenyllead oxide gave the same sublimate and a residue of lead oxide.

Dull and Simons (46) studied the pyrolysis of tetraphenyllead over a range of temperatures in sealed Pyrex bulbs which were carefully evacuated after the introduction of the sample. The yield of biphenyl was smaller as the temperature was raised and benzene and *p*-diphenylbenzene were formed at temperatures somewhat higher than the optimum for formation of biphenyl.

These same authors, in an earlier paper (45), had established for the first time the existence of the free phenyl radical. The apparatus used was made of quartz and consisted of a chamber to contain the tetraphenyllead, a short region inside an electric furnace inclined slightly from the horizontal, and a chamber to retain the liquid and crystalline products and in which mercury was kept refluxing. The sample was kept just below its melting point (215-220°) and the pyrolysis was run for six hours at an indicated pressure of 0.01 mm.

The product formed in the mercury reflux chamber was recrystallized from alcohol. Among the characteristic broad crystals of biphenyl there were scattered needle-like crystals. These proved to be diphenylmercury. As neither tetraphenyllead nor biphenyl reacts with mercury vapor, the authors believed that active phenyl radicals were present. Koton (131, 132, 133) also observed pyrolysis in tetraphenyllead.

Simons, McNamee and Hurd (196) pyrolyzed tetramethyllead by a static and a flow method and observed the different products formed. The gases produced included acetylene, isobutylene, propylene, ethylene, hydrogen, methane, and ethane.

Paneth and Hofeditz (176) demonstrated the presence of methyl radicals in the pyrolysis of tetramethyllead. Garzuly-Janke (60) also reported on pyrolysis of tetramethyllead.

Meinert (162) pyrolyzed tetraethyllead and found ethylene, ethane, butane, hydrogen, and butylenes as well as small amounts of liquid products.

Paneth and Lautsch (177) pyrolyzed tetraethyllead, tetraisobutyllead, and tetrapropyllead. While tetraethyllead gave identifiable ethyl radicals, the other two lead compounds seemed to give mixtures, indicating further decomposition of the preliminary isobutyl and propyl radicals.

In heating or distilling organolead compounds, particularly the alkyl lead compounds, the rigorous exclusion of air is a wise precaution. Krause (138) mentions a violent explosion resulting from trying to seal an ampoule of tetramethyllead. Seemingly the volatile vapors of the lead compound mixed with air and exploded when ignited. This explosion detonated the sample of tetramethyllead.

Bailie (10) studied the pyrolysis of R_6Pb_2 compounds with the view of converting them to R_4Pb types. In some cases the formation of tetravalent organolead compounds by pyrolysis of the trivalent type proceeds only with difficulty, and in the case of hexacyclohexyldilead and hexamesityldilead, quite drastic thermal conditions failed to bring about decomposition to the tetravalent compounds. This agrees with the observations of Krause and Reissaus (141) that ortho substituents in the groups attached to lead increase the stability of the trivalent compounds. Bailie found that in the pyrolysis of anisyl- and ethoxyphenyllead compounds of the R_6Pb_2 type, the ortho compounds were more resistant to heat than were the para compounds. Likewise in the case of the tolyllead compounds, the ortho substituted member showed greater stability than the para substituted member, while the meta substituted compound decomposed with the least difficulty. If a series of radicals is arranged in the order of the decreasing thermal stabilities of the R_6Pb_2 compounds containing those radicals, they fall in the following order:

mesityl, cyclohexyl, α-naphthyl > o-ethoxyphenyl, o-anisyl, o-tolyl >
p-ethoxyphenyl, p-anisyl, p-tolyl > m-tolyl, phenyl > ethyl, methyl.

The series shows only a very general correlation to the series of Kharasch and others based upon cleavage of unsymmetrical organometallic compounds (see p. 16). Steric factors must play an important role since compounds exhibiting the greatest stability are those containing radicals with substituents ortho to the lead atom. Thus, in the series given above, the o-tolyl radical is placed above the p-alkoxyphenyl radicals, whereas the reverse is found in the other series. Likewise, the cyclohexyl group is placed with the highly aromatic mesityl and α-naphthyl radicals, and is placed among the aliphatic radicals in the series determined by preferential cleavage with hydrogen chloride.

INTRODUCTION OF WATER-SOLUBILIZING GROUPS INTO ORGANOLEAD COMPOUNDS

Considerable work has been done on the introduction of the nitro group into organolead compounds and the subsequent reduction of the nitro group to an amino group.

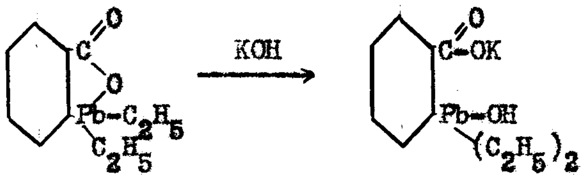
Vorländer (212) reported that there was no practical yield of nitration product in the reaction of tetraphenyllead with sulfuric-nitric acid solution. He found that diphenyllead dinitrate was converted to dinitrophenyllead dinitrate when heated with nitric acid to 100° in a sealed tube. Challenger and Rothstein (40) found that a more convenient method was to add diphenyllead dinitrate to a mixture of nitric and sulfuric acids at -15 to -10° and let the reaction mixture stand at room temperature over night. They found that nitration occurred in the <u>meta</u> position. Schmidt (192) nitrated diphenyllead diacetate with nitric acid at room temperature. Bindschadler (14) was unable to obtain a product from the reaction of triphenyllead-sodium with a nitrated aryl halide.

In the reduction of nitroaryllead compounds, Kocheshkov and Borodina (128) tried to reduce di-*m*-nitrophenyllead dibromide. Reduction with dilute hydrochloric acid and iron yielded 95% of aniline after two days of intermittent agitation. Titanium trichloride and 15% hydrochloric acid gave a 100% yield of aniline after eight days. Stannous chloride and dilute hydrochloric acid also produced aniline. Reduction with ammonium sulfide yielded lead sulfide and aniline. Schmidt (192) reduced di-m-nitrophenyllead oxide to di-m-aminophenyllead dichloride by slowly adding titanium trichloride to the lead compound dissolved in alcoholic hydrochloric acid.

Austin (6), by the permanganate oxidation of triphenylallyllead, obtained triphenyl-β,γ-dihydroxypropyllead. The chief reaction was the complete elimination of the allyl group. Ozonization of triphenylallyllead yielded a white alkali-insoluble precipitate. Stuckwisch (201), by hydrolysis of triphenylcarbethoxymethyllead, obtained triphenylcarboxymethyllead and showed that it was alkali-insoluble.

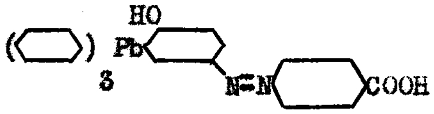
Melstrom (163) oxidized triphenyl-p-hydroxymethylphenyllead, but the sodium salt of the triphenyl-p-carboxyphenyllead was water-insoluble. Potassium permanganate oxidation in acetone solution of o- and p-tolyl groups attached to lead (6) did not yield the carboxyl compounds.

The inner anhydride of diethyl-o-carboxyphenyllead hydroxide (1) was insoluble in water and cold base, but warming the base caused it to go into solution immediately:



The inner anhydride was reformed upon acidification of the solution. The hydrated form has never been isolated.

The sodium salt of triphenyl-1-[2-hydroxy-5-(p-carboxyphenylazo)-phenyl] lead (201):



was water-soluble. When the 1-hydroxy group was replaced by a dimethylamino group, the sodium salt was still somewhat soluble in water.

Kocheshkov (125) introduced hydroxyaryl groups into tin compounds by using hydroxyarylmercury compounds:

$$R_3SnSnR_3 + (HOR')_2Hg \longrightarrow 2R_3SnR'OH + Hg$$

Analogous reactions with organolead compounds were unsuccessful.

The halogen-metal interconversion reaction (73, 215) is a method of choice for preparing organolithium compounds inaccessible through other, more direct methods. By this method organolithium compounds containing nuclear hydroxyl (2), primary amino (81, 83), and carboxyl groups (2) have been obtained. When the lithium compounds obtained by halogen-metal interconversion were used as intermediates in the preparation of lead compounds, complex mixtures were obtained (82). This may have been due in part to metal-metal interconversion (74). The difficulty may be overcome, at least in the aryllead series, by shortening the time of reaction, or by converting the organolithium compound to the Grignard reagent by means of magnesium bromide (72, 82). These may prove to be general methods for the synthesis of a variety of organolead compounds hitherto inaccessible.

ORGANOLEAD COMPOUNDS IN THE TREATMENT OF CANCER

Since its introduction in the chemotherapeutic treatment of cancer by Bell (12), lead has attracted more attention than any other metal in this particular field of therapeutics. From his observations, Bell concluded that metallic lead has a selective action upon sex cells, blood cells, nerve and embryonic cells, and tissue containing an abundance of phosphatides, especially lecithin. The action is general in young, vigorously growing tissue and local in adult cells. More lead accumulated in the cancerous tissues of men and dogs than in any other part of the body except the gonads. Bell suggested a direct chemical combination between lead and the phosphatides. Ensuing investigations (13, 173, 195, 216) gave varying degree of success.

It is common knowledge that lead compounds in general possess a high degree of toxicity. Attempts have been made to mask the lead by using it in highly complex molecules (44, 192). At the same time, it has been kept in mind that a more water-soluble molecule was also needed. Compounds can generally be made more water-soluble by the introduction of polar groups such as $-SO_3H$, $-OH$, $-COOH$, $-NH_2$, etc., but these groups are introducted into organolead compounds with great difficulty.

Schmidt reduced di-m-nitrophenyllead oxide with titanium trichloride and obtained di-m-aminophenyllead dichloride. The amino groups were detectable by diazotization and coupling and also by the formation of yellow Schiff's bases.

