ORGANOLEAD COMPOUNDS

ROBERT W. LEEPER

Pineapple Research Institute, Honolulu, Hawaii

LAWRENCE SUMMERS

Department of Chemistry, University of North Dakota, Grand Forks, North Dakota

AND

HENRY GILMAN

Department of Chemistry, Iowa State College, Ames, Iowa

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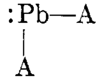
I. INTRODUCTION

Organolead compounds are substances in which at least one lead–carbon bond is present. The first such material was described one hundred years ago (238), and since that time the field of organolead compounds has become one of the most thoroughly investigated subdivisions of organometallic chemistry. Reviews of the subject (35, 87, 93, 142, 191, 194, 215, 304, 316) have appeared from time to time. The latest complete review (215) covers the literature up to about 1935, while the most recent detailed discussions (35, 142) in English date from about 1925. It seems desirable at this time to review and summarize the present state of knowledge in this field, with special emphasis on the developments of the last twenty years. This is the purpose of the present paper, in which the original literature is covered through 1951, with some additional references of later date. Tables are included which give what is believed to be an essentially complete listing of known organolead compounds, with literature references. In nearly every case all references known to the authors are given for each compound. An exception is made only for one or two compounds (notably tetraethyllead) for which the number of references is so large as to preclude a complete listing.

II. Valence States of Group IVB Elements in Neutral Molecules

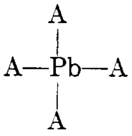
Lead, the element of atomic number 82, is a member of Group IVB of the Periodic Table. In the atom of any element of this group there are four electrons in the valence level. All orbitals in lower levels are completely occupied, so that differing valences will not be due to employment of more or fewer lower-lying orbitals in bond formation. The four valence electrons are not all equivalent. The ground state for these atoms is (in the Russell–Saunders notation) a ^3P state, derived from an s^2p^2 configuration (264). There are two electrons in the *s* subshell, necessarily with spins coupled, and in this state only the two unpaired electrons in the *p* subshell should be available for bonding. A covalence of 2 would be expected, arising from this ground state of the atom. In order to form the usual four-covalent state, it is necessary to uncouple one of the *s* electrons; the Pauli principle requires that this electron be promoted to a higher energy level. The next level is the *p* level of the same subshell, and promotion of an *s* electron to this level gives an sp^3 configuration, for which the lowest term is a ^5S state with four uncoupled electrons. To prepare the atom for bond formation the linear combinations of these sp^3 orbitals which give the best bonds are sought, and the familiar tetrahedral orbitals result. The common four-covalent state is derived from the sp^3 ^5S state of the atom, which is not the ground state but the first excited state.

Covalences of 2 and 4 would then be expected for these elements in neutral molecules (ions and radicals are discussed below). In fact, these covalences, and no others, are those which are known for elements of this group. The two-covalent state may be represented as in structure I (where A is any covalently bound atom or group) and the four-covalent state as in II. These two states are not at all analogous chemically. In structure I the central lead atom has only six electrons in the valence shell and should be able readily to accommodate another pair to form the stable octet. Also there is an "inert pair" (146, 315) of electrons not being employed in bond formation. Structure II, in contrast, is a structure with two more covalent bonds, with no inert pair of electrons, and with a complete octet around the central atom. The latter state occurs far more frequently than the former. In almost all known organolead molecules the lead atom is four-covalent.



$$:\underset{\underset{\mathrm{A}}{|}}{\mathrm{Pb}}-\mathrm{A}$$

I



$$\mathrm{A}-\overset{\overset{\mathrm{A}}{|}}{\underset{\underset{\mathrm{A}}{|}}{\mathrm{Pb}}}-\mathrm{A}$$

II

The discussion above emphasizes some similarities in compound formation by all elements of this group. Among these elements there are also differences, which lead in some cases to rather widely different chemical behavior of their compounds. First, there is considerable difference in electronegativity. Recently proposed electronegativity values are as follows: carbon, 2.55; silicon, 1.76; germanium, 1.40; tin, 1.37; lead, 1.13 (314; see also 145). The other elements of the group are considerably less electronegative than is carbon, and this should be reflected in a difference in the behavior of, for instance, carbon–carbon and lead–carbon bonds. Second, the carbon atom is in a special situation within the group. Since it is a second-period element it cannot expand its valence shell beyond eight electrons. For silicon and other elements in higher periods, such an expansion is theoretically not forbidden and may account for some of the differences between the chemistry of these elements and that of carbon. Also, carbon has that pronounced ability to form multiple bonds which is characteristic of the second-period elements. Were it not for this, it is possible that there would be in fact no known compound of divalent carbon, because all such compounds which are isolable are unsaturated (for example, carbon monoxide) and consequently have the possibility of stabilization by resonance with forms derived from the four-covalent state. Single-bonded structures such as CCl_2 have been postulated as reaction intermediates (173; see 1) but have never been isolated. Third, the ability to maintain the divalent state apparently increases, in this group, as the atomic number or atomic weight increases. Such compounds are unknown for carbon, except as noted above, and are rare for silicon. Divalent tin is more stable, and lead yet more so. Further discussion of this question is given below (Section IV).

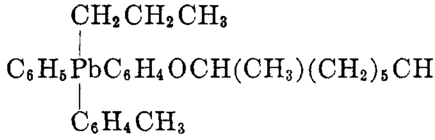
III. Organolead Compounds of Four-Covalent Lead

A. NATURE AND CONFIGURATION OF THE BONDS FORMED BY FOUR-COVALENT LEAD

The best-known organolead compounds are those of the type R_4Pb, in which the organic groups (R) may be the same or different. Examples are tetraphenyllead, $(C_6H_5)_4Pb$, tetraethyllead, $(C_2H_5)_4Pb$, and ethyltriphenyllead, $(C_6H_5)_3PbC_2H_5$. From the discussion above, it is seen that the well-known theoretical development which leads to the expectation of tetrahedral bonding for the four-covalent carbon atom should apply also to all members of Group IVB. The expected tetrahedral configuration around the lead atom is confirmed by all existing data. The tetramethyl derivatives of silicon, germanium, tin, and lead were investigated, in the vapor state, by Brockway and Jenkins (22) by electron diffraction. George (89), Giacomello (92), and Zhdanov and Ismailzade (340) investigated the structure of crystalline tetraphenyllead by means of x-ray diffraction. In all these cases the data agree with the tetrahedral configuration and the bond distances are essentially equal to the sums of the covalent radii involved. (Brockway and Jenkins do not make this calculation for their lead compound, possibly for lack of an accepted value for the lead covalent radius, but if the value 1.44 Å. is used, their data will agree well with the radius sums. Giacomello uses the value 1.6 Å. for the lead radius; if 1.44 Å. is used, his bond distance is considerably greater than the sum of the radii.)

Organolead compounds of the type R_3PbPbR_3 are also presumably covalent compounds, derived from this same four-covalent state of the lead atom. Electron diffraction measurements (319) of liquid hexamethyldilead, $(CH_3)_3PbPb(CH_3)_3$, agree with the expected configuration with the following parameters: Pb—Pb, 2.88 Å.; Pb—C, 2.25 Å.; ∠C—Pb—Pb, 109.5°. This calculation gives the present best value, 1.44 Å., for the covalent radius of lead.

The tetrahedral configuration is thus well supported by physical evidence. The best chemical evidence on this point would consist of the preparation and resolution of a compound which would exhibit optical activity due to an asymmetric configuration around the lead atom. Such a resolution has not been accomplished. Compounds having four different groups attached to the same lead atom have been prepared (12, 154, 158) but not resolved. As far as is known, the difficulties in this problem are experimental and not basic—that is, no investigator has ever suggested that there is any theoretical reason to believe that a lead atom in such a situation will not cause optical activity. Experimentally the preparation of a compound with four different groups attached to lead requires the exercise of considerable ingenuity and skill, and when such a compound is prepared it is very likely to be a liquid, not resolvable by the usual method of crystallization of diastereoisomers. Thus Austin's compound (12)



$$\begin{array}{l} \quad\;\; CH_2CH_2CH_3 \\ \quad\;\; | \\ C_6H_5PbC_6H_4OCH(CH_3)(CH_2)_5CH_3 \\ \quad\;\; | \\ \quad\;\; C_6H_4CH_3 \end{array}$$

would not crystallize. It seems likely that the resolution of a compound with optical activity due to an asymmetric lead atom will eventually be accomplished.

The types of compounds mentioned above involve a lead–carbon or a lead–lead bond. Organolead compounds in which lead forms a covalent bond to other elements than these have not been described. Such bonds would be expected only to elements (such as silicon or tin) which would not differ too greatly in electronegativity from lead. The bonds of lead to the highly electronegative elements—as, for instance, to chlorine in $(C_2H_5)_3PbCl$—are apparently ionic in those cases which have been studied. A material such as $(C_6H_5)_3PbLi$ also behaves as an ionic substance. Organolead ions are discussed in Section V.

B. SYMMETRICAL ORGANOLEAD COMPOUNDS

1. *General*

Symmetrical organolead compounds are substances of the type R_4Pb (table 1) in which the R groups are all the same. R may be alkyl or aryl. The tetraalkylleads are colorless, and are liquid up to tetratetradecyllead, m.p. 31°C. The tetra-*n*-alkyllead compounds are thermally stable up to about 100°C., and may usually be distilled at reduced pressure without decomposition. (Tetramethyllead, however, is a decidedly unstable substance (37) and may decompose explosively during attempts at distillation.) Tetra-*sec*-alkylleads are somewhat less stable than the straight-chain compounds. Tetracyclohexyllead decomposes at 160°C. without melting.

TABLE 1

R_4Pb *compounds*

COMPOUND	MELTING POINT	BOILING POINT	$n_D^{20°}$	REFERENCES
	°C.	°C.		
Tetraamyllead		170/1 mm.	1.4966	(182)
Tetra-*dl*-amyllead		150/0.5 mm.	1.4957	(182)
Tetrabenzyllead				(161, 222, 233)
Tetra(*p*-bromophenyl)lead	187			(122)
Tetrabutyllead		140/1 mm.	1.5119	(69, 182, 183, 250, 300, 311)
Tetracyclohexyllead	Decomposes at 160 without melting			(147, 161, 211)
Tetra(*p*-dimethylaminophenyl)lead	197–198			(11, 129)
Tetra(*o*-ethoxyphenyl)lead	219–220			(98)
Tetra(*p*-ethoxyphenyl)lead	110			(98)
Tetraethyllead		78/10 mm.	1.5195	(10, 16, 20, 21, 23, 24, 26, 28, 30, 38, 42, 43, 44, 47, 48, 54, 56, 57, 58, 59, 74, 75, 83, 91, 94, 96, 101, 108, 123, 136, 137, 141, 151, 158, 166, 167, 169, 174, 175, 176, 178, 179, 181, 182, 183, 186, 202, 238, 240, 249, 250, 251, 254, 255, 256, 257, 262, 274, 275, 278, 282, 283, 286, 293, 300, 302, 305, 306, 308, 311, 328, 334)
Tetra-2-furyllead		52/53 mm.		(132)
Tetraheptyllead				(183, 337)
Tetrahexadecyllead	42			(253)
Tetraisoamyllead	Decomposes on heating		1.4947	(155, 158)
Tetraisobutyllead	−23; decomposes on heating		1.5043	(155, 158, 162, 278, 311)
Tetraisopropyllead		120/14 mm.	1.5223	(79, 144, 156, 158, 311)
Tetra(*o*-methoxyphenyl)lead	148–149			(98)
Tetra(*p*-methoxyphenyl)lead	145–146			(98, 133)
Tetramethyllead	−27.5	110; 6/10 mm.	1.5128	(15, 24, 34, 38, 43, 44, 47, 54, 56, 57, 58, 59, 76, 85, 88, 108, 136, 151, 158, 162, 169, 178, 181, 182, 183, 201, 213, 229, 252, 267, 274, 276, 277, 281, 285, 305, 311, 317, 318)

TABLE 1—*Concluded*

COMPOUND	MELTING POINT	BOILING POINT	$n_D^{20°}$	REFERENCES
	°C.	°C.		
Tetraphenethyllead				(222)
Tetraphenyllead	223–225			(5, 10, 11, 17, 38, 44, 66, 70, 71, 81, 86, 96, 98, 101, 106, 114, 115, 117, 129, 136, 140, 143, 148, 161, 178, 181, 198, 203, 204, 205, 206, 208, 209, 212, 217, 221, 223, 229, 235, 244, 248, 258, 266, 268, 269, 270, 271, 280, 283, 287, 291, 303, 310, 326, 327, 330, 337, 338, 339, 340)
Tetra-*p*-phenyltrimethylammoniumlead tetraiodide	187–189			(127)
Tetrapropyllead		126/13 mm.	1.5094	(44, 47, 151, 158, 165, 183, 278, 300, 309)
Tetratetradecyllead	31			(253)
Tetra-2-thienyllead	152			(132, 218, 220)
Tetra-*o*-tolyllead	201–202			(8, 9, 98)
Tetra-*m*-tolyllead	122–123			(98)
Tetra-*p*-tolyllead	240			(9, 38, 44, 98, 114, 217, 287, 289, 327, 337)
Tetra-2,5-xylyllead	255			(224)

Tetraarylleads are white or colorless crystalline solids, usually with melting points well above 100°C. (tetraphenyllead melts at 223°C.). They are thermally stable up to the melting point. Above this temperature decomposition may occur.

R_4Pb compounds containing radioactive lead have been prepared (6, 7, 44).

Tetraalkylleads are soluble in the common organic solvents, such as ether, benzene, chloroform, or absolute ethanol. The symmetrical tetraarylleads are soluble in such solvents as acetone, chloroform (from which tetraphenyllead is crystallized), or aromatic hydrocarbons, but they are almost insoluble in alcohols or ethers. The R_4Pb compounds are in general quite insoluble in water.

These compounds are regarded, as already indicated, as possessing typical covalent bonds. They are relatively stable and are unreactive in such organometallic reactions as addition to a carbonyl group. They are not highly sensitive toward aqueous strong bases. Reaction takes place at moderate rates with aqueous strong acids (312), and the carbon–lead bond is quite sensitive toward anhydrous acids, for instance, hydrogen chloride in organic solvents. This bond is also cleaved readily and completely by the action of halogens.

Compounds of this type have been prepared in numerous ways, but only two procedures are of any great utility. These are preparations involving the action of a moderately reactive organometallic compound (such as a Grignard reagent or organolithium compound) on lead dichloride, and preparations employing lead–sodium alloy and an alkyl halide.

2. Preparation

(a) Lead dichloride and reactive organometallic compounds

One common method of preparation of organometallic compounds of heavy metals involves the treatment of the heavy metal halide with a Grignard reagent or organolithium compound. Application of this procedure in its simple form to the preparation of R_4Pb compounds would require the use of lead tetrachloride, and tetraalkylleads have been made in this way (151). Because of the unstable nature of lead tetrachloride, this is not a practical procedure. Fortunately, such organolead compounds are available from the reaction of Grignard reagents with lead dichloride (283), according to the equation:

$$4RMgX + 2PbCl_2 \xrightarrow{\text{heat}} R_4Pb + Pb + 2MgX_2 + 2MgCl_2$$

This is a common laboratory method of preparation of R_4Pb compounds in those cases in which the R_6Pb_2 compound (which is an intermediate) can be decomposed by heating.

The nature of this reaction was studied extensively by Krause and coworkers. They concluded (215) that the steps involved were

$$2RMgX + PbCl_2 \rightarrow R_2Pb + MgX_2 + MgCl_2$$

$$3R_2Pb \rightarrow R_6Pb_2 + Pb$$

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

where, in accordance with later evidence (see below), R_6Pb_2 is written rather than R_3Pb as given by Krause. It is readily possible to isolate R_6Pb_2 compounds from these reaction mixtures; when heated alone, such compounds do undergo further thermal decomposition in accordance with the equation above. Of the R_2Pb compounds presumably produced in the first reaction little is known, although one or two have been isolated from such reaction mixtures. Their nature is discussed later. Although the above formulation may be correct in its main features, other complicating reactions may also occur (98, 109).

In practice, the technique involves the addition of the Grignard solution to lead dichloride suspended in diethyl ether, followed by refluxing for several hours to decompose the R_6Pb_2 compound. In order to allow a higher temperature to be reached, toluene or xylene may be added to the mixture. For tetraarylleads, the mixture is then treated with water and the insoluble residue, containing metallic lead and any remaining R_6Pb_2, as well as the product, is filtered out and extracted with appropriate solvents. A specific example is the preparation of tetraphenyllead from lead chloride in 83 per cent yield (310). For tetraalkylleads, the mixture is hydrolyzed after the heating and the organic liquid is isolated and distilled. The crude product obtained in this way usually contains R_6Pb_2.

Repeated redistillation, during which metallic lead continues to be deposited, must be employed in order to decompose this intermediate. Specifically, the preparation of tetramethyllead (215) may be cited. Organolithium compounds can be employed, in exactly the same way as Grignard reagents, for the preparation of R_4Pb compounds (11). Use of the RLi compounds in this fashion is of advantage mainly in those cases in which the Grignard reagent is unavailable (for example, in the preparation of tetra-*p*-dimethylaminophenyllead).

If the intermediate R_6Pb_2 compound is not sufficiently decomposed by heating, this procedure cannot be applied. In such cases the crude product may be treated with bromine and then again with the Grignard reagent.

$$R_3PbPbR_3 + Br_2 \rightarrow 2R_3PbBr$$

$$R_3PbBr + RMgX \rightarrow R_4Pb + MgXBr$$

Other processes for the conversion of hexaalkyldilead to tetraalkyllead include treatment of the hexaalkyldilead with ethyl iodide (225) or percolation of the material through a column of silica-type catalyst (243).

