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MECHANISMS OF REACTIONS INVOLVED IN THE PREPARATION OF ORGANOLEAD COMPOUNDS
CONTAINING WATER-SOLUBILIZING GROUPS

by

Lawrence Summers

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INTRODUCTION

During the ninety-eight years which have elapsed since the first organometallic derivative of lead was described, the field of organolead compounds has been one of the most thoroughly investigated subdivisions of organometallic chemistry. Approximately six hundred organolead compounds have been described. A complete bibliography is a necessity to a worker in this field. Reviews of the subject[1,2,3,4] have appeared occasionally in the literature. The latest complete review[3] covers the literature up to about 1935, while the last detailed review[1] in English was published in 1925. Investigators in this Laboratory, however, have available in addition an excellent and thorough bibliography of organolead literature by Robert W. Leeper[5], in which publications through 1941, and some dated 1942, are listed. There is given also, in

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[1] G. Calingaert, *Chem. Revs.*, *2*, 43 (1925).

[2] K. A. Kocheshkov, *Uspekhi Khim.*, *3*, 83 (1934) [*C. A.*, *28*, 5402 (1934)].

[3] E. Krause and A. von Grosse, "Die Chemie der metallorganischen Verbindungen", Gebruder Borntraeger, Berlin, 1937, pp. 372-429.

[4] H. Gilman, "Organic Chemistry, An Advanced Treatise", 2nd ed., John Wiley and Sons, New York, 1943, Chapter 5, *Organometallic Compounds*.

[5] R. W. Leeper, Doctoral Dissertation, Iowa State College (1942).

tabular form, a list of all organolead compounds known up to that time.

In this thesis, therefore, the literature on organolead chemistry is reviewed from the beginning of 1942 through 1949, with some additional references from American, English, and German journals for 1950. This review forms the first part of the historical section. The literature coverage is believed to be complete and to include all references on organolead chemistry for the period indicated. The tabulation of organolead compounds which concludes the survey is arranged according to the plan used by Leeper[5], and therefore serves as an extension of the Leeper tables to the present time. All organometallic compounds of lead which have received mention in the literature during this period are listed.

This thesis, as is indicated by its title, describes some investigations of the nature, scope, and mechanisms of certain reactions useful for the preparation of organolead compounds, particularly of compounds containing functional groups which might confer the property of water-solubility. In all its stable organometallic compounds lead exhibits a covalence of four, but the common inorganic starting material for the preparation of such compounds is either lead dichloride, $PbCl_2$, or lead metal (often in the form of a lead-sodium alloy). In these preparations there is thus an oxidation step, or steps, which may involve organometallic intermediates in which the valence of lead is other than four. In an investigation concerned in part with the mechanisms of some of these reactions, it was therefore considered desirable to acquire as thorough an understanding as possible of the nature of certain valence states of lead. The second part of the historical section is devoted to a review of the theoretical and experimental literature on the valence states of the Group IV-B elements, with particular reference to lead, tin, germanium, and silicon. The second part differs from the first part in organization and purpose. Whereas the first part represents in abstract and tabular form a complete résumé of the material which has been published on organolead chemistry during the period covered, the second part on the other hand represents a discussion and critical survey, based on selected references drawn from any part of the chemical or physical literature, of the present state of knowledge on its subject.

HISTORICAL

Survey of the Literature on Organolead Chemistry from 1941 to the Present Time

Preparation and chemical properties of organolead compounds

Preparative reactions.--During this period few new synthetic methods for the preparation of organolead compounds have been described. One novel synthesis of tetraalkylleads has however been reported[6] from this Laboratory. It was found that the reaction

$$3RLi + PbX_2 + RI \longrightarrow R_4Pb + LiI + 2LiX$$

proceeded smoothly in ether to give for instance a 92% yield of tetramethyllead from methyllithium, methyl iodide, and lead iodide. The reactions were carried out by adding the organolithium compound to a mixture of the other reagents in ether, without cooling--that is, essentially at the refluxing temperature of the ether. Metallic lead was produced as an intermediate. A mechanism involving the reactions

$$4RLi + 2PbX_2 \longrightarrow R_4Pb + Pb + 4LiX$$
$$2RI + Pb \longrightarrow R_2PbI_2$$

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[6] H. Gilman and R. G. Jones, J. Am. Chem. Soc., 72, 1760 (1950).

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

is suggested. This reaction is discussed further in the discussion part of this thesis. It was also applied[5] in the aromatic series, to give an 80% yield of tetraphenyllead from phenyllithium, iodobenzene, and lead chloride. The Grignard reagent also gave, apparently, good results for alkyl compounds[6], but not for phenyl compounds[5].

Other synthetic studies during this time have described mainly the extension and perfection of previously known methods. The best procedures for the synthesis of certain basic alkyllead starting materials are described in a paper by Calingaert and others[7], in which preparations for R_3PbX and $R_2PbX'_2$ compounds (where R = alkyl, X = Cl, I, OH, $\frac{1}{2}SO_4$, $\frac{1}{2}CO_3$, HCO_3, $\frac{1}{2}S$, CN, or $OOCCH_3$, and X' = OH) are given in detail. The reactions used are not new, but since Dr. Calingaert is one of the two leading authorities on organolead chemistry these experimental details from his laboratory are very useful to the laboratory worker in this field. For R_3PbCl compounds, cleavage of R_4Pb compounds with HCl gas in hexane is recommended as giving a purer product than cleavage in ether or with aqueous hydrochloric acid. The hydroxides were prepared from wet silver oxide and the corresponding chlorides. The carbonates were prepared from the hydroxides with carbon dioxide,

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[7] G. Calingaert, F. J. Dykstra, and H. Shapiro, J. Am. Chem. Soc., 67, 190 (1945).

and the other salts by double decomposition reactions, except that the sulfate was best obtained by air oxidation of the sulfide.

Saunders[8,9,10] and co-workers have also published rather exact directions for the preparation of a large number of trialkyllead salts, where the alkyl group was ethyl, n-propyl, n-butyl, or in some cases methyl. The preparations involved usually the reaction of the trialkyllead hydroxide with the desired acid, or of the trialkyllead halide with the sodium salt of the acid. A laboratory method of preparation of tetraalkylleads from lead-sodium alloy is also given.

Aspects of the industrial synthesis of tetraethyllead have been the subject of a number of patents. In one of these[11] it is stated that lead metal in finely divided, non-oxidized form will react with ethyl or methyl chloride or bromide at 100-130° in the presence of iodine or iodides as catalysts to give tetraalkyllead compounds. The finely divided residual lead recovered from the usual commercial preparation of tetraethyllead is especially recommended. The best catalysts were iodine or lead iodide; good catalysts were

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[8] B. C. Saunders and G. J. Stacey, *J. Chem. Soc.*, 919 (1949).

[9] R. Heap and B. C. Saunders, *J. Chem. Soc.*, 2983 (1949).

[10] B. C. Saunders, *J. Chem. Soc.*, 684 (1950).

[11] H. W. Pearsall (to Ethyl Corporation), U. S. Patent 2,414,058 (1947) [*C. A.*, *41*, 2430 (1947)].

sodium iodide, potassium iodide, methyl iodide, triethyllead iodide, mercuric iodide, and cuprous iodide. Of less value were the iodides of cadmium, cerium (III), bismuth(III), caesium, zinc, arsenic(V), and antimony(V), or _n_-propyl iodide.

Standard procedures were used by Meals[12] for the synthesis of a number of organolead compounds containing long-chain normal alkyl groups. A noteworthy preparative detail here is the fact that the R_3PbCl intermediates, such as for instance tri-_n_-dodecyllead chloride, were found to result in good yield directly from the Grignard reagent and lead chloride, $PbCl_2$. (This is not the case with, for instance, triphenyllead chloride. The yield of the latter material from the direct reaction[13] is so poor that the method is useless for preparative purposes.)

The reaction of allylmagnesium bromide with lead chloride under customary conditions was studied[14]. No products were isolated.

The Nesmeyanov diazo method for the preparation of organometallic compounds was applied[15] for tetraphenyllead. Phenyldiazonium fluoborate, $C_6H_5N_2BF_4$, and lead in acetone at

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[12] R. N. Meals, _J. Org. Chem._, _9_, 211 (1944).

[13] E. Krause and O. Schlöttig, _Ber._, _58_, 427 (1925).

[14] K. V. Vijayarahavan, _J. Ind. Chem. Soc._, _22_, 227 (1945) /_C. A._, _40_, 4659 (1946)/.

[15] A. N. Nesmeyanov and K. A. Kocheshkov, _Bull. acad. sci. U. R. S. S., Classe sci. chim._, 522 (1945) /_C. A._, _42_, 5870 (1948)/.

6° gave 15% yield. In ethanol, gas was evolved only when the temperature had risen to 35°, and no tetraphenyllead resulted. In other investigations, Nesmeyanov and co-workers[16] studied the properties of bis(2-chlorovinyl)lead compounds. Bis(*trans*-2-chlorovinyl)mercury and lead tetraacetate in chloroform gave bis(2-chlorovinyl)lead diacetate. From this, derivatives such as the dichloride and sulfate were prepared. The dichloride with mercury metal gave a 99% yield of (*trans*-2-chlorovinyl)-mercuric chloride, indicating that the 2-chlorovinyl group had retained its *trans* configuration. The dichloride with excess phenylmagnesium bromide gave 84% yield of tetraphenyllead, and ethylene gas was evolved. On the basis of his work with the 2-chlorovinyl compounds of mercury, tin, and lead, Nesmeyanov concludes[17] that in electrophilic or radical substitutions at an ethylenic carbon atom the original stereochemical configuration (*cis* or *trans*) is preserved.

Cleavage reactions.--Some investigations of cleavage reactions of organolead compounds have been continued during this period. Malinovskiĭ[18] found that when tetraphenyllead

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[16] A. N. Nesmeyanov, R. Kh. Freidlina, and A. Kochetkov, *Izvest. Akad. Nauk S. S. S. R., Otdel, Khim. Nauk*, 127 (1948) /*C. A.*, **43**, 1716 (1949)/

[17] A. N. Nesmeyanov and A. E. Borisov, *Doklady Akad. Nauk S. S. S. R.*, **60**, 67 (1948) /*C. A.*, **43**, 560 (1949)/.

[18] M. S. Malinovskiĭ, *Trudy Gor'kov Gosudarst. Pedagog. Inst.*, No. **5**, p. 39 (1940); *Khim. Referat. Zhur.*, No. 2, p. 45 (1941) /*C. A.*, **37**, 3070 (1943)/.

was heated with acetyl chloride in the presence of aluminum chloride one phenyl group was split off readily (and probably others, with greater difficulty). Diphenylmercury reacted smoothly also, but tetraphenyltin gave a tar, and organophosphorus compounds did not react. Manulkin[19] studied the action of aluminum and of ferric chloride on tetraalkyl derivatives of silicon, tin, and lead. Tetraethyllead with aluminum chloride in chloroform gave 81% yield of lead chloride. Tetra-<u>n</u>-butyllead with ferric chloride in chloroform gave tri-<u>n</u>-butyllead chloride (36%), but in this case again the ethyl compound gave only lead chloride (51-66%). With mercuric chloride[20] tetraethyllead in absolute ethanol gave ethylmercuric chloride (92%) and triethyllead chloride (37%) according to the reaction

$$(C_2H_5)_4Pb + HgCl_2 \longrightarrow C_2H_5HgCl + (C_2H_5)_3PbCl.$$

Tetraphenyllead with alpha-naphthol[21] at 130° gave 29% of metallic lead, plus some naphthalene, whereas tetraphenyltin did not react. With pyrogallol, neither the lead nor the tin compound underwent any reaction.

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[19] Z. M. Manulkin, <u>Zhur</u>. <u>Obshchei</u> <u>Khim</u>., <u>18</u>, 299 (1948) /_<u>C</u>. <u>A</u>., <u>42</u>, 6742 (1948)_7.

[20] Z. M. Manulkin, <u>Zhur</u>. <u>Obshchei</u> <u>Khim</u>., <u>16</u>, 235 (1946) /_<u>C</u>. <u>A</u>., <u>41</u>, 90 (1947)_7.

[21] M. M. Koton, <u>Zhur</u>. <u>Obshchei</u> <u>Khim</u>., <u>17</u>, 1307 (1947) /_<u>C</u>. <u>A</u>., <u>42</u>, 1903 (1948)_7

In a paper on organotin compounds, Arbuzov[22] states that triphenyllead iodide heated with triethyl phosphite, $(C_2H_5O)_3P$, gave only tetraphenyllead, while triethyllead bromide gave a white amorphous solid. These compounds did not, therefore, undergo the "Arbuzov reaction", which is reported to proceed readily with organotin compounds.

$$R_3SnX + (R'O)_3P \longrightarrow R_3SnPO_3R'_2$$

The most interesting application of cleavage reactions of organolead compounds described during this time is given in a paper by Kharasch and co-workers[23], who in rather large-scale preparations obtained a 95-97% yield of ethylarsenic dichloride from arsenic trichloride and tetraethyllead. The reaction

$$2AsCl_3 + (C_2H_5)_4Pb \longrightarrow (C_2H_5)_2PbCl_2 + 2C_2H_5AsCl_2$$

was spontaneous at room temperature. The next step,

$$(C_2H_5)_2PbCl_2 + AsCl_3 \longrightarrow C_2H_5AsCl_2 + PbCl_2 + C_2H_5Cl,$$

proceeded slowly at room temperature, but rapidly above 90°. Similar reactions took place with phosphorus trichloride, to give ethylphosphorus dichloride in 89-96% yields, and with antimony trichloride (yield of $C_2H_5SbCl_2$, 71%). At 120°, the reaction

$$2C_2H_5AsCl_2 + (C_2H_5)_4Pb \longrightarrow (C_2H_5)_2PbCl_2 + 2(C_2H_5)_2AsCl$$

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[22] B. A. Arbuzov and A. N. Pudovik, Zhur. Obshchei Khim., 17, 2158 (1947) [C. A., 42, 4522 (1948)].

[23] M. S. Kharasch, E. V. Jensen, and S. Weinhouse, J. Org. Chem., 14, 429 (1949).

could be carried out.

Organolead-metal compounds.--The study of the formation of such compounds in liquid ammonia was continued in this Laboratory. It was found[24] that R_3PbNa compounds could be prepared readily by reaction of R_4Pb derivatives with sodium in liquid ammonia, as well as by the previously reported reactions involving R_6Pb_2 or R_3PbCl compounds as starting materials. The R_4Pb compounds gave the best yields (83% in the case of triethyllead-sodium). The R_6Pb_2 derivative, however, gave the purest product in the case of the phenyl compound. The best experimental conditions for the derivatization of the R_3PbM' compounds with for instance benzyl chloride or ethyl bromide in liquid ammonia or in ether-ammonia were established. The relative ease of cleavage of various groups from organolead compounds by sodium in liquid ammonia was studied. The series established was, in order of decreasing ease of cleavage, allyl, benzyl, sec-butyl, n-butyl, ethyl, methyl, phenyl, p-dimethylaminophenyl. This is almost the exact reverse of series established using hydrogen halides for cleavage. The reactions of hexaphenyldilead with lithium, sodium, potassium, rubidium, calcium, strontium, and barium in liquid ammonia were compared[5], and it was found that the yield of R_3PbM' compound was best with lithium or calcium, and

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[24] E. Bindschadler, Doctoral Dissertation, Iowa State College (1941). See Iowa State Coll. J. Sci., 16, 33 (1941) /C. A., 36, 4476 (1943)/.

decreased progressively as the atomic weight of the active metal increased within each group of the periodic table. The Group II-A metals acted as monovalent metals in this reaction--that is, for maximum yields it was necessary to use two gram-atoms of the metal per mole of hexaphenyldilead.

The reactions of diphenyllead dihalides with metals in liquid ammonia were also investigated[25,5]. Diphenyllead dibromide with four equivalents of lithium gave diphenylleaddilithium, which with ethyl bromide yielded diphenyldiethyllead. Many attempts to prepare pure diphenyllead by such reactions failed[25]. The reactions involved were rather complicated, and careful choice of experimental conditions was necessary to obtain reasonable yields of $R_2PbM'_2$ compounds.

The reactions of metals in liquid ammonia with organic compounds, including organometallics, are the subject of a recent review by Watt[26]. However, the discussion of organometallic compounds of the Group IV-B metals is limited (as the author states) to work done up to about 1935. Organolead compounds, which were not successfully cleaved in liquid ammonia until 1939, are not discussed, although they are included in tables of literature references.

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[25] L. D. Apperson, Doctoral Dissertation, Iowa State College (1940). See Iowa State Coll. J. Sci., 16, 7 (1941) [C. A., 36, 4476 (1942)].

[26] G. W. Watt, Chem. Revs., 46, 317 (1950).

Hein[27] reports that hexacyclohexyldilead, shaken with sodium in ether under nitrogen for three days or more, gave $(C_6H_{11})_3PbNa$ solutions. These are described as colorless and stable for months. Color was developed at first, and lead (at least half the total amount present) was deposited as metal. The reaction with iodine was studied. The shaking was apparently at room temperature, in the dark. If the organolead-sodium compound was actually present, this is the first record of the preparation of such a compound in ether. The solutions used were very dilute, however, and the procedure would apparently be of little value as a synthetic method.

Use of organolead compounds in the study of free radicals.--Organolead compounds have previously found use as sources of free radicals, especially alkyl radicals, as for instance in the experiments of Paneth. Semerano and Riccobini and co-workers[28,29,30,31,32], in a series of papers which were published mostly in 1941 but not received in this country until

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[27] F. Hein and E. Nebe, Ber., 75, 1744 (1942).

[28] G. Semerano and L. Riccobini, Ricerca sci., 11, 269 (1940); [Chem. Zentr. 1941, I, 350].

[29] G. Semerano, L. Riccobini, and L. Götz, Z. Electrochem., 47, 484 (1941).

[30] G. Semerano and L. Riccobini, Z. physik. Chem., A189, 203 (1941).

[31] G. Semerano and L. Riccobini, Ber., 74B, 1089 (1941).

[32] G. Semerano, L. Riccobini, and F. Callegari, Ber., 74B, 1297 (1941).

considerably later, report a study of the behavior of free alkyl radicals at low temperatures. These authors' central idea is that free alkyl radicals produced, for instance according to the Paneth technique, by pyrolysis of more stable organometallic compounds (such as dimethylmercury or tetramethyllead) are liberated only at high temperatures and therefore necessarily in highly activated states. Their reactions are then complicated by their high energy content, and to study the perhaps simpler reactions of alkyl radicals in their ground states, means must be sought whereby they can be formed at much lower temperatures. Decomposition of very unstable organometallic compounds, such as methylsilver, was the method chosen. The alkylsilver compounds were formed by the reaction of the appropriate tetraalkyllead compound with silver nitrate in ethanol or methanol at low temperatures, and were not isolated. They were instead allowed to decompose by warming, and the products were identified. The article[30] in the Z. physik. Chem. contains an extensive theoretical discussion; the experimental chemistry involving the lead compounds is essentially covered in the two papers[31, 32] in the Ber. English workers[33] have since reported an investigation covering practically the same material. In general, these researches showed that methyl radicals thus produced from methylsilver

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[33] C. E. H. Bawn and F. J. Whitby, Discussions Faraday Soc., 2, 228 (1947).

dimerized to give ethane, without disproportionation products. Higher alkyl radicals, however, gave disproportionation. Thus for instance n-propylsilver gave propane and propene as well as hexane. The use of tetramethyllead with copper salts gave a different result[33]; the methylcopper thus 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 were investigated in this Laboratory[34]. It was found that 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 both with the R_4M compound and the inorganic salt. Tetraphenylsilane and tetraphenylgermanium were not cleaved by silver nitrate. The methyl compounds were also studied.

Organolead compounds as catalysts.--In connection with the production of free radicals by organolead compounds on heating, their use as catalysts for various radical-type reactions should be mentioned. In a study[35] of the number of moles of ethylene or of propylene polymerized per mole of various catalysts at 276° and 250 atmospheres, it was found

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[34] H. Gilman and L. A. Woods, J. Am. Chem. Soc., 65, 435 (1943).

[35] P. L. Kooijman and W. L. Ghijsen, Rec. trav. chim., 66, 673 (1947).

that tetramethyllead initiated the polymerization of about 480 moles of ethylene or 1850 moles of propylene. This lead compound was in this respect the best among various metal alkyls, diazo compounds, etc., which were investigated. Tetraalkylleads are mentioned as catalysts for the production of higher alkyl chlorides from ethylene and hydrogen chloride[36], for thermal decomposition of hydrocarbons[37], and for the decomposition of organic peroxides and their formation from alkenes and atmospheric oxygen[38].

Reactions involving metallic lead.--Kocheshkov and coworkers studied the nature of the reactions of metals with organolithium compounds[39]. They were concerned mostly with tin and tin amalgams, but they found that lead powder with phenyllithium gave, in 185 hours at room temperature, a 5% yield of tetraphenyllead. The reaction of lead powder with lithium and bromobenzene in ether, however, gave a 23% yield in 25 hours. This work is of interest in comparison with the synthesis of tetramethyllead mentioned above[6], and is considered further in the discussion section of this thesis. The

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[36] W. E. Hanford and J. Harmon (to Du Pont), U. S. Patent 2,418,832 (1947) [*C. A.*, *42*, 581 (1948)].

[37] G. C. Eltenton, *J. Chem. Phys.*, *15*, 465 (1447).

[38] F. I. Berezovskaya, E. K. Varfolomeeva, and V. G. Stefanovskaya, *Zhur. Fiz. Khim.*, *18*, 321 (1944) [*C. A.*, *39*, 2024 (1945)].

[39] T. V. Talalaeva and K. A. Kocheshkov, *Zhur. Obshchei Khim.*, *12*, 403 (1942) [*C. A.*, *37*, 3068 (1943)].

reactions of lead with compounds such as diphenyllead dichloride were also investigated to some extent[40].

Reaction of lead chloride with phenyllithium.--In a brief note from this Laboratory[41], containing no experimental detail, it is stated that lead chloride reacts at -5° with phenyllithium in ether to give triphenyllead-lithium. This suggestion was the point of departure for some of the work described in the present thesis, and the nature of the reaction is discussed at length below. It is stated also that hexaphenyldilead with phenyllithium gives tetraphenyllead and triphenyllead-lithium.

Organolead metal carbonyls.--Hein and others[42,43,44] studied the reactions of some organometallic compounds of heavy metals, including lead, with iron pentacarbonyl and iron carbonyl hydride derivatives. They report that diethyllead iron tetracarbonyl results from triethyllead hydroxide and

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[40] M. M. Nad' and K. A. Kocheshkov, Zhur. Obshchei Khim., 12, 409 (1942) [C. A., 37, 3068 (1943)].

[41] E. Bindschadler and H. Gilman, Proc. Iowa Acad. Sci., 48, 273 (1941) [C. A., 36, 1595 (1942)].

[42] F. Hein and H. Pobloth, Z. anorg. allgem. Chem., 248, 84 (1941).

[43] F. Hein and E. Heuser, Z. anorg. Chem., 255, 125 (1947).

[44] F. Hein and H. Scheiter, Z. anorg. Chem., 259, 183 (1949).

calcium iron carbonyl hydride, as unstable red plates. The reactions were in general not clear-cut, and definite products were isolated in few cases.

Compounds of the type R_6Pb_2 and R_2Pb.--The intriguing problems regarding the nature and reactions of these types of lead compounds have received some further attention. Malatesta[45] reports cryoscopic molecular weight determinations on hexaphenyldilead and hexacyclohexyldilead in naphthalene and in biphenyl. The lead compounds were dimeric, even at the rather high freezing points of these solvents. Calingaert[46] found that the previously accepted formulation

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

represented correctly the result when a mixture of hexamethyldilead and hexaethyldilead was heated at 100° under nitrogen for five hours. The metallic lead found was within 5% of that required by the above equation. All the possible lead alkyls were obtained; and since lead alkyls do not undergo redistribution in the absence of a catalyst, the interchange of groups is believed to have occurred before or during the decomposition of the R_6Pb_2 compounds. (This result is to be compared with a previous report[47] that hexaphenyldilead and hexa-p-tolyldilead

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[45] L. Malatesta, Gazz. chim. ital., 73, 176 (1943).

[46] G. Calingaert, H. Soroos, and H. Shapiro, J. Am. Chem. Soc., 64, 462 (1942).

[47] H. Gilman and J. C. Bailie, J. Am. Chem. Soc., 61, 731 (1939).

heated together in refluxing xylene gave only the symmetrical products, tetraphenyllead and tetra-p-tolyllead.) Hein[48] investigated the autooxidation of hexacyclohexyldilead with atmospheric oxygen. This reaction was found to be photochemical, and to occur only under the influence of ultra-violet light, but not at all in the dark or in sodium vapor light. The probable nature of the products is discussed.

The preparation of hexacyclohexyldilead is discussed by Jensen and Clauson-Kaas[49]. They were unable to prepare diphenyllead. The results of their rather careful study of certain physical properties of lead and tin compounds of these types are described in the second part of the historical section.

Physical properties of organolead compounds

The work of Malatesta[45] on molecular weights of R_6Pb_2 compounds has been mentioned above, as has the investigation of Jensen and Clauson-Kaas[49].

The absorption spectrum of hexacyclohexyldilead in the ultraviolet and visible regions is given by Hein[48], and those of the tetraphenyl derivatives of silicon, tin, and lead from

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[48] F. Hein, E. Nebe, and W. Reimann, Z. anorg. allgem. Chem., 251, 125 (1943).

[49] K. A. Jensen and N. Clauson-Kaas, Z. anorg. allgem. Chem., 250, 277 (1943).

2100 to 3000 Å. (in chloroform and in ethanol) by Milazzo[50]. Riccobini[51] 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, 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 C-Pb or C-Sn bond. The absorption curves given by Riccobini[51] and by Hein[48] show a smooth rise to continuous absorption in the near ultraviolet for their alkyl compounds (essentially the same result which has been noted here in some measurements on phenyl derivatives). Milazzo's curves[50] 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 Riccobini, that the nature of the curves for the lead derivatives indicates dissociation. The results of these two authors, while not in conflict, appear to require some integration.

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[50] G. Milazzo, Gazz. chim. ital., 71, 73 (1941).

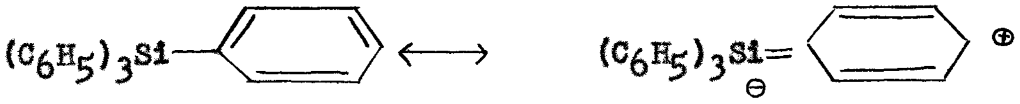
[51] L. Riccobini, Gazz. chim. ital., 71, 696 (1941).

Riccobini studied also[52] the polarography of triethyllead chloride in aqueous potassium chloride. In the reaction at the cathode the valence change was 1, and the voltage was significantly greater than for the reduction of Pb^{++}.

