[Contribution from the Chemical Laboratory of Iowa State College]

ORGANOMETALLIC COMPOUNDS OF LEAD, TIN AND GERMANIUM[1]

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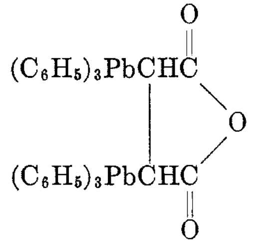
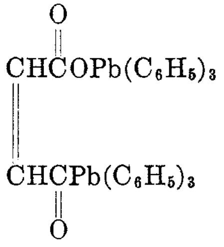
In this communication we describe the preparation of a number of new organometallic compounds of lead, tin, and germanium. Most of these compounds were prepared in connection with a program of investigation of methods of introducing water-solubilizing groups into organometallic compounds. The background of this program has been discussed previously (12, 11, 8). We report in addition the results of some studies on the relative reactivities of various Group I-A and II-A metals in cleavage of organolead compounds in liquid ammonia. These studies were also made in connection with a series of earlier investigations (10, 2, 1).

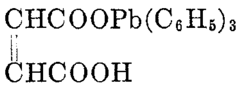
Maleic anhydride and hexaphenyldilead were found to react either when allowed to stand for extended periods of time in chloroform solution or, more rapidly, when melted together. The material obtained was apparently the compound I. Such a reaction could conceivably proceed by cleavage of the anhydride linkage, to give II, rather than by addition to the double bond. However, our product gave a sodium salt, which is evidence against structure II; and for further substantiation we prepared triphenyllead hydrogen maleate (III) and di-(triphenyllead) maleate (IV) and found them to have solubilities and melting points much different from our product.



I

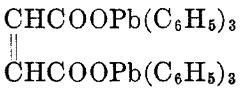


II



$$\begin{array}{l}\mathrm{CHCOOPb(C_6H_5)_3}\\ \|\\ \mathrm{CHCOOH}\end{array}$$

III



$$\begin{array}{l}\mathrm{CHCOOPb(C_6H_5)_3}\\ \|\\ \mathrm{CHCOOPb(C_6H_5)_3}\end{array}$$

IV

None of these compounds (I–IV) was water-soluble.

Conant and Chow (4) obtained α,β-di(triphenylmethyl)succinic acid as the final product of the reaction of triphenylmethyl with maleic anhydride. In the

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[1] Paper LXIX in the series: "Relative Reactivities of Organometallic Compounds." The preceding paper with Miller is in *J. Am. Chem. Soc.*, **73**, (1951).

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reaction described above, therefore, hexaphenyldilead apparently behaved like hexaphenylethane, although physical measurements (15) indicate no dissociation of the lead compound into radicals. Conant and others (4, 5) also obtained reactions between triphenylmethyl and compounds such as isoprene, other substituted 1,3-dienes, or pyrrole. We however were unable to cause similar reactions to occur with hexaphenyldilead. A further examination of the reaction between maleic anhydride types and hexaaryldileads and related organometallic compounds is in progress.

o-Hydroxyphenyltriphenyllead was prepared. This material was fairly soluble in alcohol, but insoluble in water.

One purpose in preparing water-soluble organolead compounds was to test them as possible anti-cancer agents. Several organolead compounds containing polynuclear hydrocarbon radicals were prepared. Since some polynuclear hydrocarbons are known to produce cancer, it might be interpreted as an indication of the effectiveness of organolead compounds in the treatment of cancer if such compounds showed decreased cancer-producing tendencies. 9-Phenanthryltriphenyllead, di-9-phenanthryldiphenyllead, (benz[*a*]anthracen-7-yl)triphenyllead and bis(benz[*a*]anthracen-7-yl)-diphenyllead were tested but neither the phenanthrene-[3] nor the benz[*a*]anthracene-containing compounds (6) produced cancer.

Another means of introducing organic radicals into organometallic compounds involves a reaction in liquid ammonia of the general type:

$$(R_3Pb)_2 + 2\,M \longrightarrow 2\,R_3PbM \xrightarrow{2\,R'X} 2\,R_3R'Pb + 2\,MX$$

The different liquid ammonia-soluble metals were tried. The first metal in periodic groups I-A and II-A, lithium and calcium, gave the best yields. The yields decreased progressively as one substituted metals further down each family in the periodic system (Table I). Another interesting observation was that group II-A metals acted as monovalent metals in the liquid ammonia reactions.

In attempting to extend this reaction, it was found that R_2PbX_2 compounds, when treated with metals soluble in liquid ammonia, underwent redistribution of R groups (Table II):

$$R_2PbX_2 + M \rightarrow (R_3Pb)_2 + R_4Pb$$

Liquid ammonia reactions which were attempts to prepare compounds of the type $R_2R'PbPbR'R_2$ were inconclusive in outcome. There appeared to be a reaction but the products were highly unstable.

$$2\,R_2R'PbX + 2\,M \rightarrow R_2R'PbPbR'R_2 + 2\,MX$$

Hellerman and Newman (13) observed a reaction between diazomethane and both mercuric chloride and RHgX compounds. In our studies, no such reaction was observed for either diazomethane or diazoethane and triethyllead chloride.