It has been shown (108, 129) that organolithium compounds can be used advantageously in another way for the preparation of R_4Pb compounds from lead dichloride. The overall reaction involved is

$$3RLi + PbCl_2 + RI \rightarrow R_4Pb + 2LiCl + LiI$$

The reaction is carried out by adding the organolithium solution to a mixture of the other reagents in ether, without cooling (that is, essentially at the refluxing temperature of the solution). In this way, tetramethyllead can be prepared conveniently in 92 per cent yield (108), and tetraphenyllead in 80 per cent yield (129). This is the present method of choice for these preparations. It requires a shorter time, produces a product free from metallic lead, and makes convenient the preparation of larger amounts of product (since half the lead is not lost by conversion to metallic lead). It is probable that the following reactions

$$4RLi + 2PbX_2 \rightarrow R_4Pb + Pb + 4LiX$$

$$2RI + Pb \rightarrow R_2PbI_2$$

$$2RLi + R_2PbI_2 \rightarrow R_4Pb + 2LiI$$

are involved. Grignard reagents, used in this way, give fairly good results for alkyl compounds (48, 108), but not for phenyl compounds (129).

(b) Lead–sodium alloy and organic halides

This was the reaction used in the first preparation of an organolead compound (238), and it was employed in a number of early studies (34, 91). Its main importance is due to the fact that it is used commercially for the preparation of tetraethyllead from ethyl chloride (74). Some other tetraalkylleads can be made in this way. Tetraphenyllead has been thus obtained (287) from lead–sodium alloy and bromobenzene in the presence of ethyl acetate. It has been suggested (35) that the reaction involves reduction, and that ethyl acetate, water, etc.

promote the reaction by acting as sources of hydrogen. The patent literature lists aldehydes, ketones, carboxylate esters, amides, acetals, and acid anhydrides (63, 64, 174, 286) among other materials for reducing reaction time and increasing yields.

Little new information concerning this type of reaction has appeared in published sources since the review by Calingaert (35). The use of magnesium–lead alloys or calcium–lead alloys in the preparation of organolead compounds by such procedures has recently been patented (47, 226, 311). Grignard reagents may also be employed (48). Such processes appear to be closely related to the synthesis of R_4Pb compounds from lead chloride, an alkyl halide, and an organolithium compound (108, 129) (see Section III,B,2,(a) above). On the basis of availability of materials and convenience in handling, the alloy processes cannot compete for occasional laboratory preparations with the Grignard reaction. Saunders (300) has given specific directions for a *laboratory* preparation of tetraethyllead by this process.

(c) Other methods

Numerous other methods of preparation of R_4Pb compounds from lead alloys or metallic lead have been suggested from time to time. Alkyl iodides react with metallic lead (33, 281). Calingaert (35) reports that reactions such as

$$Pb + 4C_2H_5I + 2Zn + 8NaOH \rightarrow (C_2H_5)_4Pb + 4NaI + 2Na_2ZnO_2 + 4HOH$$

give good yields. Many catalysts for the preparation of tetraalkylleads by such processes have been suggested (35, 281). Several patents claim that when a hydrocarbon mixture such as gasoline vapor is subjected to pyrolysis and the gaseous mixture containing free radicals is brought into contact with lead and quickly cooled, a solution of organolead compounds results (295, 324). Electrolysis of alkyl halides in alkaline media has also been claimed (36) as a method for the preparation of tetraethyllead.

The Nesmeyanov diazo method for the preparation of organometallic compounds has been applied (271) for tetraphenyllead. Phenyldiazonium fluoroborate, $C_6H_5N_2BF_4$, and lead in acetone at 6°C. gave a 15 per cent yield. In ethanol, gas was evolved only when the temperature had risen to 35°C., and no tetraphenyllead resulted.

Lead amalgam or metallic lead will react (327) with phenyllithium to give low yields of tetraphenyllead. Somewhat better yields result if the aryl halide is also present. Thus lithium, bromobenzene, and lead powder, refluxed for 25 hr. in ether, gave a 23 per cent yield of tetraphenyllead (327). The procedure described above (108, 129) for the preparation of R_4Pb compounds from RLi, RI, and $PbCl_2$ is a logical extension of methods such as this. In recent patents (49, 50, 51, 313) it is claimed that alkyllead compounds can be prepared, by similar processes, from metallic lead and alkylating agents in the presence of various more active organometallic compounds.

Other methods which employ lead halides as starting materials include the reaction of lead dichloride with diethylzinc (26, 83) to give tetraethyllead, or the preparation of R_4Pb compounds by dropping a mixture of organic halide and lead dichloride in toluene upon sodium in toluene (161).

Organolead halides, R_3PbX or R_2PbX_2, will react with RMgX or RLi to give R_4Pb. Such a preparation is readily carried out in good yields, and its practical utility will depend on whether the R_4Pb compound or the organolead halide is more readily obtainable. Triphenyllead chloride, $(C_6H_5)_3PbCl$, and diphenyllead dichloride, $(C_6H_5)_2PbCl_2$, have been converted to tetraphenyllead by the action of hydrazine sulfate (100, 266). Electrolysis of acetone in dilute sulfuric acid, using a lead cathode, may have given a little tetraisopropyllead (292, 325). The production of tetrabenzyllead by the pyrolysis of benzylplumbonic acid, $C_6H_5CH_2Pb(OH)_3$, is also claimed (230).

3. Physical properties

The general results of diffraction studies on these compounds (22, 86, 89, 92, 339, 340) have already been described. There is some conflict among some of the reports (89, 92, 339) concerned with x-ray diffraction studies on tetraphenyllead and similar compounds, in connection with such points as the angle of "tilt" of the aromatic rings around the carbon–lead bond. There is, however, essential agreement on bond lengths and configurations.

The absorption spectra of the tetraphenyl derivatives of silicon, tin, and lead from 2100 to 3000 Å. (in chloroform and in ethanol) are given by Milazzo (258). Riccoboni (293) discusses critically the ultraviolet absorption spectra of tetraethyllead, tetraethyltin, triethyllead chloride, triethyltin chloride, and diethyltin dichloride in hexane and in methanol. Continuous absorption was found for the lead compounds and is attributed to dissociation. It is concluded that the energy at the boundary of the continuous portion of the spectrum, diminished by the energy of activation of the radicals which are formed, is related to the energy necessary to split the first lead–carbon or tin–carbon bond. The absorption curves show a smooth rise to continuous absorption in the near ultraviolet. The curves given by Milazzo (258) are of the same type, but with some slight inflections. He compares these with the curves for his silicon and tin compounds, which show quite definite absorption bands on the rising part of the curve, and states that the bands are also suggested in the case of the lead derivative. He concludes however, like Riccoboni, that the nature of the curves for the lead derivatives indicates dissociation.

The infrared and Raman spectra of tetraethyllead and tetramethyllead have been studied by a number of investigators (72, 184, 275, 314, 317). The infrared absorption spectrum of tetramethyllead is described by Sheline and Pitzer (314), and force constants are calculated for metal–carbon bonds. From this work are obtained the electronegativity values cited above for Group IVB elements.

Tetraphenyllead is included in a discussion (280) of diamagnetic anomalies and the relation of molecular diamagnetism to structure. The magnetic susceptibilities and parachors of tetramethyllead, tetraethyllead, tetrapropyllead, tetrabutyllead, and tetraheptyllead are given by Kadomtzeff (183). The ionization potential of tetraethyllead has been reported as 12.3 v. and that of tetramethyllead (provisional) as 11.5 v. (84). The molecular volumes at 0°K. have been calculated for tetramethyllead, tetraethyllead, tetra-*n*-propyllead, *n*-propyltriethyllead, diethyldi-*n*-propyllead, ethyltri-*n*-propyllead, methyltriethyllead, and *n*-butyltriethyllead (172).

A simplified method of estimating rotational potential barriers—that is, barriers to free rotation about a single bond—is described by French and Rasmussen (85). The method having been indicated, some calculations are made for cases where data are known, and for others where they are not. These authors calculate the barrier for the tetramethyllead and tetramethyltin as approximately 0 cal., and for tetramethylgermanium as about 400 cal. These results are to be compared with the measured values of 1100–1500 cal. for tetramethylsilane and 4800 cal. for neopentane.

Equations for the calculation of boiling points of tetraalkylleads have been given (25, 43, 182).

4. Chemical properties

(a) General

Organolead compounds are to be classified among the relatively unreactive organometallic types (93). They are stable in air at ordinary temperatures. They do not exhibit such characteristic organometallic reactions as addition to a carbonyl group. The symmetrical compounds, at least, are quite resistant to the action of aqueous bases and are even somewhat resistant to aqueous acids—partly, perhaps, because the lead compound is quite insoluble in the aqueous medium.

Under more drastic conditions—at higher temperatures, or in solution in organic solvents—organolead compounds undergo a number of reactions, almost all of which involve the breaking of a carbon–lead bond. Two general types of cleavage are to be noted. In processes which presumably involve ionic mechanisms, strong acids such as hydrogen chloride in benzene, or strong bases such as organolithium compounds in ether, can readily displace an organic group from lead. Or organolead compounds may dissociate thermally, in which case a radical process is involved.

(b) Ionic cleavage reactions

The ionic cleavages with acidic reagents are usually carried out with halogens or hydrogen halides. Halogens react with R_4Pb compounds to give R_3PbX or R_2PbX_2, depending on the temperature and the concentrations of the reactants. The monohalides are presumably formed first, and are then converted to the dihalides under proper conditions (151). Cleavage with bromine at −70°C. yields R_3PbX compounds, and at −25°C., R_2PbX_2 compounds. It has been impossible to cleave three R groups and retain a stable residue. When more than two equivalents of halogen are used, the product is lead halide and the organic halide. (Methods of formation of $RPbX_3$ compounds are described in Section V,C.) Hydrogen halides also cleave R_4Pb compounds readily. The reactions may be carried out in ether, benzene, hexane, chloroform, or other similar solvents. Here, again, R_3PbX or R_2PbX_2 compounds may be obtained.

$$R_4Pb + X_2 \rightarrow R_3PbX + RX$$

$$R_4Pb + 2X_2 \rightarrow R_2PbX_2 + 2RX$$

$$R_4Pb + HX \rightarrow R_3PbX + RH$$

$$R_4Pb + 2HX \rightarrow R_2PbX_2 + 2RH$$

These R_3PbX or R_2PbX_2 compounds are useful intermediates for the preparation of unsymmetrical organolead compounds (Section III,C).

The ionic cleavage with basic reagents has been less studied. It has been shown (115) that cleavage of arylleads by alkyllithium solutions occurs with ease (see Section C below).

That aspect of all reactions involving cleavage of a carbon–lead bond which has received most study is the question of the relative ease of cleavage of different kinds of organic groups from a lead atom. Since most of this study has centered around reactions of unsymmetrical compounds, the results obtained are described below in connection with such compounds.

(c) Radical cleavage reactions

Pyrolysis of organolead compounds gives free organic radicals. This has been demonstrated for both tetraalkyl- and tetraarylleads. Paneth (276, 277, 278) pyrolyzed tetramethyllead at low pressures in a stream of an indifferent gas and was able to demonstrate that the pyrolysis products contained free methyl radicals. The technique employed, involving the reaction of the methyl radicals with metallic mirrors previously deposited on the cold parts of the tube, is now well known and has come to bear Paneth's name. This was the first demonstration of the existence of simple aliphatic free radicals. Tetraethyllead likewise gave identifiable ethyl radicals, but tetra-*n*-propyllead or tetraisobutyllead gave mixtures, indicating further decomposition of the initial *n*-propyl or isobutyl radicals. Pyrolysis of tetraalkylleads has also been studied by other workers (68, 88, 254, 318). Among the products obtained from pyrolysis of tetramethyllead, Simons, McNamee, and Hurd (318) identified acetylene, 2-methyl-2-propene, propylene, ethylene, hydrogen, methane, and ethane. Minert (254) reports ethylene, ethane, butane, hydrogen, butylenes, and small amounts of liquid products as resulting from the pyrolysis of tetraethyllead.

The simple phenyl radical was likewise first demonstrated in experiments involving an organolead compound. Dull and Simons (70) heated tetraphenyllead just below its melting point at 0.01 mm. pressure, in the presence of mercury vapor. Along with biphenyl, diphenylmercury was identified in the product. Since neither tetraphenyllead nor biphenyl reacts with mercury vapor, it was concluded that phenyl radicals were present. Further studies (71) on the pyrolysis of tetraphenyllead at various temperatures, in sealed Pyrex bulbs which were evacuated after introduction of the sample, indicated that there was an optimum temperature for maximum yield of biphenyl, and that above this temperature benzene and terphenyl began to be formed. The decomposition of tetraphenyllead to give biphenyl and lead had been known previously. Zechmeister and Csabay (338) were able to carry out bulb-to-bulb distillation of tetraphenyllead at 240°C. (15–20 mm. pressure) without decomposition occurring, but at 270°C. biphenyl in good yield appeared (plus metallic lead). Pyrolysis of tetraphenyllead was studied also by Koton (203, 204, 205).

Tetraalkyl- and tetraaryllead compounds have been reported (337) to give high yields of the R—R compound when heated under pressure in the presence of hydrogen and nickel. In the absence of nickel, simple hydrogenation took place and very little of the R—R compound was produced (90, 178). Copper did not alter the nature of the products (90).

Radicals can thus be produced thermally from organolead compounds. It would be expected that photolysis to radicals should also occur, and the nature of the ultraviolet absorption spectrum is indeed such as to indicate dissociation (see Section B,3 above). Homolytic cleavage of the carbon–lead bond may also be accomplished by chemical agents. Organolead compounds are cleaved readily by active metals in liquid ammonia (101).

$$R_4Pb \xrightarrow[NH_3]{2Na} R_3PbNa + RH + NaNH_2$$

The nature of this type of reaction is not at present clear, but it may well be a radical process. The cleavage of one or two R_4Pb compounds by sodium in ether has also been described (168, 302). Makarova and Nesmeyanov (244) obtained a quantitative yield of benzenediazonium nitrate by the action of N_2O_2 and NO upon tetraphenyllead.

Some studies reported (305, 306, 307, 308, 309) by Semerano and Riccoboni and coworkers on the behavior of free alkyl radicals at low temperature involve the use of tetraalkylleads in reactions of this sort. These authors believe that reactions of free alkyl radicals liberated at high temperatures are complicated by the high energy content of the radicals. Accordingly, studies of reactions of alkyl radicals in ground states must be conducted at lower temperatures. Decomposition of very unstable organometallic compounds, such as methylsilver, was the method chosen. The alkylsilver compounds were formed by reaction of the appropriate tetraalkyllead with silver nitrate in ethanol or methanol at low temperatures. They were allowed to decompose by warming, and the products were identified. English workers (15) have since reported an investigation covering practically the same material. In general, these researches showed that methyl radicals thus produced dimerized to give ethane, without disproportionation products. Higher alkyl radicals gave disproportionation. The *n*-propyl radical gave propane and propylene as well as hexane. The use of tetramethyllead with copper salts gave a different result (15); the methylcopper presumably produced yielded methane on decomposition. This is attributed to reaction with the solvent (ethanol or methanol), although this theory leaves certain data unexplained. Corresponding reactions in the aromatic series have also been investigated (136). In the cleavage of tetraphenyllead or tetraphenyltin with silver nitrate or copper nitrate in ethanol the amount of the various products obtained (such as benzene and biphenyl) varied with both the organic compound and the inorganic salt. With silver nitrate, tetraphenyllead gave biphenyl and triphenyllead nitrate, while tetramethyllead gave methane, ethylene, ethane, and trimethyllead nitrate. With copper nitrate, tetraphenyllead yielded *m*-dinitrobenzene in addition to the products already mentioned, and tetramethyllead gave methane, ethane, and trimethyllead nitrate. Tetraphenylsilane or tetraphenylgermanium were not cleaved by silver nitrate. Tetraphenyllead and mercuric chloride give phenylmercuric chloride and triphenyllead chloride or diphenyllead dichloride (270).

(d) Reactions not involving lead–carbon cleavage

Almost no reactions not involving lead–carbon cleavage have ever been carried out with symmetrical organolead compounds. The problem of altering the nature of a functional group in an organolead molecule without at the same time causing cleavage of the lead–carbon bond is a difficult one. Acid–base reactions may sometimes be accomplished, but cleavage is apt to accompany such changes. Tetra-*p*-dimethylaminophenyllead dissolves in aqueous hydrochloric acid and may be reprecipitated unchanged after a short time (11), but longer standing causes cleavage. Tetra-*p*-dimethylaminophenyllead may also be methylated with dimethyl sulfate, to convert the tertiary amino groups to quaternary ammonium ions (127).

There is no practical yield of nitration product in the reaction of tetraphenyllead with sulfuric–nitric acid solution (329). Attempted metalation of tetraphenyllead with organolithium compounds, and subsequent carbonation, did not introduce a carboxyl group (114, 115).

C. UNSYMMETRICAL ORGANOLEAD COMPOUNDS

1. General

In the unsymmetrical organolead compounds there are four organic groups attached to lead, but not all these groups are the same. Compounds having two, three, or four different R groups attached to the same lead atom can be prepared (see tables 2, 3, 4, and 5). In such compounds the R groups may be all alkyl, all aryl, or mixed aryl and alkyl. These compounds are usually lower melting, more soluble in organic solvents, less stable thermally, and somewhat more reactive chemically than related symmetrical compounds. The unsymmetrical tetraarylleads are solids at ordinary temperatures, while the triarylalkyl- and the diaryldialkylleads may be liquid or solid. The aryltrialkylleads are usually liquid, as are the unsymmetrical tetraalkylleads.