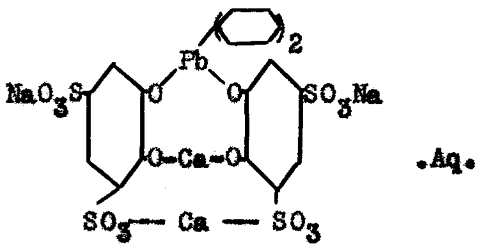
The first strictly organic lead compound of this type (82) was triphenyl-*p*-aminophenyllead. It has been diazotized and coupled with *β*-naphthol to give an azo lead dye.

Schmidt (192), in addition to a group of inorganic lead salts, tested, on experimental mouse cancer and Brown-Pearse tumor in rabbits, the following organolead compounds:

1. Trimethyllead chloride
2. Tetraphenyllead
3. Dimethyllead oxide
4. Hexaxylyldilead
5. Sodium salt of diphenyllead catecholdisulfonic acid
6. Sodium calcium salt of diphenyllead catecholdisulfonic acid
7. Sodium salt of di-*m*-aminophenyllead catechodisulfonic acid

A distinct action was obtained only with compounds 5 and 6 and to a lesser extent with 7. Using a radioactive isotope of lead failed to increase the efficacy of the compounds.

The complexity of some of these molecules containing carbon-lead linkages may be readily appreciated from the following illustration. The compound is number 6 in the list just given and the structure was arrived at from claims made by Schmidt in United States Patents 1,879,533 and 1,889,383.



Collier (41) studied eleven of the organolead compounds prepared by Krause (137). The results are given in Table 19.

The toxicity was dependent upon the structure of the compound rather than upon the solubility in water. Tri-n-propyllead fluoride was the most effective.

Buck and Kumro (17) made toxicity studies on a number of organolead compounds. They found that tetramethyllead has a relatively low toxicity and placed some hope in organolead compounds containing two or three methyl groups and having the remaining valencies of lead satisfied by an aromatic nucleus with amino or hydroxyl substituents.

In another series of toxicity studies (71), Table 20 was compiled.

Table 19. Organolead Compounds and Their Effect Upon Mouse Cancer

Compound	Number of animals	% distinct effect	% complete healing
Tri-*n*-propyllead fluoride	14	71.4	50.0
Triisobutyllead bromide	28	60.7	21.4
Triisoamyllead bromide	13	61.5	7.7
Tetraphenyllead	22	59.1	40.9
Hexaphenyldilead	18	16.6	5.5
Triphenyllead bromide	13	7.7	0.0
Triphenyllead fluoride	20	55.0	25.0
Diphenyllead dibromide	15	46.6	6.6
Hexacyclohexyldilead	13	53.8	30.7
Tricyclohexyllead iodide	16	43.8	25.0
Triphenylcyclohexyllead	20	20.0	15.0

Table 20. Toxicity of Organolead Salts

Compound	Solubility	M.T.D.	M.L.D.
Triethyllead *p*-toluenesulfonate	0.5-1.0%	12-15 mgs.	15 mgs.
Triethyllead salicylate	0.25	15-18	18-20
Triethyllead phenylacetate	0.3	12-15	15
Triethyllead furoate	0.3-0.4	12-15	15
Triethyllead *p*-aminobenzoate	0.5-1.0	12-15	15
Triethyllead furylacrylate	0.3-0.5	12-15	15-18

LEAD POISONING AND ITS TREATMENT

The dangers of lead poisoning and the early troubles in the tetraethyllead industry are now of common knowledge. Anyone who has worked with organolead compounds and has felt the pains in the stomach, the languor, and lack of appetite associated with lead poisoning can appreciate the statement that utmost cleanliness, proper ventilation, and a good diet are necessary. The diet of a worker coming in contact with lead in any form should include plenty of calcium (95) and vitamin C (113). Milk and all dairy products are good sources of calcium and the vitamin C may best enter the diet as vegetables or fruit juices. The calcium appears to prevent the deposition of lead in the bones, and vitamin C forms a poorly ionized, less toxic compound with lead that is eliminated.

In cases of lead poisoning, two procedures may be employed. The first is the storage of the lead for quick alleviation of symptoms and the second is de-leading the patient. The first method need not be carried out in a hospital but the second should. For storage of lead, calcium lactate, gluconate, chloride, glucoheptonate, glucuronate, borogluconate, ascorbic acid, ferrous ascorbate, vitamin D, calcium or sodium citrate, sodium carbonate, and sodium bicarbonate are employed. For elimination, phosphoric acid, hydrochloric acid, potassium or sodium iodide, sodium thiosulfate, ammonium chloride, magnesium sulfate, thyroid and parathyroid extracts are used (198).

An extensive study of lead poisoning, diagnosis, and treatment is also given by Gant (58).

INDUSTRIAL USES OF ORGANOLEAD COMPOUNDS

The most widely known use of an organolead compound is as an antiknock agent in motor fuel. Tetraethyllead is the compound most widely used in this respect, although tetramethyllead has found some use, according to the patent literature. Patents have also suggested unsymmetrical organolead compounds, such as diethyldimethyllead, as possible materials. Trialkyllead salts of nitrophenols have been patented for use as antiknock agents (210).

Compounds such as triethyllead phenate, triethyllead cresolate, di-triethyllead resorcinolate, and di-triethyllead pyrocatecholate have been suggested for use as disinfectants, insecticides, or as driers, antioxidants, and inhibitors (206).

Plastics have been prepared by reacting compounds such as trimethyllead bromide and potassium methacrylate to get trimethyllead methacrylate and then polymerizing this product with styrene (211).

A German patent (61) suggests the use of tetraethyllead in a process for coating iron with metallic lead.

Di-triethyllead styphnate is mentioned in a patent (209) as the main ingredient in an ignition compound suitable for use in electric blasting caps.

ANALYSIS OF ORGANOLEAD COMPOUNDS

The method of gravimetric analysis suggested by Gilman and Robinson (78) is the most convenient general method of analysis of organolead compounds. The usual method now used in these laboratories is carried out on a much smaller scale. Instead of a 400 cc. beaker and a 0.5 g. sample a Corning micro filter beaker no. 31025 and about 0.1 g. sample is used. Decomposition of the sample is first carried out with 1 cc. of concentrated sulfuric acid and finished up with the cautious addition of perhydrol. The lead sulfate is precipitated with an alcohol-water solution and the analysis completed as suggested by Gilman and Robinson.

Austin (5) has suggested a volumetric analysis of aryllead compounds using standard ammonium molybdate solution with tannic acid as the indicator.

Hein, Klein, and Mesée (111) titrated tetraethyllead in ethyl alcohol with an iodine solution and obtained good results although several hours are necessary to determine the point where a slight yellow color shows the presence of excess iodine. The reaction takes place more rapidly in methyl alcohol. Determination of tetraethyllead in gasoline is done by adding excess iodine in gasoline and titrating the excess with sodium thiosulfate.

$$(C_2H_5)_4Pb + I_2 \longrightarrow (C_2H_5)_3PbI + C_2H_5I$$

With tetraphenyllead the conditions are quite different because of the difference in solubility and slow rate of reaction. Here best results are obtained by adding excess iodine to a benzene solution of the organolead compound, heating in the presence of light, and back titrating with sodium thiosulfate solution. Under these conditions the reaction is:

$$(C_6H_5)_4Pb + 3I_2 \longrightarrow PbI_2 + 4C_6H_5I$$

Calingaert and Gambrill (30) have suggested the following method of analyzing for tetraethyllead in gasoline. The sample of gasoline containing tetraethyllead is refluxed with concentrated hydrochloric acid and the lead chloride that forms is extracted and a lead determination made by any of the standard methods. Edgar and others (48) have likewise suggested a method of analyzing for tetraethyllead in gasoline.

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INTRODUCTION

Organolead compounds have been shown to be effective in arresting cancer (see under "Organolead Compounds in the Treatment of Cancer" in the historical portion of this thesis). In the early studies of lead therapy in cancer it was found that the general insolubility of lead compounds and the slight difference between the therapeutic and toxic doses would be serious drawbacks to their widespread use.

Two methods of overcoming the insolubility of organolead compounds present themselves; the compounds may be made water-soluble or fat-soluble. In general, a molecule may be made more soluble in water by the introduction of polar groups, such as $-COOH$, $-OH$, $-SO_3H$, $-NH_2$, $-NR_2$, etc. The difficulty has been less a matter of what groups to introduce to effect water-solubility than of how to introduce the groups.

This work, then, was undertaken in order to study possible means of introducing water-solubilising groups into organolead compounds. Some studies were also made upon intermediates for future studies along this line. The other group IV-B metals, germanium and tin, were given some attention in order to observe what gradations in properties exist in this group in the periodic system of the elements.

EXPERIMENTAL

Organolead Reactions

The interaction of phenyllithium, iodobenzene, and lead chloride to produce tetraphenyllead

In a 1 l. three-necked flask was placed 12 g. (1.73 g. atoms) of finely cut lithium metal together with 500 cc. of dry ether. To this was added 125.6 g. (0.8 mole) of bromobenzene in 200 cc. of dry ether. The resultant solution was allowed to stand until clear and then was decanted, under nitrogen, into a dropping funnel.

The clear phenyllithium solution was slowly added to 200 cc. of dry ether, 69.5 g. (0.25 mole) of anhydrous lead chloride, and 56 g. (0.25 mole plus 10%) of iodobenzene in a 2 l. three-necked flask. The rate of addition was such that gentle refluxing occurred. No cooling was necessary; the reaction was not vigorous. Some bright yellow precipitate was observed after about one-third of the phenyllithium was added but no free lead was noticed.

The mixture was refluxed for two hours after the addition was completed. This did not seem to make any difference in the appearance of the mixture. It was hydrolyzed by dropwise addition of water while being cooled in an ice bath.

The ether layer was then distilled and the residue filtered and dried. This solid residue weighed 123 g. Extraction with chloroform gave 103 g. of tetraphenyllead. This was an 80% yield based upon reaction (1) of page 144 or 160% based upon the series of reactions marked (2) of page 144. There was an inorganic residue of 14.5 g. which was light grey in color and had no black color of free lead.