Dipole moments of some organolead compounds are given[53] as follows (in Debye units):

$(C_2H_5)_3PbC_6H_5$	0.86
$(C_6H_5)_3PbC_2H_5$	0.81
$(C_6H_5)_3PbCl$	4.32
$(C_2H_5)_3PbCl$	4.66
$(C_2H_5)_3PbBr$	4.88
$(C_2H_5)_3PbOH$	~2.4

The values for the halide derivatives, it is pointed out, are in the region expected for inorganic salts (NaI, 4.9; KI, 6.8), indicating that the Pb-X bond is probably essentially ionic. In this and previous work, Malatesta is seeking evidence for his belief that some of the properties of organic compounds of the Group IV-B elements can be explained on the basis of a resonance form which places a double bond on the central atom, thus:



As he himself points out, the result that these dipole moment values for such compounds as ethyltriphenyllead are in fact

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[52] L. Riccobini, Gazz. chim. ital., 72, 47 (1942).

[53] L. Malatesta and R. Pizzotti, Gazz. chim. ital., 73, 349 (1943).

somewhat greater than those for the corresponding tin compounds seems to afford poor support for this idea, since lead should be the element in this group least apt to support the resulting negative charge. Some discussion is given in an attempt to rationalize this discrepancy.

Tetraphenyllead is included in a recent tabulation[54] of diffraction data, and also in a discussion[55] of diamagnetic anomalies and the relation of molecular diamagnetism to structure. The magnetic susceptibilities and parachors of $(CH_3)_4Pb$, $(C_2H_5)_4Pb$, $(\underline{n}\text{-}C_3H_7)_4Pb$, $(\underline{n}\text{-}C_4H_9)_4Pb$, and $(\underline{n}\text{-}C_7H_{15})_4Pb$ are given by Kadomtzeff[56]. An X-ray crystal investigation of the tetraphenyl derivatives of silicon, tin, and lead, and of tetra-p-tolyltin and tetra-p-anisyltin, is reported by Zhdanov[57]. The angles of "tilt" found for the aromatic rings differ somewhat from those reported in previous work[58,59].

A simplified method of estimating rotational potential barriers--that is, barriers to free rotation about a single

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[54] L. K. Frevel, R. W. Rinn, and H. C. Anderson, Ind. Eng. Chem., Anal. Ed., 18, 83 (1946).

[55] P. Pascal, Compt. rend., 218, 57 (1944).

[56] I. Kadomtzeff, Compt. rend., 226, 661 (1948).

[57] G. S. Zhdanov and I. G. Ismailzade, Doklady Akad. Nauk S. S. S. R., 68, 95 (1949) /̲C. A., 43, 8764 (1949)̲/.

[58] W. H. George, Proc. Roy. Soc., 113A, 585 (1927).

[59] G. Giacomello, Gazz. chim. ital., 68, 422 (1938).

bond--is described by French and Rasmussen[60]. The method having been indicated, some calculations are made for cases where data are known, and for others where they are not. In particular, the authors calculate the barrier for tetramethyllead and tetramethyltin as approximately 0, and for tetramethylgermanium about 400 calories. These results are to be compared with the measured values of 1100-1500 calories for tetramethylsilane and 4800 calories for neopentane.

Lile and Menzies[61] discuss the changes in maximum covalency which occur on passing from quadrivalent platinum through trivalent gold to divalent mercury, with reference to what they call "derived organometallic pseudo-atoms" and ions. Further changes on proceeding to thallium, lead, and bismuth are then discussed. The formation of addition complexes of the organometallic compounds with amines is used as a criterion of maximum possible covalency. Tetraphenyllead, they found, did not react with ethylenediamine. Cryoscopic molecular weight determinations in benzene carried out on hexaphenyldilead (0.2-0.5 g. in 15 g. of solvent) showed it to be dimeric (found, M. W. 780-792; calculated for $(C_6H_5)_3Pb$, M. W. 438). Diphenyllead sulfide, however, was trimeric (concentration 0.5

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[60] F. A. French and R. S. Rasmussen, J. Chem. Phys., 14, 389 (1946).

[61] W. J. Lile and R. C. Menzies, J. Chem. Soc., 617 (1950).

g. in 16-23 g. of solvent; found, M. W. 1006-1019; calculated for $(C_6H_5)_2PbS$, M. W. 393).

A new application of organolead compounds is indicated in a discussion[62] of the characteristics of Geiger counters filled with tetramethyllead vapor. Counters so filled are described as particularly useful for measurements involving very high counting rates. They operated at 100% efficiency at a pressure as low as 14 mm. of mercury, and because of this low gas pressure the "dead time" was much less (about 5×10^{-5} sec.) than for counters filled with the usual mixture of argon and ethanol.

Physiological properties of organolead compounds

In 1939 a group of English chemists at Cambridge, directed by B. C. Saunders, began a project for the British Ministry of Supply in which the attention soon became focused on organolead compounds having sternutatory properties. In the period from 1939 through 1941 this group prepared and tested over one hundred such compounds, many of them new. The work began to be published in the chemical literature in 1947, and publication is continuing at the present time. The first article[63] is apparently a summary of the work and its results,

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[62] C. L. Meaker, C. S. Wu, and L. J. Rainwater, Phys. Rev., 73, 1240 (1948).

[63] H. McCombie and B. C. Saunders, Nature, 159, 491 (1947).

given without much chemical experimental data. The chemical details of the work are gradually being published in the articles[8,9,10] now appearing.

The compounds studied were almost all salts of trialkyllead hydroxides with either organic or inorganic acids. They were prepared as indicated above[8,9,10]. Salts of the trimethyl-, triethyl-, tri-n-propyl-, and tri-n-butyllead series were studied. The trimethyllead salts were very feeble sternutators[9], no matter what the acid radical was. The other types were all active sternutators[8], and a definite peak of activity was reached in the tri-n-propyllead series[8,9,10]. Salts of dialkyllead hydroxides had negligible sternutatory power[8]. Among the most active compounds studied[10] were N-trialkyllead salts of sulfonamides, of the type $RSO_2 \cdot NR' \cdot PbR''_3$. Many of these were intolerable to human volunteers at a concentration of $1:10^7$ in air. Examples are N-tri-n-propyllead methanesulfonamide, $(n\text{-}C_3H_7)_3Pb \cdot NH \cdot SO_2CH_3$, and N-tri-n-propyllead benzenesulfonamide, $(n\text{-}C_3H_7)_3Pb \cdot NH \cdot SO_2C_6H_5$. The N-tri-n-propyllead salt of saccharin was strongly sternutatory, and also very sweet. These compounds were converted by strong acids to the sulfonamides and the R_3Pb salts. It is pointed out that there remains the possibility that the compounds might have the O-Pb linkage, rather than the N-Pb*.

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*But if these are ionic crystals, then it appears that this distinction is probably meaningless. The valuable aid which could be given here by X-ray work is in fact pointed out by Saunders[10].

In the course of some other investigations[64,65] involving fluorine compounds, Saunders also prepared triethyllead salts with fluorine-containing anions. Triethyllead fluoroacetate was found[66] to have sternutatory and, on injection, convulsant properties.

Dunlap and Warren[67] report that no tumors developed at the site of subcutaneous injection in mice of two lead compounds, 7-benz[a]anthryltriphenyllead and bis(7-benz[a]-anthryl)diphenyllead, containing radicals derived from a polynuclear hydrocarbon which might be expected to have carcinogenic action.

Analysis of organolead compounds

A reportedly convenient and rapid method for the determination of lead in organolead compounds is described by Saunders[8]. The lead compound is decomposed by nitric acid and the lead is precipitated as the chromate. The precipitate is filtered out and then redissolved in strong acid, and the chromic acid is determined volumetrically.

An apparently rather lengthy volumetric method for the determination of tetraethyllead (for instance, in gasoline) is

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[64] B. C. Saunders, G. J. Stacey, F. Wild, and I. G. E. Wilding, J. Chem. Soc., 699 (1948).

[65] B. C. Saunders and G. J. Stacey, J. Chem. Soc., 1773 (1948).

[66] H. McCombie and B. C. Saunders, Nature, 158, 382 (1946).

[67] C. E. Dunlap and S. Warren, Cancer Research, 6, 454 (1946).

also described[68].

Tabulation of organolead compounds

Table I lists all references known to us for each organolead compound mentioned in the chemical literature during the period covered by this survey. The only exception to this is that not all references to tetraethyllead are given. For this one compound only references of chemical or physiological interest are included; and many patents, in particular, dealing with chemical engineering or combustion engineering aspects of the technology of the compound are omitted. A recent foreign review[69] of the technology, manufacture, and properties of this compound includes 146 references.

In Table I, the compounds listed are tabulated in sections according to chemical constitution--R_4Pb compounds, $R_3R'Pb$ compounds, etc. Within each section the order of entries is the alphabetical order of the organic radicals, with the radical present in greatest number listed first. This is the arrangement adopted by Leeper[5], and, as stated above, this tabulation therefore serves as an extension of his tables. Compounds which were previously known, and which therefore appear also in the Leeper tables, are marked with an asterisk.

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[68] F. Burriel and L. García Escolar, Anales fís. y quím. (Madrid), 42, 777 (1946) [C. A., 41, 4735 (1947)].

[69] V. V. Korshak and G. S. Kolesnikov, Uspekhi Khim., 15, 325 (1946) [C. A., 41, 701 (1947)].

Such compounds are of course included only when new work involving them has appeared during the period of the review.

Table I

Organolead Compounds Mentioned in the Chemical Literature, 1941-1950

Compound	M.p. or b.p., °C.	References
	R_4Pb compounds	
Tetra-n-butyl-*	157/5	8, 19, 56
Tetraethyl-*	78/10	6, 8, 19, 20, 23, 24, 28, 31, 32, 34, 38, 46, 48, 51, 56, 68, 69, 70, 71, 72, 73, 74
Tetra-n-heptyl-*	---	56
Tetramethyl-*	6/10	6, 11, 28, 33, 34, 35, 37, 46, 48, 56, 60, 62

*Compounds thus marked are listed also in the tables given by Leeper[5].

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[70] E. Berl (to Berl Chem. Corp.), U. S. Patent 2,270,780 (1942) /C. A., 36, 3191 (1942)/.

[71] H. Gilman and R. K. Abbott, J. Org. Chem., 8, 224 (1943).

[72] M. P. Monserrat, Combustibles (Zaragoza), 5, No. 25/6, 15; No. 27/8, 67 (1945) /C. A., 42, 8451 (1948)/.

[73] G. E. Holbrook (to Du Pont), U. S. Patent 2,464,397 (1949) /C. A., 43, 4287 (1949)/.

[74] R. J. Plunkett (to Du Pont), U. S. Patent 2,477,465 (1949) /C. A., 43, 8398 (1949)/.

Table I (continued)

Compound	M.p. or b.p., °C.	References
Tetraphenyl-*	227-9	15, 16, 17, 18, 21, 22, 34, 39, 40, 41, 50, 54, 55, 57, 61, 75, 76
Tetra-n-propyl-*	126/13	8, 29, 43, 56
Tetra-n-tetradecyl-	31	12
Tetra-p-tolyl-*	240	39
	$R_3R'Pb$ compounds	
Triethyl-p-bromophenyl-*	d. 210/3	77
Triethyl(1-diethylamino-n-propyl)-	---	77
Triethylmethyl-*	70/16	46
Triethylphenyl-*	126/6 d.	24, 53
Trimethylethyl-*	27/10	46
Triphenyl(benz/‾a‾7-anthracen-7-yl)-*	204-5	67
Triphenyl-p-bromophenyl-*	115	75
Triphenyl-p-carboxyphenyl-, methyl ester	124-6	75, 77
Triphenylethyl-*	49-50	24, 75

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[75] H. Gilman, A. H. Haubein, G. O'Donnell, and L. A. Woods, J. Am. Chem. Soc., 67, 924 (1945).

[76] M. M. Koton, Zhur. Obshchei Khim., 18, 936 (1948) /‾C. A., 43, 559 (1949)‾7.

[77] D. S. Melstrom, Doctoral Dissertation, Iowa State College (1943). See Iowa State Coll. J. Sci., 18, 65 (1943) /‾C. A., 38, 727 (1944)‾7.

Table I (continued)

Compound	M.p. or b.p., ° C.	References
Triphenyl-p-1-hydroxyethylphenyl-	68-70	77
Triphenyl-α-hydroxy-m-tolyl-	113-4	77
$R_2R'_2Pb$ compounds		
Di-(benz[a]anthracen-7-yl)diphenyl-*	295-6	67
Diethyldimethyl-*	52/14	46
Diethyldiphenyl-*	176/8	25
Diethyldi-n-propyl-*	99/10	63
R_3PbX compounds		
Tri-n-butyl- chloride*	---	8, 19, 63
Tri-n-hexadecyl- chloride	79-80	12
Tricyclohexyl- iodide*	92	27
Tri-n-dodecyl- chloride	64-5	12
Triethyl- bromide*	103-4	22, 53, 78
Triethyl- chloride*	d. 120	7, 8, 9, 10, 20, 34, 51, 52, 53, 64, 72, 78, 79
Triethyl- iodide*	19-20	7
Trimethyl- chloride*	187 subl.	7
Tri-o-methoxyphenyl-chloride	167-71	40

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[78] G. Calingaert, H. Shapiro, F. J. Dykstra, and L. Hess, J. Am. Chem. Soc., 70, 3902 (1948).

[79] C. G. Stuckwisch, Doctoral Dissertation, Iowa State College (1943). See Iowa State Coll. J. Sci., 18, 92 (1943) [C. A., 38, 728 (1944)].

Table I (continued)

Compound	M. p. or b.p., °C.	References
Tri-n-octadecyl- chloride	82-3	12
Triphenyl- bromide*	166	53, 63
Triphenyl- chloride*	206	17, 40, 53, 63, 75, 80
Triphenyl- iodide*	142	22, 63
Tri-n-propyl- bromide*	76-8	8
Tri-n-propyl- chloride*	137	8
Tri-n-tetradecyl- chloride	74-5	12
	$R_2R'PbX$ compounds	
Dimethylethyl- chloride*	---	7
Di-n-propylethyl- chloride	---	63
Diphenyl-o-carboxyphenyl- chloride	210-20	77
Diphenyl-o-carboxyphenyl- chloride, methyl ester	170-1	77
	R_2PbX_2 compounds	
Di-p-carbethoxyphenyl- dichloride	>270	40
Di-2-chlorovinyl-dichloride	d. 163	16
Dicyclohexyl- dibromide*	d. 142	25
Dicyclohexyl- diiodide*	---	27
Diethyl- dichloride*	---	8, 10
Di-o-methoxyphenyl- dichloride	188	40

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[80] H. Gilman and D. S. Melstrom, J. Am. Chem. Soc., 70, 4177 (1948).

Table I (continued)

Compound	M.p. or b.p., °C.	References
Dimethyl- dibromide*	---	6
Diphenyl- dibromide*	---	25
Diphenyl- dichloride*	d. 284	17
Diphenyl- diiodide*	101-3	25
Di-n-propyl- dichloride*	d. 228	8
	R_6Pb_2 compounds	
Hexacyclohexyldi-*	d. 196	27, 45, 48, 49
Hexaethyldi-*	d. 100/2	46
Hexamethyldi-*	37-38	48
Hexaphenyldi-*	d. 155	24, 45, 61
Hexa-p-xylyldi-*	168	48
	R_3PbY compounds	
Tri-n-butyl- acetate	86	8
Tri-n-butyl- bromoacetate	54	8
Tri-n-butyl- chloroacetate	60	8
Tri-n-butyl- β-chloropropionate	65-66	8
Tri-n-butyl- crotonate	119	8
Tri-n-butyl- hydroxide*	d. 115	8
Tri-n-butyl- iodoacetate	83	8
Tri-n-butyl- naphthalene-2-sulfonate	68	8
Tri-n-butyl- propionate	79-80	8

Table I (continued)

Compound	M.p. or b.p., °C.	References
Tri-n-butyl- p-toluenesulfonate	81	8
Tri-n-butyl- trichloroacetate	119	8
Tri-n-dodecyl- acetate	59	12
Tri-n-dodecyl- nitrate	44-5	12
Triethyl- acetate*	d. 160	8
Triethyl- acrylate	Sinters 120	9
Triethyl- anthranilate	96	8
N-Triethyl- benzenesulfonamide	132	10
Triethyl- bromoacetate*	120	9
Triethyl- chloroacetate*	147	9
Triethyl- β-chloropropionate	106	9
Triethyl- crotonate	135-6	9
Triethyl- cyanate	d. 184	9
Triethyl- cyanide*	189 d.	7, 9
N-Triethyl- ethylenesulfonanilide	116	10, 63
Triethyl- ethyl oxalate	55	9
Triethyl- ethyl sulfide	76-8/0.075	9
Triethyl- fluoroacetate	180.5 d.	65, 66
Triethyl- fluorophosphonate	>260	64
Triethyl- hydroxide*	---	7, 8, 10, 63, 78

Table I (continued)

Compound	M.p. or b.p., °C.	References
N-Triethyl- methanesulfonamide	97	10
N-Triethyl- methanesulfonanilide	115.5	10
Triethyl- naphthalene-2-sulfonate	152	9
Triethyl- phenyl sulfide*	---	9
N-Triethyl- phthalimide	131	9, 63
Triethyl- propionate*	141 d.	9
N-Triethyl- saccharin	135	10
Triethyl- selenocyanate	29.5-30.5	9
N-Triethyl- sulfanilamide	171	10
N-Triethyl- o-toluenesulfonamide	133	10
N-Triethyl- p-toluenesulfonamide	127	10, 63
N-Triethyl- p-toluenesulfonanilide	134	10
Triethyl- o-toluenesulfonate	189	9
Triethyl- p-toluenesulfonate*	170	9
N-Triethyl- p-toluenesulfon-p'-chloroanilide	111.5	10
Triethyl- thiocyanate*	35	9
Triethyl- trichloroacetate*	140	9
Trimethyl- acetate	183-4	7

Table I (continued)

Compound	M.p. or b.p., °C.	References
Trimethyl- chloroacetate	169	9
Trimethyl- formate	113	9
Trimethyl- isovalerate	160	9
Trimethyl- *p*-toluenesulfonate	<220	9
Trimethyl- trichloroacetate	>220	9
Triphenyl- hydroxide*	---	53, 63
Tri-*n*-propyl- acetate*	126-7	8
Tri-*n*-propyl- acrylate	123	8
Tri-*n*-propyl- anthranilate	57-8	8
N-Tri-*n*-propyl- benzenesulfonamide	93.5-94.5	10, 63
Tri-*n*-propyl- bromoacetate	93-4	8
Tri-*n*-propyl- *n*-butyrate	105-6	8
Tri-*n*-propyl- chloroacetate	109-10	8
Tri-*n*-propyl- β-chloropropionate	99-100	8
Tri-*n*-propyl- crotonate	135	8
Tri-*n*-propyl- cyanide	135 d.	8
Tri-*n*-propyl- hydroxide*	d. 140	8, 10, 43, 63
Tri-*n*-propyl- iodoacetate	88-89	8
Tri-*n*-propyl- isovalerate	110-111	8
N-Tri-*n*-propyl- methanesulfonamide	67	10, 63

Table I (continued)

Compound	M.p. or b.p., °C.	References
Tri-n-propyl- naphthalene-2-sulfonate	126-7	8
N-Tri-n-propyl- phthalimide		9, 63
Tri-n-propyl- propionate	121-2	8
N-Tri-n-propyl- saccharin	130	10, 63
N-Tri-n-propyl- sulfanilamide	101	10
N-Tri-n-propyl- p-toluenesulfonamide	100-1	10, 63
N-Tri-n-propyl- p-toluenesulfonanilide	104	10
Tri-n-propyl- o-toluenesulfonate	86-7	8
Tri-n-propyl- p-toluenesulfonate	82-3	8
N-Tri-n-propyl- p-toluenesulfon-p'-bromoanilide	117	10
N-Tri-n-propyl- p-toluenesulfon-p'-chloroanilide	123	10
Tri-n-propyl- trichloroacetate	139-40	8
Tri-n-propyl- xanthate	57.5	8
	R_2PbY_2 compounds	
Di-p-carbethoxyphenyl-diacetate	207-8	40
Di-2-chlorovinyl-diacetate	d. 115-130	16
Di-2-chlorovinyl-dibenzoate	d. 204-5	16

Table I (continued)

Compound	M.p. or b.p., °C.	References
Di-2-chlorovinyl-sulfate	d. 171-2	16
Diethyl- carbonate	---	7
Diethyl- dihydroxide	---	7, 78
Diethyl- di-p-nitrophenoxide	---	8
Diethyl- sulfite		63
Di-o-methoxyphenyl-diacetate	191-3 d.	40
Di-2-naphthyl- diacetate	236-6.5	40
Diphenyl- diacetate*	195	40
Diphenyl- sulfide*	d. 80-90	61
Di-n-propyl- diacetate	122 d.	8
Unclassified salts		
Diethyl-n-propyllead propionate		63
Diethyllead iron tetracarbonyl	---	42
Diphenyl-o-carboxyphenyllead hydroxide, anhydride	300-5 d.	77
Methanedi-N-(triethyllead) sulfonanilide	d. 71-180	10
Di(triphenyllead) iron tetracarbonyl	---	44

Valence States of Group IV-B Elements and Structures of Their Compounds

The elements of Group IV-B of the periodic table--carbon, silicon, germanium, tin, and lead--form compounds in which they exhibit various covalences. The common covalence is of course four, as exhibited by all these elements in the majority of their compounds. There may be cited for example, among lead compounds, the types represented by tetraphenyllead, hexaphenyldilead, lead tetrachloride, and so on. The three-covalent state is presumably represented in compounds such as $(C_6H_5)_3PbLi$, $(C_6H_5)_3SnNa$, $CsPbCl_3$, etc., although the physical data necessary to confirm the supposition do not exist for such compounds. In such cases the heavy metal is pictured as the central element of the anion. In the series Pb, Sn, Ge, Si this state is apparently increasingly difficult to attain. For the two-covalent state, compounds having stoichiometric formulas such as $(C_6H_5)_2Pb$ and $(C_6H_5)_2Sn$ are described, and in at least some cases it appears probable that such compounds can actually exist in the monomeric form under certain conditions. Among inorganic compounds the oxidation number 2 is of course well known for lead, not uncommon for tin, less stable for germanium, and practically non-existent for silicon.

(This discussion will not consider certain well-known compounds of these elements in which the element attains a covalence greater than four--for instance, Si in $SiF_6^=$, etc.).

It is of interest to inquire how these valences can arise among the Group IV-B elements, and whether the known principles of theoretical chemistry would predict their occurrence. It is found that a qualitative answer can be given, which however as in many other cases is of the nature of a correlation of existing physical and chemical data, but which serves as a useful basis for speculations.

The atoms of all these Group IV elements possess four electrons in the valence level. The levels below the valence level are complete*, so that changes of valence cannot occur in these elements (as they can, for instance, in the case of the Group IV-A elements) by placing varying numbers of electrons in a lower level. However, the four valence electrons are not all equivalent. The ground state for these atoms is (in the Russell-Saunders symbolism) a ^3P state[81], derived from an s^2p^2 configuration. That is, there are two electrons in the s subshell, necessarily with spins coupled,

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*For C, Si, and Ge the lower levels are formally complete. In the case of Sn the valence shell is the 0 shell, and there is a level in the N shell, the $4f$ level, which is not complete. Actually, however, this is a higher-energy orbital than the $5s$ or $5p$ orbitals. An analogous situation exists in the lead atom.

[81] R. F. Bacher and S. Goudsmit, "Atomic Energy States", McGraw-Hill, New York, 1933.

and in this state therefore only the two unpaired electrons in the p subshell should be available for bonding. The two-covalent state is therefore accounted for, as arising from the ground state of the atom. In order to form the usual four-covalent state, it is necessary to uncouple one of the s electrons, which in accordance with the Pauli principle requires in these atoms that it be "promoted" to a higher energy level. The next level is the p level of the same shell, and promotion of an s electron to this level gives an sp^3 configuration, from which we obtain as the lowest term 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 of these elements, with tetrahedral bonding, is therefore derived from the ^5S state of the atom, which is not the ground state but the first excited state.

The above-described "promotion" of an s electron of course requires energy. However, the atom in the resulting ^5S state is now able to form two additional bonds. It would be of interest to compare the magnitude of the energy required for the ^3P-^5S transition with the magnitudes of the bond energies in, for instance, carbon compounds. For carbon, the ^5S state has not been located experimentally. However, a theoretical calculation by Ufford[82] locates the ^5S state 3.16 electron volts (about 73 kcal./mole) above the ground state for this element, and this value is supported by certain indirect experimental evidence[83,84]. This value for the atom cannot serve as more than an approximate index of the energy difference which would exist when bonds were formed, because of the high perturbation which would result from the presence of for instance a hydrogen atom. It is, however, the only bit of quantitative information available. It is of interest to note briefly the nature of this computation, in order to understand that even this calculation is not apt to be made for an atom such as lead. The calculation of Ufford, involving rather lengthy and laborious numerical integrations, was made using one-electron functions previously given by Torrance for the carbon atom. These functions were obtained by the Hartree method, which involves repeated approximations requiring each time the integration of a number of simultaneous equations (one for each electron state in the atom). Obviously in the case of the lead atom, with its 82 electrons, the mathematical labor involved would be prohibitive. There are other possible approaches, such as the Thomas-Fermi

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[82] C. W. Ufford, Phys. Rev., 53, 568 (1938).

[83] L. H. Long and R. G. W. Norrish, Proc. Roy. Soc., 187A, 337 (1946).

[84] L. H. Long and R. G. W. Norrish, Nature, 157, 486 (1946).

statistical method, for which lead with its high atomic number might be a favorable case. It remains necessary, however, to depend on chemical and physical data to shorten the work, rather than attempting to make calculations from first principles, and theory in its present form can serve mainly in qualitative ways.

For all the elements of this group, therefore, tetrahedral bonding is expected as for carbon compounds. There is no existing experimental data which would indicate any other structure for the compounds of these elements in the four-covalent state. The tetramethyl derivatives of Si, Ge, Sn, and Pb were investigated, in the vapor state, by Brockway and Jenkins[85] by electron diffraction; and George[58] and Giacomello[59] investigated the structure of crystalline tetraphenyl derivatives of Si, Sn, and Pb by means of X-rays. Electron diffraction measurements on $PbCl_4$ are also recorded[86]. In all these cases the data agree with the tetrahedral structure, and the bond distances are essentially equal to the sums of the covalent radii of the atoms involved*. Electron diffraction data

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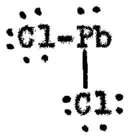
*Brockway and Jenkins do not make this calculation for their lead compound, probably for lack of an accepted value for the Pb covalent radius, but if the present best value of 1.44 Å. is used their data will agree well with the radius sums. Giacomello uses the somewhat doubtful value 1.6 Å. for the Pb radius; if 1.44 Å. is used his bond distance is considerably greater than the sum of the radii.

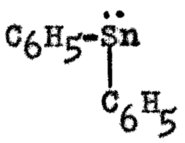
[85] L. O. Brockway and H. O. Jenkins, J. Am. Chem. Soc., 58, 2036 (1936).

[86] M. W. Lister and L. E. Sutton, Trans. Faraday Soc., 37, 393 (1941).

on liquid hexamethyldilead[87] agree with the expected structure, with the following parameters: Pb-Pb, 2.88 Å.; Pb-C, 2.25 Å.; ∠C-Pb-Pb, 109.5°. This gives the present best value, 1.44 Å., for the covalent radius of Pb.