TABLE 2

$R_3R'Pb$ *compounds*

COMPOUND	MELTING POINT	BOILING POINT	$n_D^{20°}$	REFERENCES
	°C.	°C.		
Allyltriethyllead	Decomposes at 115 without melting	86/10 mm.	1.5423	(101, 122, 126, 158)
Allyltriphenyllead	76–77			(9, 135)
(*o*-Aminophenyl)triphenyllead	164–165			(125)
(*p*-Aminophenyl)triphenyllead	166–167			(124, 125)
Amyltriethyllead		121/15 mm.	1.5097	(153, 158)
sec-Amyltriethyllead		118/13 mm.	1.5158	(156, 158)
Amyltriphenyllead	16–17			(12)
(Benz[*a*]anthracen-7-yl)triphenyllead	204–205			(73, 110)
Benzohydryltriphenyllead	122; decomposes at 130 without melting			(98)
Benzyltricyclohexyllead	228			(98)
Benzyltris(*p*-ethoxyphenyl)lead	76–77			(98)
Benzyltriethyllead		149–150.5/13 mm.	1.5843 (at 21.4°)	(101, 110, 149)
Benzyltris(*o*-methoxyphenyl)lead	80–81			(98)
Benzyltrimethyllead		124/13 mm. with decomposition		(149)
Benzyltriphenyllead	93			(98, 101, 110, 129, 135, 222)
Benzyltri-*p*-tolyllead	81–82			(98, 129)
ε-Bromoamyltriethyllead		166.8/13 mm.	1.5374	(153, 158)
p-Bromobenzyltriphenyllead	66–68			(127)
[5-(*p*-Bromophenylazo)-2-dimethylaminophenyl]triphenyllead				(125)
[5-(*p*-Bromophenylazo)-2-hydroxyphenyl]triphenyllead				(125)
(*p*-Bromophenyl)triethyllead		143/0.002 mm. (bath temperature)	1.5968	(112, 122)
(*p*-Bromophenyl)triphenyllead	115			(106, 115, 122)
3-Butenyltriethyllead		78/3 mm.	1.5230	(135)

TABLE 2—*Continued*

COMPOUND	MELTING POINT	BOILING POINT	$n_D^{20°}$	REFERENCES
	°C.	°C.		
3-Butenyltriphenyllead	84–86			(135)
Butyltriethyllead		108/13 mm.	1.5123	(101, 131, 154, 158)
sec-Butyltriethyllead		103/13 mm.	1.5186	(101, 131, 156, 158)
tert-Butyltriethyllead		76/5 mm.		(131)
Butyltriisobutyllead		145–146/10 mm.		(69)
Butyltrimethyllead		64.5/14 mm.	1.5046	(150, 158)
sec-Butyltrimethyllead		59/13 mm.	1.5133	(53, 154)
tert-Butyltrimethyllead	5.7	47/13 mm.	1.5089	(38, 44, 110)
Butyltriphenyllead	47			(130)
sec-Butyltriphenyllead	84			(130)
tert-Butyltriphenyllead	150–150.5			(130)
(Carbethoxymethyl)triphenyllead	59–60			(195, 196)
(α-Carbethoxyphenethyl)triphenyllead	82–84			(195, 196)
(*p*-Carbomethoxyphenyl)triphenyllead	125–127			(106, 112)
(Carboxymethyl)triethyllead	137 with decomposition			(126)
(Carboxymethyl)triphenyllead	194			(126)
[5-(*p*-Carboxyphenylazo)-2-dimethylaminophenyl]triphenyllead				(125)
[5-(*p*-Carboxyphenylazo)-2-hydroxyphenyl]triphenyllead				(125)
(*p*-Carboxyphenyl)triphenyllead	256–258			(106, 112)
(1-Chloroethyl)triethyllead	Decomposes at −20 without melting			(335)
(Chloromethyl)triethyllead		66/3 mm.	1.5443	(335)
[5-(*p*-Chlorophenylazo)-2-dimethylaminophenyl]triphenyllead				(125)
[5-(*p*-Chlorophenylazo)-2-hydroxyphenyl]triphenyllead				(125)
p-Chlorophenyltriphenyllead				(115)
Cyclohexyltriphenyllead	119			(66, 212, 221, 223)
2-Dibenzofuryltriphenyllead	158.5–159.5			(102)
3-Dibenzofuryltriphenyllead	125–126			(102)
4-Dibenzofuryltriphenyllead	99–100			(102)

TABLE 2—*Continued*

COMPOUND	MELTING POINT	BOILING POINT	$n_D^{20°}$	REFERENCES
	°C.	°C.		
(2-Diethylaminoethyl)triethyllead		85–90/0.001 mm. (bath temperature)	1.5235	(112)
(3-Diethylaminopropyl)triethyllead			1.5229	(112)
(3-Diethylaminopropyl)triphenyllead				(127)
(3-Diethylaminopropyl)triphenyllead, methyl iodide derivative	153–155			(127)
(3-Diethylaminopropyl)triphenyllead, methyl sulfate derivative	137–138			(127)
(2,3-Dihydroxypropyl)triphenyllead	124–125			(9) (9)
[2-Dimethylamino-5-(*p*-iodophenylazo)phenyl]triphenyllead				(125)
[2-Dimethylamino-5-(*p*-nitrophenylazo)phenyl]triphenyllead				(125)
(*p*-Dimethylaminophenyl)triethyllead		130/1 mm.	1.5442 (at 25°)	(125)
(*o*-Dimethylaminophenyl)triphenyllead	101–102			(125)
(*p*-Dimethylaminophenyl)triphenyllead	124–125			(11, 101)
(*p*-Ethoxyphenyl)triphenyllead	119–120			(223)
Ethyltriisoamyllead			1.4981	(155, 158)
Ethyltriisobutyllead			1.5064	(155, 158)
Ethyltrimethyllead		27–28/11 mm.	1.5154	(38, 43, 44, 56, 57, 58, 59, 150, 154, 158)
Ethyltriphenyllead	49–50			(81, 97, 101, 106, 129, 221, 223)
Ethyltripropyllead		118.2/14 mm.	1.5120	(44, 155, 158)
2-Furyltriphenyllead	166–167			(132)
2-Furyltris(*p*-methoxyphenyl)lead	83			(133)
[2-Hydroxy-3,5-bis(*p*-nitrophenylazo)phenyl]triphenyllead				(125)
(*p*-1-Hydroxyethylphenyl)triphenyllead	68–70			(112)

TABLE 2—*Continued*

COMPOUND	MELTING POINT	BOILING POINT	$n_D^{20°}$	REFERENCES
	°C.	°C.		
(*p*-2-Hydroxyethylphenyl)triphenyllead	87–88			(112)
[2-Hydroxy-5-(*p*-iodophenylazo)phenyl]triphenyllead				(125)
(*o*-Hydroxymethylphenyl)triphenyllead	134–136			(111, 112)
(*m*-Hydroxymethylphenyl)triphenyllead	113–114			(112)
(*p*-Hydroxymethylphenyl)triphenyllead	98–100			(111, 112)
[*o*-(2-Hydroxy-1-naphthylazo)phenyl]triphenyllead				(125)
[*p*-(2-Hydroxy-1-naphthylazo)phenyl]triphenyllead	Decomposes at 135 without melting			(124)
o-Hydroxyphenyltriphenyllead	216–218			(110, 125)
Isoamyltriisobutyllead			1.5012	(155, 158)
Isoamyltrimethyllead		69–71/12 mm.	1.4926 (at 20.3°)	(150)
Isoamyltripropyllead			1.5051	(155, 158)
Isobutyltrimethyllead		58–59/15 mm.	1.5050	(150, 158)
Isobutyltriphenyllead	68–68.5			(130)
Isobutyltripropyllead			1.5079	(155, 158)
Isopropyltrimethyllead		75/60 mm.	1.5095	(38, 44, 156, 158)
[2-Methoxy-5-(*p*-nitrophenylazo)phenyl]triphenyllead				(125)
[4-Methoxy-3-(*p*-nitrophenylazo)phenyl]triphenyllead				(125)
(*o*-Methoxyphenyl)triphenyllead	128–129			(112)
(*p*-Methoxyphenyl)triphenyllead	150–151 with slight decomposition			(112, 133)
Methyltriphenyllead		77–78/3 mm.	1.5837	(44, 149, 219)
Methyltripropyllead		106/13 mm.	1.5101	(44, 155, 158)
(*p*-Methylaminophenyl)triphenyllead	97–98			(125)
1-Naphthyltriphenyllead	101			(223)
	131			(135)

TABLE 2—*Continued*

COMPOUND	MELTING POINT	BOILING POINT	$n_D^{20°}$	REFERENCES
	°C.	°C.		
9-Phenanthryltriphenyllead	169–171			(110)
Phenethyltriphenyllead	116–117			(222)
(*p*-Phenoxyphenyl)triphenyllead	127			(221)
Phenyltri-*o*-tolyllead	161–162			(8)
Triethyl-2-hydroxyethyllead		100/2 mm.		(126)
Triethylisoamyllead		114.5/13 mm.	1.5099	(150, 154, 158)
Triethylisobutyllead		102/10 mm.	1.5127	(131, 150, 154, 158)
Triethylisopropyllead		90/13 mm.	1.5181	(156, 158)
Triethylmethyllead		70–70.5/16	1.5183	(38, 43, 44, 56, 57, 58, 59, 141, 150, 158)
Triethyl-1-naphthyllead		176/13 mm. with decomposition		(149)
Triethyloctadecyllead	73–74			(116)
Triethyl(pentamethylenemagnesium bromide)lead	Not isolated			(153)
Triethylphenyllead		135/12 mm.	1.5762	(47, 101, 149, 195, 247)
Triethyl(*p*-phthalimidophenyl)lead		100/0.0001 mm.		(125)
Triethylpropyllead		99.5/16 mm.	1.5168	(44, 150, 154, 158)
Triethyl-*o*-tolyllead		153.5/13 mm.	1.5740 (at 21.5°)	(149)
Triethyl-*p*-tolyllead		154/13 mm.	1.5695	(149)
Triisoamylisobutyllead			1.4960	(155, 158)
Triisoamylmethyllead			1.4971	(155, 158)
Triisoamylpropyllead			1.4979	(155, 158)
Triisobutylmethyllead		121/12 mm. with slight decomposition	1.5030	(155, 158)
Triisobutylpropyllead			1.5054	(155, 158)
Triisopropylmethyllead				(44)
Tri(*o*-methoxyphenyl)triphenylmethyllead	145–146			(98)
Trimethyl(*p*-triethylsilylphenyl)lead		191/17 mm.	1.54937 (at 23.8°)	(157)
Trimethyl(trimethylpentamethylenetin)lead		162/17.5 mm.	1.52282 (at 23.2°)	(159)

TABLE 2—*Concluded*

COMPOUND	MELTING POINT	BOILING POINT	$n_D^{20°}$	REFERENCES
	°C.	°C.		
Trimethylpropyllead		48–49/16 mm.	1.5095	(44, 150, 154, 158)
Trimethyl-*o*-tolyllead		117.5–118/13 mm.	1.5793 (at 21.4°)	(149)
Trimethyl-*p*-tolyllead		118–119/13 mm.	1.5732	(149)
Triphenyl(triphenylmethyl)-lead	196–197			(98)
Triphenylpropyllead	69–70			(12, 129)
Triphenyl-2-pyridyllead	220 with decomposition			(104)
Triphenyl-β-styryllead	107–109			(135)
Triphenyl-2-thienyllead	206–207			(132, 219, 220)
Triphenyl-*p*-tolyllead	125.5			(9, 11, 101, 221, 224)
Triphenyl-2,4-xylyllead	111.5–112			(223)
Triphenyl-2,5-xylyllead	104.5			(221, 223)

2. Preparation

(a) Organolead halides and reactive organometallic compounds

The most common method of preparation of unsymmetrical organolead compounds is by the reaction of an organolead halide such as triethyllead chloride, $(C_2H_5)_3PbCl$, or diphenyllead dichloride, $(C_6H_5)_2PbCl_2$, with a Grignard reagent. The organolead halides (see below) are in turn commonly prepared by reaction of a symmetrical organolead compound with halogen or hydrogen halide. The steps of a typical synthesis are as follows:

$$PbCl_2 \xrightarrow{RMgX} R_4Pb \xrightarrow{HX} R_3PbX \xrightarrow{R'MgX} R_3R'Pb$$

or

$$R_4Pb \xrightarrow{2HX \text{ or } X_2} R_2PbX_2 \xrightarrow{2R'MgX} R_2R'_2Pb$$

These reactions presumably involve nucleophilic attack by a carbon atom in the Grignard reagent upon the positive lead atom in R_3PbX or R_2PbX_2. It is usually necessary to isolate both the R_4Pb compound and then the organolead halide, in separate steps. The process may be extended, with a proper choice of groups, to yield eventually $R_2R'R''Pb$ and $RR'R''R'''Pb$ compounds.

(b) Organolead-metal compounds and organic halides

The reaction of organolead-metal compounds with organic halides is in a sense the reverse of the reaction described in part (a), since in this case the

TABLE 3

$R_2R'_2Pb$ *compounds*

COMPOUND	MELTING POINT	BOILING POINT	$n_D^{20°}$	REFERENCES
	°C.	°C.		
Bis(benz[*a*]anthracen-7-yl)-diphenyllead	295–296 with decomposition			(73, 110)
Bis(chloromethyl)diethyllead		96/2 mm.		(335)
Bis(*p*-dimethylaminophenyl)-diphenyllead	134–135			(11)
Diamyldi-*dl*-amyllead		160/1 mm.	1.4923	(182)
Diamyldibutyllead		170/1 mm.	1.4984	(182)
Di-*dl*-amyldibutyllead		135/0.5 mm.	1.4993	(182)
Diamyldiethyllead		116–118/0.5 mm.	1.5038	(182)
Diamyldihexylead		180/0.5 mm.		(182)
Diamyldiisoamyllead		160/0.5 mm.	1.4959	(182)
Diamyldiisobutyllead		140/0.5 mm.	1.4994	(182)
Diamyldimethyllead		113/4 mm.	1.5009	(182)
Diamyldipropyllead		150/1 mm.	1.5019	(182)
Dibenzyldiphenyllead	Decomposes at 200 without melting			(222)
Di(biphenylyl)diphenyllead	134–135			(134)
Di(*p*-bromophenyl)diphenyllead	123			(122)
Dibutyldiethyllead		90/1 mm.	1.5093	(182)
Di-*tert*-butyldiethyllead		80/10 mm.		(122)
Dibutyldiisoamyllead		135/0.5 mm.	1.4982	(182)
Dibutyldiisobutyllead		135/1 mm.	1.5021	(182)
Dibutyldimethyllead		108/10 mm.	1.5049	(182)
Di-*sec*-butyldimethyllead	By-product; no analytical or physical data			(53)
Dibutyldiphenyllead	Decomposes when heated *in vacuo*			(99)
Di-*sec*-butyldiphenyllead	Unstable			(99)
Di-*tert*-butyldiphenyllead	177			(99)
Dibutyldipropyllead		120/1 mm.	1.5062	(182)
Di(*p*-chlorophenyl)diphenyllead				(115)
Dicyclohexyldiphenyllead	178–180 with decomposition			(110, 147)
Diethyldiisoamyllead		142/13 mm.	1.5041	(152, 158)
Diethyldiisobutyllead		124/13 mm.	1.5086	(152, 158)
Diethyldiisopropyllead		95.5/14 mm.	1.5169	(152, 158)
Diethyldimethyllead		51/13 mm.	1.5177	(38, 43, 44, 47, 56, 57, 58, 59, 152, 158, 261)
Diethyldi-1-naphthyllead	116			(223)

TABLE 3—*Concluded*

COMPOUND	MELTING POINT	BOILING POINT	$n_D^{20°}$	REFERENCES
	°C.	°C.		
Diethyldioctadecyllead	58–60			(116)
Diethyldiphenyllead		176/8 mm.	1.5939 (at 18°)	(97, 122, 141, 261)
Diethyldipropyllead		99/10 mm.	1.5149	(38, 44, 152, 158, 163, 182, 242)
Di-2-furyldi(*p*-methoxyphenyl)-lead	72–73			(133)
Di-2-furyldiphenyllead	118			(132)
Di-2-furyldi-2-thienyllead	117–119			(132)
Diisoamyldimethyllead		122–123/13 mm.	1.5005	(152, 158)
Diisobutyldimethyllead		95.5–96/13 mm.	1.5024	(38, 44, 152, 158)
Diisobutyldiphenyllead	Unstable			(99)
Diisopropyldimethyllead				(44)
Dimethyldiphenyllead		151–152/2 mm.	1.6263	(44, 122)
Dimethyldipropyllead		72/10 mm.	1.5086	(44, 152, 158, 182)
Di-1-naphthyldiphenyllead	197			(135, 141, 223)
Di-9-phenanthryldiphenyllead	208–210			(110)
Diphenyldi-2-thienyllead	185			(132)
Diphenyldi-*o*-tolyllead	134–135			(228)
Diphenyldi-*p*-tolyllead	121–122			(11, 114)
Diphenyldi-2,5-xylyllead	94			(221)

lead is contained in a negative ion, and the reaction involved is presumably a nucleophilic attack by this ion on the carbon atom in the RX compound.

$$R_3PbM' + R'X \rightarrow R_3R'Pb + M'X$$

Here M′ is an active metal, such as sodium or lithium. The organolead-metal compounds, R_3PbM', may be obtained in two ways. Treatment of lead dichloride with phenyllithium in ether at −10°C. gives triphenylleadlithium (17, 129), which is not isolated but is used immediately for reaction with an RX compound. The overall process is

$$PbCl_2 \xrightarrow{3RLi} R_3PbLi \xrightarrow{R'X} R_3R'Pb$$

The method has the advantage that no intermediates need be isolated, and, if the halogen in R′X is moderately reactive, it is well adapted to the preparation of $R_3R'Pb$ compounds in which R′ contains no functional groups which will react with organolithium compounds. A specific example is the preparation of triphenyl-γ-diethylaminopropyllead in 91 per cent yield, calculated from lead chloride (127). Application of this technique to cases where R is alkyl has not

TABLE 4

$R_2R'R''Pb$ *compounds*

COMPOUND	BOILING POINT	$n_D^{20°}$	REFERENCES
	°C.		
Butyldiethylmethyllead	67/5 mm.	1.5125	(101)
sec-Butyldiethylmethyllead	87/10 mm.	1.5180	(101)
Cyclohexyldiphenylmethyllead			(221)
Diethyl-*sec*-amylpropyllead	121/12 mm.	1.5137	(156, 158)
Diethylbutylpropyllead	116/13 mm.	1.5094	(154, 158)
Diethyl-*sec*-butylpropyllead	115/13 mm.	1.5170	(156, 158)
Diethylisoamylisobutyllead	131/14 mm.	1.5050	(154, 158)
Diethylisoamylmethyllead	103/13 mm.	1.5082	(154, 158)
Diethylisoamylpropyllead	127.5/15 mm.	1.5075	(154, 158)
Diethylisobutylmethyllead	87/13 mm.	1.5117	(154, 158)
Diethylisobutylpropyllead	110/13 mm.	1.5115	(154, 158)
Diethylisopropylpropyllead	107/17 mm.	1.5162	(156, 158)
Diethylmethylphenyllead	132/15 mm.		(101)
Diethylmethylpropyllead	80.5/15 mm.	1.5150	(44, 101, 154, 158)
Diisoamylethylpropyllead	145.5/13 mm.	1.5034	(154, 158)
Dimethyl-*sec*-amylethyllead	90/15 mm.	1.5114	(156, 158)
Dimethyl-*sec*-butylethyllead	74/13 mm.	1.5128	(156, 158)
Dimethyl-*sec*-butylisoamyllead	111.5–112.5/ 14 mm.	1.5066	(156, 158)
Dimethylethylisoamyllead	92/14 mm.	1.5059	(154, 158)
Dimethylethylisobutyllead	74/13 mm.	1.5081	(154, 158)
Dimethylethylisopropyllead	61.2/15 mm.	1.5135	(156, 158)
Dimethylethylpropyllead	65/15 mm.	1.5118	(44, 154, 158)
Dimethylisoamylpropyllead	105/15 mm.	1.50201	(154, 158)
Dimethylphenylpropyllead	93/3 mm.		(101)
Dipropylethylmethyllead			(44)
Di-*o*-tolylphenylpropyllead	49–50 (m.p.)		(12)

TABLE 5

$RR'R''R'''Pb$ *compounds*

COMPOUND	BOILING POINT	$n_D^{20°}$	REFERENCES
	°C.		
Butylethylisoamylpropyllead	144/14 mm.	1.5035	(154, 158)
Butylethylmethylpropyllead	103/13 mm.	1.5083	(154, 158)
Ethylisoamylmethylpropyllead	115/15 mm.	1.5068	(154, 158)
(*p*-*sec*-Octyloxyphenyl)phenylpropyl-*o*-tolyllead	Oil		(12)

yet been studied. The organolead-metal compounds may also be prepared by treatment of R_4Pb, R_3PbPbR_3, or R_3PbX with active metals in liquid ammonia (101). The R_3PbM' intermediate (for instance, triethylleadsodium, $(C_2H_5)_3PbNa$) is again not isolated, but is treated with an $R'X$ compound. In this case, it is necessary first to prepare and isolate an organolead starting material, for instance, the R_4Pb compound.

$$PbCl_2 \xrightarrow{RMgX} R_4Pb \xrightarrow[(NH_3)]{Na} R_3PbNa \xrightarrow{R'X} R_3R'Pb$$

No such preparation has been described in which R′ was aryl. The direct synthesis of compounds such as $R_2R'_2Pb$ (through $R_2PbM'_2$ intermediates) has been studied (97), but has not as yet been developed into a useful synthetic method.