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[3] L. F. Fieser, private communication.

Diazoethane and tripropyltin bromide reacted but the presumed tripropyl-β-bromoethyltin was unstable.

TABLE I

REACTIONS IN LIQUID AMMONIA IN WHICH 0.0025 MOLE OF HEXAPHENYLDILEAD WAS TREATED WITH VARIOUS METALS, FOLLOWED BY BENZYL CHLORIDE

METAL	G.-ATOM OF METAL	BENZYLTRIPHENYLLEAD, %
Lithium	0.005	71; 72
Sodium	.005	60; 64
Potassium	.005	55; 57
Rubidium	.005	52
Calcium	.005	79; 81
Calcium	.0025	40; 41
Strontium	.005	67; 74
Strontium	.0025	34; 36
Barium	.005	56; 61
Barium	.0025	31; 36

TABLE II

REACTIONS IN LIQUID AMMONIA BETWEEN DIPHENYLLEAD DIHALIDES AND SEVERAL METALS

DIPHENYLLEAD DICHLORIDE		METAL		TETRAPHENYLLEAD		HEXAPHENYLDILEAD	
Grams	Mole	Grams	G.-Atom	Grams	%[a]	Grams	%[a]
		Lithium					
4.32	0.01	0.28	0.04	trace		1.75	60.0
		Calcium					
2.16	.005	.4	.01			0.60	27.4
		Calcium					
4.32	.01	.4	.01	0.22	10.0	.68	23.3
DIPHENYLLEAD DIFLUORIDE							
		Lithium					
2.00	.005	.07	.01	trace		.75	52.0
		Sodium					
2.00	.005	.23	.01	trace		.65	45.0
		Calcium					
3.99	.01	.4	.01	trace		1.70	58.0

[a] The percent yield is based upon the phenyl groups appearing in reactant and product.

Emmert and Eller (7) reacted tin and ethyl iodoacetate, isolating dicarbethoxymethyltin diiodide:

$$2\ ICH_2COOC_2H_5 + Sn \rightarrow (C_2H_5OOCCH_2)_2SnI_2$$

The action of halogenated organic compounds, especially halogenoesters, with finely divided lead would seem to offer an excellent method of introducing radicals with reactive groups into organolead compounds, and we investigated this possibility. No reaction was observed. Tin powder, however, reacted with a number of compounds containing bromine. The products were nearly always thick tars or greasy solids and decomposed upon attempted distillation under reduced pressure.

The series of compounds of the $RSnI_3$ type (19) was extended by one member. The instability was still such that no further work was undertaken.

The several new organogermanium compounds prepared had properties quite similar to the corresponding organotin compounds.

Acknowledgement. The authors are grateful to Lawrence Summers for assistance.

EXPERIMENTAL

All melting points are uncorrected and were determined on a Fisher-Johns micro-melting point apparatus.

Product from maleic anhydride and hexaphenyldilead. (a) A tube containing 4 g. (0.0045 mole) of hexaphenyldilead, 0.45 g. (0.0045 mole) of maleic anhydride, and 100 cc. of chloroform was sealed and stored in the dark. After 5 months a solid filled the lower part of the tube. On isolation this material was found to be insoluble in acetone, ethanol, dioxane, chloroform, carbon tetrachloride, benzene, and the petroleum ethers; very slightly soluble in boiling water, and soluble in glacial acetic acid. Unreacted materials were removed by boiling with chloroform and ethanol. Digestion with ammonium acetate solution removed traces of inorganic lead. The greyish-white crystalline residue turned brown at 265–270° and had not melted at 330°.

Anal. Calc'd for $C_{40}H_{34}O_4Pb_2$: Pb, 41.75. Found: Pb, 41.70.

(b) A quicker preparation was found possible by heating a quantity of maleic anhydride above its melting point (52.6°) but not near the decomposition temperature of hexaphenyldilead (160°). Hexaphenyldilead was slowly added to the molten material in small portions until the mixture became thick. The crude powder was extracted with benzene, ethanol, and ammonium acetate solution, and 4.38 g. (0.005 mole) of hexaphenyldilead yielded 4.0 g. (81%) of product.

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

Sodium salt. A quantity of the purified product of the reaction of hexaphenyldilead with molten maleic anhydride was refluxed for 8 hours with a 10% sodium hydroxide solution containing dioxane to prevent frothing. The mixture was diluted with water, filtered, and the crystalline solid washed with water until alkali free. The product was as insoluble as the starting material.

Anal. Calc'd for $C_{40}H_{32}Na_2O_4Pb_2$: Pb, 39.98. Found: Pb, 40.41.

While the analysis was 0.43% higher than the anticipated value, it was still 1.34% lower than the value of the starting material. Undoubtedly longer refluxing of this insoluble material would have given a more complete conversion of the free acid to the sodium salt.