In the two-covalent state of these elements, which is derived from the s^2p^2 ^3P ground state of the atom, bond formation is expected to utilize essentially the two *p* orbitals, the *s* orbital remaining occupied by its electron pair in the molecule as in the atom. The configuration can be represented as follows, using $PbCl_2$ and $(C_6H_5)_2Sn$ as examples:





For pure *p* bonds the bond angle would be 90°; actually *p* bonds are always distorted somewhat from this value (e. g., H-O-H in water = 104°). It is particularly to be noted that the above configurations do not represent radicals; there are no unpaired electrons.

Thus the two-valent state of these elements may be regarded as being due to a reluctance, for some reason increasingly great as the atomic number increases within the group, to "promote" the *s* electron to a higher level. This results

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[87] H. A. Skinner and L. E. Sutton, *Trans. Faraday Soc.*, *36*, 1209 (1940).

in the presence of an electron pair, in formulas such as those above, which is not functioning to form a bond. This effect was named the "inert pair" effect by Sidgwick[88], who was the first to describe it clearly, although Grimm and Sommerfeld[89] anticipated the conception in some respects. Sidgwick points out that the effect can operate in other families of the periodic table, and is especially prominent with elements of high atomic weight, so that it is quite characteristic of elements in the same period as lead. For instance, thallium has a well-known univalent state. Since the publication of Sidgwick's book this phenomenon has apparently attracted little interest, and no one has attempted to explain theoretically why it should be most characteristic of elements of high atomic number, or to discuss it in quantitative terms, except for the calculations noted above for carbon, which do not bear directly on the question.

As a matter of fact, it seems probable that the stability of the "inert pair", even in compounds of these heavy elements, may not be as great as indicated by the formulas above. These formulas would represent simple molecules of the types PbX_2 or PbR_2, but actually no volatile compounds of two-valent lead are known. All such compounds are solids,

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[88] N. V. Sidgwick, "The Electronic Theory of Valency", Oxford, 1927, pp. 178-181.

[89] H. G. Grimm and A. Sommerfeld, Z. f. Phys., 36, 36 (1926).

and it may be that in the crystal they are usually rather highly polymerized substances. The unexpected low solubility in water of the dihalides of lead (and of the monohalides of thallium) is noted in this connection. Diphenyltin is monomeric when freshly prepared, but polymerizes rapidly on standing, reaching the molecular weight of a pentamer or greater. However, two structure determinations have been reported which confirm the expected configuration for the simple molecules. Lister and Sutton[90] performed electron diffraction measurements on $PbCl_2$ vapor, in which state the compound is believed to be monomeric, and interpret their results as indicating a non-linear molecule, with a bond angle about 95°, and with bond distance Pb-Cl, 2.46 Å. The bromide and iodide gave similar results. Powell and Tasker[91] studied by X-ray diffraction crystals of compounds such as $Rb(Pb_2Br_5)$, which contains $PbBr_2$ groups in the crystal structure, and thus held rigidly so that polymerization does not occur. They found the bond angle in these groups to be 85.5 ± 2°, and the bond distances longer than the ionic radii, indicating some covalent character. The crystal structures of the polymerized solid dihalides of these elements are well known from X-ray

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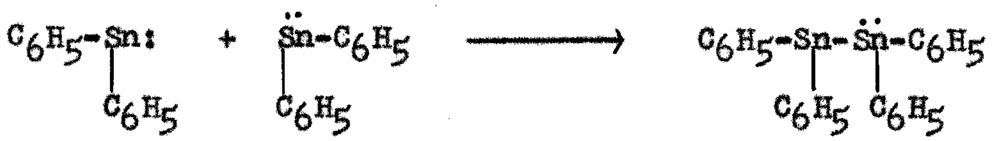
[90] M. W. Lister and L. E. Sutton, Trans. Faraday Soc., 37, 406 (1941).

[91] H. M. Powell and H. S. Tasker, J. Chem. Soc., 119 (1937).

investigations[92]. The lead chloride crystal, for instance, may be described roughly as consisting of close-packed layers of chloride ions with lead ions interspersed in the layers so that the whole structure is greatly distorted and the term "coordination number" essentially loses its meaning.

The structures drawn above for compounds of two-valent Pb and Sn show immediately a way in which polymerization can be pictured. Each Pb or Sn atom has only a sextet of electrons, and needs a pair to complete the group of eight; and also each atom has an "inert pair". Polymerization of diphenyltin, for example, may be indicated



$$C_6H_5-\underset{C_6H_5}{Sn}: \quad + \quad \underset{C_6H_5}{\ddot{Sn}}-C_6H_5 \longrightarrow C_6H_5-\underset{C_6H_5}{Sn}-\underset{C_6H_5}{\ddot{Sn}}-C_6H_5$$

and so on. Jensen and Clauson-Kaas[49] have made some measurements of the magnetic susceptibility and the dipole moment of diphenyltin. (They apparently intended to do this work also for diphenyllead, but found it impossible to obtain a homogeneous preparation of this material.) Their preparations of diphenyltin were rather carefully made, and the polymerization state was well established. For monomeric preparations as well as for polymerized material they found no paramagnetic effect at all. There was a rather small dipole moment (~1.0).

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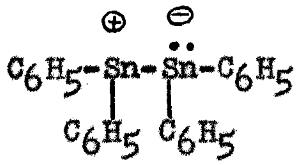
[92] R. G. W. Wyckoff, "Crystal Structures", Interscience, New York, 1948.

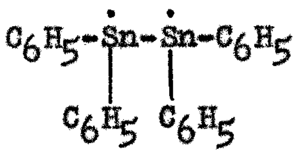
It was independent of the degree of polymerization. After some discussion the authors accept it as real and not attributable to impurities. The absence of paramagnetic effect is expected for the structures above, and confirms the formulation of $(C_6H_5)_2Sn$ as a molecule, not a radical. Jensen and Clauson-Kaas, in attempting to explain the dipole moment, consider various possible structures for the polymer. They discard the structure indicated above, because from such a structure, they state, a large dipole moment would result, due to formal charge separation.



$$C_6H_5-\overset{\oplus}{Sn}(C_6H_5)-\overset{\ominus}{\ddot{Sn}}(C_6H_5)-C_6H_5$$

(I)

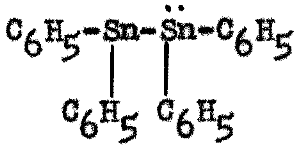
Here they are apparently ignoring the resonance possibilities which appear at first glance. They conclude that diphenyltin is best represented by a structure



$$C_6H_5-\dot{Sn}(C_6H_5)-\dot{Sn}(C_6H_5)-C_6H_5$$

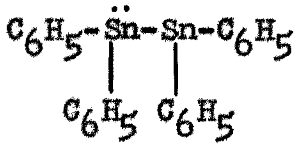
(II)

for which, as they state, it is difficult to estimate the probable dipole moment. They stipulate further that the two electrons on the Sn atoms have antiparallel spins. This would appear to mean nothing different (in the dimer) from a Sn-Sn double bond, but this last possibility they had already discarded because it would show no dipole moment. Their argument is therefore somewhat difficult to follow. It would seem that more consideration should perhaps be given to structure I. In this structure, if the two tin atoms were equivalent, then any dipole moment should be obliterated by resonance. There is little basis for guessing at the actual stereochemical configurations in such a structure as this, but the obvious assumption would seem to be a planar configuration with about 120° angles around the first Sn atom (by analogy with boron, for instance) and a pyramidal arrangement (by analogy with nitrogen) around the other Sn atom. In this case the tin atoms are not equivalent, and the alternative structures



$C_6H_5-\underset{\textstyle C_6H_5}{Sn}-\underset{\textstyle C_6H_5}{\ddot{Sn}}-C_6H_5$

or



$C_6H_5-\underset{\textstyle C_6H_5}{\ddot{Sn}}-\underset{\textstyle C_6H_5}{Sn}-C_6H_5$

would seem to involve some displacement of the phenyl groups. In other words, "steric inhibition of resonance" would seem to exist. Qualitatively, the result of this might be just such a lowering of the dipole moment, without complete obliteration, as was found. This suggestion has the advantage that it is then unnecessary to account arbitrarily for the lack of paramagnetic effect.

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 as reaction intermediates, although for the interpretation of the results reported in this thesis this has not been found necessary. For the methylene fragment, some experimental work by Burton and colleagues[93] suggests that the energy difference between molecule and diradical is little, and Long and Norrish[83] estimate it at about 15 kcal./mole.


$:\underset{\mathrm{H}}{\mathrm{C}}-\mathrm{H}$

or


$\cdot\underset{\mathrm{H}}{\dot{\mathrm{C}}}-\mathrm{H}$

This small energy requirement should make the radical state readily available in most reactions if necessary. Since data are lacking, no similar estimates can be made for compounds of other elements of the family.

In connection with the existence of simple compounds of divalent elements of this group, it is interesting to note that carbon dichloride has recently been postulated[94] as the reactive intermediate in the alkaline hydrolysis of chloroform and related compounds. The reaction scheme, which seems well supported by kinetic data, is as follows:

$$\mathrm{CHCl_3} + \mathrm{OH^-} \xrightleftharpoons{\text{fast}} \mathrm{CCl_3^-} + \mathrm{HOH}$$
$$\mathrm{CCl_3^-} \xrightarrow{\text{slow}} \mathrm{Cl^-} + \mathrm{CCl_2}$$

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[93] M. Burton, T. W. Davis, A. Gordon, and H. A. Taylor. J. Am. Chem. Soc., 63, 1956 (1941).

[94] J. Hine, J. Am. Chem. Soc., 72, 2438 (1950).

$$CCl_2 \xrightarrow[HOH]{OH^-,\ fast} CO + HCOO^-$$

(In the following parts of this thesis, some quite similar reactions involving divalent lead compounds are postulated.) The CCl_2 written above is referred to in the paper as a "radical", but in fact the author represents it always with all electrons paired, and therefore in the molecular state.

The stereochemistry of lead and similar metals is discussed by Byström[95]. He concludes that in compounds such as PbS, PbSe, PbTe, PbF_2 (both forms), $PbCl_2$, $PbBr_2$, and PbI_2 the 6s electron pair is certainly stereochemically inactive; but that in many compounds of formally bivalent lead the 6s pair is probably involved, as in tetrahedral and orthorhombic PbO, in Pb_3O_4, and in other compounds. The high molecular weight found for diphenyllead sulfide has been mentioned above[61]. It seems possible that diphenyllead oxide and other similar compounds may also be found to be polymeric, in view of their low solubilities and high melting points.

An example of the polymerization of a compound containing an element of Group IV-B in a formally divalent state is given by diphenylgermanium, whose preparation and behavior are described by Kraus and Brown[96]. Diphenylgermanium dichloride, $(C_6H_5)_2GeCl_2$, was reduced with sodium in boiling

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[95] A. Byström, Arkiv Kemi, Mineral. Geol. 25A, No. 13 (1947) [C. A., 43, 451 (1949)].

[96] C. A. Kraus and C. L. Brown, J. Am. Chem. Soc., 52, 4031 (1930).

xylene, under nitrogen. A red color developed, which gave way to yellow, very faint at the end. The solution was decanted and filtered hot, and the brown residue remaining was washed with hot xylene. On cooling, the xylene solution yielded a small quantity of white crystals. Further concentration of the solution gave only a little more material, but when the solvent was finally removed completely a viscous yellow residue remained which solidified to a resin that could be chipped and ground to a powder. Attempts to recrystallize this material yielded, in each extraction, only minute amounts of solid. The white crystalline solid analyzed for $(C_6H_5)_2Ge$ (10 to 20% yield), and the molecular weight by freezing point in benzene was that of a tetramer, $[(C_6H_5)_2Ge]_4$. The colored resinous product, however, <u>also</u> analyzed close to the required value for diphenylgermanium, and also showed the tetrameric molecular weight. Furthermore, the crystalline sample became less soluble on being isolated. (One sample of white crystals having m. p. 294-5° was obtained, but it is not quite clear whether this m. p. could be duplicated or whether it was given by only one particular sample.)

This behavior (which has been confirmed in some work reported in the experimental part of this thesis) is very reminiscent of certain well-known features of the behavior of condensation polymers of bi-functional organic molecules[97]. In such cases (e. g., anhydride polymers of dibasic organic acids) units of five or six atoms give cyclic monomers, and those of about eight atoms or more give linear polymers, but there is usually in any series an intermediate case (the seven-atom unit in the case of the anhydrides) where reversible cyclization of the linear polymer occurs. The behavior of the polymer is then very similar to that of diphenylgermanium. It seems quite possible that the colored insoluble resin is a linear form, and the color may be due to unsaturated end-atoms. To suggest that the white crystals are a cyclic form, colorless because there are no end-groups, is a rather more speculative step, although such evidence as exists would seem to justify it.

One point in connection with the structure of the compounds of these elements in the four-covalent state remains to be discussed. This is the nature of the compounds R_6M_2, where M is Pb, Sn, or Ge. Krause[3] originally supposed that these substances, like hexaphenylethane, were highly dissociated into radicals in dilute solution, and his molecular weight data showed considerable dissociation. Measurements of magnetic susceptibility made on various compounds of this

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[97] W. H. Carothers, "Collected Papers", H. Mark and G. S. Whitby, editors, Interscience, New York, 1940.

type show however no paramagnetic effect at all[98,99], and the accuracy of the measurements is good enough that radicals at least cannot be present to an extent anywhere near that assumed by Krause from the freezing-point data. However, these freezing-point data have been confirmed by several other workers[49,100], and the dissociation is apparently real. The discussion has perhaps been somewhat obscured by the idea of radicals--that is, it has been implied that if there is dissociation, then there are radicals; or that since there are no radicals, there is no dissociation. Actually, all these data seem to indicate that there is dissociation, but not into radicals. This was suggested by Morris and Selwood[99], who thought that the low molecular weights might indicate decomposition. A pertinent experiment would be to determine whether the dissociation is reversible or not, but this has apparently never been done. The report of Malatesta[45] that in higher-melting solvents certain of these compounds do not show dissociation needs to be integrated with the other data. A clearer understanding of the nature of R_6Pb_2 compounds, in particular, would be desirable. Some light might then be thrown on one of the most peculiar reactions in organolead

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[98] R. Preckel and P. W. Selwood, J. Am. Chem. Soc., 62, 2765 (1940).

[99] H. Morris and P. W. Selwood, J. Am. Chem. Soc., 63, 2509 (1941).

[100] L. S. Foster, W. M. Dix, and I. J. Gruntfest, J. Am. Chem. Soc., 61, 1685 (1939).

chemistry, namely the smooth thermal decomposition to give lead and an R_4Pb compound.

EXPERIMENTAL

Organosilicon Reactions

Application of the halogen-metal interconversion to the preparation of derivatives of m-bromoaniline

Synthetic procedures involving in general a series of reactions such as

$$XC_6H_4NH_2 \xrightarrow{RLi} LiC_6H_4NLi_2 \xrightarrow{R_3MX,\ \text{then HOH}} R_3MC_6H_4NH_2$$

(where X = halogen, M = a metal, and R = an organic group) have been applied in this Laboratory[77,79,80,101] to the synthesis of organometallic compounds of elements of Group IV-B. Similar reactions starting from halogenated phenols have also been investigated[77,79,80,102]. The products from the amines are organometallic compounds containing an aromatic amino group, and these may in some cases[80,101] be diazotized and coupled with amines or phenols, or other diazotized amines may be coupled with them, to give dyes containing an organometallic grouping. Stuckwisch[79] applied this series of reactions to o- and p-bromoaniline, and prepared in this manner

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[101] H. Gilman and C. G. Stuckwisch, J. Am. Chem. Soc., 64, 1007 (1942).

[102] H. Gilman and J. F. Nobis, J. Am. Chem. Soc., 72, 2629 (1950).

corresponding organolead compounds. He concluded, however, that m-bromoaniline did not react, since from carbonation of the intermediate he did not isolate m-aminobenzoic acid. In some cases it has been suggested that the difficulty of isolation of organometallic derivatives so prepared from o- or p-bromoaniline is due to the susceptibility to hydrolysis of such compounds. It appeared that compounds with the amino group meta to the metal atom might conceivably be less sensitive in this respect. The possibility of using m-bromoaniline for such syntheses was therefore again investigated. For this purpose organic compounds of silicon were employed, since the desired starting materials are readily available commercially.

In the experiments described below the n-butyllithium was usually prepared in accordance with a procedure recently described from this Laboratory[103], in yields varying from 74 to 81%. The solutions were analyzed by the double titration method[104]. The m-bromoaniline was redistilled from Eastman Kodak material. All operations up to the hydrolysis step were carried out in an atmosphere of pure dry nitrogen.

All melting points reported in this experimental section are uncorrected.

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[103] H. Gilman and co-workers, J. Am. Chem. Soc., 71, 1499 (1949).

[104] H. Gilman and A. H. Haubein, J. Am. Chem. Soc., 66, 1515 (1944).

Reaction of n-butyllithium with m-bromoaniline.--In carrying out this interconversion the m-bromoaniline in ether was placed in a three-neck flask equipped with stirrer and reflux condenser, and was stirred and cooled mildly with ice water while the n-butyllithium solution was added from a calibrated dropping funnel. The concentrations of the reagents are indicated below in specific experiments. Three equivalents of n-butyllithium were used per mole of m-bromoaniline. During the addition of the first equivalent of the lithium compound gas was evolved vigorously, and the solution became greenish in color. Color Test I[105] for active organometallic compounds was now negative. The addition of the rest of the n-butyllithium, in the cold, proceeded without any more evolution of gas and without the development of much heat. Color Test I became positive during the addition of the second equivalent. After all the lithium compound (three equivalents) had been added the solution was dull brown. It contained no colored precipitate, and no such precipitate formed on stirring for varying periods, up to one hour, in the cold. The reaction was finished by refluxing the mixture for 0.5-1.0 hour. During this time gas was again evolved, and a bright yellow solid precipitate appeared in the solution. This precipitate undoubtedly corresponded to

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[105] H. Gilman and F. Schulze, J. Am. Chem. Soc., 47, 2002 (1925).

the p-lithio-N,N-dilithioaniline isolated by Stuckwisch[106], and the phenomena described indicate that the reaction of the second hydrogen atom of the amino group with n-butyllithium did not occur until the solution was refluxed, and that the intermediate m-lithio-N-lithioaniline, m-LiC_6H_4NHLi, was ether-soluble.

Preparation of m-aminophenyltrimethylsilane.--In the first attempt, m-bromoaniline, 15.3 g. (0.089 mole), was treated under the conditions described above with 0.268 mole of n-butyllithium in 193 ml. of ether. To the resulting mixture, stirred and cooled in ice, there was added 19.3 g. (0.178 mole) of trimethylchlorosilane in 20 ml. of ether, at such a rate that mild refluxing was maintained. The solution was stirred for two hours longer, and then stood over night. It was hydrolyzed by slow addition of water, with ice cooling, and the ether layer was separated, washed with water, and dried on Drierite. Removal of the ether on a water bath left a dark reddish liquid, which was distilled through a 10-cm. Vigreaux column. There was collected 10.5 g. of material boiling at 80-97° (1.5 mm.). In addition there was a considerable amount of brown viscous tar left in the still pot. The distillate was redistilled twice, to give finally 2.8 g. of colorless liquid boiling at 82-86° (1.5 mm.), $n^{20}D$ 1.5472,

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[106] H. Gilman and C. G. Stuckwisch, J. Am. Chem. Soc., 71, 2933 (1949).

soluble in dilute hydrochloric acid. The b. p. of m-bromoaniline is estimated for 1.5 mm. as about 80°. Values of $n^{20}D$ from the literature are: m-Bromoaniline, 1.6260; aniline, 1.5863. Anal. Calcd. for $C_9H_{15}NSi$: Si, 17.0. Found: Si, 11.5.

The results of the first experiment indicated that a silicon-containing material was formed, but from the boiling points involved it appeared that its separation from starting material by distillation would not be possible. In a larger-scale experiment, carried out in the same way, the same results were obtained. The yield of product boiling after one distillation at 77-84° (1.5 mm.) was 11.5 g. from 28.7 g. of m-bromoaniline. This product had $n^{20}D$ 1.5472, and gave a positive test for halogen and for nitrogen on sodium fusion. Anal. Found: Si, 12.2; Br, 13.4. This analysis agreed closely with the composition of a mixture containing 70% of the desired compound and 30% of m-bromoaniline. On this basis, the yield of the desired product in the crude mixture would be 30% calculated from m-bromoaniline.

Of this product, various portions were taken and converted to solid derivatives, in order to investigate the possibility of purification by crystallization of the derivatives. These derivatives were all prepared by variations of the Schotten-Baumann technique--that is, under strongly basic conditions--since the C-Si bond is perhaps more stable to base than to acid. Benzenesulfonyl chloride gave a benzenesulfonamide, yield 0.2 g. from 1 g. of the crude amine, after recrystallization from aqueous ethanol to a constant m. p. of 100-101°. From benzoyl chloride and 1 g. of the crude material there resulted a benzamide, which after washing with dilute sodium hydroxide and with water and recrystallizing from aqueous alcohol had m. p. 121-125°. From 4 g. of the amine there was obtained, with acetic anhydride, an acetyl derivative, m. p. 114-115° after two recrystallizations from aqueous ethanol. All these derivatives crystallized as white needles. Most interest attached to the acetamide, since it should be the derivative most easily hydrolyzed to give back the desired amine. Of the recrystallized acetamide, 0.8 g. was refluxed for ten hours with 10% sodium hydroxide in 50% aqueous ethanol. The solution was then diluted with water and extracted with ether, the ether extract was treated with dilute hydrochloric acid, and finally the hydrochloric acid extract was made basic and extracted with ether. This ether solution was dried and the ether was removed, finally at 5 mm. pressure, leaving 0.2 g. of product, not enough to distill, having $\underline{n}^{20}$D 1.5318. Anal. Calcd. for $C_9H_{15}Si$: Si, 17.0. Found: Si, 16.9. This small sample was therefore apparently the desired product. In another experiment 0.6 g. of the acetyl derivative was refluxed for six hours with 20% aqueous sulfuric acid. This solution, after being made basic and worked up in the same way, yielded 0.1 g. of an amine having $\underline{n}^{20}D$ 1.5763 and containing no silicon. This was apparently aniline, produced by acid cleavage of the silicon compound. However, this was a strongly acid solution, and it appeared that the m-amino compound was in fact somewhat resistant to acid, since extractions with cold dilute hydrochloric acid could be performed without destroying the material.

Preparation of m-aminophenyltriphenylsilane.--In the experiments above the desired trimethylsilyl compound was formed, but the techniques required for its separation from unreacted starting material caused the yield to be very low. The corresponding triphenylsilyl compound was expected to be a solid, and it was hoped that its purification could be effected more simply.

m-Bromoaniline, 5.5 g. (0.032 mole) in 5 ml. of ether was treated as above with 0.096 mole of n-butyllithium in 89 ml. of ether, and to the resulting mixture there was added 18.9 g. (0.064 mole) of triphenylchlorosilane (recrystallized, m. p. 92-94°) suspended in 25 ml. of ether. The solution was then refluxed under nitrogen. Color Test I[105] was positive after one hour, negative after three hours. Hydrolysis of the mixture, followed by working up as above, gave from the ether solution a red-brown mushy residue. From this the triphenylsilanol (due to the excess triphenylchlorosilane) was distilled at 170-180° (1.5 mm.). The recovery of the silanol was 5.2 g. (67% based on the excess $(C_6H_5)_3SiCl$). It melted after recrystallization at 142-145° and contained no nitrogen or halogen. The residue was a tarry brown mass containing some solid material. An attempt was made to crystallize it from a mixture of chloroform and petroleum ether (b. p., 60-70°), but no crystals formed after four days in the refrigerator. The solution was therefore shaken with cold 5% hydrochloric acid, in an attempt to extract the amine, whereupon a solid appeared in the separatory funnel. This solid was filtered out, and the acid layer was then separated and a further amount of solid was obtained by neutralizing this acid extract. The solid fractions were combined. This material was brownish, amorphous, and gummy in character. It was dissolved in chloroform, boiled with charcoal, and filtered. The chloroform solution was then diluted with petroleum ether (b. p., 60-70°), and the product was recrystallized from the mixed solvent. This gave finally 0.25 g. (2% yield) of granular tan crystals, no longer tarry, and apparently stable in air, m. p. 248-251°. Anal. Calcd. for $C_{24}H_{21}NSi$: Si, 7.98. Found: Si, 7.79.

The product was obtained only in low yield, and the procedure was very tedious. In another experiment, an attempt was made to isolate the amine by precipitation of the hydrochloride from the ether solution with dry HCl, and thus to separate it from the tar which inhibits crystallization.

The reaction was carried out as before, using 6.7 g. of m-bromoaniline, the reaction mixture was hydrolyzed and washed, and the ether layer was separated and dried. Hydrogen chloride gas was then passed into this ether solution, cooled in ice, until no further precipitate formed. The precipitate was filtered out, to give about 5.5 g. of brown solid, which was granular while under the ether but which on exposure to air rapidly became tarry and sticky. This material was suspended in water, the suspension was made basic with 10% sodium hydroxide and stirred for one hour, and the solid was filtered out and washed with water. After drying in air, the solid material (about 3 g.) melted in the region of 120°, and was brown and sticky. It was treated in chloroform solution with charcoal, filtered, and recrystallized twice from a mixture of chloroform and petroleum ether (b. p., 60-70°). This finally gave 0.15 g. of tan powder, m. p. 248-250, which still contained however only 7.14% Si. This method of purification obviously offered no advantages.

Attempted preparation of m-aminophenyltriethylsilane.-- It appeared, therefore, that whereas the isolation of the trimethylsilyl compound was complicated by the presence of starting material boiling at nearly the same temperature, the isolation of the triphenylsilyl compound was still more difficult because of the presence of the large amount of tarry by-product. This tar was characteristic of the synthesis, and appeared also as a distillation residue in the experiments with the trimethylsilyl derivative, but the crude product could in that case be removed from the tar by distillation. It was therefore considered that this synthesis might be most suitably applied in a case where the product would be a liquid, so that it could be distilled away from the tar, but where the product might also have a boiling point differing enough from that of the starting material so that separation could be effected. The number of trialkylchlorosilanes available on the market is limited, but triethylchlorosilane is available, and an attempt was made to prepare m-aminophenyltriethylsilane from it. The procedure was exactly analogous to that used for the trimethylsilyl compound above. The triethylchlorosilane was obtained from Anderson Laboratories, Inc., Adrian, Michigan. From 27.8 g. of m-bromoaniline there was finally obtained 1.8 g. of product boiling at 94-98° at 1.0 mm., $n^{20}D$ 1.5156. Anal. Calcd. for $C_{12}H_{21}NSi$: Si, 13.5. Found: Si, 12.1. The material gave a positive test for halogen (and for nitrogen). This was not, therefore, a pure product. The behavior of the distillation indicated the presence in the mixture of another somewhat lower-boiling material of higher refractive index; this was presumably m-bromoaniline. The difference in boiling points was apparently not great enough for complete separation under the conditions of this distillation.