(c) Redistribution

The redistribution reaction (discussed below) offers the possibility of preparing large quantities of unsymmetrical organolead compounds, in favorable cases (39). The disadvantage of such a reaction as a preparative process lies in the fact that a mixture of all possible products is obtained. The separation of this mixture to give a reasonable yield of one product is not in general possible, at least on a laboratory scale. As an example, there may be cited the study by Calingaert, Beatty, and Soroos (44) involving tetraethyl-, tetramethyl-, and tetra-*n*-propyllead.

(d) Other methods

Formation of unsymmetrical organolead compounds by various other processes has been reported. These processes at present are not practical as preparative methods.

The series of reactions

$$(C_6H_5)_3PbCl + KOOCCH_2COOC_2H_5 \rightarrow (C_6H_5)_3PbOOCCH_2COOC_2H_5 \rightarrow CO_2 + (C_6H_5)_3PbCH_2COOC_2H_5$$

has been reported (196) as establishing a carbon–lead bond. Earlier attempts (175) gave no organolead product from the heating of lead tetrabenzoate or tetraacetate. Pyrolysis of the latter gave nearly quantitative yields of lead diacetate.

Mixtures of symmetrical and unsymmetrical organolead compounds were produced when hexamethyldilead and hexaethyldilead were heated together (58).

A patent (40) has described the preparation of unsymmetrical ethyl methyl compounds by the simultaneous reaction of ethyl chloride and methyl halides with sodium–lead alloy. This is a modification of the usual lead–sodium alloy method by the introduction of more than one kind of organic group into the mixture. Similarly, the reaction of Talalaeva and Kocheshkov (327) may be modified by the introduction of mixtures of organic groups; it has been found (128) that reaction of phenyllithium with lead powder in the presence of ethyl iodide gives diethyldiphenyllead (39 per cent) and no tetraphenyllead, whereas reactions involving lead powder and phenyllithium with methyl iodide or *p*-iodotoluene give considerable amounts of tetraaryllead. In all such processes as these, mixtures are obtained which in general are not separable, although in special cases separations have been worked out.

Diazomethane reacts with triethyllead chloride or diethyllead dichloride, in the presence of copper bronze, to give (chloromethyl)triethyllead or bis(chloromethyl)diethyllead (335). Diazoethane reacts similarly, but the products are less stable.

3. Physical properties

The general physical properties of unsymmetrical organolead compounds have already been indicated. Physical investigations with organolead compounds have usually employed symmetrical substances, and there are fewer data which pertain in particular to unsymmetrical compounds. Dipole moments of some such materials have been determined (247) and found to be small, as expected.

4. Chemical properties

(a) General

The chemical properties of unsymmetrical organolead compounds are basically the same as those of the symmetrical compounds. The unsymmetrical compounds are capable of being cleaved by the same ionic or radical reagents already discussed. When an unsymmetrical compound is cleaved, there arises a question as to which of the various carbon–lead bonds will be most readily attacked by a given reagent. A comparison of the relative amounts of the various possible products which result when an unsymmetrical organometallic compound is cleaved by hydrogen chloride has often been used as a criterion for the establishment of a series of relative electronegativities of various organic groups. The work of Kharasch (185, 187, 188, 189, 190) on organomercury compounds is particularly well known. Other investigations have involved organotin (19, 29) or organolead (9, 11, 12, 132, 135, 182) compounds, and sometimes different cleaving reagents (8, 141, 175, 182, 218, 219, 221, 222, 223, 224). Some of the results obtained with lead compounds are discussed here.

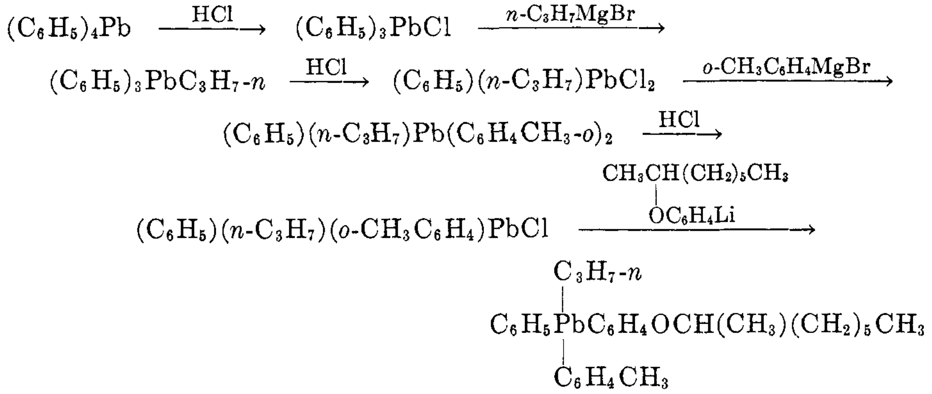
(b) Cleavage by halogen or hydrogen halide

From various studies, the following series of relative ease of cleavage have been established for organic groups in organolead compounds when treated with halogen or hydrogen halide (in each case, the most easily cleaved group is listed first):

α-naphthyl, p-xylyl, p-tolyl, phenyl, methyl, ethyl, n-propyl, isobutyl, isoamyl, cyclohexyl (221)
2-furyl, 2-thienyl, phenyl (132)
(allyl, β-styryl), phenyl, 3-butenyl (271)

Comparison of parts of these series with similar series obtained from the study of organomercury or organotin compounds indicates that there is little if any difference in the order of cleavage, providing the same cleavage reagent is used. In general (8), aromatic groups are cleaved before saturated aliphatic ones, and secondary or tertiary aliphatic groups before the corresponding primary groups. The cyclohexyl group seems much more firmly held than any other. Structures such as the 2-furyl or 2-thienyl groups are more labile than phenyl, as are also some unsaturated aliphatic structures (allyl, β-styryl).

This selectivity in cleavage is great enough so that, in properly chosen cases, it may be employed for the building up of very unsymmetrical compounds. Probably the best example of a synthetic process of this sort is the following preparation by Austin (12) (see above, Section III).



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

$$(C_6H_5)_3PbC_3H_7\text{-}n \xrightarrow{HCl} (C_6H_5)(n\text{-}C_3H_7)PbCl_2 \xrightarrow{o\text{-}CH_3C_6H_4MgBr}$$

$$(C_6H_5)(n\text{-}C_3H_7)Pb(C_6H_4CH_3\text{-}o)_2 \xrightarrow{HCl}$$

$$(C_6H_5)(n\text{-}C_3H_7)(o\text{-}CH_3C_6H_4)PbCl \xrightarrow{\substack{CH_3CH(CH_2)_5CH_3\\ |\\ OC_6H_4Li}}$$

$$C_6H_5\overset{\overset{\displaystyle C_3H_7\text{-}n}{|}}{\underset{\underset{\displaystyle C_6H_4CH_3}{|}}{Pb}}C_6H_4OCH(CH_3)(CH_2)_5CH_3$$

(c) Cleavage by other acidic reagents

Cleavage of the lead–carbon bond, in symmetrical or unsymmetrical organolead compounds, is caused by Lewis acids in general. A large number of metal halides have been used in such reactions (23, 96, 140, 143, 186, 248, 249, 250, 251). Organometallic halides also cause such cleavage, and in particular (see Section V,B) the organolead halides themselves will catalyze such processes.

When an unsymmetrical organolead compound (or a mixture of such compounds or of symmetrical compounds) is heated in the presence of a small amount of such a Lewis acid, there occurs an equilibration of groups on lead, so that the equilibrium mixture contains all the possible organolead compounds which could result from the R groups present. Here the bond types in the initial and final products are all the same (that is, all lead–carbon bonds); and if the R groups are similar, ΔH for such a change may be practically zero. The equilibrium composition would then be determined solely by the change in entropy, ΔS^0. It has been calculated (322) that the steric effects involved in the interchange could make up no more than a very small contribution to ΔS^0, so that the controlling factor in determining the equilibrium state for such reactions would be ΔS^0_σ, or randomness of distribution. The equilibrium mixture would be essentially that predicted by the laws of chance, assuming a completely random distribution of the R groups among the lead compounds.

Reactions of this type have been studied extensively by Calingaert and coworkers. The term "redistribution reaction" was applied by them to such a process, in which the interchange takes place at random as far as the experimental measurements can show. The usefulness of distinguishing by a special term what would appear to be particular cases in the large general group of such reactions has been questioned (322, 323), and the term "redistribution" is at present in common use by organic chemists to denote any reversible process of intermolecular interchange of similar groups to form products in which the bond types are the same as in the reactants, whether or not the equilibrium constant is exactly 1.0. The experimental work pertaining to this subject is nevertheless of great interest, and offers a good example of the usefulness of organometallic compounds in studies of the behavior of covalent bonds to carbon. The results have been reviewed previously (41) and will not be discussed here. The possibility of redistribution must be kept in mind in reactions involving unsymmetrical organolead compounds, since the necessary catalysts are very apt to be present in organolead reaction mixtures. The use of redistribution as a preparative method has already been mentioned (Section C,2 above).

(d) Cleavage by organolithium compounds

The cleavage series obtained by the use of alkyllithium solutions as cleavage reagents (115) differs somewhat from the acid cleavage series, although in general the aromatic groups are again much more readily cleaved. Some variation is also found when different metals, such as tin or mercury, are used.

(e) Cleavage by active metals in liquid ammonia

After it was established (101) that organolead compounds such as tetraphenyllead or tetraethyllead could be cleaved by sodium in ether–liquid ammonia, such cleavage reactions were carried out with a number of unsymmetrical lead compounds. The relative amounts of the possible organoleadsodium products were estimated by adding a reactive alkyl halide and then separating the different organolead products. The series of groups arranged in order of decreasing ease of cleavage with sodium is allyl, benzyl, *sec*-butyl, *n*-butyl, ethyl, methyl, phenyl, *p*-dimethylaminophenyl. This series is almost exactly the reverse of the series obtained with acidic reagents such as hydrogen chloride (see above). The position of the allyl group is noteworthy. In general, allyl might be expected to occupy a place near benzyl in such series, but in the cleavage studies with hydrogen halide (9, 135, 190) the allyl group shows an anomalous behavior. This has been explained (190) by assuming that a different mechanism is involved. In this series with sodium there is no suggestion of any anomaly, which perhaps indicates that the mechanism of reaction, whatever it may be, is quite uniform when sodium in liquid ammonia is the cleaving reagent.

(f) Reactions not involving lead–carbon cleavage

Few reactions not involving lead–carbon cleavage have been carried out successfully with unsymmetrical organolead compounds, because of the sensitivity of the lead–carbon bond.

By permanganate oxidation of allyltriphenyllead, Austin (9) obtained (2,3-dihydroxypropyl)triphenyllead in small yield, but the chief reaction was complete elimination of the allyl group. Permanganate oxidation of (*p*-hydroxymethylphenyl)triphenyllead gave (*p*-carboxyphenyl)triphenyllead (112). A similar reaction with the ortho isomer not only performed the expected oxidation but also cleaved one phenyl group, to give (*o*-carboxyphenyl)diphenyllead hydroxide. (*o*-Carboxyphenyl)diethyllead hydroxide (existing as the inner anhydride) was prepared in a similar manner (95).

Hydrolysis of (carbethoxymethyl)triphenyllead yielded (carboxymethyl)-triphenyllead (126). The action of organolithium compounds on (*p*-bromophenyl)triphenyllead, followed by carbonation, did not introduce the carboxyl group (114, 115), but with diethylbarium there resulted (*p*-carboxyphenyl)-triphenyllead in 1.5 per cent yield (106).

D. HEXAALKYL- AND HEXAARYLDILEAD COMPOUNDS, R_3PbPbR_3

1. General

In all known compounds of the type R_3PbPbR_3, the R groups are identical. The hexaaryldileads are crystalline solids; the hexaalkyldileads are liquids, difficult to preserve in a pure state (see table 6).

2. Preparation

Two methods for the preparation of such compounds are of practical importance. Of these, the preparation from lead chloride and the Grignard reagent has been most widely used (11, 26, 53, 138, 217, 224).

$$3PbCl_2 + 6RMgX \rightarrow R_3PbPbR_3 + Pb + 3MgX_2 + 3MgCl_2$$

The primary product of the reaction is presumably an R_2Pb compound, as already discussed. This reaction represents a step in the customary synthesis of R_4Pb compounds, and it is carried out in the same way except that the heating time is limited. The product may contain more or less R_4Pb, and the purity depends on the stability of the R_6Pb_2 compound. Hexacyclohexyldilead (211) or hexamesityldilead (98) are very stable toward further heating, and careful control of these reactions is not necessary. In such a case as hexaphenyldilead, the product will probably contain some R_4Pb compound, which is removed by fractional crystallization. With the liquid hexaalkyldileads, crystallization has not been possible. The employment of organolithium compounds in such a reaction is exemplified by the preparation of hexaphenyldilead in 79 per cent yield from lead chloride and phenyllithium (129).

A more recently developed method for the synthesis of such compounds involves presumably the reaction of an R_3PbX compound with an R_3PbM' compound. This method is best carried out in liquid ammonia, using as starting material for the R_3PbM' compound the R_3PbX compound itself (35, 98).

$$2R_3PbI + 2Na \rightarrow R_3PbPbR_3 + 2NaI$$

If triphenyllead chloride is used in place of the iodide in the preparation of hexaphenyldilead, the reaction does not proceed as smoothly. This is possibly due to the lower solubility of the chloride in liquid ammonia (81). If the alloy

TABLE 6

R_6Pb_2 *compounds*

COMPOUND	MELTING POINT	REFERENCES
	°C.	
Hexaamyldilead		(193)
Hexabutyldilead	Not isolated	(69)
Hexacyclohexyldilead	Decomposes at 196 without melting	(66, 98, 168, 169, 180, 211, 212, 246, 265)
Hexa-*o*-ethoxyphenyldilead	170–171 with decomposition	(98)
Hexa-*p*-ethoxyphenyldilead	178–179 with decomposition	(98)
Hexaethyldilead	Decomposes at about 100/2 mm.	(26, 53, 58, 98, 166, 193, 238, 257)
Hexaisopropyldilead		(144)
Hexamesityldilead	Melts above 325	(98)
Hexa-*o*-methoxyphenyldilead	201 with decomposition	(98)
Hexa-*p*-methoxyphenyldilead	138–140	(98, 133)
Hexamethyldilead	37–38; decomposes at 238	(53, 58, 166, 169, 319)
Hexa-1-naphthyldilead	Decomposes at 255 without melting	(98)
Hexaphenethyldilead		(222)
Hexaphenyldilead	Decomposes at 155 without melting	(66, 81, 96, 98, 101, 113, 129, 212, 217, 221, 234, 235, 246, 290)
Hexa-*m*-tolyldilead	109; decomposes at 116–117	(98, 260)
Hexa-*o*-tolyldilead	Decomposes at 240 without melting	(8, 9, 96, 98, 217)
Hexa-*p*-tolyldilead	Decomposes at 193 without melting	(9, 98, 114, 217)
Hexa-2,4-xylyldilead	233.5 with decomposition	(138)
Hexa-2,5-xylyldilead		(169, 217, 224, 303)
	167.5; decomposes at 195	(217)
	225 with decomposition	(224)
Related compounds		
Hexacyclohexyldilead·iron tetracarbonyl		(164)
Hexaphenyldilead·iron tetracarbonyl		(164, 171)

Na_4Pb_9 is used in place of sodium, the yield of R_6Pb_2 is much improved. For such a preparation, the use of triphenyllead chloride and triphenylleadlithium prepared in ether (129) has not been satisfactory (128), because of reaction of the triphenyllead chloride with the phenyllithium component of the equilibrium (see Section V,D). Also, attempts to prepare compounds of the type $R_2R'PbPbR'R_2$ by the reaction of $R_2R'PbX$ compounds with sodium in liquid ammonia have not been successful (110).