The interaction of phenyllithium, bromobenzene, and lead chloride to produce tetraphenyllead

This reaction was the same as that on page 108 except that 39.2 g. (0.25 mole) of bromobenzene was substituted for the iodobenzene.

As the phenyllithium was added, a greyish precipitate was noticed, while the solution took on a yellow-orange color. Upon further addition of phenyllithium this color disappeared with the formation of a lead mirror and a black solution. The mirror slowly disappeared. When the addition of the phenyllithium was completed, the mixture was stirred with refluxing for two hours. The deep black suspension was slowly converted to a grey-black suspension. There was a strong positive color test number one at the end of this time.

The mixture was cooled in an ice bath and hydrolyzed by the addition of water. The reaction was much more vigorous than in the preceding one where iodobenzene was used.

After hydrolysis, the ether was distilled and the solid residue in the water layer filtered and dried. It only weighed 77 g. Eighteen grams of bromobenzene was recovered. The extracted tetraphenyllead weighed 32 g. which was a 24.8% yield based upon reaction (1) of page 144. The inorganic residue had a greenish cast without evidence of any free lead.

The interaction of phenyllithium and lead chloride to produce tetraphenyllead

This was the same size reaction as that of page 108 with the exception that no iodobenzene or bromobenzene was used.

A black suspension resulted upon the addition of the phenyllithium, after the momentary formation of a bright yellow-orange solution. After two hours refluxing the black color had changed to dark grey. There was a positive Color Test I.

Hydrolysis was effected by the cautious addition of water to the stirred mixture cooled in an ice bath. After addition of 250 cc. of water, the mixture was stirred for an hour, the ether distilled, and the solid residue filtered from the water. The dried solid weighed 89.5 g.

Chloroform extraction gave 30 g. of tetraphenyllead and 33 g. of a light green inorganic powder. This represents a 41% yield of tetraphenyllead figured upon reaction (1) of page 144, for comparative purposes.

The interaction of phenylmagnesium bromide, iodobenzene, and lead chloride to produce tetraphenyllead

The Grignard reagent prepared from 157 g. (1 mole) of bromobenzene and 24.3 g. (1 g. atom) of magnesium in 350 cc. of ether was slowly added to a mixture of 93 g. (0.3 mole) of lead chloride and 68 g. (0.3 mole) of iodobenzene in 350 cc. of toluene. The first few drops of Grignard reagent caused a bright yellow-orange color but this was soon replaced by the characteristic black of the ordinary tetraphenyllead preparations. The black mixture was refluxed with stirring for five hours. The mixture did not get thick as in the ordinary tetraphenyllead preparations. It was hydrolyzed by pouring upon iced ammonium chloride. After standing over night, the reaction mixture was filtered and the organic portion of the filtrate was distilled. The residue from this distillation was added to the original filtered solid and the whole mass extracted with chloroform, in a Soxhlet extractor.

In this manner 63.5 g. of tetraphenyllead was obtained together with a residue of 53 g. of black inorganic material. This was a 37% yield based upon reaction (1) on page 144 or 74% based upon the series of reactions marked (2) on page 144.

In a check experiment in which the reaction mixture was stirred for two hours and only ether was used as a solvent, a 34% yield of tetraphenyllead (based upon reaction (1) of page 144) was obtained.

Reaction of hexaphenyldilead with maleic anhydride

In chloroform. In reactions between maleic anhydride and hexaphenyldilead, small amounts of maleic acid or traces of water were found to cause a flocculate precipitate. To avoid this, the maleic anhydride was heated in a test tube suspended in an oil bath.

In a dry tube was placed 4 g. (0.0045 mole) of hexaphenyldilead, 0.45 g. (0.0045 mole) of maleic anhydride, and 100 cc. of dry chloroform. The tube was sealed, shaken well, and placed in a warm laboratory desk. After fifteen minutes only a slight precipitate had formed. Five months later a slightly brownish-grey solid filled the lower part of the tube. This material was insoluble in acetone, ethyl alcohol, dioxane, chloroform, carbon tetrachloride, benzene, and the petroleum ethers. It was slightly soluble in boiling water and dissolved in glacial acetic acid.

Any unreacted materials were removed by boiling, first with chloroform and then with alcohol. Digestion with an ammonium acetate solution removed traces of inorganic lead. The material was then a greyish-white color. When viewed under a microscope, it was seen to possess a cubic structure similar to salt. When heated, it turned brown at 265-270° and had not melted at 330°. This product was believed to be $\underline{\alpha,\beta}$-di(triphenyllead)succinic acid. Because of the very limited solubility of the compound, it was impossible to run a neutral equivalent upon it. Anal. Calcd. for $C_{40}H_{34}O_4Pb_2$: Pb, 41.75. Found: Pb, 41.70.

In molten maleic anhydride. In the course of investigating the possible structure of the compound formed by the long-time interaction of hexaphenyldilead and maleic anhydride in chloroform solution, it was found possible to prepare this product in a much shorter length of time. A quantity of maleic anhydride was heated somewhat above its melting point (52.6°) but not too close to the decomposition temperature of hexaphenyldilead (160°). To the molten solution was slowly added hexaphenyldilead in small quantities. Too large individual additions caused local formation of a deep purple or red color. Additions were suspended when the mixture became thick. Gentle heating was continued for fifteen minutes and then the crude α,β-di(triphenyllead)succinic acid was progressively extracted with benzene, alcohol, water, and ammonium acetate solution. The product from this treatment was a greyish-white powder which proved to be as insoluble in solvents as the product from the previous reaction. From 4.38 g. (0.05 mole) of hexaphenyldilead was obtained 4.0 g. (81% yield) of product.

Anal. Calcd. for $C_{40}H_{34}O_4Pb_2$: Pb, 41.75. Found: Pb, 41.95.

Sodium salt of α,β-di(triphenyllead)succinic acid

Since, in the above experiments, the hexaphenyldilead could have reacted with either the double bond or the anhydride linkage in maleic anhydride, a method of differentiating between the two possible structures had to be found. The material was too insoluble to attempt to run a neutral equivalent. An alternative procedure would be to attempt to prepare the sodium salt of the acid form, by prolonged boiling of a sodium hydroxide solution with the unknown product.

A quantity of the purified product of the reaction of hexaphenyldilead with molten maleic anhydride was refluxed for eight hours with a 10% sodium hydroxide solution. Some dioxane was added to the refluxing mixture to prevent undue foaming. After the eight hours of refluxing, the mixture was diluted with water and filtered. The solid that separated was washed repeatedly with water until the filtrate was alkali free. It was then washed with alcohol and air-dried to give a crystalline product that sparkled in the sunlight. The product was as insoluble as the starting material.

Anal. Calcd. for $C_{40}H_{32}O_4Pb_2Na_2$: Pb, 39.98. Found: Pb, 40.41.

While the analysis was 0.43% higher than the anticipated value, it was still 1.34% lower than theoretical value of the starting material. It burned with a strong sodium flame. Undoubedly longer refluxing of the solution would have given more complete conversion of the free acid to the sodium salt.

Triphenyllead-sodium and ethyl α,β-dibromosuccinate

First attempt. Three grams (0.0034 mole) of hexaphenyldilead was dissolved in 150 cc. of liquid ammonia in a 250 cc. three-necked round-bottomed flask equipped with a stirrer. To this solution was added 0.157 g. (0.0068 g. atom) of sodium cut into small pieces. This was followed by 1.14 g. (0.0034 mole) of ethyl α,β-dibromosuccinate, added in small quantities. The ammonia boiled vigorously when this last material was added.

After the ammonia had boiled off the residue was extracted successively with chloroform, ammonium acetate solution, and alcohol. There was a very small residue of shiny colorless plates that melted at a high temperature to give a black melt. They burned on a spatula with a small flame, leaving a residue of lead. The sample was too small for an analysis.

Second attempt. Triphenyllead-sodium was prepared by adding 0.262 g. (0.0114 g. atom) of sodium to 5 g. (0.0057 mole) of hexaphenyldilead in 200 cc. of liquid ammonia. When about half of the ammonia had evaporated, 50 cc. of anhydrous ether was added and then the rest of the ammonia was evaporated. The last traces were removed by immersing the reaction flask in warm water and refluxing the ether. A green oil was observed under the clear ether layer.

To this mixture was added 1.89 g. (0.0057 mole) of ethyl $\underline{\alpha},\underline{\beta}$-dibromosuccinate dissolved in 20 cc. of anhydrous ether. The ether in the flask clouded up at once and the green oil disappeared with the formation of a brown and then a red scale upon the sides of the flask. The reaction was refluxed in a water bath for one-half hour. It was then worked up by filtering the ether and extracting the residue successively with chloroform, ammonium acetate solution, and alcohol. The residue after this treatment was a grey powder that analyzed 5½% low for lead content, for the compound where each bromine was replaced by a triphenyllead unit.

Triphenyllead acid maleate

Five grams (0.011 mole) of triphenyllead hydroxide was dissolved in 250 cc. of boiling, absolute alcohol. To this solution was added 1.07 g. (0.011 mole) of maleic anhydride and the mixture was boiled for ten minutes. The milky solution was filtered and the filtrate was distilled until a precipitate started to form. A white solid was filtered from the cooled solution. This solid was dissolved in hot alcohol and treated with alcoholic potassium hydroxide while still hot. Addition of a little water and cooling caused the potassium salt to precipitate. The product was filtered, redissolved in hot alcohol, and acidified to Congo red paper with hydrochloric acid. Addition of water precipitated the free acid, which was filtered, washed with water, and air-dried. It melted at 207° and weighed 5.3 g. which represents a 90% yield.

Anal. Calcd. for $C_{22}H_{18}O_4Pb$: Pb, 38.64. Found: Pb, 38.80.

Neutral Equivalent. Calcd: 536. Found: 525.

The solubility, analysis, and melting point of triphenyllead acid maleate are decidedly different from the corresponding figures for the product from hexaphenyldilead and maleic anhydride.