Preparation of some organosilicon compounds by Williamson-type reactions

The functional groups which are introduced into organic molecules in order to increase water-solubility may be classified as anionic, cationic, or neutral. A classification on this basis is often used for synthetic detergents, for instance. Most attempts to introduce solubilizing functions into organolead or organosilicon compounds have been concerned with anionic or cationic groups, such as the amino, phenolic, or sulfonic acid groupings. A difficulty which is encountered in many such cases is that the organometallic linkage is susceptible to the action of such groups themselves, and is cleaved by them, so that the desired compound is difficult to obtain. Or, in the case of basic groups such as the amino group, the compound must be treated with acid to bring it into solution, and cleavage may result, as was found by Austin[107] when he attempted to prepare a salt of triphenyl-*p*-aminophenyllead with even such a weak acid as acetic acid. These considerations of course do not indicate that attempts to solubilize sensitive organometallic compounds by means of ionic groups will not ultimately prove successful. However, it appeared that means for the introduction of neutral water

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[107] P. R. Austin, *J. Am. Chem. Soc.*, *54*, 3726 (1932).

solubilizing groups into such molecules might also be worthy of investigation, and some experiments in this direction were carried out.

Preparation of triphenyl-alpha-glyceroxysilane.--Triphenylsilanol, 2.8 g. (0.01 mole) was refluxed with 0.5 g. of sodium metal in 50 ml. of dry toluene for one hour. The solution was then filtered hot through glass wool into a 100-ml. three-neck flask equipped with stirrer and reflux condenser, and cooled. There was added 1.1 g. (0.01 mole) of glycerol alpha-chlorohydrin (prepared in 42% yield according to Conant and Quayle[108]). The precipitated triphenylsilanolate dissolved and the cold solution became clear. The mixture was stirred and refluxed for forty-five minutes, and the hot solution was filtered to remove the sodium chloride which had formed. Thereafter the solution was concentrated by distilling off solvent, and cooling in ice yielded 1.5 g. of triphenylsilanol, m. p. 154-155° after another crystallization, identified by mixed m. p. with an authentic sample. Since sodium chloride was formed, a reaction had obviously occurred, but not to give the desired product. It is probable that the result of this reaction was epoxide formation from the chlorohydrin,

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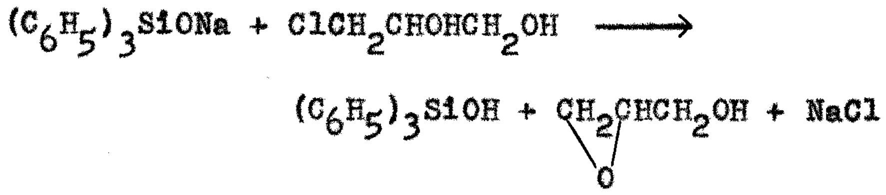
[108] J. B. Conant and O. R. Quayle, Organic Syntheses, Coll. Vol. I, 2nd ed., John Wiley and Sons, New York, 1941, p. 294.



$$(C_6H_5)_3SiONa + ClCH_2CHOHCH_2OH \longrightarrow (C_6H_5)_3SiOH + \underbrace{CH_2CHCH_2OH}_{O} + NaCl$$

since the tendency of glycerol alpha-monochlorohydrin to yield glycide when treated with sodium hydroxide, sodium ethoxide, or other bases is well-known.

Since the above experiment did not give the desired result, an attempt was made to carry out the coupling in the reverse manner. To 4.2 g. (0.014 mole) of triphenylchlorosilane in 40 ml. of benzene there was added 1.6 g. (0.014 mole) of alpha-monosodium glyceroxide, prepared according to Fairbourne and Toms[109]. The mixture was stirred one hour at room temperature. Reaction apparently occurred, with some warming and with the deposition of sodium chloride. The solution stood over night, and was then warmed to refluxing for fifteen minutes and filtered hot. When it was then cooled, it became turbid and 1.6 g. of sticky white crystals, m. p. about 120-135°, was obtained. Another crystallization did not improve much the character of this material. The difficulty apparently was that the impurity was glycerol, which is insoluble in benzene. The product was therefore crystallized from absolute ethanol, in two small portions, to give altogether 0.35 g. of white crystals melting at 135-7° with some preliminary softening. A 50:50 mixture of this

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[109] A. Fairbourne and H. Toms, J. Chem. Soc., 119, 1035 (1921).

material with triphenylsilanol (m. p. 153-4°) melted over a range from 110 to 146°.

In order to obtain a larger sample of this product, the above experiment was repeated with 16.0 g. of triphenylchlorosilane, and 9.0 g. of the crude sticky crystals was obtained from the hot benzene solution on cooling. This material was recrystallized from absolute ethanol. However, the first crop (2.2 g.) thus obtained melted from 69 to 120°, and a second crop (1.2 g.) melted at 65-7°. This second crop was identified, by a mixed melting point determination with an authentic sample[110], as triphenylethoxysilane. Apparently an interchange occurred on heating the product with ethanol. The reason why this was not noticed in the first experiment probably was that the amounts concerned were very small and the heating time required to effect solution in ethanol was only a few seconds.

These experiments suggested a suitable method of purification of the product. To 14.7 g. (0.05 mole) of triphenylchlorosilane in 100 ml. of dry benzene there was added 5.7 g. (0.05 mole) of alpha-monosodium glyceroxide, and the mixture was stirred at room temperature for two hours, then warmed to refluxing for fifteen minutes. The solid dissolved at first, then gradually a heavy white precipitate appeared, most of

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[110] L. F. Cason, Doctoral Dissertation, Iowa State College (1948).

which went into solution during the refluxing, leaving the sodium chloride as a sticky ball. The hot solution was filtered, and on cooling yielded 4.6 g. of sticky white crystals. This material was placed in a small conical flask and stirred for three minutes with absolute ethanol, with ice cooling. It was then filtered out, and the treatment was repeated. This removed the glycerol, apparently, since it was now possible to crystallize the material from benzene in pure form. The yield was 3.2 g. (18%), m. p. 139-142°. Anal. Calcd. for $C_{21}H_{22}O_3Si$: Si, 8.01. Found: Si, 7.93.

Preparation of triphenyllead triphenylsilanolate.--Triphenylsilanol, 1.85 g. (0.007 mole), was refluxed for thirty minutes in 25 ml. of dry toluene with 0.5 g. of sodium. The hot solution was decanted from the sodium into another reaction flask, and there was added 3.2 g. (0.007 mole) of triphenyllead chloride (prepared by the method of Gilman and Robinson[111]). The mixture was refluxed for forty-five minutes, with shaking. The sodium chloride which formed was filtered out of the hot solution. From the filtrate there separated on cooling 2.7 g. (56%) of white crystals, m. p. 125-7°. After crystallization from 1:5 chloroform-petroleum ether (b. p., 60-70°) the m. p. was 123-4°. Anal. Calcd. for $C_{36}H_{30}OPbSi$: Pb, 29.0; Si, 3.9. Found: Pb, 29.4; Si,

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[111] H. Gilman and J. D. Robinson, J. Am. Chem. Soc., 51, 3112 (1929).

4.0. The analysis was carried out by fusing the sample with sodium peroxide in a Parr bomb, dehydrating the silica with perchloric acid, and determining the lead as chromate in the filtrate from the silica.

Attempted reaction of lead chloride with sodium triphenylsilanolate.--The solution of sodium triphenylsilanolate prepared as above from 0.5 g. of sodium and 2.8 g. (0.01 mole) of triphenylsilanol in 25 ml. of toluene was stirred and refluxed for four hours with 1.3 g. (0.005 mole) of lead chloride, $PbCl_2$. There was no evidence of reaction. The residue remained unchanged, and was filtered out and identified as lead chloride. From the toluene solution, after hydrolysis with water, triphenylsilanol, m. p. 148-151°, was recovered.

Organolead Reactions

When the attention was now turned to lead compounds, the first necessity was to prepare a stock of starting materials such as tetraphenyllead and triphenyllead chloride. The synthesis of tetraphenyllead by the usual procedure[112] from the Grignard reagent and lead chloride is quite convenient. However, some work in this Laboratory[6] (at that time unpublished) had shown, as discussed in the historical section,

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[112] W. C. Setzer, R. W. Leeper, and H. Gilman, J. Am. Chem. Soc., 61, 1609 (1939).

that the reaction of an RLi compound with lead chloride in the presence of the RI compound could give very high yields of R_4Pb compounds. The reaction had been applied by R. W. Leeper[5] to the synthesis of tetraphenyllead in 80% yield, and this method appeared to be potentially the most convenient procedure available for the preparation of such compounds. This proved to be the case, and some further investigations into the nature and scope of the reaction were undertaken.

The aryllithium solutions, for all the work described below, were prepared as in the following example: To 6 g. (0.86 g. atom) of lithium metal, cut into small pieces and stirred mechanically in 250 ml. of dry ether, there was added a solution of 62.8 g. (0.40 mole) of bromobenzene in 100 ml. of ether, at such a rate that steady refluxing was maintained throughout the addition. After the reaction was completed, the stirring was stopped and the solution was allowed to settle. In about nine out of ten cases, the solid material settled out completely from the phenyllithium solution in an hour or two, leaving a perfectly clear light brown solution. In a few cases, however, the preparations remained turbid, and would not settle completely. This difference was thought to be due perhaps to the bromobenzene used, although the point was never investigated. The solution was decanted through glass wool, under nitrogen, into a calibrated dropping funnel. For standardization, 2-ml. aliquots of the RLi preparation were pipetted into water and the resulting mixture was titrated with 0.1 N sulfuric acid, using phenolphthalein (or, in the case of p-dimethylaminophenyllithium, thymol blue) as indicator. The yields were always between 90 and 95%, so that the solutions were approximately 1 M.

In reactions involving organolithium compounds, the preparation of the RLi solution and all subsequent operations were carried out in an atmosphere of dry nitrogen.

The lead chloride was ordinary reagent grade material, used directly from the bottle without special drying.

In the experiments involving lead or lead chloride there was employed a glass stirrer with a heavy shaft and a semicircular glass blade which fit closely the contour of the bottom of the flask. Efficient stirring was an important point in the technique.

Studies on the preparation of R_4Pb compounds by the Jones-Leeper technique

Preparation of tetraphenyllead.--This was carried out according to the directions previously given[5]. To 69.5 g. (0.25 mole) of lead chloride, 56 g. (0.25 mole plus 10%) of iodobenzene, and 200 ml. of ether in a three-neck flask there was added a solution of phenyllithium prepared from 126 g. (0.8 mole) of bromobenzene and 12 g. (1.73 g. atom) of lithium. Addition was at room temperature, without cooling.

Mechanical stirring was employed. The mixture was then refluxed for two hours, cooled in ice, hydrolyzed by addition of ice water, and filtered to remove the crude product. After drying, this residue was extracted for twenty-four hours with 300-400 ml. of chloroform in a Soxhlet extractor. Filtration of the chloroform extract, after cooling, yielded in several experiments always about 100 g. (about 80%) of tetraphenyllead. During the preparation there was observed at first a fleeting yellow color, and occasionally during the reaction some traces of gray which then disappeared, but essentially the mixture remained nearly white throughout. The heating effect during the addition of the phenyllithium was small, but was sufficient to cause the solution to reflux in runs of this size.

Effect of reflux time.--Tetraphenyllead was prepared by the procedure above, using 13.9 g. (0.05 mole) of lead chloride, 10.2 g. (0.05 mole) of iodobenzene, and 0.15 mole of phenyllithium in ether. After addition was complete the mixture was refluxed only fifteen minutes. Since there had been no particular change in the appearance of the preparation above after the completion of the addition, it was thought that perhaps the two-hour refluxing period was unnecessary. However, when this mixture was worked up as above the yield of tetraphenyllead obtained from the chloroform extract was only 8.2 g., or 32%. The ether layer was dried and the ether distilled off, and petroleum ether (b. p., 60-70°) was added to precipitate traces of tetraphenyllead. This was filtered out, and by distillation of the remaining solution there was obtained 4.7 g. (46% recovery) of iodobenzene.

Effect of a deficiency of phenyllithium.--Certain conceivable mechanisms which might be suggested for this reaction would involve as intermediates compounds such as triphenyllead iodide, formed during reactions such as

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

$$(C_6H_5)_2Pb + C_6H_5I \longrightarrow (C_6H_5)_3PbI$$

$$C_6H_5Li + (C_6H_5)_3PbI \longrightarrow (C_6H_5)_4Pb + LiI$$

If only two equivalents of phenyllithium, for instance, were used for the reaction, it might be expected that stable intermediates of this nature, if formed, could be isolated. The preparation was therefore carried out using different ratios of phenyllithium to lead chloride and iodobenzene.

To 13.5 g. (0.05 mole) of lead chloride and 10.2 g. (0.05 mole) of iodobenzene in 40 ml. of ether there was added 0.10 mole (2 equivalents) of phenyllithium in 95 ml. of ether. The mixture was refluxed for one hour. Color Test I[105] was positive after 0.5 hour, negative after one hour. The reaction was worked up as above. The yield of tetraphenyllead was 15.1 g. This is 88% based on the equation

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

The residue from the ether layer, after removal of 0.2 g. of tetraphenyllead by treatment with petroleum ether (b. p., 60-70°), gave 3.1 g. (0.015 mole) of iodobenzene, b. p. 48-9° (4.5 mm.). The excess of iodobenzene present, according to the reaction above, was 0.017 mole. Obviously essentially all the phenyl groups were accounted for, and any organolead product other than tetraphenyllead could scarcely have been present in any significant amount. No triphenyllead iodide was found.

In another experiment, there was used 13.9 g. (0.05 mole) of lead chloride, 10.2 g. (0.05 mole) of iodobenzene, and 0.05 mole (1 equivalent) of phenyllithium in 45 ml. of ether. The reaction was worked up in the same way, and there was obtained 6.3 g., or 73% yield based on the reaction given, and again no other organolead product was found present.

Redissolution of metallic lead.--The most probable mechanism[6] for the reaction under consideration involves metallic lead as an intermediate. This formulation is supported by the observation[6] that in the case of the alkyl compounds black lead is formed and then redissolves as reaction proceeds. With the phenyl compound this is less easy to see, because this compound is insoluble in ether, so that a dense white precipitate is always present. An experiment bearing on this point was performed. To 11.1 g. (0.04 mole) of lead chloride in 30 ml. of ether, stirred and cooled at -10° in ice-salt, there was added 0.08 mole (2 equivalents) of phenyllithium in 76 ml. of ether. This gives a preparation which is essentially diphenyllead, as will be described below. Color Test I was negative. The yellow mixture was now refluxed for one hour to precipitate metallic lead. The result finally was a black suspension in a dark brown liquid. To this mixture, at room temperature, was added 0.04 mole (1 equivalent) more of phenyllithium and 0.04 mole, plus 10%, of iodobenzene, and stirring was continued. The mixture became white, and considerable refluxing occurred. Although some gray remained and apparently not all the lead dissolved, hydrolysis and working up of the product gave 16.2 g. of tetraphenyllead (78% based on the reaction above, or essentially the same yield as when the preparation was carried out directly).

This experiment was in agreement with the results of Gilman and Jones[6]. Previous experiments by Kocheshkov[39,113] had also demonstrated that metallic lead as such (i. e., not necessarily prepared by the decomposition of intermediates formed from lead chloride) would react with phenyllithium, much more readily in the presence of a phenyl halide than alone. For the preparation of the symmetrical R_4Pb compounds this latter method seemed to be of little practical interest,

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[113] T. V. Talalaeva and K. A. Kocheshkov, Zhur. Obshchei Khim., 8, 1831 (1938) [C. A., 33, 5819 (1939)].

but it was considered possible that studies employing lead powder and using different organic radicals in the RLi compound and in the iodo compound might throw some light on the nature of the reaction, and might also serve to indicate whether this would be a practical method of preparation of compounds of the type $R_2R'_2Pb$ directly from lead. Such reactions had not been reported previously.

Reaction of phenyllithium with lead powder in the presence of ethyl iodide.--To 10.4 g. (0.05 g. atom) of lead metal powder (Metals Disintegrating Co., Elizabeth, New Jersey, MD 205, Lot No. 1177-F) stirred vigorously in 50 ml. of dry ether, there was added 15.6 g. (0.10 mole) of ethyl iodide, and the mixture was refluxed for one hour. There was no visible evidence of reaction, and the lead apparently remained unaltered. A solution of 0.10 mole of phenyllithium in 98 ml. of ether was then added rapidly to the refluxing solution. A white cloudiness developed, which gave way quickly to a black suspension, and heat was evolved. Stirring and refluxing were continued for four hours. Color Test I[105] was now negative. The mixture was cooled in ice and hydrolyzed by addition of water. The whole mixture was filtered with suction. There remained on the filter 4.1 g. of black lead. The ether layer of the filtrate was separated and dried, and the ether distilled. There remained 15.7 g. of yellow oil. An attempt was made to distill this oil through a 10-cm. Vigreaux column. At 35-5° (15 mm.) there was obtained about

0.5 g. of ethylbenzene, n^{20}D 1.4977, formed presumably by reaction of phenyllithium with the ethyl iodide. Distillation was continued at 5 mm. pressure, but little distillate passed over, and finally at a pot temperature of 180-190° extensive decomposition began to occur, with deposition of a lead mirror on the flask. The b. p.'s involved are: Tetraethyllead, 68° (5 mm.); triethylphenyllead, 126° (6 mm.); diethyldiphenyllead, 176° d. (8 mm.); ethyltriphenyllead, solid, m. p. 49-50°, not distillable without decomposition according to our experience. The result therefore indicated the presence of diethyldiphenyllead, and the absence of tetraethyllead.

The experiment was repeated. In the second trial, the residue of unattacked lead powder weighed only 1.8 g., and the residual oil from the ether weighed 18.2 g. It was distilled this time from a small flask with no column. Even under these conditions distillation was troublesome, and extensive decomposition occurred. Only one drop of material corresponding to ethylbenzene was obtained, and 8.2 g. of colorless liquid, boiling at 177-185° (5 mm.) was obtained in two fractions, n^{20}D 1.6172 and 1.6188 respectively. Anal. Calcd. for $(C_2H_5)_2Pb(C_6H_5)_2$: Pb, 49.4; for $C_2H_5Pb(C_6H_5)_3$: Pb, 44.3. Found: Pb, 48.6. This material was therefore largely diethyldiphenyllead (crude yield, 39%), from the b. p. and analysis. The decomposition during distillation, however, made a clean separation of the products impossible. This decomposition has been noted before[114,115].

Reaction of phenyllithium with lead powder in the presence of p-iodotoluene.--For a study of $R_2R'_2Pb$ compounds, where R is to be an aryl group, the number of choices of R' which can be made so that separation of the products will conceivably be possible is small. If R' is an alkyl group larger than methyl or ethyl, the products will be oils which according to the literature cannot be distilled without decomposition, and our experience showed that even in the case where R' was ethyl a good separation could not be obtained. If for R' another aryl radical should be chosen, it would be expected that all the products would be solids. Furthermore, it might be anticipated that in such a case halogen-metal interconversion and displacement reactions would lead to bad mixtures even if the primary reaction should proceed as desired. Nevertheless the experiment was tried. To 10.4 g. (0.05 g. atom) of the lead powder, stirred in 50 ml. of ether, there was added 21.8 g. (0.10 mole) of p-iodotoluene, and the mixture was refluxed. No apparent action occurred. To the refluxing solution there was added 0.10 mole of phenyllithium in 94 ml. of ether, and refluxing was continued for 1.5 hours. A white precipitate formed, in addition to the black lead.

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[114] S. Möller and P. Pfeiffer, Ber., 49, 2441 (1916).

[115] A. E. Goddard and D. Goddard, J. Chem. Soc., 121, 482 (1922).

The mixture was cooled in ice, hydrolyzed with water, and filtered. The residue (nearly white, about 4 g.) from the filtration was extracted with 50 ml. of chloroform, which left only 0.5 g. of lead powder. The ether layer in the filtrate was separated and dried, and to it was added the chloroform extract. The solvents were removed, and the product extracted with hot absolute ethanol to remove unsymmetrical lead compounds. Cooling of the ethanol extract gave 6.8 g. of white crystals, m. p. 125-36°. Repeated crystallizations did not effect purification; the last product still melted at 131-138°. The residue unextracted by the ethanol melted, after crystallization from ethanol-chloroform, at 220-235°. Apparently this reaction did give a mixture of the possible products, and purification was impossible beyond the separation of the symmetrical from the unsymmetrical compounds. Failure to separate this mixture has been reported by previous investigators[116].

Reaction of phenyllithium with lead powder in the presence of methyl iodide.--The only remaining choice of radicals appeared to be the phenyl-methyl combination. The mixture involved was separated by Calingaert[116]. Other drawbacks were apparent, however, such as the fact that methyl iodide couples rather rapidly with phenyllithium, and that the behavior of the methyl group in some organometallic

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[116] G. Calingaert, H. A. Beatty, and H. Soroos, J. Am. Chem. Soc., 62, 1099 (1940).

compounds (e. g., methyllithium) is unlike that of other alkyl groups. To 20.8 g. (0.10 g. atom, excess) of lead powder and 14.1 g. (0.10 mole) of methyl iodide in refluxing ether there was added, over a period of twenty minutes, 0.10 mole of phenyllithium in ether. The appearance of the reaction was the same as in the experiments involving ethyl iodide. The mixture was cooled in ice and hydrolyzed. Filtration left a partly white residue, indicating the presence of tetraphenyllead. This residue was extracted with chloroform, leaving 15.0 g. of unreacted lead, and the chloroform was distilled off to leave 3.0 g. (23%, calculated on the basis of the phenyl groups present in the phenyllithium) of tetraphenyllead, m. p. 226-8°, identified by mixed m. p. with an authentic specimen. Presumably this amount of tetraphenyllead cannot be due to a reaction involving only lead and phenyllithium, since Kocheshkov[39] obtained only a 5% yield of tetraphenyllead from phenyllithium and lead powder in 185 hours at room temperature. The residue from the ether layer yielded about 2 g. of toluene, 1 g. of distillate boiling indefinitely up to 100° (5 mm.), and 1 g. of residue in the pot. This reaction apparently proceeded to give mainly tetraphenyllead and toluene (by coupling), plus a small amount of impure volatile lead compounds. It is noteworthy that in the two reactions involving ethyl iodide (above) there was no evidence of tetraphenyllead, although it was sought for. The suggestion is that the methyl group behaved more like the p-tolyl than like the ethyl group (except for the coupling reaction).

Preparation of tetra-p-dimethylaminophenyllead.--This compound was desired for use in some of our experiments. It had been prepared previously[107] by the reaction

$$4\ \underline{p}\text{-}(CH_3)_2NC_6H_4Li + 2PbCl_2 \longrightarrow [\underline{p}\text{-}(CH_3)_2NC_6H_4]_4Pb + Pb + 4LiCl$$

in 17% yield. Its synthesis by the reaction

$$3\ \underline{p}\text{-}(CH_3)_2NC_6H_4Li + PbCl_2 + \underline{p}\text{-}(CH_3)_2NC_6H_4I \longrightarrow [\underline{p}\text{-}(CH_3)_2NC_6H_4]_4Pb + 2LiCl + LiI$$

was now investigated. The p-iododimethylaniline was prepared by halogen-metal interconversion between iodobenzene and p-dimethylaminophenyllithium[117].

To 11.1 g. (0.04 mole) of lead chloride and 9.9 g. (0.04 mole) of p-iododimethylaniline in 30 ml. of ether there was added at room temperature, with stirring, a solution of 0.12 mole of p-dimethylaminophenyllithium in 113 ml. of ether, over a period of thirty minutes. A transient yellow color, followed by a deep brown, appeared during the addition of the first portions of the organolithium solution. These colors gave way to a greenish gray (not the dense black of precipitated

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[117] H. Gilman and L. Summers, J. Am. Chem. Soc., 72, 2767 (1950).

lead). The mixture was stirred one hour at room temperature, then refluxed for two hours. It was cooled in ice and hydrolyzed by addition of ammonium chloride solution, and the precipitated material was filtered out with suction. This grayish-white powder, weight 15 g., was extracted with chloroform in a Soxhlet extractor for twenty-four hours. Removal of the chloroform from the extract left a pasty grayish solid, which was not completely soluble in benzene when crystallization was attempted. It was therefore washed twice by decantation with boiling petroleum ether (b. p., 60-70°). Most of the color passed into the petroleum ether, and a nearly white powder, 8.4 g., remained. This now dissolved in 75 ml. of hot benzene, and was boiled with charcoal and filtered. To the hot filtrate there was added 100 ml. of the petroleum ether. Cooling yielded 4.7 g. of white crystals, m. p. 184-189°. A second crop was taken, weighing 0.7 g. and having the same melting point. The total yield was 20%. The original ether layer was worked up as usual, and gave a dark brown residue, which was treated with petroleum ether (b. p., 60-70°) to remove any of the lead compound present. About 1 g. of crude tetra-p-dimethylaminophenyllead precipitated and was filtered out. On removal of the solvent there now remained a dark brown liquid residue containing no lead, probably dimethylaniline.

In a second experiment the reaction was carried out as above, with the same amounts of starting materials, but the refluxing time was extended to 5.5 hours. The residue after hydrolysis (16 g.) was, in this case, given a pre-extraction with petroleum ether (b. p., 60-70°) for six hours in a Soxhlet extractor, in order if possible to remove the colored impurity which had caused trouble before. From the petroleum ether extracts there crystallized a few tenths of a gram of yellow needles, which were impure product, m. p. 165-190°. The chloroform extraction was then performed, but there was still some yellow color present. The solid from the chloroform was washed with petroleum ether (b. p., 60-70°), then crystallized from benzene-petroleum ether to give 7.4 g. (27%) of tetra-p-dimethylaminophenyllead, m. p. 189-191°. As before, the original ether layer was found to contain a little impure product, not enough to justify purification.

These experiments indicated a procedure which was tried and found to be suitable for the preparation of tetra-p-dimethylaminophenyllead in good yield on this scale. Apparently the reaction was very slow, and the crude product was contaminated with dimethylaniline and with small amounts of a yellowish impurity, not very soluble in benzene, which interfered with the purification. (This latter impurity was probably related to the diaryllead compound whose existence is indicated by experiments described below.) The following procedure was therefore adopted: A mixture of 11.1 g. (0.04 mole) of lead chloride and 10.9 g. (0.04 mole plus 10%) of p-iododimethylaniline was stirred and heated to refluxing in a three-neck flask while 0.12 mole of p-dimethylaminophenyllithium in 110 ml. of ether was added over a period of 1.5 hour. The color, which was very dark as addition proceeded, lightened at the end of the addition. Refluxing was continued for twenty-four hours. Color Test I[105] was still positive, although weak. The mixture was cooled and poured into ice water. The precipitate was filtered out and the filtrate (including the ether layer) discarded. The residue, after standing on filter paper for two hours, was washed once by decantation with 95% ethanol (for removal of water), then once by the same procedure with petroleum ether (b. p., 60-70°) (for removal of residual amines and of the colored impurity). The 30 g. of whitish powder remaining was dissolved in 300 ml. of benzene, boiled with charcoal, and filtered. To the hot filtrate there was added 500 ml. of warm petroleum ether (b. p., 60-70°). The solution was cooled, finally in the refrigerator, and the crystals were filtered out and washed with the petroleum ether. The yield was 17.4 g. (63%) of soft white needles, m. p. 187-9°. Anal. Calcd. for $C_{32}H_{40}N_4Pb$: Pb, 30.1. Found: Pb, 29.9.