Other methods which have been reported as producing compounds of the present type include the electrolysis of R_3PbOH in alcoholic solution (257), or the electrolytic reduction of ketones in sulfuric acid (325), using lead electrodes. Chemical reduction of acetone in sulfuric acid with lead–sodium alloy led to hexaisopropyldilead (144). The initial product of the action of lead–sodium alloy on alkyl halides (see above) also contains such compounds.

3. Physical properties

Electron diffraction measurements (319) on hexamethyldilead have already been mentioned. The results indicate nothing unexpected in the structure of the compound. Hein, Nebe, and Reimann (169) give data on the absorption of hexacyclohexyldilead in the ultraviolet. The dipole moment of hexaphenyldilead is zero (234).

Most of the physical-chemical investigations of such compounds have centered around the problem of their dissociation in solution and will therefore be discussed below.

4. Chemical properties

(a) General

All the reported chemical reactions of substances of the type R_3PbPbR_3 involve cleavage of the lead–lead bond. The two most characteristic features of the chemistry of these compounds are (*a*) a dissociation which occurs in solution at ordinary temperatures, without deposition of lead, and (*b*) thermal dissociation at high temperatures, either in a high-boiling solvent or alone, to give lead metal and R_4Pb compounds. In addition, most of the reagents which cleave lead–carbon bonds will also cleave these compounds. The action of halogen or hydrogen halides upon R_6Pb_2 compounds in solution leads to mixtures of PbX_2, R_2PbX_2, and R_3PbX, in proportions varying with the conditions and the reactants (8, 98, 217). Hexaphenyldilead is cleaved readily by phenyllithium in ether, to give $(C_6H_5)_3PbLi$ (17).

(b) Dissociation in solution

Hexaphenyldilead is nearly white with a slight yellow color. In organic solvents it forms yellow solutions. In the dark the solid compound is stable, but the solutions react gradually with atmospheric oxygen. Cryoscopic molecular-weight determinations in concentrated solution give a value approaching that calculated for R_6Pb_2, but upon dilution the molecular weight decreases and approaches that required for R_3Pb (81, 217). Other hexaaryldileads (and hexacyclohexyldilead) behave similarly.

In view of these properties, and of the formal analogy of the R_6Pb_2 compounds with hexaarylethanes, it was supposed (215) that these substances were highly dissociated into radicals of the type $R_3Pb\cdot$ in dilute solution. Measurements of magnetic susceptibility made on various compounds of this type show, however, no paramagnetic effect at all (265, 290). The accuracy of the measurements is good enough so that radicals at least cannot be present to an extent anywhere near that assumed from the freezing-point data. Nevertheless, these latter data have been confirmed by several other workers (81, 180), and the dissociation is apparently real. The discussion has perhaps been somewhat obscured by the idea of radicals. Actually, all these data seem to indicate that there is decomposition, but not into stable radicals. This was suggested by Morris and Selwood (265), who thought that the low molecular weights might indicate decomposition. A pertinent experiment would be to determine whether or not the dissociation is reversible, but this has apparently not been done. The report of Malatesta (246) that in higher-melting solvents certain of these compounds do *not* show dissociation needs to be integrated with the other data.

Thus the supposition that free organolead radicals exist in these solutions is not supported by the physical evidence. Their chemical properties are nevertheless very reminiscent of those of solutions of the triarylmethyls. They react rapidly with halogen, undergo autoöxidation, and react with alcoholic silver nitrate to produce unstable colored precipitates. They may react also with the magnesious iodide system ($Mg + MgI_2$) to give RMgX compounds, presumably through R_3PbMgX intermediates (98). Addition of hexaphenyldilead to the carbon–carbon double bond, as in maleic anhydride, has been reported (110). The autoöxidation of hexacyclohexyldilead has been studied at length by Hein (169). It was found to be photochemical and to occur only under the influence of ultraviolet light, but not at all in the dark or in sodium vapor light. Reactions in the presence of compounds such as carbon tetrachloride were also studied.

(c) Thermal dissociation

When R_3PbPbR_3 compounds are heated to temperatures in the neighborhood of 200°C., they undergo a decomposition which is represented by the equation

$$2R_3PbPbR_3 \rightarrow 3R_4Pb + Pb$$

The temperature required depends on the nature of the R groups. Hexaalkyldileads undergo such a decomposition on distillation, although the ease of decomposition decreases as the molecular weight of the R group increases, in straight-chain compounds. The solid hexaaryldileads decompose on or before melting, with deposition of lead; the resulting product then melts at the melting point of the R_4Pb compound. Heating in a high-boiling solvent (toluene, xylene, pyridine) may also effect the decomposition. The ease with which this reaction may be carried out depends on the nature of the organic groups, and the series

ethyl, methyl > *m*-tolyl, phenyl > *p*-tolyl, *p*-ethoxyphenyl, *p*-methoxyphenyl > *o*-tolyl, *o*-ethoxyphenyl, *o*-methoxyphenyl > cyclohexyl, mesityl, α-naphthyl

(where the organic groups are listed in order of decreasing ease of pyrolysis of their R_6Pb_2 compounds) represents some results reported (98).

Yields of R_4Pb from such a decomposition may be of the order of 90 per cent (98). The correctness of the rather complicated stoichiometry indicated by the equation above is shown by some work of Calingaert, Soroos, and Shapiro (58), who heated a mixture of hexamethyldilead and hexaethyldilead under nitrogen at 100°C. and obtained metallic lead in an amount within 5 per cent of that required. All the possible lead alkyls resulted; and since lead alkyls do not undergo redistribution in the absence of a catalyst, the interchange of groups was believed to have occurred before or during the decomposition of the R_6Pb_2 compounds. However, when hexa-*p*-tolyldilead and hexa-*p*-methoxyphenyldilead were heated together (98), only the symmetrical compounds, tetra-*p*-tolyllead (65 per cent yield) and tetra-*p*-methoxyphenyllead (57 per cent yield), could be isolated.

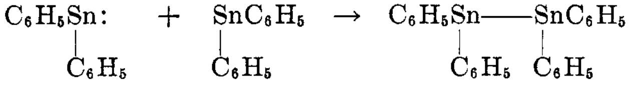
This curious type of thermal decomposition is not characteristic of organometallic compounds of the other Group IVB elements. It is more nearly duplicated in some properties of organothallium compounds. No explanation of the nature of the changes involved has been offered. When all the R groups in the molecule are the same, the nature of the products does not shed much light on the reaction path. It would be desirable to study such reactions with unsymmetrical compounds, but no such compound has yet been made.

IV. ORGANOLEAD COMPOUNDS OF TWO-COVALENT LEAD

A. NATURE AND CONFIGURATION OF THE BONDS FORMED BY TWO-COVALENT LEAD

The two-covalent state of the Group IVB elements has been described above as arising from the $s^2p^{2\,3}P$ ground state of the atom. This state is represented in structure I (page 103). The expected bond angle would be 90° (for p^2 bonding). Electron diffraction measurements on lead dihalides in the vapor state (where the compounds are believed to be monomeric) support this expectation (236). It is particularly to be noted that structure I is not a radical; there are no unpaired electron spins.

However, it seems probable that the stability of the inert pair may not be as great, even for such a heavy atom as lead, as is represented in structure I. This structure would represent a simple molecule of the type PbX_2 or R_2Pb. So little is known about R_2Pb compounds that no direct experimental evidence can be cited. Diphenyltin (62, 180, 214) and diphenylgermanium (210) are better known and are polymeric substances, the former yellow and the latter existing in both colored and colorless forms. The careful measurements of Jensen and Clauson-Kaas (180) on diphenyltin are especially illuminating. This material is monomeric when freshly prepared, but polymerizes rapidly to reach the molecular weight of a pentamer or greater. Measurements of magnetic susceptibility showed no paramagnetic effect at all, either for monomeric preparations or for more highly polymerized material. There was a dipole moment (~1.0), small but apparently real, and independent of the degree of polymerization. Jensen and Clauson-Kaas offer an explanation, based on biradicals with formal bonds, for these observations. It appears that a different interpretation is possible. Inspection of structure I shows that the polymerization of diphenyltin might be pictured as follows:



$$C_6H_5\underset{\textstyle C_6H_5}{\underset{|}{Sn}}: \;+\; \overset{..}{\underset{\textstyle C_6H_5}{\underset{|}{Sn}}}C_6H_5 \rightarrow C_6H_5\underset{\textstyle C_6H_5}{\underset{|}{Sn}}\text{——}\overset{..}{\underset{\textstyle C_6H_5}{\underset{|}{Sn}}}C_6H_5$$

III

and so on. The absence of a paramagnetic effect would be expected for structure III. In this structure as written there is a formal charge separation which should

TABLE 7

R_2Pb *compounds*

COMPOUND	COMMENTS	REFERENCES
Di-*sec*-butyllead	No analysis but derivatives were prepared	(292)
Dicyclohexyllead	No analysis	(168)
Diisopropyllead		(79, 144, 325)
Dimethyllead		(259)
Di-3-pentyllead	No analysis but derivatives were prepared	(292)
Diphenyllead	Decomposes around 100°C.	(217, 261)
Di-*p*-tolyllead		(217)
Related compounds		
Dibutyllead·iron tetracarbonyl		(164)
Diethyllead·iron tetracarbonyl	Darkens at 110°C., decomposes at 138°C.	(170)
Dimethyllead·iron tetracarbonyl		(164)
Dipropyllead·iron tetracarbonyl		(164, 165)

result in a large dipole moment. If, however, the tin atoms were configurationally identical, this dipole moment would be obliterated because of hybridization. There is little basis for guessing at the actual stereochemical configurations, but the most obvious assumptions might be a planar configuration around the first tin atom in III, and a pyramidal configuration around the other. Then the two would not be identical, and some steric inhibition of the hybridization might exist. The result would be such a lowering of the dipole moment, without complete obliteration, as was observed.

This theory does not account for the yellow color of diphenyltin. In connection with the non-radical formulation of these divalent compounds in general, it should be noted that such formulations for the molecules in resting states do not necessarily preclude the consideration of activated radical forms, which could arise by unpairing of the *s* electrons (in a monomer). The energy barrier between the states $:CH_2$ and $\cdot\dot{C}H_2$ of the methylene fragment is small (32), perhaps about 15 kcal./mole (239).

This discussion of other elements of the group has been given because it serves as useful orientation for consideration of lead compounds, where data are mostly lacking.

B. PREPARATION AND PROPERTIES OF R_2Pb COMPOUNDS (TABLE 7)

1. General

It is assumed that R_2Pb compounds are the first products of the reaction of lead chloride with active organometallics,

$$2RMgX + PbCl_2 \rightarrow R_2Pb + MgX_2 + MgCl_2$$

and that their presence is indicated by the transient brown or red colorations which appear during the preparation of R_4Pb compounds. However, the only examples which have been isolated are diphenyllead and di-*o*-tolyllead. The easy thermal dissociation of R_2Pb compounds (presumably to R_6Pb_2 and lead) has usually prevented their isolation.

2. Diphenyllead and di-o-tolyllead

Diphenyllead and di-*o*-tolyllead were obtained by Krause and Reissaus (217) by reaction of lead chloride with the Grignard reagent at 2°C. The yields were about 4 per cent. At higher temperatures decomposition was presumably too rapid, and even at 2°C. most of the product was R_4Pb and R_6Pb_2, whereas at lower temperatures the Grignard reagent essentially did not react with lead chloride. The products were solids, deep blood-red in color. This difficult work was painstakingly carried out, and the diphenyllead was characterized by analyses for lead, carbon, and hydrogen and by cryoscopic molecular-weight determinations in benzene which showed the compound to be monomeric. The results cannot be questioned, but attempts (97, 180) to duplicate this preparation have never been successful. Krause and Reissaus themselves experienced difficulty in duplicating the synthesis, and gave some discussion of the probable reasons.

It might be supposed that organolithium compounds would react more readily with lead chloride, at temperatures low enough that decomposition of the R_2Pb compound could be avoided. There is considerable evidence (129) that in the reaction of phenyllithium with lead chloride at -10°C. diphenyllead is the first product, and that it can be maintained in the mixture as long as the temperature is kept low. The main point of discrepancy here is that the material believed to represent diphenyllead is not red, but bright yellow when freshly formed. This difference may not be of great significance. The work of Krause and Reissaus has sometimes been interpreted as indicating that diarylleads are, typically, well-defined red crystalline monomers; but this would be in contrast to R_2M compounds of other elements of Group IVB, which, as discussed above, are somewhat ill-defined solid polymers, yellow to brownish in color. Under other reaction conditions Krause and Reissaus did observe yellow intermediates in their solutions. It is conceivable that the degree (and the nature) of the polymerization may influence the color of the product. The intermediate product from *o*-tolyllithium and lead chloride is indeed blood-red (129). It seems probable that further investigation might lead to the actual isolation of diarylleads, in some form, from the reactions of aryllithium compounds with lead dichloride.

3. Other R_2Pb *compounds*

Electrolytic reduction of ketones in sulfuric acid, with use of a lead cathode, is believed to give dialkylleads, among other products. In this manner diisopropyllead has been prepared but not isolated (325).

Reaction of dialkyllead dihalides with sodium in liquid ammonia (35) has not led to the isolation of dialkylleads. Use of diaryllead dihalides in such a reaction also does not give diarylleads.

Recent studies (259) have suggested that the first product of the reaction of alkyl radicals with a lead mirror in the Paneth apparatus may be an R_2Pb compound, since lead or tellurium mirrors are removed at the same rate when hot acetone or dimethyl ether is passed through the tube.

4. Chemical properties

The R_2Pb compounds decompose readily on heating, and this is their best-known chemical characteristic. Diphenyllead on heating in a capillary tube (217) turned pale and decomposed at about 100°C. The decomposition product turned yellow at 120°C., melted above 200°C., and turned black at 260°C. These observations do not lend support to the series of equations given above to explain the formation of R_4Pb compounds. Hexaphenyldilead was formed from diphenyllead by refluxing an ether–benzene solution of diphenyllead and phenylmagnesium bromide. The yellow product obtained from phenyllithium and lead chloride does decompose readily (129) on brief refluxing of the solution in which it was made, to give lead and hexaphenyldilead in good yield. Thermal decomposition to give the free metal is not characteristic of R_2M compounds of other elements of Group IVB (however, compare the rapid decomposition of the analogous phenylthallium (107), even at -70°C.).

It is postulated (129) that diphenyllead can add phenyllithium to form triphenylleadlithium, $(C_6H_5)_3PbLi$. Such reactions would be expected, in view of the electronic configuration indicated for R_2Pb molecules. The reaction is apparently reversible.

V. IONIC ORGANOLEAD COMPOUNDS

A. NATURE AND TYPES OF LEAD-CONTAINING IONS

The organolead compounds already discussed contain only lead–carbon or lead–lead bonds, which are apparently typical covalent bonds. The bonds formed by lead to highly electronegative or electropositive elements may in contrast be essentially ionic. The lead atom may then be the central element in either a cation [as in $(C_6H_5)_3PbCl$ or $(C_2H_5)_3PbOH$] or an anion [as in $(C_6H_5)_3PbLi$]. Many compounds containing organolead cations, such as R_3Pb^+, are well-known, isolable, stable substances, whose formulation in this fashion is supported by physical-chemical data and by their general behavior. Compounds containing anions such as $(C_6H_5)_3Pb^-$ have not been isolated, although they are becoming fairly well known as reaction intermediates in solution.

Tables 8 through 19 contain information as to the melting and boiling points of many ionic organolead compounds, together with literature references.

B. R_3PbAn AND R_2PbAn_2 COMPOUNDS

Here R is any organic group, and the R groups in the same molecule need not be alike. "An" is any anion.