Di-triphenyllead maleate

To a hot solution of 4.55 g. (0.01 mole) of triphenyllead hydroxide was added an alcoholic solution of 0.58 g. (0.005 mole) of maleic acid. The solution was distilled until material started to precipitate. The mass of crystals produced upon cooling was filtered and air-dried to give 3.9 g. (82% yield) of a white product sintering at 198-199°.

Anal. Calcd. for $C_{40}H_{32}O_4Pb_2$: Pb, 41.84. Found: Pb, 42.30.

The properties and analysis of this compound, likewise, do not agree with those of the product from the reaction of hexaphenyldilead and maleic anhydride.

Attempts to induce a reaction between hexaphenyldilead and various unsaturated organic compounds

Dry benzene solutions of the proper molecular proportions of hexaphenyldilead and isoprene, pyrrole, styrene, 1,4-diphenylbutadiene-1,3, and furan were sealed and stored in the dark for five months. There was no reaction in any case.

Triphenyl-o-hydroxyphenyllead

Upon 0.88 g. (0.126 g. atom) of lithium chips in 50 cc. of anhydrous ether was slowly dropped 5.48 g. (0.04 mole) of n-butyl bromide in 25 cc. of anhydrous ether. The mixture was stirred for one-half hour after the addition was completed and then the excess lithium was filtered out. Into the stirred solution of n-butyllithium was slowly dropped 2.25 g. (0.013 mole) of o-bromophenol in 25 cc. of ether. Stirring was continued for one-half hour after the addition was completed.

To the o-lithio lithium phenoxide thus formed was added 4.74 g. (0.01 mole) of triphenyllead chloride. After 100 cc. of benzene was added, the mixture was gently refluxed for one hour. The mixture was then filtered and the filtrate hydrolyzed with water slightly acidulated with hydrochloric acid. The solvent layer was separated and distilled. The residue was washed with cold alcohol and then recrystallized from this solvent. There was obtained 0.64 g. (12% yield) of triphenyl-o-hydroxyphenyllead, m.p. 216-218°.

Anal. Calcd. for $C_{24}H_{20}OPb$: Pb, 38.98. Found: Pb, 39.22.

Triphenyl-9-phenanthryllead

The Grignard reagent was prepared by refluxing 3.67 g. (0.0143 mole) of 9-bromophenanthrene and 0.35 g. (0.0143 g. atom) of magnesium in a mixture of 15 cc. of dry benzene and 15 cc. of anhydrous ether. To this was added 5.18 g. (0.1 mole) of triphenyllead bromide. The mixture was refluxed for twenty-four hours and then was hydrolysed with a dilute hydrochloric acid solution. The ether layer was separated and evaporated to give a brown oil which slowly crystallized. This material was insoluble in alcohol, pet. ether (bp, 60-68°), acetone, and dioxane. The brown color of the oil was removed by dissolving the oil in benzene and passing the solution through a column of activated alumina. The benzene was then distilled and the residue recrystallized from ethyl acetate to give a product melting at 169-171°. There was 3.5 g. (57% yield) of material with a slightly yellowish cast.

Anal. Calcd. for $C_{32}H_{24}Pb$: Pb, 33.66. Found: Pb, 33.47.

Di-9-phenanthryldiphenyllead

The Grignard reagent was prepared by refluxing for twenty-four hours a mixture of 7.34 g. (0.0286 mole) of 9-bromophenanthrene and 0.70 g. (0.287 g. atom) of magnesium in 60 cc. of a 1:1 benzene-ether mixture. To this was added 20 cc. of ether and 5.21 g. (0.1 mole) of diphenyllead dibromide. After refluxing for twenty-four hours, it was hydrolyzed with dilute hydrochloric acid and filtered. The ether layer was evaporated to give a clear brown liquid that precipitated colorless crystals upon adding ethyl acetate. The crude product weighed 4.86 g. (68%). Recrystallization from ethyl acetate gave material with a greyish cast and melting at 208-210°.

Anal. Calcd. for $C_{40}H_{28}Pb$: Pb, 28.95. Found: Pb, 28.93.

When 0.5 g. (0.0007 mole) of di-9-phenanthryldiphenyllead was dissolved in 30 cc. of boiling chloroform and dry hydrogen chloride bubbled in, a precipitate formed. The precipitate was filtered and dried to give 0.29 g. (97% yield) of diphenyllead dichloride, identified by refluxing with phenylmagnesium bromide and making a mixed melting point determination with known tetraphenyllead. The chloroform solution was evaporated to recover the cleaved phenanthrene, which was identified by a mixed melting point determination.

Attempted preparations of tetra-9-phenanthryllead

To the Grignard reagent prepared in 50 cc. of benzene-ether from 2.57 g. (0.01 mole) of 9-bromophenanthrene and 0.25 g. (0.01 g. atom) of magnesium was added 25 cc. of benzene and 1.2 g. (0.0043 mole) of dry lead chloride. The solution turned orange and after a few minutes heating on a hot plate it was deep red. After refluxing five hours, the color had disappeared and the sides of the flask were coated with a solid. The mixture was hydrolyzed with an ammonium chloride solution, filtered, and the ether layer evaporated. The residue did not contain lead.

In another run of the same size, the reactants were refluxed for one hour on a steam bath. The mixture turned from bright red to black and a precipitate appeared on the sides of the flask. This time the reaction was hydrolyzed with dilute hydrochloric acid. Evaporation of the ether layer did not give any material containing lead. One gram of phenanthrene was recovered.

Triphenyl-7-(1,2-benzanthryl) lead

To the *n*-butyllithium solution prepared in 30 cc. of ether by the reaction of 1.5 g. (0.011 mole) of *n*-butyl bromide with 0.17 g. (0.025 g. atom) of lithium metal was added 1 g. (0.00325 mole) of 7-bromo-1,2-benzanthracene. The reaction mixture was stirred for *two minutes* and then 1.5 g. (0.00325 mole) of triphenyllead chloride was added. Stirring was continued for ten minutes before hydrolyzing with water. The resultant mixture was filtered and washed with ether. The residue was recrystallized from ethyl acetate. The product melted at 204-205°, which was the same melting point as triphenyllead chloride. A mixed melting point, however, was depressed. There was 1.13 g. of product which was a 52% yield.

Anal. Calcd. for $C_{36}H_{26}Pb$: Pb, 31.12. Found: Pb, 30.90.

When dry hydrogen chloride was passed into a chloroform solution containing 0.2 g. (0.0003 mole) of triphenyl-7-(1,2-benzanthryl)lead a white precipitate formed. This precipitate was filtered and dried to give 0.12 g. (92% yield) of diphenyllead dichloride. This product was identified by refluxing it with a phenylmagnesium bromide solution, hydrolyzing, and working up in the customary manner. The tetraphenyllead thus obtained was identified by a mixed melting point with a known sample of tetraphenyllead. The chloroform was evaporated from the 1,2-benzanthracene formed by the hydrogen chloride cleavage to give 0.07 g. (quantitative yield) of 1,2-benzanthracene. It was identified by a mixed melting point with a known sample of 1,2-benzanthracene.

Di-7-(1,2-benzanthryl)diphenyllead

To the *n*-butyllithium prepared in 40 cc. of ether by the reaction of 3.0 g. (0.022 mole) of *n*-butyl bromide with 0.033 g. (0.048 g. atom) of lithium metal was added 2.5 g. (0.0081 mole) of 7-bromo-1,2-benzanthracene. The mixture was stirred for *two minutes* and then 1.75 g. (0.004 mole) of diphenyllead dichloride was added. Stirring was continued for ten minutes before hydrolyzing with water.

The resultant mixture was filtered and the solid extracted with benzene. When the benzene solution was concentrated and alcohol added, small slightly yellow needles formed. These needles melted with some decomposition at 295-296° (micro melting point). There was only 0.3 g. (3.6% yield) of di-7-(1,2-benzanthryl)diphenyllead.

Anal. Calcd. for $C_{48}H_{32}Pb$: Pb, 25.39. Found: Pb, 25.40.

Reactions in liquid ammonia between hexaphenyldilead and several metals, derivatized with benzyl chloride

The following is a typical procedure in the reaction of hexaphenyldilead with metals in liquid ammonia, using benzyl chloride to derivatize the product thus formed.

A 250 cc. three-necked flask was fitted with a mechanical stirrer and the side-necks were equipped with stoppers. Through one of the side-necks was added 2.19 g. (0.0025 mole) of hexaphenyldilead and 150 cc. of liquid ammonia.

While this mixture was stirred, 0.035 g. (0.005 g. atom) of lithium, cut into small pieces, was slowly added. The solution was stirred for five minutes after the addition was completed and then 1 cc. (excess) of benzyl chloride was introduced, dropwise. Evaporation of the ammonia left a residue which was extracted with ether. The ether solution was evaporated and the residue washed with 10 cc. of alcohol. There remained 1.9 g. (72% yield) of triphenylbenzyllead, melting at 91-92°.

Table 1. Reactions in Liquid Ammonia in Which 0.0025 Mole of Hexaphenyldilead was Treated With Various Metals Followed by Benzyl Chloride

Metal	g. atom of metal	% Triphenylbenzyllead
Lithium	0.005	71 ; 72
Sodium	0.005	60 ; 64
Potassium	0.005	55 ; 57
Rubidium	0.005	52
Cesium	-----	---
Calcium	0.005	79 ; 81
"	0.0025	40 ; 41
Strontium	0.005	67 ; 74
"	0.0025	34 ; 36
Barium	0.005	56 ; 61
"	0.0025	31 ; 36

Reaction in liquid ammonia between 0.1 mole of triethyllead chloride and 0.2 g. atom of lithium gave a 40% yield of triethylbenzyllead when benzyl chloride was added.

When 0.2 g. atom of calcium was substituted for the lithium, the yield was only 13%.

Reactions in liquid ammonia between diphenyllead dihalides and several metals

The following is a typical reaction in liquid ammonia between a diphenyllead dihalide and a liquid ammonia soluble metal. Actually, only diphenyllead dichloride and diphenyllead difluoride were used. Calcium, lithium, and sodium were the metals used.