This is a heterogeneous reaction, and quite slow, as these and other experiments demonstrate. It would be expected that for larger batches the time would be much increased. This was found to be the case. A preparation was carried out using the same procedure as above but starting from 45.9 g.

(0.165 mole) of lead chloride and 44.8 g. (0.165 mole) of p-iododimethylaniline in 130 ml. of ether, and adding 0.495 mole of p-dimethylaminophenyllithium in 498 ml. of ether. The product, after working up as before, weighed 25.6 g. (23% yield). To obtain a good yield from a batch of this size would probably require several days' refluxing.

Preparation of tetra-p-dimethylaminophenyllead tetramethiodide.--Tetra-p-dimethylaminophenyllead is soluble in acids such as hydrochloric acid, and can be precipitated unchanged after short periods of time by bases[107]. On standing in the acid solution, however, it decomposes. A way was sought in which this amino-lead compound could be converted to salts which would be soluble in water at a pH closer to 7.0, in order to avoid this acid cleavage. Since quaternary ammonium hydroxides are strong bases, their salts with the common strong acids would be expected to give nearly neutral solutions. The preparation of a methiodide of tetra-p-dimethylaminophenyllead was therefore undertaken. Methyl iodide reacted rapidly with this compound, and in no case was there any difficulty with this part of the preparation. The difficulty arose from the presence of four tertiary amino groups in this molecule. It was difficult to obtain a product analyzing for the tetramethiodide, apparently because when some of the tertiary amino groups had been converted, the molecule became so strongly polar that it precipitated from the organic solvents and was thus removed from the field of action of the methyl iodide. The adoption of rather drastic conditions finally gave the desired product.

In the first experiment 5.0 g. (excess) of methyl iodide in 25 ml. of benzene was added to 3.4 g. (0.005 mole) of tetra-p-dimethylaminophenyllead in 25 ml. of benzene, and the solution was stirred and refluxed for one hour. The white precipitate was filtered out and recrystallized from methanol, to give 1.3 g. of white crystals, m. p. 185-190°; mixed m. p. with the starting material, 185-192°; m. p. of the starting material, 189-191°. This product, insoluble in hot benzene and crystallizable from methanol, obviously was not starting material. The m. p. determinations were therefore taken as indicating that the product decomposed to give starting material somewhere below the m. p. of the latter. Anal. Calcd. for $C_{36}H_{52}NI_4Pb$: I, 40.4. Found: I, 32.3. From the benzene filtrate, on standing, more solid precipitated, indicating that the time allowed for reaction had been too short.

In another experiment the reaction was carried out in a 50:50 benzene-methanol mixture, with six hours' refluxing followed by sixteen hours' standing at room temperature. The yield was 2.5 g. of recrystallized material from 3.4 g. of tetra-p-dimethylaminophenyllead. The m. p. was as before. Anal. Found: I, 21.6.

Next the following procedure was tried: Tetra-p-dimethylaminophenyllead, 3.4 g. (0.005 mole) was dissolved in 25 ml. of methyl iodide in a small flask, and the solution was warmed for a minute or two. It became a solid paste. Then 300 ml. of methanol was added and the mixture was refluxed for 2.5 hours. The solid passed mostly into solution. The solution was filtered hot and the filtrate cooled, finally in the refrigerator, to give 3.5 g. of light yellow needles. Another crystallization gave 1.3 g. of white crystals, m. p. 187-190°. *Anal.* Found: I, 39.9. This method was apparently capable of yielding the desired product.

The final preparation was carried out as follows: Tetra-*p*-dimethylaminophenyllead, 13.8 g. (0.020 mole) was dissolved in 50 ml. of methyl iodide in a 2000-ml. three-neck flask equipped with stirrer and reflux condenser. The solution was warmed slightly and stirred, then let stand for one hour. A precipitate appeared gradually, and finally the whole mass became a whitish paste. Now 1000 ml. of methanol was added and the mixture was refluxed, with stirring, for twelve hours. The hot solution was filtered, leaving much undissolved residue. On cooling, finally in an ice-salt bath, the filtrate gave 9.9 g. of slightly yellow needles, which were recrystallized from 820 ml. of methanol to give 5.3 g. of product. The residue from the first filtration of the reaction mixture was replaced in the reaction flask and refluxed again with 1000 ml. of methanol containing 10 ml. of methyl iodide. Hot filtration now left little residue, and the filtrate on cooling yielded a second crop of 7.9 g. of pure white crystals. The total yield was thus 13.2 g. (53% calculated from the tetra-p-dimethylaminophenyllead). Both crops melted at 187-189°. Anal. Found: First crop, I, 40.7; second crop, I, 40.0.

This material was soluble in water or in cold methanol to the extent of about 0.5 g. per 100 ml. of solvent at room temperature, and somewhat more soluble in either solvent hot. It was soluble in ethylene glycol, and insoluble in benzene or ether. The saturated aqueous solution had pH 7.5. On standing for a month it gave no precipitate, and the pH rose only to 8.1.

Of this material, a sample was submitted to Dr. Jonathan L. Hartwell, of the National Institutes of Health, for testing against mouse sarcoma. The following letter from Dr. Hartwell to Professor Gilman contains a preliminary report of the results:

August 17, 1950

Professor Henry Gilman
Iowa State College of
Agriculture and Mechanic Arts
Ames, Iowa

Dear Professor Gilman:

I am sorry so much time has elapsed since your letter of July 11th, requesting information on your organolead compound, but I have been on a rather extended vacation.

The compound was injected subcutaneously in a dose (75 mg. per kg. body weight) which killed half the sarcoma-bearing mice, yet no damage was observed in the tumors. The slides have not come through yet but if there should be any evidence of histologic damage we will let you know.

In spite of this result, it might be well for us to study a few other water-soluble organo-lead compounds since this is an interesting class of compounds and one can not draw conclusions from one member of a class.

With best regards,

Sincerely yours,

/s/ Jonathan L. Hartwell
National Institutes of Health
Bethesda, Md.

Studies on the nature and reactions of triphenyllead-lithium in ether

In the course of experiments on reactions of the type described above, some experiments were performed in which lead chloride in ether was treated with phenyllithium at low temperatures. It was found that under these conditions decomposition of the intermediate did not occur, and no metallic lead was produced. Instead, the reaction proceeded smoothly to form triphenyllead-lithium, using three equivalents of the organolithium compound.

$$3C_6H_5Li + PbCl_2 \longrightarrow (C_6H_5)_3PbLi + 2LiCl$$

Such a reaction had been suggested previously[41], but any experimental details were lacking. Since this appeared to be a promising approach to the preparation of unsymmetrical organolead compounds directly from lead chloride, investigations of the course of the reaction were undertaken. Later it was applied for the synthesis of some organolead compounds of interest to us.

Preparation of triphenyllead-lithium in ether.--The general procedure which was used for the preparation of triphenyllead-lithium on a 0.04 mole scale was as follows: The phenyllithium solution, about 1 M, was prepared as described above, decanted into a calibrated dropping funnel, and titrated to determine its strength. The calculated volume of this solution necessary to give 0.120 mole of phenyllithium was added dropwise, over a period of about one hour, to 11.1 g. (0.04 mole) of dry lead chloride in 30 ml. of ether in a three-neck flask. The operations were of course carried out under nitrogen. During the addition the mixture was cooled in an ice-salt bath whose temperature was kept near -10°. Mechanical stirring was employed, and again it should be mentioned that efficient stirring is one of the most important points in the technique. The stirrer blade must fit the flask closely, otherwise the very dense lead chloride merely collects on the bottom of the flask and the reaction proceeds irregularly. The most efficient type of stirrer for such work, from the mechanical point of view is the Hershberg type. In these stirrers, however, the blades are made from metal wire, and the use of the metal always introduces some uncertainty, especially when unusual results are obtained from the experiment. Therefore it is probably best, in general, to employ a glass stirrer of the type described above (e. g., Ace Glass Co. stirrer, catalog number 8245).

The phenomena which occurred during the addition of the phenyllithium were as follows: The first few ml. produced no visible effect. Within a short time, however, a yellow color developed and deepened to a bright orange-yellow. This color, which is believed to indicate diphenyllead, increased in amount up to two equivalents of phenyllithium if the latter was added slowly enough so that it could react as added. If at any time the phenyllithium was added much faster than indicated above, the color would disappear and then reappear when addition was slowed. Color Test I[105] for reactive organometallic compounds remained negative up to about 0.110 mole of phenyllithium. Between 0.110 and 0.120 mole the yellow color disappeared and did not reappear; and at the same time Color Test I became positive. The final mixture contained a heavy, grayish-white precipitate (not black) in a light yellowish solution, and reacted as triphenyllead-lithium. These phenomena were confirmed carefully in at least four different runs, and were observed in general in numerous other experiments.

This preparation was repeated many times, for various studies, using quantities of lead chloride up to 0.1 mole. Runs up to this size caused no trouble if stirring and cooling were efficient. If however, due to heat of reaction or to any other cause, the internal temperature rose locally much above that indicated, some decomposition with deposition of lead took place. Whether or not the phenyllithium was added slowly enough that it could react as formed made a difference in the appearance of the solution during the reaction, as noted above, but it is believed that it would make no difference in the final result if the temperature could be kept down. That is, the rate of addition recommended above is governed largely by the efficiency of temperature control. If, however, the temperature was held too far below that indicated, the first part of the reaction proceeded rather slowly.

In the working up of reaction mixtures obtained from triphenyllead-lithium reactions, the procedure used varied according to the nature of the reaction. In general, the reaction mixtures after hydrolysis were filtered to remove tetraphenyllead and hexaphenyldilead, which are not very soluble in ether, and also to remove precipitated inorganic material. From these residues the organolead compounds were extracted with hot chloroform, and the tetraphenyllead was allowed to crystallize from the chloroform extract. From the chloroform filtrate any hexaphenyldilead could then be precipitated with ethanol. Tetraphenyllead can be identified, and a fair estimate of its purity can be formed, by the m. p. and mixed m. p. with authentic tetraphenyllead. Since hexaphenyldilead decomposes on heating at 155-160°, its m. p. behavior cannot be used as a criterion of purity. This behavior is, however, characteristic, and it is useful as a means of identification. From the ether extracts of these preparations the ether was removed, and petroleum ether (b. p. 60-70°) was added to precipitate traces of tetraphenyllead or hexaphenyldilead. Commonly, traces of tetraphenyllead were present in the preparations. Hexaphenyldilead was usually noted only in cases where reaction of the triphenyllead-lithium with the alkyl halide, for instance, had been incomplete (see below, under "Hydrolysis").

<u>Preparation of triphenylbenzyllead</u>.--Benzyl chloride was the reagent usually employed for the characterization of the triphenyllead-lithium preparations. Triphenyllead-lithium was prepared, as described above, by addition of 0.120 mole of phenyllithium in 115 ml. of ether to 11.1 g. (0.04 mole) of lead chloride in 30 ml. of ether at -10°. To this preparation there was then added 6.1 g. (0.04 mole plus 20%) of redistilled benzyl chloride in 50 ml. of ether, still in the cold. There was little heating effect. The mixture was stirred for fifteen minutes in the cold and then refluxed for 1.5 hours. The gray appearance of the precipitate gave way to the dead-white color of lithium chloride. The mixture was cooled in ice-salt and hydrolyzed by slow addition of cold saturated aqueous ammonium chloride solution. The hydrolysis left only traces of solid, not enough to require filtration. The ether layer was separated, washed with water, and dried on Drierite. The ether was removed on a water bath, and

finally by evacuation at a water pump at room temperature. This left a solid residue weighing 20.6 g., which was boiled with 150 ml. of hot 95% ethanol. The hot extract was filtered rapidly and then cooled to room temperature, and yielded 14.7 g. (69%) of triphenylbenzyllead as white crystals, m. p. 91-93°; mixed m. p. with an authentic specimen[118], 91-93°; m. p. of the reference sample, 91-93°.

Solubility of triphenyllead-lithium in ether.--It would in some cases be advantageous, in using these preparations of triphenyllead-lithium, if the solution could be decanted off the solid residue and then added to the other reactant, like an organolithium solution. This possibility was tested. Triphenyllead-lithium was prepared as above, using 11.1 g. (0.04 mole) of lead chloride, and after the preparation was complete the stirring was stopped and the gray-white solid allowed to settle out. The yellowish supernatant liquid was decanted through glass wool, under nitrogen, into a calibrated separatory funnel. The total volume was 104 ml. Of this, 52 ml. (one half) was run into ice water. There was only a trace of red color, and very little precipitate. (Triphenyllead-lithium on hydrolysis gives, as will be described below, a voluminous yellow or orange precipitate, accompanied by transient deep red colorations in the ether.) The other 52

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[118] H. Gilman, E. B. Towne, and H. L. Jones, J. Am. Chem. Soc., 55, 4689 (1933).

ml. of the decantate was placed in a three-neck flask under nitrogen and cooled in ice while 3.0 g. (0.02 mole plus 20%) of benzyl chloride in 32 ml. of ether was added. The experiment was then finished as in the preparation of triphenylbenzyllead. There was obtained finally 0.2 g. of impure triphenylbenzyllead, m. p. 85-90°.

When ice water was added for disposal of the residue remaining in the original reaction flask, the voluminous orange solid appeared, and the transient intense blood-red color.

Stability to heat at the diphenyllead stage.--The bright yellow intermediate which was present in the triphenylleadlithium preparations was believed to be diphenyllead in some form. Whatever its nature, the mixture at this stage was unstable to heat. In one experiment, 0.16 mole (2 equivalents) of phenyllithium in 150 ml. of ether was added at -10° to 22.2 g. (0.08 mole) of lead chloride in 65 ml. of ether. The color was now bright yellow, and Color Test I[105] was negative. This mixture was refluxed for one hour, with stirring. The color changed rapidly through brown to deep black, as in an ordinary preparation of tetraphenyllead from the Grignard reagent[3,112]. Stirring was stopped and the solid allowed to settle, and the ether solution was then decanted off. The solid was stirred with hot benzene, and this in turn was decanted. The black lead remained in the flask. From the combined extracts there was isolated 18.5 g. (79%) of hexaphenyldilead, d. 155°.

Stability to heat at the triphenyllead-lithium stage.--When three equivalents of phenyllithium had been added in the cold, and the yellow color was no longer present, the triphenyllead-lithium preparations were (rather unexpectedly) stable on heating, or at least decomposed only slowly. In one experiment triphenyllead-lithium was prepared as above, in the cold, and the mixture was then refluxed for two hours with stirring. There was no visible change, and no black precipitate. In another case, triphenyllead-lithium was prepared in ether as usual from 11.1 g. of lead chloride, and to the preparation there was then added 150 ml. of dry toluene, to raise the boiling point. The mixture was now refluxed with stirring for five hours, without visible change. It was cooled in ice, and there was added 6.1 g. (0.04 mole plus 20%) of benzyl chloride. The experiment was continued as in the preparation of triphenylbenzyllead. The residue of black lead on hydrolysis was filtered out, and weighed only 0.3 g. The yield of triphenylbenzyllead was 13.4 g. (65%).

Hydrolysis of the triphenyllead-lithium preparations.--Hydrolysis of various reaction mixtures obtained from lead chloride and phenyllithium at -10°, whether at a stage corresponding to diphenyllead or to triphenyllead-lithium, gave no well-defined products. The behavior of such mixtures on hydrolysis, however, was on the whole reproducible and distinctive enough that it would be used on occasion to give an indication of the completeness or the probable course of a reaction. Addition of these mixtures, at the diphenyllead or at the triphenyllead-lithium stage, to water gave a copious precipitate, varying in color from light yellow to orange. This precipitate undoubtedly contained inorganic material, although it was in part organic. During the hydrolysis a deep blood-red color often developed in the ether, or in benzene when this was present. This color faded rapidly to yellow. These organic extracts contained some unstable material of unknown nature, since on storage even under nitrogen they continued for several days to deposit a solid material which was originally whitish, but which turned yellow on ageing. Attempts to work up these different fractions gave usually in the organic part only some hexaphenyldilead. An experiment to be described below, which involved hydrolysis of the reaction product of p-dimethylaminophenyllithium with lead chloride, gives a good example of the indefinite behavior of these materials.

Carbonation experiments.--The theory was developed that in the triphenyllead-lithium preparations there existed an equilibrium between diphenyllead and phenyllithium, on the one hand, and triphenyllead-lithium on the other,

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

ordinarily far displaced toward triphenyllead-lithium. The reactions with benzyl chloride and with other alkyl halides (below) served to characterize the triphenyllead-lithium. Phenyllithium fortunately does not react exceedingly rapidly with most alkyl halides. For characterization of the phenyllithium, the carbonation reaction was employed.

Triphenyllead-lithium was prepared by addition of 0.120 mole (3 equivalents) of phenyllithium in 112 ml. of ether to 11.1 g. (0.04 mole) of lead chloride in 30 ml. of ether at -10°. Color Test I[105] was positive, and the mixture was gray-white, with no yellow solid remaining. Dry carbon dioxide gas was then led over the solution, still stirred in the cold, for five hours. The ether carried out by the gas stream was replaced. The yellow color gradually returned to the mixture. Hydrolysis with ice water gave the above-mentioned yellow precipitate, and the deep red color in the ether layer. The precipitate was filtered out with suction, and the water layer of the filtrate was separated and washed out again with ether. The combined ether layers were extracted once more with 5% sodium hydroxide, this extract was added to the previous aqueous extract, and the combined solutions were acidified with dilute nitric acid (white precipitate) and extracted twice with ether. These ether extracts were dried on Drierite and the ether was distilled off, leaving 2.4 g. of snow-white crystals, m. p. 115-121°, which after crystallization from water melted at 120-121°; mixed m. p. with an authentic specimen of benzoic acid, 120-121°. This is 0.020 mole of benzoic acid, or 49% yield calculated on the amount of phenyllithium present over two equivalents. A check experiment, performed in exactly the same way, gave 2.7 g. (55%, on the same basis) of benzoic acid.

In the first experiment, the original ether layer after hydrolysis and filtration was dried on Drierite and distilled, leaving 2.0 g. (11%) of hexaphenyldilead, d. 155° (see the remarks above under "Hydrolysis"). The solid residue from the hydrolysis was mostly inorganic, probably a basic carbonate of lead, judging from its evolution of carbon dioxide when treated with dilute nitric acid.

When exactly three equivalents of phenyllithium were used, per mole of lead chloride, in the preparation of triphenyllead-lithium, Color Test I was positive as usual in this case, indicating a small amount of free phenyllithium. In the next experiment, carbonation was performed on a preparation made using an intermediate amount of phenyllithium, not enough to cause a positive Color Test. To 11.1 g. (0.04 mole) of lead chloride in 30 ml. of ether there was added, at -10°, 0.104 mole (2.6 equivalents) of phenyllithium. Color Test I was negative, and some yellow color remained in the mixture. Carbon dioxide gas was now passed over the cold solution for five hours, during which time the yellow color deepened. Hydrolysis and working up as above gave 1.3 g. of benzoic acid, or 44% based on the amount (0.024 mole) of phenyllithium present in excess of two equivalents.

Any conclusions from these results would be vitiated if it should prove that diphenyllead itself could also react with carbon dioxide to give benzoic acid. A fourth experiment was therefore performed to test this possibility. Phenyllithium, 0.080 mole (2 equivalents) was added to 11.1 g. (0.040 mole) of lead chloride in 30 ml. of ether. Color Test I was negative, and the mixture was bright yellow in color. The carbonation and working up were carried out as before. No benzoic acid resulted. The final ether extract left no residue on distillation.

These results may be summarized as follows:

Equivs. C_6H_5Li per mole $PbCl_2$	Equivs. C_6H_5COOH per mole $PbCl_2$	Yield of C_6H_5COOH (basis: C_6H_5Li over 2 equivs.)
2.0	0.00	--
2.6	0.26	44%
3.0	0.55	55
3.0	0.49	49

That is, no benzoic acid resulted at the diphenyllead stage, but from any amount of phenyllithium present over two equivalents benzoic acid was obtained in 44-55% yields.

The equilibrium theory suggested above seemed to indicate that in a case where different aryl groups having about the same ionic character were used in forming the triaryllead-lithium compound an equilibrium among these groups would occur, and carbonation should give a mixture of acids (see discussion part). This was also tested. To 16.7 g. (0.060 mole) of lead chloride in 50 ml. of ether there was added 0.120 mole (2 equivalents) of phenyllithium in 115 ml. of ether, at -10°. The mixture had the appearance expected at the diphenyllead stage. Color Test I was negative. There was now added, still at -10°, 0.060 mole (1 equivalent) of p-tolyllithium. The yellow color disappeared, and the appearance of the mixture was the same as a triphenyllead-lithium preparation. Carbonation and working up were carried out as before. The crude acids thus obtained (7.9 g.) melted over a 10-degree range in the neighborhood of 80°. The composition of the mixture was determined by an oxidation procedure based on a method previously described from this Laboratory[119]. The mixed acids were boiled for three hours in 100 ml. of 10% sodium hydroxide containing 10 g. of potassium permanganate. The excess permanganate was destroyed with a drop of ethanol and the manganese dioxide was filtered out. The solution was made acid and filtered, and the white precipitate was extracted with two portions (25 and 50 ml.) of warm chloroform. This left 2.1 g. of an acid which did not melt at 280°. This was certainly terephthalic acid (0.013 mole), from oxidation of p-toluic acid, and no further attempt was made to identify it because p-toluic acid would have been formed in any case. The important point was whether benzoic acid would be formed

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[119] H. Gilman and J. E. Kirby, J. Am. Chem. Soc., 54, 345 (1932).

also. It was already known that the mixture at the diphenyllead stage would give no benzoic acid, and since the phenyllithium was added only in the first two equivalents, the formation of benzoic acid during carbonation would indicate equilibration between the phenyl and p-tolyl groups. The filtrate from the terephthalic acid was extracted with chloroform, and the chloroform extracts were combined and distilled, leaving 1.2 g. (0.010 mole) of benzoic acid, m. p. after recrystallizing from water 120-122°, identified by mixed m. p. with an authentic sample.

Preparation of tri-p-tolylbenzyllead.--In order to illustrate some simple examples of preparative applications of triaryllead-lithiums in ether, some reactions were carried out in which well-known compounds were prepared using other aryllithium components, and also some using other RX compounds. In one such experiment, 0.120 mole (3 equivalents) of p-tolyllithium in 114 ml. of ether was added, at -10°, to 11.1 g. (0.04 mole) of lead chloride in 30 ml. of ether. The appearance of the reaction at all stages was exactly the same as in the case of the phenyl compound. The intermediate diaryllead stage was yellow in this case also, and the final mixture gray-white. There was added, all in one portion, 5.6 g. (0.040 mole plus 10%) of benzyl chloride, and the mixture was then refluxed for 1.5 hours, cooled, hydrolyzed, and worked up as for triphenylbenzyllead (above). The crude product was extracted with 100 ml. of hot absolute ethanol, from which it crystallized on cooling as long flat rods, m. p. 81-83°. It was identified by mixed m. p. with an authentic sample[47].

In other experiments, described below, lead chloride was treated under the same conditions with o-tolyllithium. In this case it was noteworthy that the color in the diaryllead stage was a deep blood-red, rather than yellow.

Preparation of triphenylethyllead.--For this preparation there was used 13.9 g. (0.050 mole) of lead chloride in 50 ml. of ether, 0.150 mole of phenyllithium in 139 ml. of ether, and finally 7.8 g. (0.050 mole) of ethyl iodide. The reaction was carried out essentially as previously described for the other compounds, to give as crude product, after removal of the ether, a yellow liquid. To this there was added 50 ml. of petroleum ether (b. p., 60-70°), and the precipitate (0.2 g.) of tetraphenyllead was filtered out. The petroleum ether was removed, and the remaining oil was dissolved in 25 ml. of hot 95% ethanol. On cooling this solution the product appeared as an oil, which solidified in the refrigerator to white crystals, m. p. 48-50°, yield 10.5 g. (45%). This m. p. is higher than the values recorded in the literature, which vary from 39° to 42°. However, it was checked on different thermometers; and when the material was compared with an authentic specimen[120] all three samples (this preparation, the

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[120] J. D. Robinson, Doctoral Dissertation, Iowa State College, 1929.

reference material, and the mixture), heated simultaneously, melted at 48-50°. The lead content was also determined. Anal. Calcd. for $C_{20}H_{20}Pb$: Pb, 44.3. Found: Pb, 44.0.

Preparation of triphenyl-n-propyllead.--Triphenyllead-lithium was prepared from 11.1 g. (0.04 mole) of lead chloride in 30 ml. of ether and 0.120 mole of phenyllithium in 113 ml. of ether, and to this was added 4.9 g. (0.04 mole) of n-propyl bromide, all in one portion, in the cold. The mixture was in this case refluxed for only 0.5 hour, after which it was cooled, hydrolyzed, and worked up as in the case of triphenylbenzyllead, to give a pure-white solid as crude product. This was dissolved in 50 ml. of hot absolute ethanol, and on cooling this solution to room temperature there was obtained 11.1 g. of small white crystals, m. p. 67-8° (lit., 69-70°). Cooling the mother liquor in the refrigerator gave a second crop, 1.0 g., m. p. 66-68°. The total yield, 12.1 g., was 63%. Anal. Calcd. for $C_{21}H_{22}Pb$: Pb, 43.0. Found: Pb, 42.7.

Reaction of p-dimethylaminophenyllithium with lead chloride.--p-Dimethylaminophenyllithium reacted very much more slowly with lead chloride than did the other aryllithium compounds. When an ether solution of this lithium compound was added to 11.1 g. (0.04 mole) of lead chloride in ether at -10°, Color Test I[105] became positive with the first few ml. of the organolithium solution. Two equivalents (0.080 mole) of the RLi compound was added, and the mixture was stirred in the cold for five hours and finally refluxed for sixty hours before the Color Test became negative. Upon addition of the first portions of the RLi solution the mixture became a deep violet blue in color, so that visual observation could not detect whether a colored intermediate, or metallic lead, was produced. This deep violet color is characteristic of some reactions involving this lithium compound. Small samples withdrawn and hydrolyzed with water, however, showed no lead, and there was apparently gradually built up in the mixture an orange-red intermediate. Because of this behavior, it was not readily possible in the case of the p-dimethylaminophenyl compound to distinguish the stages in the reaction or to demonstrate distinct mechanisms. Unsymmetrical derivatives containing the p-dimethylaminophenyl group were not obtained by use of reactions involving triaryllead-lithiums. The reaction of the lithium compound with lead chloride was so slow* that complicating side reactions led, instead, to by-products when the RX component was present. In one case an attempt was made to prepare phenyl-tri-p-dimethylaminophenyllead, the only unknown member of the group of phenyl-p-dimethylaminophenyllead derivatives. Instead of the desired reaction with lead chloride, the p-dimethylaminophenyllithium

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*Unpublished studies by G. E. Dunn in this Laboratory have shown that p-dimethylaminophenyllithium reacts at a similarly slow rate with silicon tetrachloride.

underwent a halogen-metal interconversion with the iodobenzene, and the main product isolated was p-iododimethylaniline. (This side reaction was later developed into a convenient laboratory method for the preparation of the latter compound[117].)