TABLE 8

R_3PbX *compounds* (X = *halide*)

COMPOUND	MELTING POINT	REFERENCES
	°C.	
Tribenzyllead bromide	Decomposes at 150 without melting	(222)
Tribenzyllead chloride		(215)
Tributyllead bromide		(67, 69, 261)
Tributyllead chloride	109–111; b.p., 147–149/5–7 mm.	(24, 77, 242, 250, 284, 300)
Tri-*sec*-butyllead chloride	Decomposes at 130 without melting	(292)
Tricyclohexyllead bromide	Decomposes at 210 without melting	(211)
Tricyclohexyllead chloride	Decomposes at 236 without melting	(14, 169, 211)
Tricyclohexyllead fluoride	Decomposes at 198 without melting	(216)
Tricyclohexyllead iodide	91.7; decomposes at 125 without melting	(66, 98, 168, 211, 212)
Tridodecyllead chloride	64–65	(253)
Triethyllead bromide	103–104	(5, 38, 44, 52, 56, 67, 98, 151, 234, 238, 247, 321, 325)
Triethyllead chloride		(10, 23, 24, 27, 28, 38, 42, 44, 45, 52, 56, 96, 118, 125, 131, 136, 141, 143, 151, 162, 166, 175, 234, 238, 247, 249, 251, 257, 262, 283, 293, 294, 298, 300, 301, 320, 321, 334)
Triethyllead fluoride	Decomposes at 240 without melting	(216)
Triethyllead iodide	Freezes at 19–20	(33, 45, 192, 193, 237, 238)
Trihexadecyllead chloride	79–80	(253)
Triisoamyllead bromide	132–133	(66, 155, 212)
Triisoamyllead chloride		(193)
Triisoamyllead fluoride	Decomposes at 251 without melting	(216)
Triisoamyllead iodide		(193)
Triisobutyllead bromide	107–108	(66, 155, 212)
Triisobutyllead chloride	122 with decomposition	(155)
	Darkens at 145	(162)
Triisobutyllead fluoride	Decomposes at 230 without melting	(216)
Triisobutyllead iodide	Unstable	(155)
Triisopropyllead bromide		(144)
Triisopropyllead chloride		(144, 325)
Triisopropyllead iodide	Unstable	(325)
Trimesityllead iodide	200–201	(98)
Trimethyllead bromide	133 with decomposition	(34, 38, 56, 151, 227)
Trimethyllead chloride	Sublimes at 187; melts at 190 with decomposition	(24, 34, 38, 44, 45, 56, 151, 162, 234, 303, 321)

TABLE 8—*Concluded*

COMPOUND	MELTING POINT	REFERENCES
	°C.	
Trimethyllead fluoride	Volatile on slight heating; decomposes at 305 without melting	(216)
Trimethyllead iodide		(34, 44, 53)
Trioctadecyllead chloride	82–83	(253)
Triphenethyllead bromide	91–92	(222)
Triphenyllead bromide	166	(66, 148, 212, 221, 234, 242, 247, 321)
Triphenyllead chloride	206	(10, 11, 80, 81, 82, 96, 100, 106, 111, 119, 148, 198, 199, 221, 234, 242, 243, 247, 266, 268, 270, 272, 320, 321)
Triphenyllead fluoride	Decomposes at 318 without melting	(66, 212, 216)
Triphenyllead iodide	138–139	(5, 80, 81, 98, 148, 217, 234, 242, 321)
Tripropyllead bromide		(67, 284, 300)
	76–78	(300)
	81–82	(284)
Tripropyllead chloride		(24, 151, 284, 300)
	137	(284)
	133–134	(300)
Tripropyllead fluoride	Explodes at 235	(66, 212, 216)
Tris(*p*-ethoxyphenyl)lead iodide	99–100	(98)
Tris(*o*-methoxyphenyl)lead chloride	167–171	(266)
Tris(*o*-methoxyphenyl)lead iodide	122–123	(98)
Tris(*p*-methoxyphenyl)lead bromide		(133)
Tris(*p*-methoxyphenyl)lead chloride	152–153	(133)
Tritetradecyllead chloride	74–75	(253)
Tri-*m*-tolyllead bromide	146–147	(98)
Tri-*o*-tolyllead bromide	126–127	(8, 9)
Tri-*o*-tolyllead chloride	141–142	(9, 96)
Tri-*p*-tolyllead chloride	140–141	(9)
Tri-*p*-tolyllead fluoride	Decomposes at 280 without melting	(216)
Tri-*p*-tolyllead iodide	115	(98, 217)
Tri-2,5-xylyllead bromide	177	(224)
Tri-2,5-xylyllead chloride	167.5	(217)

TABLE 9

$R_2R'PbX$ *compounds*

COMPOUND	MELTING POINT	REFERENCES
	°C.	
(*o*-Carbomethoxyphenyl)diphenyllead chloride	170–171	(112)
(*o*-Carboxyphenyl)diphenyllead chloride	210–220	(112)
Diamylmethyllead chloride	Decomposes at 121–122 without melting	(182)
Dicyclohexylphenyllead chloride	Decomposes at 205 without melting	(110)
(3-Diethylaminopropyl)diphenyllead chloride, hydrochloride	Decomposes	(127)
Diethyl-ε-bromoamyllead bromide		(153)
Diethylbutyllead bromide	Not isolated	(154)
Diethylisoamyllead bromide	Not isolated	(154)
Diethylisobutyllead bromide	Not isolated	(154)
Diethylmethyllead chloride		(56)
Diethylphenyllead chloride		(110)
Diethylpropyllead bromide	Not isolated	(154, 156)
Diisoamylethyllead bromide	Not isolated	(154)
Dimethyl-*sec*-butyllead bromide	Not isolated	(156)
Dimethylethyllead bromide	Not isolated	(154)
Dimethylethyllead chloride		(38, 45, 56)
Dimethylpropyllead bromide	Not isolated	(154)
Diphenylamyllead chloride	123 with decomposition	(12)
Diphenylbenzyllead bromide	143 with decomposition	(222)
Diphenylbenzyllead chloride	Sinters at 157	(135)
Diphenyl-3-butenyllead chloride	134–135 with decomposition	(135)
Diphenylcyclohexyllead bromide	135	(221)
Diphenylethyllead bromide	119; decomposes at 130–135	(221)
Diphenylethyllead chloride	Decomposes at 146–147 without melting	(102)
Diphenylmethyllead bromide	118; decomposes at 124	(221)
Diphenylphenethyllead bromide	119 with decomposition	(222)
Diphenylpropyllead chloride	141 with decomposition	(12)
Diphenyl-2-pyridyllead iodide	137–140	(104)
Diphenyl-2,5-xylyllead bromide	90	(221)
Dipropylethyllead chloride		(163, 242)
Di-*o*-tolylphenyllead bromide	117–118	(8)
Di-*o*-tolylphenyllead chloride	113–114	(10)

TABLE 10

$RR'R''PbX$ *compounds*

COMPOUND	MELTING POINT	REFERENCES
	°C.	
Cyclohexylmethylphenyllead bromide	93–94	(221)
Ethylisobutylpropyllead bromide	Not isolated	(154)
Isoamylmethylpropyllead chloride	Not isolated	(154)
Phenylpropyl-*o*-tolyllead chloride	103–104	(12)

TABLE 11

R_2PbX_2 *compounds*

COMPOUND	MELTING POINT	REFERENCES
	°C.	
Bis(*m*-aminophenyl)lead dichloride		(303)
Diamyllead dibromide	Decomposes at 89 without melting	(182)
Diamyllead dichloride	Decomposes at 123–125 without melting	(182)
Di-*dl*-amyllead dichloride	Decomposes at 67 without melting	(182)
Dibutyllead dibromide		(69, 182)
Di-*sec*-butyllead dibromide		(292)
Dibutyllead dichloride	Decomposes at 180 without melting	(77, 182)
Bis(*p*-carbethoxyphenyl)lead dichloride	Does not melt at 270	(266)
Bis(2-chlorovinyl)lead dichloride	Decomposes at 163–167 without melting	(269)
Dicyclohexyllead dibromide		(97, 147, 211)
	Decomposes at 225 without melting	(147)
	Decomposes at 142 without melting	(211)
Dicyclohexyllead dichloride	Decomposes at 180 without melting	(147, 169)
Dicyclohexyllead diiodide	Decomposes under 100	(147, 168, 211)
Diethyllead dibromide		(52, 151, 261, 318)
Diethyllead dichloride		(10, 52, 120, 141, 143, 151, 163, 175, 234, 261, 298, 300, 320, 334)
Diethyllead diiodide		(151)
Diisoamyllead dibromide		(155)
Diisoamyllead dichloride	Decomposes at 108 without melting	(155)
Diisobutyllead dibromide	Decomposes at 102–103 without melting	(155)
Diisobutyllead dichloride	Decomposes above 100 without melting	(155)
Diisopropyllead dibromide		(156, 325)
Diisopropyllead dichloride	Unstable	(325)
Diisopropyllead diiodide	No analysis	(325)
Bis(*o*-methoxyphenyl)lead dichloride	187–188.5	(266)
Bis(*p*-methoxyphenyl)lead dichloride		(133)
Bis(*p*-methoxyphenyl)lead diiodide	122–123	(98)
Dimethyllead dibromide	Unstable	(108, 151)
Dimethyllead dichloride		(151, 303)
Dimethyllead diiodide	Unstable	(151)
Bis(*m*-nitrophenyl)lead dibromide		(197)
Bis(*m*-nitrophenyl)lead dichloride	Sublimes at 250	(110)
	Decomposes at 285–288 without melting	

TABLE 11—*Concluded*

COMPOUND	MELTING POINT	REFERENCES
	°C.	
Bis(*m*-nitrophenyl)lead diiodide	Decomposes at 135 without melting	(110)
Di-3-pentyllead dibromide		(292)
Diphenyllead dibromide		(66, 97, 212, 222, 261, 284, 287, 288, 310, 338)
Diphenyllead dichloride	Decomposes at 284–286 without melting	(10, 96, 98, 100, 119, 139, 140, 198, 199, 244, 268, 270, 272, 284, 288, 300, 321, 330, 338)
Diphenyllead difluoride		(310)
Diphenyllead diiodide	101–103	(97, 287, 288, 289, 310, 338)
Dipropyllead dichloride	Decomposes at 228 without melting	(151, 300)
Di-2-thienyllead dichloride	Decomposes at 202 without melting	(132)
Di-*o*-tolyllead dibromide	150–151	(8)
Di-*o*-tolyllead dichloride	178–179	(9, 10)
Di-*p*-tolyllead dibromide		(289)
Di-*p*-tolyllead dichloride		(9, 10)
Di-2,4-xylyllead dichloride		(138)
Di-2,5-xylyllead dibromide	120 with decomposition	(224)
	Related compounds	
Diethyllead bromide chloride		(215)
Diisobutyllead bromide chloride	Decomposes at 110 without melting	(155)

TABLE 12

$RR'PbX_2$ *compounds*

COMPOUND	MELTING POINT	REFERENCES
	°C.	
3-Butenylethyllead dichloride		(135)
3-Butenylphenyllead dichloride	Unstable	(135)
ε-Chloroamylethyllead dichloride	Decomposes at 120 without melting	(153)
Ethylisoamyllead dichloride	Decomposes at 128 without melting	(154)
Ethylisobutyllead dibromide	Unstable	(154)
Ethylmethyllead dichloride		(154)
Ethylmethyllead diiodide		(154)
Isoamylisobutyllead dibromide	Decomposes at 95 without melting	(155)
Isoamylpropyllead dichloride		(154)
Isobutylpropyllead dibromide	Remarkably stable	(154)
Isobutylpropyllead dichloride	Very stable	(155)
Phenylpropyllead dichloride		(12)
Phenyl-*o*-tolyllead dibromide	116–117	(8)

TABLE 13

R_3PbE *compounds* (E = *anion other than halide*)

COMPOUND	MELTING POINT*	REFERENCES
	°C.	
Tributyllead acetate	86	(300)
Tributyllead bromoacetate	54–55	(300)
Tributyllead chloroacetate	60	(300)
Tributyllead β-chloropropionate	65–66	(300)
Tributyllead crotonate	119	(300)
Tributyllead hydroxide		(284, 300)
Tributyllead iodoacetate	83	(300)
Tributyllead 2-naphthalenesulfonate	68	(300)
Tributyllead propionate	79–80	(300)
Tributyllead *p*-toluenesulfonate	81–82	(300)
Tributyllead trichloroacetate	119	(300)
Tricyclohexyllead hydroxide		(14, 211)
Tridodecyllead acetate	59	(253)
Tridodecyllead nitrate	44–45	(253)
Triethyllead acetate	160	(23, 123, 193, 200, 300)
Triethyllead acid oxalate	Not melted 300	(95, 123)
Triethyllead acid succinate	304 with decomposition	(95)
Triethyllead acid tartrate		(193)
Triethyllead acrylate	Sinters at 120	(162)
Triethyllead *p*-aminobenzoate	84–86 (monohydrate)	(105, 121, 123)
Triethyllead 1-amino-4-naphthalenesulfonate	238–240 with decomposition	(123)
Triethyllead 2-amino-5-toluenesulfonate	210 with decomposition	(123)
Triethyllead *p*-anisate	97–98	(123)
Triethyllead anthranilate	96	(300)
Triethyllead benzenesulfonamide	132	(298)
Triethyllead benzoate	127	(23, 163, 193)
Triethyllead β-benzoylacrylate	139–141 with decomposition	(123)
Triethyllead bicarbonate	Impure	(45)
Triethyllead bromoacetate	121	(23, 162)
Triethyllead *m*-bromobenzoate	113–114	(123)
Triethyllead *o*-bromobenzoate	134–135	(123)
Triethyllead *p*-bromobenzoate	127–128	(123)
Triethyllead butylmercaptide	82–83/0.5 mm. (b.p.)	(95)
Triethyllead butyrate	107.9–108.5	(23, 193)
Triethyllead *d*-camphor-10-sulfonate	172 with decomposition	(123)
Triethyllead caproate	94.7–95.8	(23)
Triethyllead caprylate	85–87.5	(23)
Triethyllead chloroacetate	147	(23, 162)
Triethyllead *p*-chlorobenzoate	123–124	(123)
Triethyllead α-chlorocrotonate	153–155	(123)
Triethyllead β-chloropropionate	106	(162)
Triethyllead cinnamate	122–123 with decomposition	(123)
Triethyllead cresolate		(60)
Triethyllead crotonate	135–136	(162)
Triethyllead cyanate		(162)

TABLE 13—*Continued*

COMPOUND	MELTING POINT*	REFERENCES
	°C.	
Triethyllead cyanide		(23, 45, 162, 193)
	194	(23)
	189 with decomposition	(162)
Triethyllead cyclohexylsulfinate	132–134	(123)
Triethyllead dibromoacetate	98.6–101.8	(23)
Triethyllead dichloroacetate	113.5–114.5	(23)
Triethyllead diphenylacetate	164–165	(123)
Triethyllead ethoxide	18	(95)
Triethyllead *N*-ethylcarbazole-2-carboxylate	195 with decomposition	(123)
Triethyllead ethylenesulfonanilide	116	(242, 298)
Triethyllead 2-ethylhexyl maleate		(13)
Triethyllead ethylmercaptide	76–78/0.075 mm. (b.p.)	(162, 242)
Triethyllead ethyl thioglycolate	94–96/0.5 mm. (b.p.)	(95)
Triethyllead ferricyanide	Impure	(23)
Triethyllead ferrocyanide	Impure	(23)
Triethyllead 9-fluorenecarboxylate	Decomposes at 195–208	(123)
Triethyllead fluoroacetate	180.5 with decomposition	(241, 299)
Triethyllead fluorophosphonate	260	(301)
Triethyllead formate		(193)
Triethyllead furoate	156–157 with decomposition	(105, 121, 123)
Triethyllead furylacrylate	132–133 with decomposition	(105, 121, 123)
Triethyllead heptoate	90–90.8	(23)
Triethyllead heptylmercaptide	114–115/0.5 mm. (b.p.)	(95)
Triethyllead hexyl maleate		(13)
Triethyllead hydroxide		(23, 27, 28, 45, 52, 166, 193, 216, 242, 257, 298, 300)
Triethyllead *m*-iodobenzoate	135–136	(123)
Triethyllead *o*-iodobenzoate	138.5–139	(123)
Triethyllead *p*-iodobenzoate	129.5–130.5	(123)
Triethyllead isobutyrate	119.4–121.8	(23)
Triethyllead isovalerate	119.4–119.8	(23)
Triethyllead lepidine-2-carboxylate	153–155	(123)
Triethyllead *N*-methylanthranilate	133 with decomposition	(123)
Triethyllead methylsulfonamide	97	(298)
Triethyllead methylsulfonanilide	115.5	(298)
Triethyllead methyl thiosalicylate	91–93/0.008 mm. (b.p.)	(95)
Triethyllead monoethyl oxalate	55	(162)
Triethyllead 2-naphthalenesulfonate	152	(162)
Triethyllead β-2-naphthoylpropionate	134.5	(123)
Triethyllead nitrate		(175, 238)
Triethyllead *o*-nitrobenzoate	142–143 with decomposition	(123)
Triethyllead *m*-nitrobenzoate	172–173	(123)
Triethyllead *p*-nitrobenzoate	168–169 with decomposition	(123)
Triethyllead pelargonate	88–90	(23)
Triethyllead phenoxide	75/0.5 mm. (b.p.)	(60, 95)
Triethyllead phenylacetate	101–106	(105, 121)

TABLE 13—*Continued*

COMPOUND	MELTING POINT* °C.	REFERENCES
Triethyllead *N*-phenylanthranilate	124.5–125.0	(123)
Triethyllead phenylmercaptide	111–113/0.5 mm. (b.p.)	(95, 162)
Triethyllead phenylpropiolate	149–150 with decomposition	(123)
Triethyllead phthalimide	131	(162, 242)
Triethyllead primary phosphate	Not melted at 250	(24, 121, 193)
Triethyllead propionate	141 with decomposition	(23, 162)
Triethyllead saccharide	135 142–143	(298) (95)
Triethyllead salicylate	93	(105, 121, 123, 162)
Triethyllead selenocyanate	33–34	(123, 162)
Triethyllead sulfanilamide	171	(123, 298)
Triethyllead thioacetate	45	(163)
Triethyllead thiocyanate	35	(123, 162, 193)
Triethyllead thiosalicylate	97–99	(121)
Triethyllead *p*-toluenesulfinate	86–88	(123)
Triethyllead *o*-toluenesulfonamide	133	(298)
Triethyllead *p*-toluenesulfonamide	127	(242, 298)
Triethyllead *p*-toluenesulfonanilide	134	(298)
Triethyllead *o*-toluenesulfonate	189	(162)
Triethyllead *p*-toluenesulfonate	170	(105, 121, 162)
Triethyllead *p*-toluenesulfon-*p*-bromoanilide	117	(298)
Triethyllead *p*-toluenesulfon-*p*-chloroanilide	111.5	(298)
Triethyllead *p*-tolylthiosulfonate	109	(123)
Triethyllead trichloroacetate	141	(29, 162)
Triethyllead triphenylacetate	134–136 with decomposition	(123)
Triethyllead valerate	115.5–117	(23)
Triisoamyllead hydroxide	Oil	(155, 193, 216)
Triisobutyllead acetate	117	(162)
Triisobutyllead butyrate	119	(162)
Triisobutyllead hydroxide	Decomposes at 115 without melting	(216)
Triisobutyllead propionate	118	(162)
Triisobutyllead *o*-toluenesulfonate		(162)
Triisobutyllead *p*-toluenesulfonate		(162)
Trimethyllead acetate	194	(45, 162)
Trimethyllead chloroacetate	169	(162)
Trimethyllead formate	113	(162)
Trimethyllead hydroxide		(166, 216)
Trimethyllead isovalerate	160	(162)
Trimethyllead methacrylate		(227)
Trimethyllead nitrate		(136)
Trimethyllead *p*-toluenesulfonate	Melts above 220	(162)
Trimethyllead trichloroacetate	Not melted at 220	(162)
Tris-*m*-nitrophenyllead nitrate		(110)
Triphenyllead acetate	206–207	(9, 10)
Triphenyllead acid maleate	207	(110)