To 3.99 g. (0.01 mole) of diphenyllead difluoride suspended in 200 cc. of liquid ammonia in a three-necked flask, was slowly added 0.4 g. (0.01 g. atom) of calcium metal. The suspension was stirred during the whole procedure and a deep red coloration was noticed about each piece of metal. At times the whole suspension took on a momentary reddish-brown color. When about half the metal had been added, the ammonia solution became blue and stayed that color. The ammonia was allowed to evaporate and the whitish residue extracted with chloroform. Fractional crystallisation of the chloroform solution gave crops of tetraphenyllead and hexaphenyldilead.

The following Table 2 gives the data on the various reactions of this type that have been run. The per cent yield was based upon the amount of phenyl radicals appearing in the reactant and in the product.

Table 2. Reactions in Liquid Ammonia Between Diphenyllead Dihalides and Several Liquid Ammonia Soluble Metals

Diphenyllead dichloride		Metal		$(C_6H_5)_4Pb$		$((C_6H_5)_3Pb)_2$	
grams	mole	g.	g.atom	g.	%	g.	%
		Lithium					
4.32	0.01	0.28	0.04	trace		1.75	60.
		Calcium					
2.16	0.005	0.4	0.01			0.60	27.4
		Calcium					
4.32	0.01	0.4	0.01	0.22	10.	0.68	23.3
Diphenyllead difluoride							
		Lithium					
2.00	0.005	0.07	0.01	trace		0.75	52.
		Sodium					
2.00	0.005	0.23	0.01	trace		0.65	45.
		Calcium					
3.99	0.01	0.4	0.01	trace		1.70	58.

Attempts to prepare compounds of the type $R_2R'PbPbR'R_2$

sym-**Tetracyclohexyldiphenyldilead.** Dicyclohexyldiphenyllead (prepared in 65% yield from diphenyllead dichloride and cyclohexylmagnesium bromide) was dissolved in pet. ether (b.p., 28-38°) and a slow stream of dry hydrogen chloride was passed in until a precipitate no longer formed. Too rapid addition of hydrogen chloride cleaved two phenyl radicals. The precipitate that formed was filtered and recrystallized from chloroform to yield crystals of dicyclohexylphenyllead chloride that sintered slightly at 195° and started to decompose at 205°.

Anal. Calcd. for $C_{18}H_{27}PbCl$: Pb, 42.63. Found: Pb, 42.58.

To a suspension of 9.76 g. (0.02 mole) of dicyclohexylphenyllead chloride in 350 cc. of liquid ammonia was slowly added 0.46 g. (0.2 g. atom) of sodium, cut into small pieces. The liquid ammonia became colored a deep red. The ammonia was allowed to evaporate and the solid residue was extracted with chloroform to give a deep red solution. Exposure of this solution to sunlight caused an immediate disappearance of the red color and the formation of a precipitate. Even evaporation of the chloroform in the dark did not keep the solution from slowly losing its color. A lead analysis was run upon the supposed *sym*-tetracyclohexyldiphenyldilead.

Anal. Calcd. for $C_{18}H_{27}Pb$: Pb, 46.00. Found: Pb, 41.83.

sym-Tetraphenyldiethyldilead. An 81% yield of diphenylethyllead chloride was obtained by slowly bubbling dry hydrogen chloride into a solution of triphenylethyllead in pet. ether (b.p., 28-38°). The precipitate that formed was recrystallized from alcohol to give a white crystalline product which sintered at 142° and decomposed at 146-147°. Anal. Calcd. for $C_{14}H_{15}PbCl$: Pb, 48.70. Found: Pb, 48.37.

No particular color changes were noticed when 4.25 g. (0.01 mole) of diphenylethyllead chloride suspended in 250 cc. of liquid ammonia was treated with 0.23 g. (0.01 g. atom) of sodium. The yellowish solution obtained by chloroform extraction of the residue after the ammonia had evaporated could not be concentrated without decomposition taking place.

Attempted sulfonation of tetraphenyllead

To ice cold 30% fuming sulfuric acid was slowly added 1 g. (0.0019 mole) of finely powdered tetraphenyllead. The material dissolved at once. After allowing the solution to come to room temperature, it was poured upon ice. Only inorganic lead was obtained.

Attempted nitration of tetraphenyllead

To a solution of 45 cc. of fuming nitric acid and 35 cc. of conc. sulfuric acid cooled to -50° in an acetone-dry ice bath was slowly added some powdered tetraphenyllead. The solution immediately turned brown and soon became black, whereupon the addition was stopped. Upon allowing the mixture to come to room temperature, considerable gas was evolved so the material was poured upon ice. Some gummy material was obtained together with unreacted tetraphenyllead, lead sulfate, and nitrobenzene.

Nitration of diphenyllead dichloride

A solution of 45 cc. of fuming nitric acid and 35 cc. of conc. sulfuric acid was cooled to -50° in an acetone-dry ice bath. Upon slowly adding 10 g. (0.019 mole) of diphenyllead dichloride a thick grey paste formed. There was a strong odor of chlorine, indicating replacement of the chlorine by the nitrate group. The paste was allowed to stand over night at room temperature and was then poured upon ice. The solid that separated was filtered, washed with water, and air-dried.

An analysis indicated 33.34% lead. This is lower than any of the most likely possibilities. $(\underline{m}\text{-}NO_2C_6H_4)_2PbCl_2$ contains 39.65% lead; $(\underline{m}\text{-}NO_2C_6H_4)_2Pb(NO_3)_2$ has 36.00%; and $(C_6H_5)_2Pb(NO_3)_2$, 42.68%.

Di-m-nitrophenyllead dichloride

The method of Setzer, Leeper, and Gilman[1] was followed for preparing diphenyllead dinitrate. This was converted to di-m-nitrophenyllead dinitrate following the general method of Challenger and Rothstein.[2] They

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[1] Setzer, Leeper, and Gilman, J. Am. Chem. Soc., 61, 1609 (1939).

[2] Challenger and Rothstein, J. Chem. Soc., 1258 (1934).

recommended using a bath temperature of -10 to -15° but it was found that lowering it to -50° enabled faster addition of diphenyllead dinitrate without danger of decomposition.

To about 200 cc. of boiling water was added 10 g. (0.02 mole) of di-m-nitrophenyllead dinitrate. A clear solution resulted. To this was added a solution of 2.9 g. (0.05 mole) of sodium chloride. There was an immediate formation of a white precipitate. The mixture was cooled, filtered, and washed with a little water. Yield, 10.1 g. (97%). It was soluble in alcohol and recrystallized from ethyl acetate in small colorless plates. When observed under a micro melting point apparatus, these plates sublimed at 250° and decomposed at 285-288°.

Anal. Calcd. for $C_{12}H_8O_4N_2PbCl_2$: Pb, 39.65; N, 5.36.
Found: Pb, 39.33; N, 5.35.

Di-m-nitrophenyllead diiodide

Di-m-nitrophenyllead diiodide was prepared in 95% yield similarly to the method used for the dichloride. The diiodide was a bright yellow crystalline material which decomposed around 135°. Like diphenyllead diiodide it tended to decompose upon attempted recrystallization, but to a lesser extent.

Anal. Calcd. for $C_{12}H_8O_4N_2PbI_2$: Pb, 29.36. Found: Pb, 30.05.

Triphenyllead nitrate

To a solution of 1. g. (0.0022 mole) of triphenyllead hydroxide dissolved in 30 cc. of hot alcohol was added 0.5 cc. of conc. nitric acid dissolved in 10 cc. of alcohol. The solution was brought to a brisk boil on a hot plate and then allowed to cool. There was only a small amount of a crystalline product so the solution was evaporated to a small volume on a steam plate. Upon cooling, small colorless crystals appeared. These were filtered, washed with a little alcohol, and air-dried. They sintered with some decomposition between 220-225°.
Anal. Calcd. for $C_{18}H_{15}O_3NPb$: Pb, 41.40. Found: Pb, 41.07.

When conc. sulfuric acid was added to the sample for analysis, it burst into flames and evolved considerable smoke. The low analysis may have been due to volatilization of some of the lead.

Nitration of triphenyllead nitrate

The general procedure (p. 128) used in the nitration of diphenyllead dinitrate was followed. No color developed until the cooling bath was removed, whereupon the solution slowly turned dark blue. When poured upon ice the next morning, the color disappeared and a grey-white crystalline mass precipitated. This was filtered, washed with water, and air-dried. The dry product was extracted with ethyl acetate and the residue of tri-m-nitrophenyllead nitrate was analyzed for lead.
Anal. Calcd. for $C_{18}H_{12}O_9N_4Pb$: Pb, 32.44. Found: Pb, 32.45.

After standing a month in a screw cap bottle in a drawer, the material had turned a dirty grey. It partly dissolved in glacial acetic acid. The residue dissolved in ammonium acetate solution and gave a heavy precipitate with sodium chromate solution. This is the usual test for inorganic lead.

Nitration of triphenyllead chloride

The general procedure (p. 128) employed in the nitration of diphenyllead dinitrate was followed. Twenty grams of triphenyllead chloride was slowly added to the nitration mixture, with stirring. After the first addition, evolution of gas was noted, and the mixture became dark. At the end of the reaction the solution was dark brown and quite viscous (130 cc. of solution). The mixture was allowed to come to room temperature and stand for two hours. It was then poured upon ice and the precipitate filtered. The grey-brown precipitate was washed well with water and dried to give 28 g. (98%) of product.

The theoretical lead content for tri-m-nitrophenyllead nitrate is 32.29% while an analysis on the above material indicated only 27.9%. This is far below the lead content for any possible nitrated lead compound. As evidenced by the dark color produced during the nitration, considerable decomposition must have occurred.