Since the reaction with lead chloride was so slow, it was thought that the diaryllead compound might in this case be correspondingly stable, and perhaps capable of isolation in a well-defined form. This idea was given support by the fact that no lead could be detected when these reaction mixtures were heated. A solution of 0.120 mole of p-dimethylaminophenyllithium was added to 11.1 g. (0.04 mole) of lead chloride in 30 ml. of ether and the mixture was refluxed with stirring for forty hours. The solid was allowed to settle and the liquid was decanted off into a separatory funnel and then added, under nitrogen, to ice water. There resulted 6.0 g. of a bright orange-red precipitate, which did not change in appearance on exposure to air. The dry powder was washed three times by decantation with ether. The residue contained nitrogen (and no halogen), and the Pb content was near that calculated for di-p-dimethylaminophenyllead. Anal. Calcd. for $C_{16}H_{20}N_2Pb$: Pb, 46.3. Found: Pb, 49.3. The material could not be purified without change. One gram of it was extracted with 150 ml. of hot benzene, and to the warm filtrate there was added 160 ml. of petroleum ether (b. p., 60-70). The solution, on cooling to room temperature, deposited 0.3 g.

of microcrystalline material of a clear deep brick-red color. However, the Pb content was now considerably lower. Anal. Found: Pb, 39.2.

Attempted preparation of an $R_2R'R''Pb$ compound from lead chloride.--The next point investigated was whether compounds of this type could be obtained directly from lead chloride, by the use of two different aryllithium compounds in succession. The only known material of this type which is a solid is phenyl-n-propyldi-o-tolyllead[121], and it was therefore chosen for the study. To 11.1 g. (0.040 mole) of lead chloride in 30 ml. of ether, at -10°, there was added 0.080 mole of o-tolyllithium in ether. Color Test I was negative, and the mixture was deep red in color. Then, still at -10°, there was added 0.040 mole of phenyllithium in ether. The color disappeared, and the Color Test became positive. To this preparation was added 12.3 g. (0.10 mole, excess) of n-propyl bromide, and the reaction was completed and worked up as described above for triphenylbenzyllead. The first crop of crystals from ethanol weighed 8.9 g., and melted at 53-79°. Recrystallization from a methanol-petroleum ether (b. p., 60-70°) mixture gave 4.3 g., melting at 44-92°. The material was obviously a mixture. A consideration of the m. p.'s recorded in the literature, and of the solubility characteristics (the material was completely soluble in the

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[121] P. R. Austin, J. Am. Chem. Soc., 55, 2948 (1933).

petroleum ether) indicated that the mixture could hardly contain tetraaryllead compounds, and probably consisted largely of triaryl-n-propylleads. In such a case the least symmetrical compounds of the type $Ar_2Ar'Pb$-n-C_3H_7 (Ar = aryl) might be expected to concentrate in the most soluble fractions. The ethanol mother liquor from the first crystallization was therefore concentrated and cooled in the refrigerator. The oil which separated would not crystallize. (The m. p. of the desired compound is 49-50°.)

The experiment was repeated as above, except that the n-propyl bromide was added beforehand to the reaction mixture. The result was however essentially the same.

Reaction of triphenyllead-lithium with iodobenzene.--To 11.1 g. (0.04 mole) of lead chloride in 30 ml. of ether there was added, at -10°, 0.120 mole of phenyllithium in 111 ml. of ether. To this preparation of triphenyllead-lithium there was added 9.0 g. (0.04 mole plus 10%) of iodobenzene. The mixture was refluxed for two hours, then cooled and hydrolyzed by addition of ice water. The residue was filtered out, dried, and extracted with chloroform in a Soxhlet extractor for twenty-four hours. The chloroform extract, cooled and filtered, yielded 13.5 g. (66%) of tetraphenyllead, m. p. 225-228°. This was a wider m. p. range than usual, and also the chloroform extract was somewhat turbid and yellowish (see under "Hydrolysis" above), although the crystals were white. The high-temperature reaction[5] previously studied gave a better yield of somewhat purer product.

Reaction of triphenyllead-lithium with *m*-bromoaniline.-- To the triphenyllead-lithium preparation obtained from 11.1 g. (0.04 mole) of lead chloride and 0.120 mole of phenyllithium there was added, still at -10°, a solution of 6.9 g. (0.04 mole) of *m*-bromoaniline in 25 ml. of ether. The mixture gradually became yellow again, indicating reaction of the phenyllithium component with the amine. After all the amine was in, enough more phenyllithium solution was added to discharge the yellow color. This required just 0.040 mole (1 equivalent) more. The mixture was stirred for forty-five minutes in the cold, then for forty-five minutes at room temperature, with no visible change. It was then refluxed for forty-five minutes, whereupon the bright yellow color was restored. Hydrolysis now gave the voluminous yellow precipitate and deep red colors which indicate (see above) that no reaction with triphenyllead-lithium has occurred, and the only organolead compound found in the mixture was hexaphenyldilead in small amounts.

These phenomena were interpretable in terms of what was known about the behavior of *m*-bromoaniline with organolithium compounds, as described in the section on organosilicon reactions. It was known that the first hydrogen atom of the amino group reacted rapidly with organolithium compounds at low temperatures, but that the product remained ether-soluble. It was also known that on heating the second hydrogen atom was attacked. An experiment was performed in which heating was avoided, and four equivalents of phenyllithium were used (one for the first hydrogen atom of the amine). That is, this was essentially an attempt to perform a reaction between triphenyllead-lithium and m-bromo-N-lithioaniline, m-BrC_6H_4NHLi. The mixture was stirred for one hour in the ice bath and then twenty-four hours at room temperature. There was now a slight yellowish tint. Hydrolysis and working up were carried out as usual, but no organolead products were isolated except for 1.3 g. of hexaphenyldilead, d. 155°.

Reaction of triphenyllead-lithium with p-nitrobenzyl chloride.--To 11.1 g. (0.04 mole) of lead chloride in 30 ml. of ether there was added 0.120 mole of phenyllithium in 112 ml. of ether, at -10°. To this preparation of triphenyllead-lithium there was now added, still at the same temperature, 7.5 g. (0.04 mole, plus 10%) of p-nitrobenzyl chloride in 100 ml. of ether. The color became violet briefly, then a red-brown precipitate appeared. The reaction was allowed to continue for 1.5 hours, then the mixture was poured onto ice and the residue was filtered out. This solid was extracted with chloroform, and after distillation of the chloroform the material recovered from it was extracted with ethanol (the desired unsymmetrical product should be crystallizable from this solvent). The ethanol extract yielded only 0.3 g. of hexaphenyldilead, d. 155°. There remained undissolved by the ethanol 11.2 g. more of the same material.

The ether layer from the original reaction mixture yielded a crude material which after several crystallizations using ethanol, methanol, and petroleum ether gave 1.0 g. of material, m. p. 69-71°; mixed m. p. with p-nitrobenzyl chloride, 71-74°; m. p. of the reference sample, 74-75°.

Preparation of triphenyl-γ-diethylaminopropyllead.-- It appeared that the reactions involving triphenyllead-lithium should be well adapted for the preparation of this compound, since the RX component, γ-diethylaminopropyl chloride, would contain a moderately reactive halogen and no functional group which would react rapidly with phenyllithium. Melstrom[77] had reported the preparation of γ-diethylaminopropyllithium from the chloride in 10% yield, and its reaction with triphenyllead chloride to give an unidentified oil. The same worker obtained an impure sample (lead analysis 5% high) of triethyl-γ-diethylaminopropyllead from the chloride and triethyllead-sodium prepared in liquid ammonia.

γ-Diethylaminopropyl chloride was prepared by the following modification of a previously described procedure[122]: A mixture of 120 ml. of chloroform and 29 g. of thionyl chloride was cooled in ice and stirred while 15.7 g. of γ-diethylaminopropanol in 26 ml. of chloroform was added. The solution was then refluxed for two hours, and the solvent and

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[122] H. Gilman and D. A. Shirley, J. Am. Chem. Soc., 66, 888 (1944).

most of the thionyl chloride were distilled off on a boiling water bath. The residue was shaken in an ice bath while 30 ml. of sodium hydroxide (4 g. of NaOH per 6 ml. of water) was added. A 100-ml. portion of ether was added to the flask, the mixture was shaken and allowed to settle, and the ether was decanted off. Then enough water just to dissolve the precipitated sodium chloride was added, and the solution was extracted once more with ether in a separatory funnel. The combined ether extracts were dried on Drierite for one to two hours (no longer), the ether was removed under reduced pressure at 30°, and the crude product distilled. It boiled at 76-77° (35 mm.). Distillation of the brown crude product was usually accompanied by foaming and bumping, and required the use of a large flask and some care. The product was colorless, and the yield from a preparation of this size was about 11 g. This material was stored in the refrigerator until needed, and immediately before use it was redistilled. The second distillation proceeded smoothly, with no foaming.

To 11.1 g. (0.04 mole) of lead chloride in 30 ml. of ether there was added, at -10°, a solution of 0.120 mole of phenyllithium in 114 ml. of ether. To this preparation of triphenyllead-lithium there was added 6.6 g. (0.04 mole plus 10%) of γ-diethylaminopropyl chloride in 25 ml. of ether. The mixture was stirred ten minutes in the cold, then refluxed for 1.5 hours, cooled in ice, and hydrolyzed by addition of cold dilute ammonium chloride solution. There was only an incidental trace of insoluble residue. The ether layer was separated and dried and the ether was removed, finally in vacuo. There remained 19 g. of yellow-brown nitrogen-containing oil. It would not solidify, even in Dry Ice, and attempts to crystallize it from ethanol or from petroleum ether (b. p., 60-70°) were fruitless. The material was characterized as described below. It was crude triphenyl-γ-diethylaminopropyllead.

The reaction was repeated several times, with the same result. In the largest preparation the triphenyllead-lithium was made from 27.8 g. (0.10 mole) of lead chloride and 0.30 mole of phenyllithium, and to this there was poured in all at once 15.0 g. (0.10 mole) of γ-diethylaminopropyl chloride. The reaction was completed as above, and after the ether was finally pumped out there remained 50.5 g. (91%) of the crude triphenyl-γ-diethylaminopropyllead as a yellow oil. Anal. Calcd. for $C_{25}H_{31}NPb$: Pb, 37.5. Found: Pb, 36.0. On standing, this oil developed a small amount of white precipitate (presumably tetraphenyllead). When this was removed by treatment with petroleum ether and the oil was then recovered, the precipitate developed again in time.

From the experience of Melstrom[77], it had been expected that the product would be an oil. The main interest, however, was not in this compound itself but in the possibility that some of its derivatives might be soluble enough in water to permit physiological testing. Crystalline derivatives were readily obtained.

Preparation of triphenyl-γ-diethylaminopropyllead methiodide.--To triphenyl-γ-diethylaminopropyllead obtained as above, starting from 0.02 mole of lead chloride, there was added 10 ml. of methyl iodide. There was some warming, and a clear solution resulted, which after ten minutes' standing set up to a solid white mass on being shaken. The mass was treated with 75 ml. of petroleum ether (b. p., 60-70°), the lumps broken up, and the suspension filtered. The residue was washed in the same way with ethyl ether, and there remained a white granular solid, 7.5 g. Part of the material was recrystallized from water, but this was not a very suitable solvent, and the crystals were sticky, due probably to insolubility of the trace impurities also. A mixture of 20 ml. of absolute ethanol and 25 ml. of petroleum ether (b. p., 60-70°) was a suitable solvent for recrystallization. The product appeared as beautiful pearly plates with a yellowish shine in bulk, m. p. 153-155°. Iodine and nitrogen were found present. Anal. Calcd. for $C_{26}H_{34}NIPb$: Pb, 29.8. Found: Pb, 29.4.

In a larger preparation, the triphenyl-γ-diethylaminopropyllead obtained starting from 8.3 g. (0.03 mole) of lead chloride was dissolved in 20 ml. of methyl iodide, and after ten minutes the solid was treated with 100 ml. of petroleum ether (b. p., 60-70°), filtered, and then washed in the same way with 100 ml. of ethyl ether. The crude product (20 g.) was dissolved in 200 ml. of hot absolute ethanol, filtered hot, and allowed to crystallize after addition of 250 ml. of hot petroleum ether (b. p., 60-70°). The yield was 15.3 g. (74% calculated from lead chloride) of the small shining plates, m. p. 153-155°.

The methiodide was essentially insoluble in water at room temperature. Since quaternary ammonium hydroxides are usually very soluble in water, experiments were carried out to determine whether such a derivative could be isolated. In one case, 3.5 g. (0.005 mole) of the methiodide in 50 ml. of methanol was stirred with the moist silver oxide prepared from 1.7 g. (0.01 mole) of silver nitrate. No change occurred at room temperature. When the solution was warmed, a dense black precipitate appeared, and a metallic mirror formed on the flask. The decomposition of lead compounds caused by silver salts in alcohols has been mentioned in the historical section[31,32,33,34]. In the next experiment water was used as the solvent. The methiodide, 3.5 g. (0.005 mole), and the silver oxide from 1.7 g. (0.01 mole) of silver nitrate were stirred for five hours at room temperature in 50 ml. of water. A brown precipitate formed, and the solution became strongly basic. It was filtered three times for clarification, and evaporated to about 15 ml. Cooling still gave no precipitate. The solution apparently contained the quaternary ammonium hydroxide, but the latter was too soluble for isolation, as is the case with many such compounds. Dilute hydrochloric acid gave a white precipitate. Dilute sulfuric acid, however, did not; and when the sulfate solution was treated with aqueous potassium iodide a white precipitate resulted which after recrystallization proved to be the methiodide.

This method did not seem to offer much promise for preparative purposes. The experiments suggested, however, that the sulfate salts of this base must be quite soluble in water. Therefore a methosulfate derivative was prepared.

Preparation of triphenyl-γ-diethylaminopropyllead methosulfate.--In the first experiment, triphenyl-γ-diethylaminopropyllead, prepared starting from 0.03 mole of lead chloride, was dissolved in 50 ml. of petroleum ether (b. p., 60-70°) and stirred for 1.5 hours at room temperature with 2.5 g. of freshly distilled dimethyl sulfate. (The petroleum ether proved to be a poor solvent for this reaction, because the dimethyl sulfate was not soluble in it. However, because the product was also extremely insoluble, crystals resulted immediately.) The white, sticky precipitate was collected, washed by decantation with ethyl ether, and crystallized from 50 ml. of benzene. This gave 7.5 g. of white crystals, m. p. 136-138°, apparently $[(C_6H_5)_3PbCH_2CH_2CH_2N(C_2H_5)_2CH_3]^{+}\,OSO_2OCH_3^{-}$.

Anal. Calcd. for $C_{27}H_{37}O_4NSPb$: Pb, 30.5; S, 4.7. Found: Pb, 30.2; S, 4.9.

In the second experiment the triphenyl-γ-diethylaminopropyllead was prepared from 20.9 g. (0.075 mole) of lead chloride. The yellow oil was dissolved in 75 ml. of benzene, and this solution was added to a solution of 10.4 g. (0.075 mole, plus 10%) of freshly distilled dimethyl sulfate in 25 ml. of benzene, with mild cooling in water. The reaction mixture was stirred for fifteen minutes at room temperature, without further cooling. Seeding with one crystal of the methosulfate caused the product to precipitate from the super-saturated benzene solution as a white mass, apparently filling the flask. After an hour's additional stirring the mixture was heated just to refluxing to dissolve the precipitate, and the solution was transferred to a crystallization flask and allowed to cool to room temperature. The 40 g. of white crystals which resulted was recrystallized from 100 ml. of benzene. The yield was 36.0 g. (70% calculated on the lead chloride), m. p. 137-138°. Anal. Found: Pb, 30.2.

The methosulfate was very soluble in methanol or ethanol, soluble in ethylene glycol or in hot benzene, insoluble in cold benzene or in petroleum ether (b. p., 60-70°). It was extremely soluble in water. A sample of the solid moistened with even a few drops of water passed into a clear solution. The material was not, however, extremely hygroscopic. It was apparently surface-active, since aqueous solutions on shaking formed foam or suds like solutions of detergents. A solution containing 5 g. of the material in 25 ml. of water had pH 5.7; after four days this had risen to 6.9, but thereafter on standing for a week longer the solution showed little further change (pH 7.2). After three months there was no visible precipitate in this solution.

Reaction of triphenyl-γ-diethylaminopropyllead with hydrogen chloride in benzene.--The triphenyl-γ-diethylaminopropyllead prepared from 0.02 mole of lead chloride was dissolved in 100 ml. of benzene containing some petroleum ether (to keep the benzene from freezing), and dry hydrogen chloride was passed in slowly for fifteen minutes while the solution was stirred and cooled in an ice bath. A precipitate formed, gummy-appearing in the solution, but a granular white powder after filtration, weight 5.0 g. The benzene filtrate, after washing with water and drying, left no residue on distillation. The precipitate appeared to be lead chloride contaminated with probably some aliphatic amine hydrochloride. Crystallization from aqueous ethanol gave 1.2 g. of pure crystalline inorganic material, apparently lead chloride.

Preparation of diphenyl-γ-diethylaminopropyllead chloride hydrochloride.--Since hydrogen chloride in benzene apparently gave complete decomposition of the lead compound, aqueous hydrochloric acid was tried. The triphenyl-γ-diethylaminopropyllead prepared from 0.03 mole of lead chloride was dissolved in 100 ml. of ether and shaken in a separatory funnel with two successive 50-ml. portions of cold 5% hydrochloric acid. Addition of the acid caused an immediate precipitate of a heavy oil, insoluble in both layers, in the separatory funnel. The oil settled rapidly to the bottom, and was withdrawn with the aqueous layer into a conical flask. The flask was shaken for about fifteen minutes, whereupon the oil changed into a crystalline solid. This was filtered out, washed on the filter with ethanol and with ether, and crystallized from 200 ml. of 95% ethanol. The yield was 8.5 g. of white crystals. Sodium fusion showed nitrogen and halogen present. Heated in a capillary tube, this material gradually turned brown, but did not melt up to 250°. The lead content found did not agree with that required for the hydrochloride, $(C_6H_5)_3PbCH_2CH_2CH_2N(C_2H_5)_2HCl$, of the original material, and the chlorine content was much too high. It was therefore probable that cleavage of a phenyl group had occurred, and that this product was the hydrochloride, $(C_6H_5)_2Pb(Cl)CH_2CH_2CH_2N(C_2H_5)_2HCl$, of diphenyl-$\gamma$-diethylaminopropyllead chloride. This was in agreement with the lead and chlorine values. Anal. Calcd. for $C_{19}H_{27}NCl_2Pb$: Cl, 12.9; Pb, 37.8. Found: Cl, 12.7; Pb, 38.2.

In a second preparation, 30.0 g. of crude triphenyl-γ-diethylaminopropyllead was dissolved in 200 ml. of ether and washed twice with 100-ml. portions of cold 5% hydrochloric acid. The oil which formed was withdrawn with the water layers and shaken under the acid until crystallization was complete (thirty minutes). The product was filtered out and recrystallized from 450 ml. of 95% ethanol. The yield was 18.2 g. (61%). *Anal.* Found: Cl, 12.8; Pb, 38.0.

Reaction of diphenyl-γ-diethylaminopropyllead chloride hydrochloride with phenyllithium.--In order to establish more securely the structure indicated for this compound, it was re-converted with phenyllithium to the starting material, which was identified as the methosulfate derivative. Two equivalents of the lithium compound were used, one for neutralization of the hydrochloride group. Diphenyl-γ-diethylaminopropyllead chloride hydrochloride, 1.1 g. (0.002 mole) was suspended in 35 ml. of ether and cooled in ice while 0.004 mole of phenyllithium in ether was added with stirring. The mixture was refluxed for twenty minutes, cooled, and hydrolyzed, and the ether layer was worked up as usual. The residue from the ether was dissolved in 2.5 ml. of benzene and added to a solution of 0.8 ml. of dimethyl sulfate in benzene in a test tube. The solution was warmed for ten minutes, cooled, and seeded with one small crystal of the methosulfate. There crystallized 0.4 g. of white solid, which was collected on a filter and washed with ether. M. p. 139-140°; mixed m. p. with triphenyl-γ-diethylaminopropyllead methosulfate, 136-140°; m. p. of the reference sample, 136-138°.

Reaction of diphenyl-γ-diethylaminopropyllead chloride hydrochloride with ethylmagnesium iodide.--All the data on this rather unusual material indicated that it was a stable, crystallizable salt of a lead compound having three different groups attached to the lead atom. If the series of reactions could be repeated through one more step, after replacing the chlorine atom with a different group, the resulting derivative would have four different groups around lead, besides a basic group through which resolution might be possible. Some experiments in this direction were attempted. To 5.5 g. (0.01 mole) of diphenyl-γ-diethylaminopropyllead chloride hydrochloride suspended in 50 ml. of ether there was added 0.02 mole, plus 10%, of ethylmagnesium iodide, with cooling and stirring. The solid dissolved. The solution was cooled and hydrolyzed with dilute ammonium chloride, and the ether layer was separated and dried and the ether removed. Attempts to crystallize the remaining oil proved fruitless. It was therefore dissolved in ether and treated in a separatory funnel with two portions of cold 5% hydrochloric acid. As before, an oil separated immediately and was withdrawn with the aqueous layer. In this case, however, this oil would solidify only to a small extent on standing, scratching, and cooling in ice. Finally the mixture was warmed for five minutes on a steam bath. The gum dissolved, but the pure-white crystals which now separated on cooling proved to be inorganic, apparently lead chloride.

Reaction of diphenyl-γ-diethylaminopropyllead chloride hydrochloride with benzylmagnesium chloride.---To 5.5 g. (0.01 mole) of diphenyl-γ-diethylaminopropyllead chloride hydrochloride suspended in 50 ml. of ether there was added 0.02 mole, plus 10%, of benzylmagnesium chloride in ether, with cooling and stirring. Color Test I[105] was negative at 1.75 equivalents of the Grignard reagent. When all the organomagnesium compound had been added (10% over 2 equivalents) the Color Test was faintly positive. Working up of the reaction mixture in the usual manner gave 3.1 g. of yellow oil which could not be crystallized. This oil was separated into three portions of about 1 g. each, which were treated as follows: (a) One portion was refluxed for one hour in 25 ml. of benzene with 1 ml. of dimethyl sulfate. After the solution had stood over night the benzene was distilled off. The residue would not solidify. It was triturated under ether to remove impurities, but still did not crystallize. It was insoluble in the ether, a fact which indicated that reaction had occurred, since the starting material had been obtained out of an ether extract. (b) A portion was dissolved in 2 ml. of methyl iodide in a test tube, warmed, and allowed to stand two hours at room temperature. There was no precipitate, even when the solution was cooled in ice. The methyl iodide was evaporated off, and the residue allowed to stand for two days. It formed a glass, which was dissolved in hot ethanol-petroleum ether. The product came out as an oil, which crystallized after one week in the refrigerator to give yellowish crystals in the solvent. When these were filtered out, however, they softened to a gum, and could not be identified. (c) The third portion was dissolved in ether and shaken with a little cold 5% hydrochloric acid in a separatory funnel. As usual, an oil separated, and was withdrawn with the aqueous layer. On standing, this sample formed some white crystals, but remained mostly gummy.

Preparation of triphenyl-p-bromobenzyllead.--To 11.1 g. (0.04 mole) of lead chloride in 30 ml. of ether there was added, at -10°, 0.120 mole of phenyllithium in 113 ml. of ether. To this preparation of triphenyllead-lithium there was now added, still in the cold, 9.0 g. (0.04 mole plus 10%) of p-bromobenzyl chloride in 50 ml. of ether. The solution was refluxed for one hour, cooled in ice, and hydrolyzed by addition of dilute ammonium chloride solution. There was almost no residue on hydrolysis. After the ether layer was separated and dried, removal of the ether left the crude product as a yellow liquid containing mushy white crystals. It was crystallized from 80 ml. of absolute ethanol, and came out first as an oil, which solidified on cooling in the refrigerator. Yield, 16.3 g. (67%); m. p. 66-68°. Because of the oiling out, the product appeared as lumps. A sample of it was therefore recrystallized by dissolving it in petroleum ether (b. p., 60-70°), cooling rapidly in ice-salt to freeze the precipitate, and then adding ethanol to prevent redissolution on warming. This sample was mostly white crystals, m. p. unchanged at 66-68°. *Anal.* Calcd. for $C_{25}H_{21}BrPb$: Br, 13.1; Pb, 34.1. Found: Br, 13.2; Pb, 34.3.

Attempted reaction of triphenyl-p-bromobenzyllead with magnesium.--Triphenyl-*p*-bromobenzyllead, 6.1 g. (0.01 mole) in 35 ml. of ether was refluxed and stirred under nitrogen for three hours with 0.5 g. of magnesium turnings. Iodine was added as catalyst. Color Test I[105] remained negative, and there was no suggestion of reaction. A few drops of methylmagnesium iodide solution were finally added, but this also did not catalyze the reaction. The mixture was treated with water and worked up as usual, to give only starting material.

Attempted reaction of triphenyl-p-bromobenzyllead with lithium.--Triphenyl-*p*-bromobenzyllead, 6.1 g. (0.01 mole) was stirred for two hours at room temperature in 60 ml. of ether, under nitrogen, with 0.3 g. of lithium metal, freshly cut into small pieces. Since there was no evidence of reaction, the mixture was refluxed for five hours. The lithium became coated black, first on the freshly cut edges, but no other change was apparent. Working up of the mixture gave only recovered starting material. The appearance of a black coating on freshly cut sodium metal when heated with organolead compounds has been noted before[24].

The failure of the triphenyl-*p*-bromobenzyllead to give a Grignard reagent was in accordance with previous results . No organolead compound containing a halogen atom attached to an aromatic ring has been converted unambiguously to an organomagnesium derivative, although in one case[77] a positive Color Test I has been obtained. Organolead compounds containing aliphatic halogen have been described in only one paper[123], but in this case the ready formation of a Grignard reagent from triethyl-ϵ-bromoamyllead was reported. The possibility that triphenyllead-lithium could be used for the preparation of compounds having an aliphatic halogen atom was investigated. 1-Bromo-3-chloropropane is known to react with bases to give preferential displacement of the bromine atom--for instance, with sodium ethoxide there results 1-chloro-3-ethoxypropane, and with potassium cyanide 1-chloro-3-cyanopropane is formed. Such reactions were attempted with triphenyllead-lithium. For reference, it was necessary during this work to prepare the fully substituted derivatives, such as 1,3-bis(triphenyllead)propane, $(C_6H_5)_3PbCH_2CH_2CH_2Pb(C_6H_5)_3$.