TABLE 13—*Concluded*

COMPOUND	MELTING POINT*	REFERENCES
	°C.	
Triphenyllead ethyl benzylmalonate	131–132	(195, 196)
Triphenyllead ethyl malonate	159–160	(195, 196)
Triphenyllead hydroxide		(14, 148, 216, 221, 247)
Triphenyllead hyponitrite	222–224	(95)
Triphenyllead laurate	91	(103)
Triphenyllead myristate	102–103	(103)
Triphenyllead nitrate	Decomposes at 220–225	(110, 136)
Triphenyllead palmitate	110	(103)
Triphenyllead stearate	112	(103)
Tripropyllead acetate	128	(162, 163, 284, 300)
Tripropyllead acrylate	123	(300)
Tripropyllead anthranilate	57–58	(300)
Tripropyllead benzenesulfonamide	96	(242, 298)
Tripropyllead bromoacetate	93–94	(300)
Tripropyllead butyrate	105–106	(300)
Tripropyllead chloroacetate	109–110	(163, 300)
Tripropyllead β-chloropropionate	99–100	(300)
Tripropyllead crotonate	135	(300)
Tripropyllead cyanide	135 with decomposition	(300)
Tripropyllead hydroxide	Decomposes at 140 without melting	(165, 216, 242, 284, 298, 300)
Tripropyllead iodoacetate	88–89	(300)
Tripropyllead isovalerate	110–111	(300)
Tripropyllead methylsulfonamide	67	(242, 298)
Tripropyllead 2-naphthalenesulfonate	126–127	(300)
Tripropyllead phthalimide		(162, 242)
Tripropyllead propionate	121–122	(300)
Tripropyllead saccharide	130	(242, 298)
Tripropyllead sulfanilamide	101	(298)
Tripropyllead *p*-toluenesulfonamide	100–101	(242, 298)
Tripropyllead *p*-toluenesulfonanilide	104	(298)
Tripropyllead *o*-toluenesulfonate	86–87	(162, 300)
Tripropyllead *p*-toluenesulfonate	73–74.5	(162)
	82–83	(300)
Tripropyllead *p*-toluenesulfon-*p*-bromoanilide	117	(298)
Tripropyllead *p*-toluenesulfon-*p*-chloroanilide	123	(298)
Tripropyllead trichloroacetate	139–140	(300)
Tripropyllead xanthate	57.5	(300)
Tri-*p*-tolyllead acetate	161–162	(9)
Tri-*p*-tolyllead hydroxide		(216)

*** The values given are melting points except as otherwise noted.**

TABLE 14

$R_2R'PbE$ *compounds* (E = *anion other than halide*)

COMPOUND	MELTING POINT	REFERENCES
	°C.	
Butyldiethyllead chloroacetate	82–83	(163)
o-Carboxyphenyldiethyllead hydroxide (as inner anhydride)	208–209	(95)
o-Carboxyphenyldiphenyllead hydroxide	300–305	(112)
Diethylpropyllead chloroacetate	112	(163)
Diethylpropyllead propionate	86	(163, 242)
Ethyldipropyllead *p*-toluenesulfonamide	94.5	(163)

TABLE 15

$(R_3Pb)_2E$ *and* $(R_3Pb)_3E$ *compounds* (E = *anion other than halide*)

COMPOUND	MELTING POINT	REFERENCES
	°C.	
Tributyllead fumarate		(13)
Triethyllead *d*-camphorate		(123)
Triethyllead carbonate		(23, 45, 52, 238)
Triethyllead chromate	Poor analysis; explodes at 190	(23)
Triethyllead fumarate	Decomposes at 163 without melting	(123)
Triethyllead oxalate	Dihydrate	(193)
Triethyllead oxide		(193, 238)
Triethyllead pyrocatecholate		(60)
Triethyllead resorcinolate		(60)
Triethyllead sulfate		(28, 45, 192, 193, 238)
Triethyllead sulfide	Freezes at −45.1	(45, 193)
Triisoamyllead oxide		(193)
Triisoamyllead sulfate		(193)
Triphenyllead carbonate	231	(125)
Triphenyllead maleate	198–199	(110)
Triphenyllead oxide		(9, 14, 148)
Triphenyllead sulfide		(148)
Tripropyllead sulfate		(284)
Triethyllead citrate		(123)

1. *General and physical properties*

Three or four hundred R_3PbAn and R_2PbAn_2 compounds are known, including about 150 in which An is a halide ion. In general, they are solid, crystalline, salt-like substances, many of which melt with difficulty or decompose on heating. In other cases, especially if An is an organic anion, they may exhibit fairly low melting points. They are in general non-volatile (reported exceptions include trimethyllead fluoride and chloride, which sublime). Some of them are somewhat soluble in water, depending on the nature of the R groups and of An. The solubility in organic solvents is limited, depending again on the specific com-

TABLE 16

R_2PbE_2 *compounds* (E = *anion other than halide*)

COMPOUND	MELTING POINT	REFERENCES
	°C.	
Bis(*m*-aminophenyl)lead dihydroxide		(303)
Bis(*p*-carbethoxyphenyl)lead diacetate	207–208	(266)
Bis(2-chlorovinyl)lead diacetate	Decomposes at 115–130 without melting	(268, 269)
Bis(2-chlorovinyl)lead dibenzoate	Decomposes at 204–204.5 without melting	(269)
Bis(2-chlorovinyl)lead sulfate	Darkens at 171–172	(269)
Bis(*o*-methoxyphenyl)lead diacetate	191–193 with decomposition	(266)
Bis(*p*-methoxyphenyl)lead diacetate		(133)
Bis(*m*-nitrophenyl)lead dinitrate		(61, 110, 329)
Bis(*m*-nitrophenyl)lead oxide		(303)
Diamyllead dihydroxide	Not isolated	(182)
Diamyllead dinitrate	Anhydrous Dihydrate; sinters at 96–98	(182)
Diamyllead sulfate	Sinters at 177	(182)
Dibutyllead dihydroxide		(182)
Dibutyllead dinitrate	Anhydrous, 123–125 Dihydrate; sinters at 116–117	(182)
Dibutyllead dioctoxide		(65)
Dicyclohexyllead oxide		(169)
Dicyclohexyllead sulfide	Decomposes at a little over 100	(147)
Diethyllead bis(chloroacetate)	176–177	(279)
Diethyllead carbonate		(45, 52)
Diethyllead diacetate	200–201	(266)
	130	(279)
Diethyllead dibenzoate	168	(163)
Diethyllead di-*m*-bromobenzoate	178–179	(123)
Diethyllead di-*N*-butylanthranilate	169–169.5 with decomposition	(123)
Diethyllead dichloroacetate	180 with decomposition	(163)
Diethyllead di-*p*-chlorobenzoate	185 with decomposition	(123)
Diethyllead dihydroxide	Hexahydrate; loses H_2O at 120 to yield oxide	(45, 52, 163)
Diethyllead dinicotinate	143 with decomposition	(123)
Diethyllead dinitrate		(175)
Diethyllead di-*m*-dinitrobenzoate	179–180	(123)
Diethyllead di-*p*-nitrophenate		(300)
Diethyllead selenite	Does not melt at 286	(123)
Diethyllead dithioacetate	84.5–85	(163)
Diethyllead di-*p*-toluate	186 with decomposition	(123)
Diethyllead di-*o*-toluenesulfonate	Decomposes at 165 without melting	(163)
Diethyllead di-*p*-toluenesulfonate		(163)
Diethyllead di(trichloroacetate)	151 with decomposition	(163)
Diethyllead oxide		(238)
Diethyllead sulfite		(163, 242)

TABLE 16—*Continued*

COMPOUND	MELTING POINT	REFERENCES
	°C.	
Diisopropyllead chromate	Impure	(325)
Diisopropyllead dinitrate		(325)
Diisopropyllead oxide	Not isolated	(144, 325)
Diisopropyllead sulfide	No analysis	(325)
Dimethyllead chromate		(151)
Dimethyllead oxide		(151, 303)
Dimethyllead sulfide		(151)
Di-2-naphthyllead diacetate	236–236.5	(266)
Diphenyllead bis(chloroacetate)	Decomposes at 185–205 without melting	(279)
Diphenyllead chromate		(288)
Diphenyllead diacetate	Dihydrate; anhydrous compound melts at 200–201	(200, 206, 266, 279, 288)
Diphenyllead dibenzoate	231–232	(207)
Diphenyllead dibenzyloxide	240	(279)
Diphenyllead dibutyrate	132–134	(207)
Diphenyllead dicaproate	Yellow oil	(207)
Diphenyllead dicyanide	Decomposes at 245–255 without melting	(338)
Diphenyllead diformate	Monohydrate	(206, 288)
Diphenyllead di-α-hydroxybutyrate	198–201 with decomposition	(207)
Diphenyllead diiodate		(140)
Diphenyllead diisovalerate	166–168	(207)
Diphenyllead dilactate	212–215 with decomposition	(207)
Diphenyllead dimethacrylate	Decomposes at 205–212 without melting	(279)
Diphenyllead dinitrate	Dihydrate	(24, 61, 113, 284, 287, 288, 310, 338)
Diphenyllead di-*p*-nitrobenzoate	256 with decomposition	(140)
Diphenyllead dipropionate	170–172	(24, 140, 207)
Diphenyllead distearate		(336)
Diphenyllead dithiocyanide		(288)
Diphenyllead di(trichloroacetate)	Decomposes at 210 without melting	(140)
Diphenyllead divalerate	168–170	(140)
Diphenyllead oxalate	Trihydrate Decomposes at 293–295 without melting	(140)
Diphenyllead oxide		(272, 288, 338)
Diphenyllead sulfide	Decomposes at 80–90 without melting	(235, 288)
Dipropyllead diacetate	122	(163, 300)
Dipropyllead dinitrate	Dihydrate; melts at 87–89	(182)
Di-*o*-tolyllead dinitrate	Not isolated	(8)
Di-*p*-tolyllead chromate		(289)
Di-*p*-tolyllead diacetate	183.5	(279, 289)
Di-*p*-tolyllead diformate	Decomposes at 233 without melting	(289)
Di-*p*-tolyllead diisobutyrate	202–203	(279)

TABLE 16—*Concluded*

COMPOUND	MELTING POINT	REFERENCES
	°C.	
Di-*p*-tolyllead dinitrate	Trihydrate	(279, 289)
Di-*p*-tolyllead sulfide	98 with decomposition	(289)
Related compounds		
Diphenyllead basic carbonate		(288)
Diphenyllead basic cyanide		(288, 338)
Diphenyllead basic nitrate		(287)
Di-*p*-tolyllead basic nitrate		(289)

TABLE 17

$RR'PbE_2$ *compounds* (E = *anion other than halide*)

COMPOUND	MELTING POINT	REFERENCES
	°C.	
Ethylmethyllead chromate		(154)
Ethylmethyllead sulfide		(154)
Isoamylpropyllead sulfide	No analysis	(154)
Isobutylpropyllead sulfide	No analysis	(154)
Phenyl-*o*-tolyllead dinitrate	Dihydrate	(8)

TABLE 18

$RPbE_3$ *compounds* (E = *anion other than halide*)

COMPOUND	MELTING POINT	REFERENCES
	°C.	
Phenyllead triacetate	101–102	(279)
Phenyllead tribenzyloxide	149.5–151.0	(279)
Phenyllead tributyrate	77–78	(279)
p-Tolyllead triacetate	86–88	(279)
p-Tolyllead trimethacrylate		(279)

pound. The R_2PbAn_2 salts are less soluble in all solvents than the R_3PbAn types. Trialkyllead hydroxides, such as $(C_2H_5)_3PbOH$, are fairly strongly basic in aqueous solution. Such solutions absorb carbon dioxide from the air to form carbonates, precipitate hydroxides from solutions of heavy metal ions, and release ammonia from ammonium salts. The triaryllead hydroxides are not water-soluble and are more weakly basic. Diethyllead dihydroxide has been described (45). Diphenyllead dihydroxide is unknown, but the corresponding oxide, $(C_6H_5)_2PbO$, is easily prepared.

Dipole moments of such compounds have been measured (234, 247, 320, 321). The values for the halide derivatives are in the region expected for inorganic salts—e.g., NaI, 4.9; $(C_2H_5)_3PbBr$, 4.88; $(C_6H_5)_3PbCl$, 4.3; $(C_6H_5)_3PbC_2H_5$, 0.81 (247)—indicating that the lead–halogen bond is largely ionic.

TABLE 19

Additional organolead compounds

COMPOUND	MELTING POINT	BOILING POINT	$n_D^{20°}$	REFERENCES
	°C.	°C.		
Allylplumbonic acid				(230)
Benzylplumbonic acid				(230)
Butylplumbonic acid				(230)
Ethylplumbonic acid	No analysis			(230)
Isopropylplumbonic acid				(230)
Methylplumbonic acid	No analysis			(230)
Propylplumbonic acid				(230)
Butyllead triiodide	No analysis			(231)
Ethyllead triiodide	Decomposes at 90; no analysis			(231)
Propyllead triiodide	No analysis			(231)
Methyllead tribromide				(232)
Methyllead trichloride				(232)
Triethyllead sodium				(101, 112)
Triphenyllead lithium				(129)
Triphenyllead sodium				(81, 98, 101, 110)
(2-Bromoethyl)(pentamethyl)-ethylenedilead				(331)
1,2-Bis(triphenyllead)succinic acid				(110)
Diethylcyclopentamethylenelead		111/13.5 mm.	1.5484	(153, 158)
Methylenebis(trimethyllead)				(331)
Pentamethylenebis(trimethyllead)		166.5/14 mm.	1.5556	(158, 159)
p-Phenylenebis(triphenyllead)	285–288			(112)
Methylenebis(triethyllead sulfonanilide)	180			(298)
Tetramethylenebis(triphenyllead)	134–136			(127)
Trimethylenebis(triphenyllead)	94–95			(127)
Tris(diphenyllead)diphosphate				(288)

In a study (294) of the polarography of triethyllead chloride in aqueous potassium chloride, Riccoboni found that the valence change at the cathode was 1, and that the voltage was significantly greater than for the reduction of Pb^{++}. Costa (67) discusses the polarography of triethyl-, tripropyl-, and tributyllead bromides.

The data on ultraviolet spectra given by Riccoboni (293) include also some results for triethyllead chloride.

All the above results indicate the ionic nature of these compounds. There are apparently no data on the configuration of the ions. An ion such as R_3Pb^+ is analogous to a carbonium ion, and a planar configuration might be expected. A prediction as to the structure of a compound such as diphenyllead dichloride would be difficult to make. Diphenyllead sulfide has been found to be trimeric in solution (235) (0.5 g. in 16–23 g. of solvent), and it would not be surprising if diphenyllead oxide is also polymeric.

2. Preparation

(a) General

Compounds of the R_3PbAn type may be prepared by double decomposition reactions from the corresponding hydroxide, or oxide, or from other salts.

$$R_3PbAn + Y^- \rightarrow R_3PbY + An^-$$

$$R_3PbAn + OH^- \rightarrow R_3PbOH + An^-$$

$$R_3PbOH + HY \rightarrow R_3PbY + HOH$$

As starting material for such metathetical processes, it is necessary to obtain some initial R_3PbAn or R_2PbAn_2 material in some other way. This starting material is commonly a halide (occasionally a nitrate or other salt), and is obtained by cleavage of an appropriate R_4Pb compound with an acidic reagent such as halogen or hydrogen halide. The common methods of preparation of compounds like these fall into two classes: (*a*) cleavage and (*b*) metathesis. The employment of these reactions for the preparation of a variety of such compounds is well exemplified in the description given by Calingaert, Dykstra, and Shapiro (45) of selected methods for the preparation of some R_3PbAn and $R_2PbAn'_2$ compounds (where R was alkyl; An was Cl, Br, I, OH, $\frac{1}{2}SO_4$, $\frac{1}{2}CO_3$, HCO_3, $\frac{1}{2}S$, CN, or $OOCCH_3$; and An′ was OH).

(b) Cleavage reactions

The effect of various organic groups on cleavage reactions which lead to R_3PbAn or R_2PbAn_2 compounds has already been discussed. Cleavage may be carried out with almost any acidic reagent, including halogens, hydrogen halides, inorganic oxygen acids, carboxylic acids, acidic metal halides such as aluminum chloride, organometallic halides, and so on. For preparative purposes, halogen or hydrogen halide is most commonly employed. Cleavage of R_4Pb by halogen to R_2PbX_2 proceeds readily, even at very low temperatures, and care must be exercised if it is desired to stop at the R_3PbX stage. Inorganic oxygen acids (e.g., nitric acid) also tend to give R_2PbX_2 compounds. Cleavage may more readily be stopped at the R_3PbX stage if the cleaving agent is hydrogen halide, although the product usually contains R_2PbX_2 or lead halide as well, and there may be difficulty in determining the proper end point for the reaction. The preparation of triethyllead chloride by hydrogen chloride cleavage of tetraethyllead in hexane (45), or of triphenyllead chloride similarly from tetraphenyllead in benzene (119), are typical examples. The R_2PbX_2 compounds may be obtained by further cleavage with hydrogen halide (119). Continued action of cleavage reagents on R_2PbX_2 does not lead to $RPbX_3$ compounds; the next product is PbX_2.

The many other cleavage reagents mentioned above are not usually employed for the preparation of organolead halides. They may on occasion be used for the preparation of another product of the reaction: for example, tetraethyllead and arsenic trichloride give ethylarsenic dichloride in 95–97 per cent yield (186), and tetraethyllead and ferric chloride give very pure anhydrous ferrous chloride in 90 per cent yield (96). The action of metal halides with R_4Pb compounds has been rather extensively studied (23, 96, 140, 143, 186, 248, 249, 250, 251).

(c) Metathetical reactions

Metathetical processes involving reactions of organolead hydroxides or oxides with acids, or of R_3PbX or R_2PbX_2 compounds with other anions, scarcely require detailed discussion. Good examples of their use are given in the publications of Saunders and coworkers (162, 298, 300), as well as in the previously cited paper by Calingaert, Dykstra, and Shapiro (45).