Triethyllead chloride and diazomethane

Into 16.48 g. (0.05 mole) of triethyllead chloride in 50 cc. of dry benzene was passed the diazomethane prepared from 6.2 g. (0.06 mole) of nitrosomethylurea. After standing over night, most of the benzene was evaporated off and the residual crystals filtered and air-dried. A lead analysis agreed with that for the starting material and not for the expected triethyl-$\underline{\alpha}$-chloromethyllead.

Triethyllead chloride and diazoethane

In a similar experiment in which diazoethane was generated from 5.85 g. (0.05 mole) of nitrosoethylurea, a lead analysis indicated that the triethyllead chloride was recovered unchanged.

Attempted reactions of halogenoesters and lead powder

Ethyl $\underline{\alpha}$-bromopropionate. The lead powder used in the following experiments was obtained from the Metals Disintegrating Company, Elizabeth, New Jersey as a product designated MD 105. It was claimed that 70% of the material consisted of a powder less than fifteen microns in diameter.

A mixture of 10.35 g. (0.05 g. atom) of lead powder and 18.1 g. (0.1 mole) of ethyl $\underline{\alpha}$-bromopropionate was heated to reflux for twelve hours. The heating was interrupted three times while the coating of lead on the walls of the flask was scraped loose. Upon vacuum distillation the ester was recovered quantitatively.

Bromomethyl acetate. A mixture of 5.17 g. (0.025 g. atom) of lead powder and 7.65 g. (0.05 mole) of bromomethyl acetate was heated without solvent on a hot plate for ten hours. There was no reaction.

Ethyl bromoacetate. A mixture of 5.17 g. (0.025 g. atom) of lead powder and 8.35 g. (0.05 mole) of ethyl bromoacetate was heated without solvent on a hot plate for eight hours. There was no reaction.

Organogermanium Reactions

Action of iodine upon tetra-*n*-butylgermanium

Anhydrous germanium tetrabromide was prepared according to the directions of Laubengayer and Brandt[3]. The general method of preparing tetraalkylgermanium compounds[4] was used to prepare tetra-*n*-butylgermanium. From one mole of *n*-butyl bromide, 54 g. (80% yield) of tetra-*n*-butylgermanium, b.p. 127-128° at 4 mm., was obtained.

To 10 g. (0.033 mole) of tetra-*n*-butylgermanium was added 8.38 g. (0.066 g. atom) of iodine crystals. The first few crystals turned the solution a murky red and seemed to go into solution. The mixture was warmed on a hot plate, with occasional shaking, for eight hours.

Vacuum distillation gave 10 g. (69% yield) of material boiling at 126-128° at 4 mm. This is the boiling point of tetra-*n*-butylgermanium but addition of bromine to the distillate caused evolution of iodine fumes.

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[3] Laubengayer and Brandt, *J. Am. Chem. Soc.*, **54**, 622 (1932).

[4] Tabern, Orndorff, and Dennis, *ibid.*, **47**, 2039 (1925).

Preparation of tri-n-butylgermanium iodide through tri-n-butylgermanium bromide

Orndorff, Tabern, and Dennis[5] mention that ethylene bromide solutions of tetraphenylgermanium are rapidly brominated whereas other solvents require days for complete reaction.

To 10 g. (0.033 mole) of tetrabutylgermanium in 25 cc. of ethylene bromide was added 5.28 g. (0.066 g. atom) of bromine in 25 cc. of ethylene bromide. The solution was refluxed four hours at the end of which time no bromine vapor was apparent over the surface of the boiling liquid.

The ethylene bromide was distilled and the residue shaken with a potassium hydroxide solution. The product was then taken up in pet. ether (b.p., 75-115°), dried with sodium sulfate, and distilled under reduced pressure. The oxide had a camphor-like odor.

The oxide was shaken with hydrogen iodide solution, dried over calcium chloride, and distilled. It boiled at 125-127° at 4 mm. There was obtained 6 g. (49%) of tributylgermanium iodide.

Anal. Calcd. for $C_{12}H_{27}GeI$: I, 34.25. Found: I, 34.11.

Tetra-2-furylgermanium

To a mixture of 20.8 g. (3.0 g. atoms) of lithium chips, 1 l. of ether, and 117 g. (1.5 mole) of furan was slowly added 163 g. (1.5 moles) of ethyl bromide in 200 cc. of ether. When the reaction was completed, the mixture was filtered, 500 cc. of benzene added, and the ether distilled.

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[5] Orndorff, Tabern, and Dennis, ibid., 49, 2512 (1927).

To this solution was slowly added 85 g. (0.217 mole) of germanium tetrabromide in 100 cc. of benzene. There was moderate refluxing during the addition. The mixture was heated to reflux for 4 hours, with stirring. It was then allowed to settle and cool, the liquid layer was separated and the benzene distilled.

The residue from the benzene distillation was vacuum distilled from an oil bath. In this distillation, no material came over until the oil bath commenced to smoke, then a quantity of slightly yellow liquid suddenly shot over into the receiver and solidified. There was 20 g. of this solid. Upon redistillation, this material distilled smoothly at 163° at 1 mm. Seemingly an initial complex had to be broken up by heating.

After three distillations and seven recrystallizations, the material still melted over the range of from 65° to 80°. There was no Beilstein test for halogen so all of the material from the various recrystallizations was gathered together and heated for 3 days in a benzene solution. The product from this treatment melted at 99-100° after recrystallizing from 60-68° b.p. petroleum ether. Seemingly the initial product was contaminated with hexafuryldigermanium. There was 18 g. (24.3% yield) of pure material.

Anal. Calcd. for $C_{16}H_{12}O_4Ge$: Ge, 21.07. Found: Ge, 21.04.

In a check experiment, the product exhibited the same type of superheating in the first distillation. The product then distilled at 163° at 1 mm. and melted at 99-100° upon recrystallizing from 60-68° petroleum ether. No prolonged heating in a benzene solution was required this time. The yield was 32%.

Organotin Reactions

n-Butyltin triiodide

$KSnCl_3$ was prepared according to the directions of Reinbach and Fleck[6]. Concentrated solutions of equimolecular amounts of potassium chloride and stannous chloride were mixed and cooled in ice water. The crystalline product that separated was filtered and dried in an oven at 105°.

Tchakirian, Lesbre, and Lewinsohn[7] prepared the lower members of the $RSnI_3$ series from alkyl iodides and $KSnCl_3$. The exact mechanism of the reaction is not yet clear. The suggestions of these authors were followed in preparing the n-butyltin triiodide.

To 15 g. (0.0568 mole) of powdered $KSnCl_3$ in a Carius tube was added 35 cc. (excess) of n-butyl iodide. The tube was sealed and heated seventy-two hours at 90°. The tube was then opened and the liquid decanted from the solid. The solid was extracted with pet. ether (b.p., 28-38°) and the two liquids combined and fractionated. There was 8 g. (25% yield) of material boiling at 154° at 5 mm. This liquid had a clear red color, even after treatment with bone black, and would not wet glass. Decomposition set in within a few minutes after isolation, with deposition of stannous iodide.

Anal. Calc. for $C_4H_9SnI_3$: Sn, 21.33. Found: Sn, 21.62.

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[6] Rimbach and Fleck, Z. anorg. Chem., 94, 139 (1916).

[7] Tchakirian, Lesbre, and Lewinsohn, Compt. rend., 202, 138 (1936).

Tri-n-propyltin bromide and diazoethane

To 25 g. of nitrosoethylurea suspended in 150 cc. of n-butyl alcohol was gradually added a solution of sodium n-butoxide in the alcohol. This was done at reduced pressure and the gases distilling were passed through a tube filled with solid potassium hydroxide and then condensed in a trap cooled in an acetone-dry ice bath. To the yellow liquid which condensed was slowly added tri-n-propyltin bromide. There was a vigorous reaction which was best controlled by frequent immersion of the reaction flask in the acetone-dry ice cooling bath. Addition of the tin compound was discontinued when the yellow color left the solution. The product was a pasty white liquid. This was vacuum distilled but the volume of liquid was too small for an accurate thermometer reading. The temperature seemed to be about 130-135° at 3 mm. The product was a clear colorless liquid without the sharp unpleasant smell of the starting tin compound.

The material was placed in a nitrogen filled glass stoppered bottle. The sample commenced to turn yellow and deposit a white solid before an analysis could be run. A qualitative test did indicate that chlorine was present.

Reactions of halogenated compounds with tin powder

Ethyl bromoacetate. The tin powder used in the following reactions was obtained from the Metals Disintegrating Company, Elizabeth, New Jersey.

The product was designated MD 105 and it was claimed that all of it was less than 325 mesh.

A mixture of 5.93 g. (0.05 g. atom) of tin powder and 16.7 g. (0.1 mole) of ethyl bromoacetate was heated to reflux for five and one-half hours. The layer of tin upon the bottom of the flask slowly disappeared. Upon allowing the reaction mixture to cool, crystals appeared in the thick black liquid. The liquid portion was washed out with ether and the crystals remaining behind were recrystallized from benzene. This colorless crystalline material melted at 139°. There was 3.5 g. (15.5% yield) of product. Assuming that this compound has a structure similar to that of the material isolated from the reaction of ethyl iodoacetate and tin[8] this compound would be called dicarbethoxymethyltin dibromide. _Anal._ Calcd. for $C_8H_{14}O_4SnBr_2$: Sn, 26.22. Found: Sn, 26.22.

Bromomethyl acetate. A mixture of 5.93 g. (0.05 g. atom) of tin powder and 15.3 g. (0.1 mole) of bromomethyl acetate appeared to start reacting as soon as mixed. The mixture was heated for five and one-half hours to give a black solution. While most of the tin had disappeared, it was impossible to isolate any organotin compound by either crystallization or distillation. Distilling the mixture at reduced pressure caused the mixture to foam and deposit inorganic tin.

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[8] Emmert and Eller, _Ber._, _44_, 2328 (1911).