Preparation of 1,3-bis(triphenyllead)propane.--Triphenyllead-lithium was prepared by the addition of 0.120 mole of phenyllithium in 113 ml. of ether to 11.1 g. (0.04 mole) of lead chloride in 30 ml. of ether at -10°. There was then added 4.0 g. (0.02 mole) of 1,3-dibromopropane and the mixture was stirred for fifteen minutes in the cold and then refluxed for one hour. It was cooled in ice, hydrolyzed with

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[123] G. Grüttner and E. Krause, Ber., 49, 2666 (1916).

ammonium chloride solution, and worked up in the usual manner. The crude product consisted of an oil plus some mushy crystals. It was extracted with two portions (100 and 50 ml.) of hot ethanol. The extracts on cooling yielded the product as an oil which solidified in the refrigerator, weight 8.4 g. The residue unextracted by the ethanol all dissolved readily in petroleum ether (b. p., 60-70°) (indicating no tetraphenyllead), and by addition of ethanol and crystallization from the hot mixed solvent there was obtained an additional 2.2 g. of product. The total weight was thus 10.6 g. (58%). The m. p. of both samples was 90-92°. Because the material oiled out on cooling, the final purification for analysis required four more crystallizations, from ethanol-petroleum ether mixtures. The final sample crystallized initially, at room temperature, as white crystals, m. p. 94-95°. (The m. p. after the previous crystallization had been 93-95°.) <u>Anal</u>. Calcd. for $C_{39}H_{36}Pb_2$: Pb, 45.1. Found: Pb, 44.9.

<u>Reaction of triphenyllead-lithium with 1-bromo-3-chloropropane</u>.--Triphenyllead-lithium was prepared by the addition of 0.180 mole of phenyllithium in 171 ml. of ether to 16.7 g. (0.06 mole) of lead chloride in 48 ml. of ether at -10°. To this preparation there was added 9.5 g. (0.06 mole) of 1-bromo-3-chloropropane (Eastman Kodak, freshly redistilled, b. p. 141-142°). The mixture was refluxed for 1.5 hours, then hydrolyzed and worked up as usual. Hydrolysis left almost no

residue. The crude product was extracted with 150 ml. of hot 95% ethanol. On cooling, finally in the refrigerator, the extract yielded 10.5 g. of white crystals, m. p. 68-71°. Anal. Calcd. for $C_{21}H_{21}PbCl$: Pb, 40.2; Cl, 6.9. Found: Pb, 40.1; halogen calculated as Cl, 6.4. The analysis was thus close to that required for triphenyl-γ-chloropropyllead, but the material did not give any evidence of active halogen. In an attempted reaction with magnesium turnings in ether there was no evidence of reaction, and no positive Color Test I, and the recovered material appeared to be the same as this sample. In an attempted conversion to the iodide with potassium iodide in acetone there was also no evidence of any reaction. The m. p. above is the same as that of triphenyl-n-propyllead (69-70°), and is considerably below that of the bis compound, which was 94-95°.

The reaction was repeated, using triphenyllead-lithium prepared from 0.04 mole of lead chloride. In this case the 1-bromo-3-chloropropane (12.6 g., 0.08 mole) was used in 100% excess over the theoretical amount, to encourage reaction with the bromine only, and the reaction time was limited to twenty minutes in the cold. Reaction was complete in this time, as judged by the absence of any red color and the appearance of only traces of precipitate on hydrolysis. The crude product was recrystallized as before, to give 28.2 g. of white solid, m. p. 65-71 . Of this material, 5 g. was dissolved in 5 ml. of petroleum ether (b. p., 60-70) and the solution was cooled rapidly in ice-salt with vigorous shaking, which gave crystals almost immediately (i. e., rather than oil). Ethanol, 30 ml., was added, and the product filtered out. It weighed 2.7 g. and had a m. p. of 56-65°.

The explanation of these results was not clear. It was obvious, however, that there was probably reaction at both ends of the 1-bromo-3-chloropropane molecule. The m. p. around 70° was apparently that of a mixture, containing probably some of the bis compound along with lower-melting material. In the halogen analysis the calculation of the result as chlorine gave nearly the correct value, but if some of this halogen was bromine, then the agreement was of course only fortuitous. The experiment was thus complicated by the possibility of formation of, not two, but three different products. Experiments were next attempted in which the dihalide contained only one halogen.

Reaction of triphenyllead-lithium with 1,3-dibromopropane.--Triphenyllead-lithium was prepared from 11.1 g. (0.04 mole) of lead chloride. To the cold solution there was added 8.9 g. (0.04 mole, plus 10%) of 1,3-dibromopropane. The reaction was allowed to continue for fifteen minutes without heating, and the mixture was then hydrolyzed and worked up as above to give a yellow oil as crude product. This was crystallized from alcohol, to give 7.3 g. of white powder, m. p. 65-80°. Further attempts to purify this material by crystallization gave no product having a definite melting point.

Preparation of 1,4-bis(triphenyllead)butane.--Triphenyllead-lithium was prepared from 0.04 mole of lead chloride, and to this preparation there was added dropwise, over a period of forty minutes, 3.4 g. (0.02 mole) of 1-bromo-4-chlorobutane (Columbia Chemical Co., Charleston, S. C.). The mixture was refluxed one hour, then cooled, hydrolyzed with dilute ammonium chloride, and worked up as usual. The crude product from the ether was a solid, weight 13.7 g., m. p. about 130-140°. It was extracted with 75 ml. of hot petroleum ether (b. p., 60-70°) and filtered. About 2 g. dissolved, and there crystallized 1.8 g. of small white crystals, m. p. 132-136°. (The petroleum ether was tried because ethanol had not been completely satisfactory for these crystallizations.) The residual solid was dissolved in chloroform, filtered for clarification, and crystallized from a mixture of 20 ml. of chloroform and 25 ml. of absolute ethanol, to give 8.5 g., m. p. 134-137°. In this experiment there had been some white residue on hydrolysis; this was apparently essentially the same material, precipitated because of its rather low solubility in ether. By recrystallization of this material, along with the first crop from petroleum ether (b. p., 60-70°), there was obtained a further 2.4 g. of product, m. p. 134-136°. The total yield of recrystallized material was 8.6 g. (46%). Anal. Calcd. for $C_{40}H_{38}Pb_2$: Pb, 44.4. Found: Pb, 44.2.

Reaction of triphenyllead-lithium with 1-bromo-4-chlorobutane.--Triphenyllead-lithium was prepared from 0.04 mole of lead chloride, and to it was added, all at once, 13.7 g. (0.08 mole, 100% excess) of 1-bromo-4-chlorobutane. The mixture was stirred twenty minutes in the cold, then hydrolyzed (little residue, filtration unnecessary) and worked up. The crude product was a yellow liquid. This was washed twice in a separatory funnel with ethanol (to remove unreacted halide), then treated with petroleum ether (b. p., 60-70°) to precipitate any R_4Pb compound, and filtered (residue, 0.2 g., white). To the petroleum ether solution (15 ml.) there was added 10 ml. of absolute ethanol. The product came out as an oil, which solidified with difficulty in the refrigerator to give 5.7 g. of rather sticky crystals, m. p. indefinite, about 55 or 60°, melt turbid. Another crystallization from petroleum ether (b. p., 60-70°) gave 1.2 g. of material melting over a 20 or 30 degree range up to about 125°. This obviously was the wrong end of the crystallization, since this product was approaching the m. p. of the bis derivative (above). Attention was turned to the more soluble fractions, and from the mother liquor of this crystallization there was obtained, by addition of ethanol and cooling in ice-salt, 2.2 g. of white crystals having m. p. about 56-61°.

Reaction of triphenyllead-lithium with triphenyllead chloride.--Compounds of the R_6Pb_2 type containing more than one kind of R group in the molecule have never been prepared. The possibility of preparing compounds of the $R_3PbPbR'_3$ type from R_3PbLi and R'_3PbX was investigated briefly. First, however, the present orientation experiment was carried out. Triphenyllead-lithium was prepared as usual, at -10°, from 8.3 g. (0.03 mole) of lead chloride. To this preparation there was added 14.2 g. (0.03 mole) of triphenyllead chloride and the mixture was stirred for 1.5 hours, still in the cold. The bright yellow color reappeared. The mixture was hydrolyzed by pouring it into dilute ammonium chloride solution and the residue was filtered out. After drying it weighed 25.2 g., and was a bright orange-yellow color. This material was extracted successively with petroleum ether (b. p., 60-70°) and hot ethanol, and then dissolved in chloroform and filtered, to leave only 0.7 g. of inorganic residue. The yellow color had faded during the ethanol treatment (this was the first point at which heat had been applied during this preparation). The chloroform solution was concentrated by distillation, and on cooling developed a persistent turbidity which remained troublesome throughout the following operations. Addition of ethanol gave 13.4 g. of white crystals. Heated in a capillary, a sample of these crystals developed a few dark specks at 155-160°, but did not behave much like hexaphenyldilead. On further heating the sample changed to yellowish and then to a brown mass, without melting. Recrystallization from a hot mixture of 85 ml. of chloroform and 100 ml. of absolute ethanol gave 9.0 g. of small white crystals which now decomposed extensively at 155-160°, like hexaphenyldilead. The petroleum ether and ethanol extracts of the original crude product gave, on working up, only some further amounts of these same crystals. The total yield of the material was 14.8 g. (56% calculated as hexaphenyldilead).

Reaction of triphenyllead-lithium with triethyllead chloride.--To the triphenyllead-lithium prepared from 0.04 mole of lead chloride, there was added 13.2 g. (0.04 mole) of triethyllead chloride (prepared according to Calingaert and co-workers[7]). The mixture became bright yellow. After 0.5 hour in the cold it was hydrolyzed by pouring it into ice water, and filtered. The ether layer of the filtrate was separated; it continued to deposit solid, and was filtered twice more on the same filter. The total residue amounted to 9.2 g. of crystalline crusts. This residue, treated as above, gave only hexaphenyldilead, 2.1 g. (12%). The ether solution, after drying and distillation, yielded a residue of oil containing white crystals. To this was added 50 ml. of absolute ethanol (with which triethylphenyllead is miscible, while tetraphenyllead and hexaphenyldilead are insoluble), and the solution was filtered from 1.2 g. of white solid. The filtrate again became turbid and continued for many days to deposit white solid. No definite product was isolated from it.

Other organolead reactions

Preparation of triphenyl-p-dimethylaminophenyllead.--Triphenyl-p-dimethylaminophenyllead was prepared as indicated by Austin[107]. Since he does not give complete details, the procedure which was used here is described in full. Triphenyllead chloride, 23.7 g. (0.05 mole), in 200 ml. of benzene plus 100 ml. of ether, was stirred and heated to refluxing while 0.06 mole (20% excess) of p-dimethylaminophenyllithium in 50 ml. of ether was added dropwise. Working up as usual (no residue on hydrolysis) gave a white solid as crude product from the organic layer. This was dissolved in 300 ml. of hot petroleum ether (b. p. 60-70°) containing 20 ml. of benzene, filtered for clarification, and allowed to crystallize in the refrigerator. There resulted about 20 g. (72%) of white solid, which, however, was still somewhat sticky. Recrystallization from 250 ml. of the petroleum ether containing 5 ml. of benzene, with charcoal, gave 8.4 g. of soft white powder, m. p. 128-130°. A second crop (m. p. 129-131°) raised the yield to 10.1 g. (Austin[107] gives the m. p. as 124-125°, and the yield as 77%.)

Preparation of triphenyl-p-dimethylaminophenyllead methosulfate.--Triphenyl-p-dimethylaminophenyllead, 8.4 g. (0.015 mole) in 25 ml. of benzene was added rapidly with shaking at room temperature to 1.9 g. (0.015 mole plus 10%)

of dimethyl sulfate in 10 ml. of benzene in a small conical flask. The solution stood one hour at room temperature. Only a slight precipitate formed. Twenty minutes' refluxing, however, caused a white solid to precipitate out, apparently filling the flask. The mixture was cooled and filtered, and the precipitate was washed with ether. Weight 4.2 g., m. p. 240-242° to a viscid, brownish melt. The filtrate, on standing over night, yielded 1.2 g. more product. The combined material was recrystallized from 250 ml. of absolute ethanol, with slow cooling, to give 3.5 g. (34%) of white, pearly, very fine fibers or needles, m. p. 241-243°. *Anal.* Calcd. for $C_{28}H_{31}O_4NSPb$: S, 4.7; Pb, 30.3. Found: S, 4.6; Pb, 29.8. This was apparently the expected compound, $[(C_6H_5)_3PbC_6H_4N(CH_3)_3]^+OSO_2OCH_3^-$. Its solubility in water was less than 0.1 g. per 100 ml. of water. (There was nevertheless foaming and suds when the material was shaken with water, as there had been with the triphenyl-gamma-diethylaminopropyllead methosulfate, above.)

Reaction of triphenyl-p-dimethylaminophenyllead with methyl iodide.--Triphenyl-*p*-dimethylaminophenyllead, 1.0 g., was dissolved in 2 ml. of methyl iodide in a 25 ml. flask, warmed to boiling, and allowed to stand at room temperature for two hours. Ether, 15 ml., was added and the product was filtered out. It was recrystallized from 20 ml. of absolute ethanol, to give 0.5 g. of white crystals which apparently decomposed on heating, so that the m. p. was not reproducible (e. g., heated rapidly from 27°, melted about 180°; heated at 2° per minute starting at 168°, melted at 173°; heated at 1° per minute, starting at 155°, melted about 165°). The analysis did not correspond for the expected methiodide. Both the lead and the iodine values were low, but the Pb:I ratio was correct. This indicated of course a content of inert material, possibly solvent of crystallization. The analysis in fact was close to that required for a dialcoholate, $(C_6H_5)_3PbC_6H_4N(CH_3) I\cdot 2C_2H_5OH$. Anal. Calcd. for $C_{31}H_{40}O_2NIPb$: Pb, 26.1; I, 16.0. Found: Pb, 25.9; I, 15.6.

Organogermanium Reactions

The studies described above on the reaction of phenyllithium with lead chloride stimulated interest in the nature of the reactions of organolithium compounds with derivatives of the other Group IV-B elements in the divalent state. Investigations in this Laboratory[124] showed that stannous chloride in ether reacts with three equivalents of phenyllithium, presumably to form triphenyltin-lithium, but that the latter reacts very slowly with RX compounds. Investigations carried out elsewhere[125] suggested that diphenyltin with phenyllithium gave triphenyltin-lithium.

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[124] S. D. Rosenberg, unpublished work.

[125] G. Wittig, Z. angew. Chem., 62, 231 (1950).

A brief investigation of the behavior of germanium in such reactions was therefore undertaken. (Part of this work was carried out in association with S. D. Rosenberg.) Germanium dichloride is very difficult to obtain, but the diiodide, GeI_2, is a stable material, and was therefore employed in this research. It was prepared, in about 40% yield, from sublimed germanium(II) sulfide, GeS*, with hydriodic acid[126]. Anal. Calcd. for GeI_2: I, 77.8. Found: I, 78.2, 78.4.

Reaction of germanium diiodide with phenyllithium in ether

Germanium diiodide, 5.9 g. (0.018 mole), was suspended in 20 ml. of ether and stirred and cooled in an ice-salt bath at -10°. Phenyllithium in ether was added. When 0.018 mole (1 equivalent) of phenyllithium in 16 ml. of ether had been added, Color Test I[105] was negative and there had developed a deep blood-red color. Addition of another 0.018 mole (1 equivalent) of the organolithium compound caused little change in the color, but some deep-red precipitate appeared on the sides and bottom of the flask. After one hour, Color Test I was still strongly positive. The cooling bath was removed, and the mixture was stirred thereafter at room temperature. After two hours more Color Test I was negative. Then additional portions of phenyllithium were added, and the mixture was

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*We are very grateful to Dr. D. F. Hornig of Brown University for the gift of the germanium sulfide.

[126] E. A. Flood, L. S. Foster, and E. W. Pietrusza, Inorg. Syntheses, 2, 106 (1946).

stirred each time until the Color Test became negative. At 2.5 equivalents, 20 hours were required; at 2.75 equivalents, 32 hours additional time. The other 0.25 equivalent was added (total, three equivalents) and the mixture was stirred for 34 hours longer. Color Test I remained positive. During the absorption of the third equivalent of phenyllithium the red color gradually lightened and the red precipitate dissolved, to leave a mixture containing a light orange-brown precipitate. There was now added 2.5 g. (0.018 mole plus 10%) of benzyl chloride in 25 ml. of ether, and the mixture was refluxed for 1.5 hours, cooled in ice, hydrolyzed with water, and filtered. The residue melted indistinctly around 220°. It was recrystallized from benzene, and gave 0.4 g. of small white prisms, m. p. 228-230°. Recrystallized again, it melted still at the same temperature. Mixed m. p. with an authentic specimen of tetraphenylgermanium, 232-235°; m. p. of the reference sample*, 232-235°.

The ether layer in the filtrate from the original reaction mixture was separated, dried on Drierite, and the ether distilled off on a water bath. This left a mush of discolored crystals in a yellow or reddish oil, the whole weighing 6.6 g. It was extracted twice with 20 ml. of hot isopropyl alcohol, which is the recommended solvent[127] for

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*Prepared by R. W. Leeper.

[127] C. A. Kraus and C. S. Sherman, J. Am. Chem. Soc., 55, 4694 (1933).

triphenylbenzylgermanium. The residue was now a brittle solid resin, weighing 1.9 g., burnt-orange in color. It was chipped out of the flask and preserved. It smelt strongly of benzyl chloride. From each of the isopropyl alcohol extracts there crystallized on cooling a gummy yellow material. This was extracted again with three successive 5-ml. portions of isopropyl alcohol, and each portion on cooling deposited a few milligrams of white, waxy crystals. All these extracts were poured through the same filter, but on the filter these soft crystals pressed together into an amorphous mass, m. p. about 70-190° when heated on a Fisher-Johns melting-point block.

These phenomena agree well with the behavior recorded for the diphenylgermanium polymer by Kraus[96], except that he records the white crystalline portion as melting (in one case) at 294-295°.

The experiment was repeated with essentially the same results, except that the third equivalent of phenyllithium required longer to react (about 40 hours at 2.5 equivalents and 64 hours at 2.75 equivalents; the mixture was stirred for 48 hours after adding all the organolithium compound).

DISCUSSION

Synthesis of Organolead Compounds

The most widely useful method for the preparation of organometallic derivatives of the heavier metals involves the reaction of a more reactive organometallic type, such as a Grignard reagent or an organolithium compound, with a halide of the heavier metal. For example, organomercury or organotin compounds are conveniently prepared by reactions such as

$$2RMgX + HgCl_2 \longrightarrow R_2Hg + MgX_2 + MgCl_2$$

$$4RMgX + SnCl_4 \longrightarrow R_4Sn + 2MgX_2 + 2MgCl_2$$

Organometallic derivatives of tetravalent lead may be obtained in an analogous manner[128], but the method is not used for preparative purposes because of the instability and treacherous nature of lead tetrachloride. Fortunately, such organolead compounds are available from the reaction of Grignard reagents with lead dichloride[129], according to the overall reaction

$$4RMgX + 2PbCl_2 \xrightarrow{\text{Heat}} R_4Pb + Pb + 2MgX_2 + 2MgCl_2 \qquad (I)$$

This is the common laboratory method of preparation of tetraarylleads. Unsymmetrical lead compounds are then usually

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

[129] P. Pfeiffer and P. Truskier, Ber., 37, 1125 (1904).

obtained by reactions such as the following (X = halogen):

$$R_4Pb + HX \longrightarrow R_3PbX + RH \qquad (II)$$

or $$R_4Pb + X_2 \longrightarrow R_3PbX + RX \qquad (III)$$

then $$R_3PbX + R'MgX \longrightarrow R_3PbR' + MgX_2 \qquad (IV)$$

Organolead compounds (except tetraethyllead) are not commercially available, and the investigator must therefore prepare for himself the intermediates indicated above. Improvements in the methods for their preparation are therefore always of interest.

The nature of the reaction of Grignard reagents with lead chloride was studied extensively by Krause and co-workers. They concluded[3] that the steps involved were

$$2RMgX + PbCl_2 \longrightarrow R_2Pb + MgX_2 + MgCl_2 \qquad (V)$$

$$3R_2Pb \longrightarrow R_6Pb_2 + Pb \qquad (VI)$$

$$2R_6Pb_2 \longrightarrow 3R_4Pb + Pb \qquad (VII)$$

(where, in accordance with later evidence[98,99,49], 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 if the heating time is limited, and when heated alone such compounds do undergo further thermal decomposition in accordance with reaction VII above[47,46]. Of the R_2Pb compounds presumably produced in reaction V, however, the only examples which have been isolated are diphenyllead and di-p-tolyllead. These were obtained[130] by the reaction of lead chloride with the Grignard reagent at 2°. The yields were only about 4%. At higher temperatures the decomposition was presumably too rapid, and even at 2° 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.

Organolithium compounds can be employed, in exactly the same way as Grignard reagents, for the preparation of R_4Pb derivatives[107].

$$4RLi + 2PbCl_2 \longrightarrow R_4Pb + Pb + 4LiCl \qquad \text{(VIII)}$$

The RLi compounds, used in this manner, offer no particular advantage over the Grignard reagent except in certain cases where the latter is unavailable (for example, in the preparation of tetra-p-dimethylaminophenyllead). However, the experiments of Jones[6] and of Leeper[5] in this Laboratory showed that organolithium compounds could also be used in another way for the preparation of R_4Pb derivatives. The overall reaction involved was

$$3RLi + PbCl_2 + RI \longrightarrow R_4Pb + 2LiCl + LiI \qquad \text{(IX)}$$

and it was suggested[6] that the steps involved were

$$4RLi + 2PbCl_2 \longrightarrow R_4Pb + Pb + 4LiCl \qquad \text{(X)}$$

$$2RI + Pb \longrightarrow R_2PbI_2 \qquad \text{(XI)}$$

$$2RLi + R_2PbI_2 \longrightarrow R_4Pb + 2LiI \qquad \text{(XII)}$$

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[130] E. Krause and G. G. Reissaus, Ber., 55, 888 (1922).

In this thesis it is shown that organolithium compounds, applied in yet another way, serve also as very useful tools for the synthesis of some unsymmetrical organolead derivatives. The reactions involve as intermediates R_3PbLi compounds, prepared in ether from lead chloride and RLi.

$$3RLi + PbCl_2 \longrightarrow R_3PbLi + 2LiCl \qquad (XIII)$$

The R_3PbLi compound is not isolated, but is instead treated with an organic halide, to give R_3PbR' compounds in good yields.

$$R_3PbLi + R'X \longrightarrow R_3PbR' + LiX \qquad (XIV)$$

The great advantage of this method of synthesis of such unsymmetrical organolead types of course lies in the fact that the preparation proceeds directly from lead chloride, and avoids the necessity of isolation of the R_4Pb compounds and then of the R_3PbX derivative (reactions I and II above). Another advantage is that it is not necessary to convert the R'X component to a Grignard reagent (as for reaction III) or organolithium compound, so that the method is well adapted for some cases where R'X does not react well with magnesium or with lithium to give an organometallic derivative. An example is the preparation, described above, of triphenyl-γ-diethylaminopropyllead. Another example is found in the preparation of compounds such as 1,3-bis(triphenyllead)propane, $(C_6H_5)_3PbCH_2CH_2CH_2Pb(C_6H_5)_3$. On the other hand, this synthetic method has certain limitations. It is well adapted for the preparation of R_3PbR' types in cases where $R'X$ contains a halogen atom attached to an aliphatic carbon atom. No compounds of this type in which R' is an aryl group have been obtained by this reaction. Also, the reaction becomes complicated if R' contains functions, such as amino or nitro groups, which react with organolithium compounds. Lastly, this is apparently not a generally useful method for the preparation of less symmetrical derivatives (for instance, of the type $R_2R'R''Pb$). The reasons for these limitations will be discussed below. In all cases studied in the work reported in this thesis, the group R was aromatic.

Mechanisms of Organolead Reactions

Many of the investigations reported in the experimental section were carried out for the purpose of throwing some light on the mechanisms involved in the preparation of organolead compounds by the various reactions considered. From these experiments, taken together with those of other workers, certain conclusions can be drawn. The mechanisms will be discussed with reference to the phenyl derivatives.

It appears that in the action of phenyllithium on lead chloride the key reaction is the formation of diphenyllead.

$$2RLi + PbCl_2 \longrightarrow R_2Pb + 2LiCl \qquad (XV)$$

Although the diphenyllead thus produced is not used as such, it is presumably the intermediate which on the one hand decomposes at higher temperatures, to give metallic lead (reaction VI); and which on the other hand, if the mixture is kept cold, reacts with additional phenyllithium to give triphenyllead-lithium.

$$(C_6H_5)_2Pb + C_6H_5Li \longrightarrow (C_6H_5)_3PbLi \qquad (XVI)$$

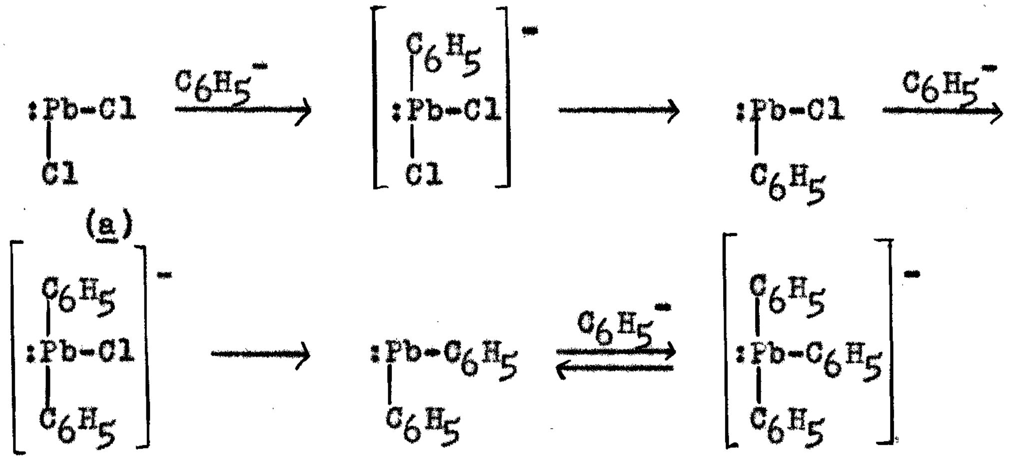
The peculiar usefulness of organolithium compounds in the latter application, as compared to the Grignard reagent, lies in the fact that they are active enough to react smoothly with lead chloride at temperatures low enough that decomposition does not occur. The low reactivity found for the Grignard reagent at such temperatures has been mentioned above. Reaction XV followed by Reactions XVI and XIV leads to the low-temperature synthesis of R_3PbR' compounds. Reaction XV followed, on heating, by reactions VI and VII leads to the classic synthesis of R_4Pb compounds. And, finally, reaction XV is of course included in reaction X, which initiates the preparation of R_4Pb compounds by the procedure of Jones[6] and Leeper[5].