(d) Direct preparation of R_3PbX from lead halide

Among the products of the direct reaction of lead chloride with a Grignard reagent is the R_3PbCl compound (221). The yield is so low in such cases as that of triphenyllead chloride that the method is useless for preparative purposes. Better than 50 per cent yields of some R_3PbCl compounds have, however, been obtained in this way (253). Although the method is far from being generally applicable, in cases where it applies it may shorten the synthetic procedures considerably, and this is important enough in practice to justify separate mention of this preparation.

(e) Other methods

Reactions of the type

$$(RN_2Cl)_2 \cdot PbCl_4 \rightarrow R_3PbCl$$

or

$$RN_2Cl \cdot PbCl_2 \rightarrow R_2PbCl_2$$

have been reported (199), but the yields are only a few per cent. The general procedure is to add a powdered metal such as tin, zinc, or copper to a suspension of the diazonium chloride–lead chloride complex and then to heat the mixture. Heating of $(RN_2Cl)_2 \cdot PbCl_4$ complexes without catalysts gave no organolead product (297). Reaction of diazonium chlorides with lead powder (245) also gave no such product.

Under special conditions (169) hexacyclohexyldilead reacts with carbon tetrachloride to yield tricyclohexyllead chloride and dicyclohexyllead dichloride. Carbon tetrabromide or hexabromoethane reacts with hexacyclohexyldilead, hexa-*p*-xylyldilead, tetramethyllead, or tetraethyllead, to yield the R_2PbBr_2 compounds.

3. Chemical properties

(a) Displacement of An^-

The most important chemical property of the organolead halides is their ready reaction with a Grignard reagent (or organolithium solution) to form new lead–carbon bonds.

$$R_3PbX + R'MgX \rightarrow R_3R'Pb + MgX_2$$

$$R_2PbX_2 + 2R'MgX \rightarrow R_2R'_2Pb + 2MgX_2$$

In such reactions X is nearly always halogen. The generality and ease of application of reactions of these types are so marked that little discussion is necessary. Most of the unsymmetrical organolead compounds whose preparation has been recorded have been obtained by such reactions, plus reactions involving cleavage of lead–carbon bonds (see Section II,C above).

(b) Cleavage reactions

Like other organolead compounds, these substances may undergo cleavage of lead–carbon bonds. The R_3PbX compounds are cleaved readily to R_2PbX_2, and the latter, with more difficulty, to lead chloride. This type of reaction has already been discussed (Section III).

Among the long list of reagents which will cleave lead–carbon bonds are organometallic halides such as R_3PbX. That is, the R_3PbX or R_2PbX_2 compounds will function as catalysts for their own redistribution, disproportionation, or decomposition. For instance, the equilibrium

$$(C_6H_5)_3PbX + (C_6H_5)_3PbX \rightleftarrows (C_6H_5)_2PbX_2 + (C_6H_5)_4Pb$$

has been demonstrated (10). A general discussion of the stability and decomposition of organolead chlorides, carbonates, and hydroxides has been given (52). Because of reactions of this sort, unsymmetrical organolead halides—for instance, $R_2R'PbX$ compounds—must be freshly prepared when they are used for synthetic purposes; otherwise, low yields and impure end products result (154).

(c) Reactions not involving bonds to lead

Diphenyllead dinitrate is converted to bis(*m*-nitrophenyl)lead dinitrate when it is heated to 100°C. in a sealed tube with nitric acid (329). A more convenient method is to add diphenyllead dinitrate to a sulfuric acid–nitric acid mixture at $-15°$ to $-10°$C. and allow the reaction mixture to stand at room temperature overnight (61). Diphenyllead diacetate may be nitrated with nitric acid at room temperature (303).

In the reduction of bis(*m*-nitrophenyl)lead dibromide (197), only aniline resulted when the reducing agent was dilute hydrochloric acid and iron, titanium trichloride, or stannous chloride. Reduction by ammonium sulfide also yielded aniline. Bis(*m*-nitrophenyl)lead oxide in alcoholic hydrochloric acid slowly treated with titanium trichloride gave bis(*m*-aminophenyl)lead dichloride (303).

c. $RPbAn_3$ COMPOUNDS

The formation of alkylplumbonic acids by reaction of an alkyl iodide with an alkaline solution of lead oxide at 5°C. has been claimed (230, 233), as has the preparation of alkyllead trihalides (231, 232) from an alkyl halide and a salt such as $CsPbCl_3$ (which is obtained from cesium chloride and lead chloride).

$$RI + NaPb(OH)_3 \rightarrow RPb(OH)_3 + NaI$$

$$RI + CsPbCl_3 \rightarrow RPbI_3$$

One $RPbCl_3$ compound, methyllead trichloride, is mentioned (232). Because of the lack of experimental data in these reports, little can be said concerning the nature of these compounds (see footnote 9 in reference 52). If they exist, they are probably not closely related to the R_3PbX and R_2PbX_2 compounds, in which the lead is in the cation. Instead, they are reported to be obtained from lead-containing anions of the type PbX_3^-, but the product may be covalent (like $PbCl_4$) or may ionize in some other fashion. The information available gives no basis for judgment.

Panov and Kocheshkov (279) have described the preparation of better-characterized aryllead compounds of the type $RPbAn_3$, where An is carboxylate or alkoxide. They were prepared by the reaction

$$R_2PbAn_2 + HgAn_2 \xrightarrow{CH_3COOH} RPbAn_3 + RHgAn$$

where R was phenyl or *p*-tolyl and An was acetate or butyrate. The products were apparently stable solids with definite melting points. They would undergo double decomposition reactions to produce other similar compounds.

$$RPbAn_3 + 3HAn' \rightarrow RPbAn'_3 + 3HAn$$

(Here An was methacrylate or benzyloxide.)

D. R_3PbM' AND $R_2PbM'_2$ COMPOUNDS[1]

1. *General*

Although no compound of this type has been isolated, the use of such substances as synthetic intermediates for the preparation of unsymmetrical organolead compounds is recently becoming fairly well understood (97, 101, 127, 129). The R_3PbM' compounds are presumably to be formulated as $M'^+(R_3Pb)^-$, although physical data in support of this formulation are not available. The R_3Pb^- ion would then be analogous to a carbanion and would be a strong nucleophilic reagent. This is the essential chemical nature of these substances, which are especially useful for the establishment of a lead–carbon bond by nucleophilic displacement on carbon. Used in this way, these nucleophilic lead-containing anions can serve to complement the electrophilic lead-containing cations of the R_3PbX compounds. Syntheses which would be very difficult through one type of reagent may sometimes be accomplished easily through the other.

The preparation and chemical properties of R_3PbM' and $R_2PbM'_2$ compounds have been studied under two main conditions: (*a*) in liquid ammonia or mixed solvents containing liquid ammonia and (*b*) in diethyl ether.

2. *Preparation*

(a) In liquid ammonia

In 1939, the preparation of triphenylleadsodium by the action of sodium in liquid ammonia on hexaphenyldilead or triphenyllead halides was described

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[1] R is any organic group and M′ is an active metal.

(81, 98). Further investigation (110) showed that lithium, potassium, rubidium, calcium, strontium, or barium would react in similar fashion with hexaphenyldilead, and also that trialkyllead-metal compounds such as triethylleadlithium could be obtained from trialkyllead chlorides. Trialkyl- and triaryllead-metal compounds were also prepared (101) by the reaction of R_4Pb compounds with sodium.

$$R_3PbPbR_3 + 2Na \xrightarrow{NH_3} 2R_3PbNa$$

$$R_3PbCl + 2Na \xrightarrow{NH_3} R_3PbNa + NaCl$$

$$R_4Pb + 2Na + NH_3 \rightarrow R_3PbNa + RH + NaNH_2$$

A comparative study of these various methods of preparation has been reported (101). The relative yields of R_3PbM' compounds produced when various metals were used (with hexaphenyldilead) have also been studied (110). It is noteworthy that, in this latter study, the Group IIA metals acted as monovalent metals, that is, for maximum yields it was necessary to use two gram-atoms of metal per mole of hexaphenyldilead. The yields in all such studies are estimated by treating the R_3PbM' compound with an alkyl halide and determining the amount of $R_3R'Pb$ formed. Ethyl bromide or, preferably, benzyl chloride is the halide commonly used.

The reactions of diphenyllead dihalides with metals in liquid ammonia were also investigated (96, 110). Diphenyllead dibromide with four equivalents of lithium gave diphenylleaddilithium, which with ethyl bromide yielded diphenyldiethyllead, among other products. Many attempts to prepare pure diphenyllead by such reactions failed (97). The reactions involved were rather complicated, and careful choice of experimental conditions was necessary to obtain reasonable yields of $R_2PbM'_2$.

(b) In diethyl ether

Lithium derivatives of the type of triphenylleadlithium can be obtained from the reaction of aryllithium solutions with lead dichloride in ether at low temperatures (17, 127, 129). This reaction proceeds (129) in two distinguishable stages, corresponding to the following equations:

$$2C_6H_5Li + PbCl_2 \rightarrow (C_6H_5)_2Pb + 2LiCl$$

$$(C_6H_5)_2Pb + C_6H_5Li \rightarrow (C_6H_5)_3PbLi$$

The first reaction is irreversible and produces a yellow intermediate which is believed to be diphenyllead in some form. The second reaction is apparently reversible, so that these preparations can react either as triphenylleadlithium or as phenyllithium. The preparation of R_3PbLi compounds in this manner is simple and proceeds directly from lead chloride; the technique is perhaps more convenient than that employing liquid ammonia. For these reasons, preparation of the R_3PbLi compound in ether, when possible, is probably more desirable for practical purposes than the preparation in liquid ammonia.

The formation of tricyclohexylleadsodium by long-continued shaking of hexacyclohexyldilead with sodium in ether has been reported (168).

3. Chemical properties

(a) Displacement of M′

The most important chemical property of R_3PbM' compounds is their reaction with an alkyl halide to produce a new lead–carbon bond.

$$R_3PbM' + R'X \rightarrow R_3R'Pb + M'X$$

With organoleadlithium compounds in ether, this reaction proceeds rapidly and smoothly, to give high yields of $R_3R'Pb$ (127, 129), if the halogen in R′X is reactive or moderately so and if R′ is such that it will not react with the organolithium component of the equilibrium. In liquid ammonia, this type of reaction gives results which are somewhat more variable. Suitable experimental conditions for the reaction of R_3PbM' compounds in liquid ammonia with benzyl chloride or ethyl bromide have been described (101).

The results of reactions such as

$$R_2PbM'_2 + 2R'X \rightarrow R_2R'_2Pb + 2M'X$$

in liquid ammonia (96, 110) are variable and seem to indicate that the exact nature of the $R_2PbM'_2$ compounds requires further investigation. Such reactions are at present not very useful for synthetic purposes.

(b) Cleavage reactions

The behavior of the triphenylleadlithium system in ether (129) indicates that there is spontaneous cleavage of a phenyl anion from the triphenyllead anion; that is, that triphenylleadlithium exists in equilibrium with diphenyllead and phenyllithium.

$$(C_6H_5)_3PbLi \rightleftarrows (C_6H_5)_2Pb + C_6H_5Li$$

The chemical evidence for this equilibrium includes the demonstration that either phenyllithium or triphenylleadlithium is available in such a preparation, although the diphenyllead component has not yet been isolated in pure form.

This reaction is of interest in that it represents a spontaneous and reversible change between two-covalent lead (structure I, page 103) and an anion derived from the four-covalent state (structure II, page 103). This spontaneous cleavage of an R group from R_3Pb^- also has practical importance because of certain limitations which it places on the types of unsymmetrical lead compounds which can be satisfactorily prepared by use of triphenylleadlithium as an intermediate. Thus, attempts (128) to convert triphenylleadlithium to $(C_6H_5)_3PbR'$ types in which R′ contained any group (such as NO_2, NH_2, etc.) which would be expected to react rapidly with phenyllithium have not been successful. (This statement also holds for R_3PbM' compounds in liquid ammonia, although the occurrence in this solvent of an equilibrium like that above has not been suggested.) Also, triarylleadlithium preparations of the type $R_2R'PbLi$ in ether do not give pure $R_2R'R''Pb$ compounds, but lead instead to mixtures, because of equilibration of the groups (129). That is, a process very similar to redistribution occurs with these organolead anions (as with the cations in the R_3PbX compounds).

VI. Physiological Properties of Organolead Compounds

The poisonous nature of alkyllead compounds is well known and must be borne in mind during experimental work with these compounds. This toxicity is exhibited by all such compounds, but most of the available data pertain to tetraethyllead. Tetraethyllead poisoning differs (256) from chronic lead poisoning due to inorganic lead. The symptoms of the former are a marked drop in blood pressure, a drop in body temperature, sleeplessness, headaches, nightmares, hallucinations, and finally insanity and death. These emotional and nervous disturbances are not especially characteristic of inorganic lead poisoning, and they point up the fact (35) that tetraethyllead is a stable, covalent, lipid-soluble organic substance which may be absorbed rapidly by the soft tissues of the body and which apparently concentrates in nervous tissue. Autopsies (273) have shown that after death from tetraethyllead poisoning a high concentration of lead occurs in the brain tissue and in the liver and kidneys. Tetraethyllead may be taken into the body by absorption through the skin or by breathing the vapor. The lethal dose, for one exposure, is relatively large as compared to other poisons, so that the material is not intensely toxic. On the other hand, the effect is cumulative, and continued exposure to small doses (for instance, continued breathing of the vapor of the substance over a period of time) will result in serious poisoning. Elimination of the lead from the body is very slow, because of the resistance of tetraethyllead to hydrolysis and the insoluble nature of the resulting inorganic lead compounds. Treatment is therefore difficult and tedious, and the employment of proper precautions beforehand is much the better course. Work should be carried on in well-ventilated hoods, preferably with intakes at table level, and all parts of the body should be protected against contact with the material—for instance, by use of rubber gloves in good condition.

The aryllead compounds are less hazardous because of their much lower volatility. There is no reason to suppose that they are inherently any less toxic than the alkylleads, and suitable precautions should be observed. Spilling of solutions in organic solvents, particularly on the hands or body, should be guarded against, and the dispersal of dusts should be avoided.

The organolead halides of the type R_3PbX possess another disagreeable physiological property, in that they are active sternutators. Some of them can make an atmosphere irrespirable when they are present in even very low concentrations. The effect of structural changes in organolead salts upon the sternutatory properties was studied extensively by Saunders and coworkers (162, 298, 300, 301), and the results have been summarized by McCombie and Saunders (242).

Lead compounds have been suggested for pharmacological use against cancer, and organolead compounds have been tested for this purpose (18, 212). Research along this line is continuing, although the toxicity of the lead compounds, and the relative insolubility of many of them in water, lead to difficulties in such applications.

VII. ANALYSIS OF ORGANOLEAD COMPOUNDS

Organolead compounds are analyzed quantitatively for lead by conversion of the lead to an inorganic form in which it is weighed. This is accomplished usually by treatment with concentrated hydrochloric acid, with halogen, or with nitric or nitric–sulfuric acids. Decomposition by halogen in the cold (150) is the best general method for the analysis of the volatile alkyllead compounds. The lead is weighed as PbX_2 (150), or the determination may be completed volumetrically (35). For the aryllead compounds the best method involves cleavage and oxidation by nitric–sulfuric acid (or by nitric acid alone, where applicable; or by sulfuric acid followed by 30 per cent hydrogen peroxide). This determination, also, may be completed either gravimetrically (118) or volumetrically (300). The nitric–sulfuric acid method (118) is inapplicable for many compounds containing more than two alkyl groups, because of loss of sample by volatilization before decomposition.

Analysis of dilute solutions containing tetraethyllead (3, 4, 46) presents a special problem of technical importance.

Quantitative analysis of organolead compounds for elements other than lead (for instance, halogen or sulfur) is by the usual methods involving combustion or sodium peroxide fusion. The solution from the sodium peroxide fusion may also be analyzed for lead, but the acid decompositions mentioned above are more rapid and convenient if lead alone is to be determined.

Qualitative tests for lead in organic compounds or solutions (35) present no particular difficulties.

VIII. USES OF ORGANOLEAD COMPOUNDS

The employment of tetraethyllead as an antiknock agent in motor fuel is a fairly large-scale use of an organometallic compound. In 1950 the United States consumed 114,000 tons of lead in the production of tetraethyllead. This represents approximately 10 per cent of the total United States consumption of lead. Numerous other organolead compounds are suggested in patents for employment as antiknock agents.

The patent literature contains numerous references to other suggested applications of organolead compounds. In the absence of any published information that lead compounds are actually being employed in these ways, it must probably be assumed that these are mostly "protection" patents. Thus, organolead compounds have been suggested for disinfectants and insecticides, or as driers, antioxidants, and inhibitors (2, 60). Polymers containing organolead structures have been described (227), and the use of organolead compounds for the stabilization of vinyl resins has been mentioned (13, 65, 296, 336). Tetraethyllead can catalyze radical polymerization (78, 201), as well as other types of reactions (160). Its use in a process for coating iron with metallic lead has been described (177). Use of some organolead compounds in explosive compositions has been patented (31, 333).

In the laboratory, the uses of organolead compounds are somewhat limited. They are not widely employed, as are some organometallic compounds, for organic synthetic purposes, for reasons which will be clear from the description above of their chemical nature. Perhaps their chief laboratory use is as a source of alkyl or aryl radicals. The catalysis of radical polymerization (78, 201) has already been mentioned, and it was found (201) that for the polymerization of ethylene or propylene, tetramethyllead was the best catalyst among a group of various metal alkyls, diazo compounds, etc. which were investigated. Tetraalkylleads have been used as catalysts for the thermal decomposition of hydrocarbons (76), and for the decomposition of organic peroxides and their formation from alkenes and atmospheric oxygen (16). The use of organolead compounds in the early studies of alkyl and aryl radicals (70, 276, 277, 278) has been mentioned; in later studies they have also been used, indirectly, for similar purposes (15, 307).

Geiger counters filled with tetramethyllead vapor, instead of the usual mixture of argon and ethanol, operated at 100 per cent efficiency at pressures as low as 14 mm. of mercury. The "dead time" was therefore very short (about 5×10^{-5} sec.), and the counting rate could be very high (252).

It is probable that as ways are devised for the synthesis of more specifically constructed organolead molecules containing varied types of functional groups, new applications will be found for the resulting compounds.

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