Phenacyl bromide. A mixture of 5.93 g. (0.05 g. atom) of tin powder and 19.9 g. (0.1 mole) of phenacyl bromide was heated on a hot plate. Shortly after the organic material had melted, a bright green solution formed. After two hours heating, this solution had turned very dark. At the end of four and one-half hours, all of the tin seemed to have disappeared. Upon allowing the reaction mixture to cool, the black liquid set to a glassy solid. Attempts to recrystallize the material, or distil it with a mercury vapor pump, were unsuccessful.

β-Bromoethyl acetate. A greyish suspension formed when a mixture of 5.94 g. (0.05 g. atom) of tin powder and 16.7 g. (0.1 mole) of the ester were mixed. After fifteen minutes of heating, a clear solution formed over the precipitated tin. The resultant clear solution slowly reacted with the tin during the course of eighteen hours, to give a black solution. Upon cooling, this black solution solidified.

Petroleum ether (b.p., 60-68°) would not dissolve this solid but benzene proved an excellent solvent. A dark thick oil resulted from attempts to decolorize a benzene solution of the product. When the oil would not crystallize, vacuum distillation was attempted with a mercury vapor pump. The oil decomposed without distilling. The foamy solid residue from the attempted distillation was dissolved in ethyl acetate but would not crystallize.

Ethyl α-bromopropionate. In an oil bath, a mixture of 2.95 g. (0.025 g. atom) of tin powder and 20 cc. of the ester were heated for twenty hours at 150°. At the end of this time, all of the tin had disappeared and a dark brown solution remained.

Vacuum distillation of the dark solution gave two fractions. The first fraction was colorless and consisted of unreacted ester. The second fraction was clear brown in color. There was only 3 cc. of the second fraction and a correct thermometer reading could not be made, but it seemed to be about 82-85° at 1.5 mm. There was a solid residue of 6 g. The second fraction to distil was assumed to be the expected di-*α*-methyl-*α*-carbethoxymethyltin dibromide.

Anal. Calcd. for $C_{10}H_{18}O_4SnBr_2$: Sn, 23.71. Found: Sn, 23.24.

In a second trial, heated at 180° for eight hours, it was noticed that more undesirable solid appeared the longer the heating was continued. The optimum time of heating is most likely four to five hours.

Diethyl α-bromosuccinate. A mixture of 5.95 g. (0.05 g. atom) of tin powder and 25.3 g. (0.1 mole) of the ester was heated in an oil bath for six hours. About fifteen minutes after heating was started, a little extra vigorous boiling of the liquid was noticed for a while. Vacuum distillation of the product gave 16 g. of a colorless liquid with an ester-like odor, boiling at 58-60° at 1.5 mm. The expected product was the ethyl ester of the di(*α*-succinic acid)tin dibromide.

Anal. Calcd. for $C_{16}H_{26}O_8SnBr_2$: Sn, 19.00. Found: Sn, 13.96.

The sample was redistilled and the middle half collected separately for another analysis. This time the tin content was 13.87%. There is no reasonable explanation for the consistently low analysis except on the ground of an impure sample. The cause of the impurity may be due either to partial decomposition of the sample during distillation, or to incomplete fractionation of the reaction mixture. The theoretical analysis for tin in the compound having four ester radicals and no bromine attached to tin, is 14.64%.

Ethyl dibromomalonate. A mixture of 3 g. (0.025 g. atom) of tin powder and 25 g. (0.079 mole) of ethyl dibromomalonate was heated in an oil bath at 130°. The reaction suddenly became vigorous about fifteen minutes after heating was started. The oil bath was removed and the reaction mixture allowed to cool. The product was a dark brown exceedingly viscous oil. This oil was readily soluble in 25 cc. of ether. Only a trace of unreacted tin settled out. When distillation was attempted, using a mercury vapor pump, the material decomposed before distilling.

2-Bromopyridine. A mixture of 12.2 g. (0.1038 g. atom) of tin powder and 32.8 g. (0.2076 mole) of 2-bromopyridine was heated to reflux for one and one-half hours. The mixture slowly turned dark and the solid tin disappeared. Upon cooling, a very viscous substance resulted. Attempted distillation removed a small amount of unreacted 2-bromopyridine but the main portion of the material would not distil. The residue from this attempted distillation was melted and poured from the flask as a high-melting, glassy, black mass.

The product was insoluble in the petroleum ethers, benzene, alcohol, glacial acetic acid, ethyl acetate, and chloroform. The material would not distil.

1-Chloro-2-iodoethane. When a mixture of 42.7 g. (0.224 mole) of 1-chloro-2-iodoethane and 17.7 g. (0.149 g. atom) of tin powder was heated to reflux on a hot plate, the mixture turned a green color in about fifteen minutes. There was no further color change and after five hours of refluxing, most of the liquid had disappeared. The residue was vacuum distilled from an oil bath. There was considerable decomposition as evidenced by the coating of the distilling flask with stannic iodide (m.p., 142-143°). A small amount of a light red liquid distilled at 65-70° at 1 mm. In an attempted redistillation, most of the liquid decomposed, leaving an orange solid. A small amount of the red liquid, when exposed to the air fumed considerably and decomposed leaving an orange solid. The most likely compound formed is di-β-chloroethyltin diiodide.

Anal. Calcd. for $C_4H_8SnCl_2I_2$: Sn, 23.76. Found: Sn, 25.90.

Evidently some decomposition occurred in the analytical sample between the time it was distilled and the time the sample was weighed.

1-Bromo-2-chloroethane. A suspension of 11.87 g. (0.1 g. atom) of tin powder and 28.7 g. (0.2 mole) of 1-bromo-2-chloroethane was sealed in a Carius tube and heated in a furnace at 145° for twenty-six hours. There was no reaction.

The same quantities of materials were heated in the same manner at 180° for six hours. The cooled tube was then opened and the contents were filtered. Distillation of the filtrate gave only unreacted 1-bromo-2-chloroethane. The solid reaction product was extracted with alcohol and the alcohol distilled. There was a residue of one-half gram of a colorless thick oil. The most likely compound formed was di-β-chloroethyltin dibromide.

Anal. Calcd. for $C_4H_8SnBr_2Cl_2$: Sn, 29.27. Found: Sn, 35.00.

While this analysis was carried out upon material that had been neither distilled nor recrystallized, the analysis as determined was too far off for there to be even a faint possibility of its being the desired compound. Even tetra-β-chloroethyltin would only have 31.85% tin. The sample must have contained inorganic tin as well as an organotin compound. The material burned with a faint flame when heated upon a spatula.

When the same quantities of starting materials were heated twenty hours at 180°, the 1-bromo-2-chloroethane was completely decomposed.

When the same quantities of starting materials were heated for ten hours at 195°, the 1-bromo-2-chloroethane was completely decomposed.

1-Bromo-3-chloropropane. A mixture of 17.9 g. (0.15 g. atom) of tin powder and 50 g. (0.312 mole) of 1-bromo-3-chloropropane was heated in an oil bath at 140° for seventy-two hours. Upon distilling the reaction products, 47 g. (94%) of the 1-bromo-3-chloropropane was recovered.

The same quantities of materials sealed in a Carius tube were heated in a furnace for twenty-four hours at 250°. The 1-bromo-3-chloropropane was completely decomposed.

DISCUSSION

Tetraphenyllead was used as the starting material in a number of the experiments in the course of this research. Since comparatively large quantities of tetraphenyllead were needed, variations in methods of preparation were tried in an effort to obtain improved yields. An interesting development of these attempts was the formation of tetraphenyllead by the action of phenyllithium upon lead chloride in the presence of iodobenzene. The general equation for such a reaction can be written:

$$(1)\quad 3RLi + RI + PbCl_2 \longrightarrow R_4Pb + 2LiCl + LiI$$

In the ordinary method of preparing R_4Pb compounds by use of the Grignard reagent (an organolithium compound is sometimes used instead) theoretically only half of the lead used in the reaction can appear in the product in the form of an organolead compound. This is apparent from the following series of equations which is commonly used to explain the course of the reaction.

$$(2)\quad 12RMgX + 6PbCl_2 \longrightarrow 6R_2Pb + 12Mg(X)Cl$$

$$6R_2Pb \longrightarrow 2R_6Pb_2 + 2Pb$$

$$2R_6Pb_2 \longrightarrow 3R_4Pb + Pb$$

A characteristic feature of such a method of preparing R_4Pb compounds is the development of a black suspension due to the formation of finely divided lead. This black color of the reaction mixture is missing, or at most only present as a fleeting trace at the start of the reaction, when the reaction is carried out in the presence of an organic iodide as in reaction (1).

The fact that there are occasional indications of the momentary presence of finely divided lead in these reactions might lead one to believe that the organic iodide reacted with the finely divided lead, perhaps in the following manner:

$$2RI + Pb \longrightarrow R_2PbI_2$$

That this was not the case is evident from the reaction where the Grignard reagent was substituted for the organolithium compound. In that case the yield of tetraphenyllead was much lower and a black reaction mixture was formed.

Substitution of an organic bromide for the organic iodide in a reaction using an organolithium compound likewise did not prevent the formation of free lead. Here, however, refluxing of the reaction mixture caused most of the free lead to disappear slowly. This difference in the length of time that the free lead was present may have been due to the lower rate of reactivity of organic bromides as compared to organic iodides. It is more likely that the reaction took a different course since the yield of tetraphenyllead was very low.

From these observations it is evident that the best yields of R_4Pb compound are reached when an organolithium compound is used in conjunction with an organic iodide. The mechanism of the reaction might conceivably involve the formation of free radicals:

$$(3) \quad RLi + RI \longrightarrow 2 \quad [R-] \quad + LiI$$

The free radicals might then react with the finely divided lead formed by the thermal decomposition of diphenyllead:

(4) $2\ [R-] + Pb \longrightarrow R_2Pb$

This can hardly be considered the main reaction, however, since the presence of free lead has only been observed occasionally and never for any length of time. It seems more likely that the main reaction involves the action of free radicals, formed as in reaction (3), upon diphenyllead, formed as in reaction (2):

(5) $2\ [R-] + R_2Pb \longrightarrow R_4Pb$

Perhaps some idea of the actual mechanism involved could be gained by use of an organic radical in the organic iodide different from that used in the organolithium compound. This might also prove to be a most convenient method of preparing unsymmetrical organolead compounds.