It is believed, then, that when phenyllithium reacts with lead chloride in ether at low temperatures to form triphenyllead-lithium the reaction proceeds in the two stages represented by equations XV and XVI. The stages are readily distinguishable by the color phenomena described above. The bright yellow intermediate which appears and increases in amount up to two equivalents of phenyllithium is believed to represent diphenyllead, in some form. As the third equivalent of phenyllithium is added, this color fades out, and finally disappears from the precipitate (although if the mixture is allowed to settle a faint yellow color is still seen in the solution). Furthermore, it is believed that while reaction XV is irreversible, reaction XVI is reversible, so that the final preparation, containing exactly 3 equivalents of phenyllithium per mole of lead chloride, is regarded as an equilibrium system, far displaced toward the triphenyllead-lithium side.

$$(C_6H_5)_2Pb + C_6H_5Li \rightleftharpoons (C_6H_5)_3PbLi \qquad (XVI)$$

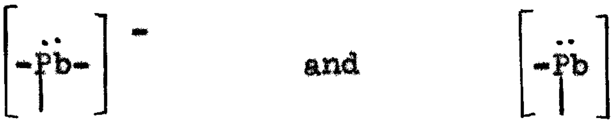
This formulation explains very well most of the behavior observed for the triphenyllead-lithium preparations. Addition of reagents containing functional groups known to react rapidly with RLi compounds always caused the reappearance, in a short time, of the yellow color, indicating a displacement of the above system to the left. This was the case, for instance, in the experiments with *m*-bromoaniline, with triethyllead chloride, and with carbon dioxide. In the case of carbon dioxide, it was found that phenyllithium added up to two equivalents was not available for carbonation to benzoic acid; but that whatever amount of phenyllithium was present *over* two equivalents could be carbonated to give, under the conditions used, always about 50% yield of benzoic acid. It is these reactions, plus the positive Color Test I[105] which develops between 2.7 and 3.0 equivalents of phenyllithium, which establish the availability of phenyllithium in these preparations. The belief in the presence of triphenyllead-lithium is of course based on the reactions with R'X compounds to give R_3PbR' derivatives.

From the discussion of divalent lead compounds given in the historical section, it is seen that monomolecular lead chloride is to be pictured as in formula a below, and that since only six electrons are present around the lead atom it should be able to accept an electron pair readily. If the organolithium compound is represented as reacting essentially as a phenyl anion, the changes involved may be as follows:



This is a formalized representation in that it shows the divalent lead compounds as monomers, whereas they are undoubtedly polymerized; and also in that it represents the organolithium compound as reacting as a simple anion, whereas the evidence available[125] suggests that it is actually a complex such as

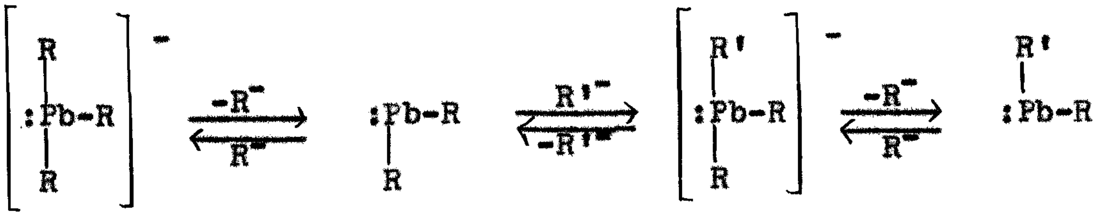
$[(C_6H_5)_2Li]$ Li. In the main, the formulation above points out that the occurrence of these reactions is the result of the small energy difference between the states



$$\left[-\ddot{P}b-\right]^- \quad \text{and} \quad \left[-\ddot{P}b\right]$$

It is the ready transformations between these two states which lead finally to the desired product. It would clearly be expected that the first two steps, involving displacement of chlorine by phenyl, might be essentially irreversible, because of the relatively high stability of chlorine as an anion. In the last step, however, there is no remaining chlorine atom. All the groups are now phenyl groups. Elimination of any anionic group at this point, therefore, would simply give back the reactants (diphenyllead and phenyllithium) and the indicated equilibrium would result. The position of this equilibrium would vary according to the nature of the R group.

The case would be different when two different organolithium compounds were present in the reaction mixture. There would then be a possibility of interchange of R groups on the lead atom, as for example



and so on, resulting in a mixture of various types of organolead intermediates. This is apparently what occurred in the attempts to prepare di-o-tolyl-n-propylphenyllead. Also, the occurrence of an equilibration of this sort is demonstrated by the appearance of benzoic acid in the mixed acids resulting from carbonation of the diphenyl-p-tolyllead-lithium preparation.

This equilibration of groups is the reason for one of the above-mentioned limitations on preparations involving triaryllead-lithiums. The other limitations indicated are due to the availability of RLi from the preparations. If R' in R'X contains a functional group which reacts rapidly with organolithium compounds, as in the experiments with m-bromoaniline or p-nitrobenzyl chloride, a complicated reaction will result. Fortunately alkyl halides do not in general react rapidly with aryllithium compounds, while apparently the reaction of triphenyllead-lithium with such halides is quite rapid, judging from the experiments in which complete reaction apparently resulted in ten or fifteen minutes in the cold. From the experiment in which triphenyllead-lithium with iodobenzene gave 66% of tetraphenyllead, it appears that reaction with aromatic halogen is also possible, although somewhat slower. The suggestion that in synthetic applications R' should be aliphatic is based, not on the lower reactivity of aromatic halogen toward the triphenyllead anion, but on the probability of occurrence of halogen-metal interconversion if

R' is aromatic. Thus for instance phenyllithium (available from the reversible reaction XVI) reacts rapidly with p-bromotoluene as follows[131]:

$$C_6H_5Li + \underline{p}\text{-}CH_3C_6H_4Br \rightleftarrows C_6H_5Br + \underline{p}\text{-}CH_3C_6H_4Li$$

This would lead finally to a mixture of products. (The case where R = R', and the product is therefore the symmetrical R_4Pb compound, would of course be an exception; but in this case the high-temperature technique is probably the method of practical choice.)

The two stages (equations XV and XVI) in the formation of triphenyllead-lithium are also distinguishable by the different behavior of the mixture on heating. Heating at the diphenyllead stage caused decomposition with deposition of lead and formation of hexaphenyldilead, as expected. Heating at the triphenyllead-lithium stage, however, did not cause decomposition. It has been pointed out[132] that this result requires consideration, since if the equilibrium XVI occurs then diphenyllead should be available in some amount even at the triphenyllead-lithium stage, and some decomposition might be expected. It may be that the equilibrium is ordinarily shifted far to the right as written, and that the time allowed for our experiments was not enough to detect decomposition

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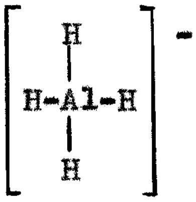
[131] H. Gilman and R. G. Jones, J. Am. Chem. Soc., 63, 1439, 1441, 1443 (1941).

[132] Private communication from Dr. George Calingaert to Professor Gilman.

under the existing conditions. It is also possible that there is a favorable temperature effect on the equilibrium.

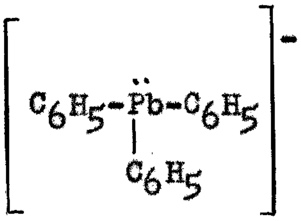
The Triphenyllead Anion and Other Organometallic Anions

Triphenyllead-lithium, $(C_6H_5)_3PbLi$, is an example of a type of complex in which a considerable amount of interest has recently developed (although such compounds have actually been known for many years). It is obvious that the reaction of phenyllithium with lead chloride in ether is quite analogous for instance to the reaction of lithium hydride with aluminum chloride in the same solvent to form lithium aluminum hydride[133]. In either case the chlorine atoms are displaced, and then finally the anion from one additional equivalent of the lithium compound adds to the central metal atom to complete the valence shell and form a univalent anion (b or c below). Similarly, methyllithium can react with trimethylaluminum[134] to give tetramethylaluminum-lithium



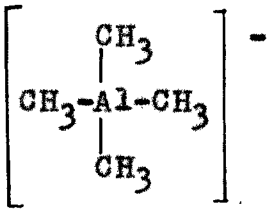
$$\left[\begin{array}{c} H \\ | \\ H\text{-}Al\text{-}H \\ | \\ H \end{array}\right]^-$$

(b)



$$\left[\begin{array}{c} C_6H_5\text{-}\ddot{P}b\text{-}C_6H_5 \\ | \\ C_6H_5 \end{array}\right]^-$$

(c)



$$\left[\begin{array}{c} CH_3 \\ | \\ CH_3\text{-}Al\text{-}CH_3 \\ | \\ CH_3 \end{array}\right]^-$$

(d)

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[133] A. E. Finholt, A. C. Bond, K. E. Wilzbach, and H. I. Schlesinger, J. Am. Chem. Soc., 69, 2692 (1947).

[134] D. T. Hurd, J. Org. Chem., 13, 711 (1948).

(anion, formula d). Many other examples of such compounds are now known, and their properties are discussed in a group of recent papers by Wittig and co-workers[125,135,136]. They may be prepared in general by reaction of a neutral organometallic molecule with an RLi compound (e. g., reaction XVI above), or by reaction of the RLi compound with an inorganic halide (e. g., reaction XIII). In the latter case the neutral molecule is an intermediate. It is of interest to compare the properties of triphenyllead-lithium with those of other complexes. (Lead complexes have not, up to the present time, been among those discussed by other authors).

Wittig[125] describes the behavior of the phenyl complexes of boron, aluminum, beryllium, and zinc, and mentions also triphenyltin-lithium. In general, in the cases investigated in detail, the compounds did not behave like triphenyllead-lithium. Tetraphenylboron-lithium, $(C_6H_5)_4BLi$, was a very unreactive material, crystallizable, and soluble in water without decomposition. During its preparation, Color Test I remained negative exactly up to the stoichiometric equivalence point (1 mole of phenyllithium to 1 mole of triphenylboron), and then became strongly positive. The compound did not react with ketones or with acyl chlorides. In fact, it showed none of the properties of phenyllithium, and there was no

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[135] G. Wittig, G. Keicher, A. Rückert, and P. Raff, Ann., 563, 110 (1949).

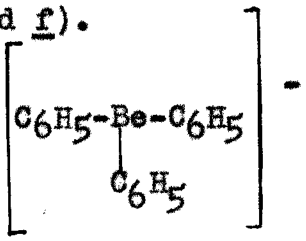
[136] G. Wittig and A. Rückert, Ann., 566, 101 (1950); G. Wittig and O. Bub, Ann., 566, 113 (1950).

evidence of any equilibrium corresponding to reaction XVI. Tetraphenylaluminum-lithium was hydrolyzed by water, and reacted with acyl chlorides to give ketones; but it did not react with ketones, and the evidence seemed to indicate that the reactions described were due to the complex itself rather than to phenyllithium. That is, the point of attack was probably the central aluminum atom (more vulnerable than the atom of the first-period element boron). Triphenylberyllium-lithium was more reactive yet, but there was still evidence against phenyllithium as the reactive species.

Furthermore, studies by S. D. Rosenberg in this Laboratory have thus far not demonstrated the availability of the phenyllithium in preparations of triphenyltin-lithium in ether, and the color phenomena and Color Test results are similar to those described by Wittig for his compounds. The single experiment recorded in this thesis with germanium indicates that this element might be found to behave in the same way as tin. It might in fact be expected that the behavior of R_3MLi derivatives of the elements of Group IV-B would be analogous to that of the R_4MLi derivatives of the Group III-A elements. The electron arrangement in the assumed structures is the same (see formulas c and d), with an octet around the central atom in either case, and the only difference is that in the case of the Group IV-B elements one pair of electrons (the "inert pair") binds no other atom.

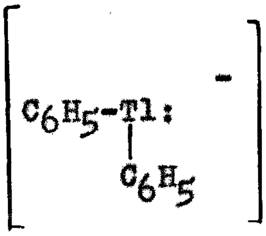
Thus it appears that while the properties of triphenyltin-lithium[124] (and probably of triphenylgermanium-lithium) are about as might be expected by analogy with other complexes, triphenyllead-lithium shows in certain respects a different behavior, as described in this thesis. The theory of a reversible reaction which has been advanced seems at present to give the most adequate explanation of this behavior, although this theory remains of course subject to revision in the light of future experimental data. An explanation on a more fundamental physical basis of this and other singularities in the behavior of lead compounds will be aided, of course, by the development of quantitative information on the energy states of the Group IV-B elements. The nature of this problem, and the difficulties involved, are indicated in the historical section.

From a preparative point of view, it is perhaps fortunate that triphenyllead-lithium differs in behavior from the $(C_6H_5)_3MLi$ derivatives of other metals of this group, since triphenyltin-lithium[124] and triphenylgermanium-lithium (this thesis) apparently do not react well with R'X compounds. It has been pointed out in the historical section that certain properties of lead in its compounds (such as the "inert pair" effect) are characteristic not so much of elements in a given group in the periodic table as of elements of high atomic number or atomic weight in general. Thus it is conceivable that analogies for lead should in some cases be sought in the same period, rather than in the same group. A knowledge of the behavior of thallium(I) in some of these reactions would be of interest for comparison with the behavior of lead(II). The results with thallium would be difficult to predict, because actually such a complex as diphenylthallium-lithium, $(C_6H_5)_2TlLi$, would not be analogous in electronic structure to triphenyllead-lithium and tetraphenylaluminum-lithium, but rather to triphenylberyllium-lithium (structures e and f).



$$\left[C_6H_5{-}\underset{\substack{| \\ C_6H_5}}{Be}{-}C_6H_5\right]^-$$

(e)



$$\left[C_6H_5{-}\underset{\substack{| \\ C_6H_5}}{Tl}{:}\right]^-$$

(f)

However, it would be of some interest if it could be shown that diphenylthallium-lithium could react smoothly with R'X compounds to give R_2TlR' derivatives. Unfortunately, the intermediate phenylthallium is so very unstable that it decomposes immediately even at -70°, and the complex anion f cannot be obtained[137].

Diphenyllead

The bright yellow intermediate which develops when lead chloride is allowed to react with two equivalents of phenyllithium at -10°, or which can be regenerated from the

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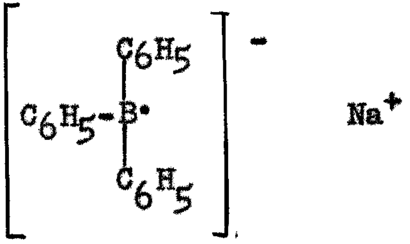
[137] H. Gilman and R. G. Jones, J. Am. Chem. Soc., 62, 2357 (1940).

triphenyllead-lithium preparations by reagents which are known to react with phenyllithium, has been referred to in this discussion as diphenyllead. The only reported isolation of diarylleads, by Krause and Reissaus[130], has already been mentioned. The material isolated by them was described as deep blood-red in color. It was characterized by lead, carbon, and hydrogen analyses, and by molecular weight determination (cryoscopic, in benzene; monomeric). The question which arises, therefore, is why the intermediate in the triphenyllead-lithium preparations should differ in color from the diphenyllead isolated by the other workers. To this question no specific answer can be given, but some discussion concerning diphenyllead can be offered.

A difficulty of course arises in any attempt to study this question directly, because diphenyllead in either form cannot be isolated as a well-defined material. The difficulties involved with triphenyllead-lithium preparations have been described in the experimental section. Attempts[25,49] to duplicate the work of Krause and Reissaus[130] with the Grignard reagent have likewise never been successful. These authors themselves, in fact, stated that the preparation could not be duplicated with any certainty. Their technique involved the addition of lead chloride to the Grignard solution. It is to be noted that in some of their experiments, when the reverse mode of addition was employed, they also observed a bright yellow intermediate which they did not isolate. They believed that this intermediate might represent the theoretical first step in the reaction, phenyllead chloride, C_6H_5PbCl. The results reported in this thesis do not support such a formulation. The yellow intermediate apparently increases in amount up to <u>two</u> equivalents of phenyllithium, and thereafter decreases. Furthermore, the orange-red material obtained by hydrolysis of the *p*-dimethylaminophenyl preparation did not contain halogen. In the mechanism indicated above for phenyllithium and lead chloride, there is a phenyllead chloride stage, but in practice it seems impossible to discern any phenomena which distinguish this stage as a separable step, whereas the diphenyllead stage is clearly distinguishable in practice. It is assumed that phenyllead chloride is very reactive toward phenyllithium.

The intermediate in the reaction of lead chloride with *o*-tolyllithium was deep red in color. *p*-Tolyllithium however gave a yellow intermediate. It should be noted that transient deep red colors do appear during the hydrolysis of triphenyllead-lithium preparations; and that the color observed in the intermediate, while bright yellow if the preparation is carried out as above, will vary under other conditions through orange to an orange-brown.

The reason why the color phenomena merit consideration at any length is of course that variations in color in compounds of this sort presumably reflect variations in the electronic state of the molecules involved, and color itself is usually attributed to the presence of labile or "odd" electrons in the molecule. Triphenyllead-lithium, it would seem, should be colorless if its electronic structure is as represented above (formula c), with no unpaired electrons and the stable octet arrangement around the central atom. This agrees with the observations recorded in this thesis. Tetraphenylboron-lithium, with an analogous structure, is isolable[125] as colorless needles and is extremely unreactive, as described above. There is, however, another type of phenylboron complex anion, present in compounds like triphenylboron-sodium[138]. These compounds are colored and highly reactive toward radical reagents such as oxygen, triphenylmethyl, etc. The properties of such materials undoubtedly indicate that they contain a radical-ion, with an unpaired electron (structure g). Triphenylboron-sodium is bright yellow.



$$\left[\begin{array}{c} \quad\ C_6H_5 \\ C_6H_5-\overset{|}{\underset{|}{B}}\cdot \\ \quad\ C_6H_5 \end{array}\right]^{-} \quad Na^{+}$$

(g)

For triphenylboron-lithium, colors varying from yellow through ruby-red to olive-green are mentioned. Another example of such a structure is probably present in the

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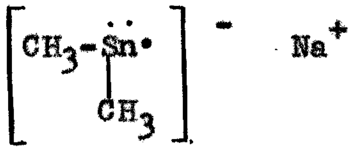
[138] E. Krause and H. Polack, Ber., 61, 271 (1928).

intermediate produced by the reaction of dimethyltin with sodium in liquid ammonia[139]. The first stage (1 g. atom of Na:1 mole of $(CH_3)_2Sn$) in this reaction gives an orange solution which reacts as would be expected if it contained dimethyltin-sodium (formula *h*). When tin[139] or germanium[96]



$$\left[\begin{array}{l}CH_3-\ddot{Sn}\cdot\\ \qquad|\\ \qquad CH_3\end{array}\right]^- \quad Na^+$$

(*h*)

compounds of this sort are treated with *two* gram-atoms of sodium, the resulting derivative is usually deep red in color. Tri-alpha-naphthylboron-disodium etherate, however, is black[140,141,142].

Thus it appears that variations in color in the lead preparations may indicate variations in electronic structure of the groups involved. At present it is not possible to give a consistent explanation of all the results observed. Further consideration may show that these color phenomena can be a useful aid to speculations on certain of the chemical

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[139] C. A. Kraus and W. N. Greer, *J. Am. Chem. Soc.*, *47*, 2568 (1925).

[140] H. E. Bent and M. Dorfman, *J. Am. Chem. Soc.*, *54*, 2132 (1932).

[141] H. E. Bent and M. Dorfman, *J. Am. Chem. Soc.*, *57*, 1924 (1935).

[142] H. E. Bent and M. Dorfman, *J. Am. Chem. Soc.*, *57*, 1259 (1935).

problems--for instance, the distinct difference in sequence of color changes between the experiments with lead on the one hand and germanium or tin[124] on the other may prove to be a guide to an understanding of the obvious differences in nature of the preparations.

The work of Krause and Reissaus[130] has been interpreted by some succeeding workers as indicating that diphenyllead is characteristically a well-defined red crystalline solid, monomeric in molecular composition. For diaryltins[143,144,49] and diphenylgermanium[96], where more results are available, it is clear that this is not the case. These materials are characteristically ill-defined polymers, varying from yellowish-white to orange in the solid and from yellow to red in solution, which on extraction yield the monomer only with difficulty (the tetramer in the case of the germanium compound). The monomer polymerizes rapidly in solution[49]. It is not immediately clear why diphenyllead should differ so considerably in these respects from the other compounds, and actually the behavior described in the experimental section for the lead chloride-phenyllithium mixtures after hydrolysis indicates that it does not. When the yellow ether layers from mixtures believed to contain diphenyllead were allowed to stand, after hydrolysis and drying, they continued for

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[143] E. Krause and R. Becker, Ber., 53, 173 (1920).

[144] R. Chambers and P. Scherer, J. Am. Chem. Soc., 48, 1054 (1926).

several days to deposit a precipitate which varied in color from yellowish-white to a brownish yellow. This material on heating in a capillary did not melt, nor did it decompose cleanly, like hexaphenyldilead. After treatment with solvents the material yielded only hexaphenyldilead. It is likely that these solutions actually contained diphenyllead, that the slow precipitation was a result of gradual polymerization, and that the yellowish solid precipitated was very likely a diphenyllead polymer. The observations suggest that there may be some process by which this intermediate can change in part to hexaphenyldilead by reactions not involving the formation of lead. In cases where the nature of a preparation is such that some of this rather intractable intermediate is left in the crude product after hydrolysis, it interferes with the straightforward working up of the reaction. The traces of yellow impurity whose removal from the tetra-p-dimethylaminophenyllead preparations is described above were apparently of this nature. If the preparation of tetraaryl-leads is carried out by treatment of R_3PbLi with the aromatic RX compound (as in the experiment involving iodobenzene), some of the intermediate may apparently remain in the product unless considerable time is allowed for the reaction. This is the reason for the statement above that such preparations are better carried out by the higher-temperature refluxing technique[5], rather than through the R_3PbLi compound.

Other Conclusions

Reactions involving metallic lead

The reaction scheme (equations X, XI, and XII) previously advanced[6] for the synthesis of R_4Pb compounds by the higher-temperature refluxing technique is in agreement with all the observations reported in this thesis. Other workers[113,39] had already established that metallic lead could react with phenyllithium to form tetraphenyllead, more readily in the presence of a phenyl halide. The purpose of the experiments involving lead powder which are described above was to determine whether this reaction would be a useful method of synthesis of $R_2PbR'_2$ compounds. From the results obtained it appears that, at least in simple cases, the customary techniques proceeding from R_2PbX_2 compounds will be preferable. Even though the primary reaction with the lead powder may proceed as desired (reaction XI), the possibility of occurrence of secondary reactions such as displacement or redistribution leads to the formation of products which are difficult or impossible to purify, when more than one kind of R group is present.

Water-soluble organolead compounds

The experiments with the quaternary ammonium derivatives demonstrate that the formation of such derivatives from organolead compounds containing tertiary amino groups is a useful method of increasing the solubility in water of the lead compound. The aqueous solutions of the resulting products had pH values near 7.0, and precipitates indicating hydrolysis of the Pb-C bond were not noted in these solutions. No attempt was made, in this work, to manufacture any large number of such compounds. Some comparisons may be made among those which were prepared. When the lead atom held four aryl groups it was difficult to obtain a very soluble derivative. Both the methiodide and the methosulfate from triphenyl-p-dimethylaminophenyllead were essentially insoluble in water. Even the tetramethiodide of tetra-p-dimethylaminophenyllead was soluble only to the extent of about 0.5%, although in this case the charge on the positive ion (+4) would be large. In contrast, the methosulfate from triphenyl-γ-diethylaminopropyllead was so highly soluble in water that the problem of solubility essentially disappeared here; and it might apparently be possible to vary this structure, within reason, in any such way as might be desired for pharmacological reasons. The resemblance of this lead compound to the surface-active quaternary ammonium bacteriostatic agents which are in current use[145] is of course of interest. The methiodide of this compound, although crystallizable from water, was not appreciably soluble in water at room temperature.

These results suggest perhaps that to bring the heavy organolead ions into solution in water very strongly hydrophilic groups are required. Another type of group which would be of interest is the sulfonic acid group. Sulfonic acids are strong acids, so that their salts with bases such as sodium hydroxide should be soluble in water at pH values near 7.0. Attempts[77,79] to solubilize organolead compounds by introduction of aromatic sulfonic acid groups into the molecule have met with some success. The comparisons given above for the quaternary ammonium salts may indicate that an aliphatic sulfonic acid would be more effective as a water-solubilizing function. Aliphatic sulfonic acids are usually prepared (in the laboratory) by reaction of an alkyl halide with sodium sulfite, which gives the sodium salt directly. Whether such a reaction could be carried out with an organolead compound is unknown, but at least it involves a basic reagent, which is a favorable condition. The attempts described above to prepare organolead compounds containing an aliphatic halogen atom, such as triphenyl-γ-chloropropyllead, were made partly with this idea in mind. However, the

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[145] C. A. Lawrence, "Surface-Active Quaternary Ammonium Germicides", Academic Press, New York, 1950.

desired products were not obtained. To date, the only lead compounds containing aliphatic halogen atoms which have been described[123] are triethyl-ϵ-bromoamyllead and its derivatives, and this preparation involved a special reaction which probably could not be applied at all for aromatic derivatives.

Physiological action

Of the lead compounds prepared, two were soluble enough in water to permit physiological testing. These compounds were the tetramethiodide of tetra-p-dimethylaminophenyllead and the methosulfate of triphenyl-γ-diethylaminopropyllead. They were submitted to government laboratories for testing against cancer, and a preliminary report on tetra-p-dimethylaminophenyllead tetramethiodide is given on page 89 of this thesis.

SUMMARY

The reaction of phenyllithium with lead chloride at -10° has been studied and found to proceed in two distinguishable stages, corresponding to the reactions

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

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

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 triphenyllead-lithium or as phenyllithium. The reaction of triphenyllead-lithium with alkyl halides

$$(C_6H_5)_3PbLi + R'X \longrightarrow (C_6H_5)_3PbR' + LiX$$

is a useful and general method for the preparation of $(C_6H_5)_3PbR'$ compounds (R' = alkyl) when the alkyl group does not contain functions reactive toward phenyllithium. This type of reaction has been applied to the preparation of some organolead compounds which would not be readily available by other methods. Reactions of this sort also proceed readily with o- or p-tolyllithium. p-Dimethylaminophenyllithium reacts very slowly, although probably in the same way.

Organolead derivatives containing tertiary amino groups have been converted into quaternary ammonium salts, and this has been found to be a useful method for conferring water-solubility on organolead compounds. Two such salts have been submitted to United States government laboratories for physiological testing. One in particular of these, the methosulfate from triphenyl-gamma-diethylaminopropyllead, was extremely soluble in water.

Investigations of the reaction of phenyllithium, RI compounds (where R was not phenyl), and metallic lead have been carried out. The results agree with some reaction formulations advanced by previous investigators in this Laboratory. These reactions did not serve well for the practical preparation of $R_2PbR'_2$ compounds.

The use of halogen-metal interconversion reactions involving m-bromoaniline and n-butyllithium for the preparation of some organosilicon derivatives has been investigated. The results establish that interconversion does occur with m-bromoaniline. The organosilicon derivatives were obtained only in small yield because of difficulties in the purification steps. New organosilicon compounds obtained by Williamson-type reactions are also described.

The literature on organolead chemistry from 1941 to the present time has been surveyed, and the organolead compounds which have received mention in the literature during this

period are tabulated. A survey, with selected references, of the literature material pertaining to some valence states of the Group IV-B elements is also given.