When methyllithium and methyl iodide were reacted with lead chloride Jones[9] was able to obtain a nearly quantitative yield of tetramethyllead.

The change of lead from Pb^{++} to Pb^{++++} requires that simultaneous reduction also take place in this reaction. This is probably best explained by assuming that the R groups undergo a change from R^+ in RI to R^- in R_4Pb.

In the course of attempting to introduce water-solubilizing groups into organolead compounds, the action of maleic anhydride upon hexaphenyldilead was investigated. After the reaction mixture had stood for five months at room temperature a solid material separated from the

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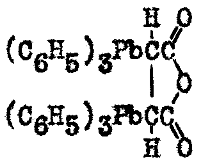
[9] Jones, R.G., unpublished work.

reaction solution. The same product was also formed (and more rapidly) when hexaphenyldilead was added to molten maleic anhydride. There were two possible positions for the organolead compound to react with maleic anhydride. One position involved the double bond and the other position involved the anhydride linkage.



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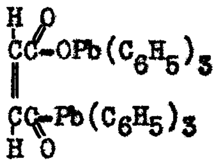

II

Hexaphenyldilead has often been incorrectly called triphenyllead although recent studies tend to discount the possibility that free radicals exist to any great extent. This nomenclature does, on the other hand, help to point out a possible relationship with triphenylmethyl, a free radical known to exist to a considerable extent in equilibrium with hexaphenylethane.

Conant and Chow[10] were able to obtain a product from the reaction of triphenylmethyl with maleic anhydride and to show that this product was *α,β*-di(triphenylmethyl)succinic acid. Presuming that a similar reaction occurred in the reaction of hexaphenyldilead with maleic anhydride, figure I would indicate the product formed. Conant and Chow converted their product to the sodium salt and found that the salt was insoluble in water.

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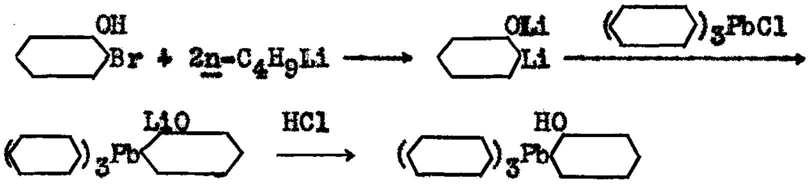
[10] Conant and Chow, *J. Am. Chem. Soc.*, *55*, 3475 (1933).

It was found in this research that the free acid was very insoluble in water, as would be expected from a compound with a molecular weight of 992. The sodium salt was formed with difficulty when the free acid was boiled with a sodium hydroxide solution. The sodium salt was also very insoluble in water. The actual formation of a sodium salt indicated that structure II was not the correct structure of the product.

Several additional experiments were carried out with the hope of finding further similarities between hexaphenyldilead and triphenylmethyl in their reactions with various compounds containing active groupings. Conant and co-workers[10,11] obtained reactions between triphenylmethyl and compounds such as pyrrole, isoprene, and other substituted 1,3-dienes but in similar reactions with hexaphenyldilead no reactions occurred.

Another method of introducing water-solubilizing groups involves the use of an organolithium compound. The single reaction of this type that was investigated can best be illustrated by the following outline of reactions:



The product, triphenyl-o-hydroxyphenyllead, was not water-soluble but the method as a means of introducing water-solubilizing groups shows promise.

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[11] Conant and Scherp, ibid., 53, 1941 (1931).

A number of different active groups have been introduced in this manner and greatly improved yields have been realized[12,13,14] within the last year or so.

The main purpose of preparing water-soluble organolead compounds was in order to test them as possible anti-cancer agents. Polynuclear hydrocarbons are known to cause cancer and it was believed wise to prepare several organolead compounds containing polynuclear hydrocarbon radicals in order to have them tested for possible cancer-producing activity. If such compounds showed decreased cancer-producing tendencies it might be interpreted as an indication of the effectiveness of organolead compounds in the treatment of cancer. With this in mind triphenyl-9-phenanthryllead, di-9-phenthryldiphenyllead, triphenyl-7-(1,2-benzanthryl)lead, and di-7-(1,2-benzanthryl)diphenyllead were prepared and sent to Dr. Louis F. Fieser for testing in mice. After six months thirty-nine out of a total of forty mice injected with the organolead compounds containing the phenanthryl radical (twenty mice on each compound) were still alive and showed no evidence of tumor development. Unfortunately, no information has been received on the organolead compounds containing the 1,2-benzanthryl radical. 1,2-Benzanthracene is known to produce cancer while there is no such knowledge in the case of pure phenanthrene.

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[12] Arntzen, Doctoral Disseration, Iowa State College (1942).

[13] Melstrom, unpublished work.

[14] Stuckwisch, unpublished work.

In studies on the feasibility of using reactions in liquid ammonia as a means of introducing organic radicals into organolead compounds, the effect upon the yield of product caused by different liquid ammonia-soluble metals was investigated. From these studies it became very apparent that the first metal in Groups I-A and II-A, lithium and calcium, gave the best yields. The yield then progressively decreased as one went down each group in the periodic system of the elements.

Another interesting observation was that the Group II-A metals seemed to act as monovalent metals in the liquid ammonia reactions. Thus, the reaction of calcium can be represented by the equation:

$$(C_6H_5)_3PbPb(C_6H_5)_3 + 2Ca \longrightarrow (C_6H_5)_3PbCaCaPb(C_6H_5)_3$$

rather than by the equation:

$$(C_6H_5)_3PbPb(C_6H_5)_3 + Ca \longrightarrow (C_6H_5)_3PbCaPb(C_6H_5)_3$$

If the quantity of calcium represented by the second equation above was used, the yield of product upon derivatizing with benzyl chloride was half the yield one would get if twice as much calcium had been used.

The reactions between compounds of the type R_2PbX_2 and metals in liquid ammonia were a continuation of studies made by Apperson.[15] No additional information has been found to add to the discussion found in his thesis.

The action of halogenated organic compounds, especially halogenoesters, with metallic lead would seem to offer an excellent method of introducing

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[15] Apperson, Doctoral Dissertation, Iowa State College (1940).

water-solubilizing groups into organolead compounds, providing lead in a finely divided state has sufficient reactivity towards halogens. Robinson[16] tried a Reformatsky type of reaction with ethyl bromoacetate or ethyl α-bromopropionate and magnesium upon triethyllead chloride or triethyllead bromide. He was unable to isolate an organolead ester but thought that a reaction had occurred. Emmert and Eller[8] reacted tin with ethyl iodoacetate and obtained a product that they believed was $I_2Sn(CH_2COOC_2H_5)_2$.

With the hope of getting an analogous reaction to take place between very finely powdered lead and bromoesters, ethyl α-bromopropionate, bromomethyl acetate, and ethyl bromoacetate were refluxed with lead powder. There was no evidence of a reaction.

When tin powder was tried in place of lead powder, reactions occurred with ethyl bromoacetate, bromomethyl acetate, phenacyl bromide, β-bromoethyl acetate, ethyl α-bromopropionate, diethyl α-bromosuccinate, ethyl dibromomalonate, and 2-bromopyridine. In some cases the reaction was quite exothermic and without exception the tin powder was used up. The products were nearly always thick tars or glassy solids and decomposed upon attempted distillation under reduced pressure. The relative instability of these products was also illustrated by their decomposition with deposition of stannous bromide if the reaction mixture was refluxed too long. Further investigation would surely disclose some suitable method of separating the pure products. It was the intention in this

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[16] Robinson, Doctoral Dissertation, Iowa State College (1929).

work to react the products (essentially R_2SnBr_2 types) with an organometallic compound such as diethylzinc which is unreactive toward the ester grouping. The product from such a reaction, a $(C_2H_5)_2SnR_2$ compound, would then be hydrolyzed to the free acid for further study.

Reactions of tin powder with compounds such as 1-chloro-2-iodoethane, 1-bromo-2-chloroethane, and 1-bromo-3-chloropropane were unsuccessful. There were indications of some reaction but seemingly the product formed was quite unstable at the temperatures required for a reaction to take place. The purpose of these experiments was to get a compound of the general type $X_2Sn\ [(CH_2)_nX]$ and finally to replace the halogen attached to carbon by water-solubilizing groups.

The reactions of R_3PbX and R_3SnX compounds with diazomethane and diazoethane were further variations in the attempt to produce an organometallic compound with a halogen attached to carbon. The compound expected would have the general formula $R_3M(CH_2)_nX$. Hellerman and Newman[17] had observed this type of reaction between diazomethane and mercuric chloride or RHgX compounds.

In the present experiments there was no indication of a reaction with the lead compounds and the product with tri-n-propyltin bromide, formed in small amounts, was unstable.

Tchakirian, Lesbre, and Lewinsohn[18] prepared compounds of the general type $RSnI_3$ where the R group was methyl, ethyl, and n-propyl. These

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[17] Helleman and Newman, J. Am. Chem. Soc., 54, 2859 (1932).

[18] Tchakirian, Lesbre, and Lewinsohn, Compt. rend., 202, 138 (1936).

compounds were quite unstable. With the hope of preparing a more stable compound of this type n-butyltin triiodide was made. This, too, started to decompose within a few minutes after isolation.

The attempted preparation of R_6Pb_2 compounds with two different organic radicals was discontinued after two of the experiments gave materials of very low stability. One very interesting observation was that sym-tetracyclohexyldiphenyldilead, a highly colored material in solution, was instantly decolorized with decomposition upon exposure to light. The speed with which this decomposition took place was amazing.

SUMMARY

A survey of the literature of organolead compounds has been made. All materials with a Pb-C bond have been listed in tabular form.

Several methods leading to the introduction of water-solubilizing groups into organolead compounds have been investigated. Some studies have been made on organogermanium and organotin compounds for comparison with related organolead preparations.