Triphenyllead acid maleate. To 5 grams (0.011 mole) of triphenyllead hydroxide in 250 cc. of boiling absolute ethanol was added 1.07 g. (0.011 mole) of maleic anhydride, and the mixture refluxed for 10 minutes. The milky solution was filtered and the filtrate distilled until a precipitate commenced to form. After cooling, the colorless solid was dissolved in hot ethanol and neutralized with alcoholic potassium hydroxide. Addition of a little water and cooling caused the potassium salt to precipitate. This product was redissolved in hot ethanol and acidified to Congo Red with hydrochloric acid. Addition of water precipitated the free acid which was washed with water and air-dried. Yield, 5.3 g. (90%); m.p. 207°.

Anal. Calc'd for $C_{22}H_{10}O_4Pb$: Pb, 38.64. Found: Pb, 38.80.

Neutral equivalent, Calc'd: 536. Found: 525.

Di(triphenyllead) maleate. To a hot solution of 4.55 g. (0.01 mole) of triphenyllead hydroxide was added an alcoholic solution of 0.58 g. (0.005 mole) of maleic acid. The solution was distilled until material commenced to precipitate. The crystalline mass of di(triphenyllead) maleate produced upon cooling was air-dried. Yield, 3.9 g. (82%); m.p. 198–199°.

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

o-Hydroxyphenyltriphenyllead. To the organolithium reagent (9) prepared by the action of 0.88 g. (0.126 g.-atom) of lithium and 5.48 g. (0.04 mole) of butyl bromide with 2.25 g. (0.013 mole) of *o*-bromophenol, was added 4.74 g. (0.01 mole) of triphenyllead chloride. After adding 100 cc. of dry benzene, the mixture was refluxed 1 hour, filtered, the filtrate hydrolyzed with dilute hydrochloric acid, and the solvent layer separated and distilled. The residue was washed with cold ethanol and recrystallized from ethanol, yielding 0.64 g. (12%) of *o*-hydroxyphenyltriphenyllead, m.p. 216–218°.

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

9-Phenanthryltriphenyllead. The Grignard reagent was prepared by refluxing for 24 hours 3.67 g. (0.0143 mole) of 9-bromophenanthrene and 0.35 g. (0.0143 g.-atom) of magnesium in 30 cc. of a 1:1 mixture of dry benzene and anhydrous ether. To this was added 5.18 g. (0.1 mole) of triphenyllead bromide. The mixture was refluxed for 24 hours and then was hydrolyzed with dilute hydrochloric acid. The organic layer was separated and evaporated to give a brown oil which slowly crystallized. It was insoluble in ethanol, petroleum ether (b.p. 60–68°), acetone, or dioxane. The brown color was removed by dissolving the oil in benzene and passing the solution through a column of activated alumina. The benzene was distilled and the residue recrystallized from ethyl acetate to give 3.5 g. (57%) of 9-phenanthryltriphenyllead, m.p. 169–171°.

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

Di-9-phenanthryldiphenyllead. The Grignard reagent was prepared as above, from 7.34 g. (0.0286 mole) of 9-bromophenanthrene and 0.7 g. (0.0287 g.-atom) of magnesium. To this was added 20 cc. of anhydrous ether and 5.21 g. (0.01 mole) of diphenyllead dibromide. After refluxing for 24 hours, the mixture was hydrolyzed with dilute hydrochloric acid. The organic layer was evaporated to give a clear brown liquid that precipitated colorless crystals of di-9-phenanthryldiphenyllead upon addition of ethyl acetate. The crude product weighed 4.86 g. (68%). Recrystallization from ethyl acetate gave m.p. 208–210°.

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

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

Attempted preparation of tetra-9-phenanthryllead. To the Grignard reagent prepared as above, from 2.57 g. (0.01 mole) of 9-bromophenanthrene and 0.25 g. (0.01 g.-atom) of magnesium, was added 25 cc. of benzene and 1.2 g. (0.0043 mole) of lead chloride. The solution turned orange and after a few moments heating on a hot plate was deep red. After refluxing 5 hours the color had disappeared. The mixture was hydrolyzed with ammonium chloride solution, filtered and the organic layer evaporated. The residue did not contain lead. One gram of phenanthrene was recovered. This experiment has not yet been checked.

(Benz[a]anthracen-7-yl)triphenyllead. To a butyllithium solution, prepared in 30 cc. of ether by the reaction of 1.5 g. (0.011 mole) of *n*-butyl bromide with 0.17 g. (0.025 g.-atom) of lithium, was added 1 g. (0.00325 mole) of 7-bromobenz[*a*]anthracene. The reaction mixture was stirred for 2 minutes and then 1.5 g. (0.00325 mole) of triphenyllead chloride was added. Stirring was continued 10 minutes before hydrolyzing with water. The resultant mixture was filtered, washed with ether, and the residue recrystallized from ethyl acetate, yielding 1.13 g. (52%) of (benz[*a*]anthracen-7-yl)triphenyllead, m.p. 204–205°. This is the same melting point as triphenyllead chloride but a mixed melting point was depressed.

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

When hydrogen chloride was passed into a chloroform solution containing 0.2 g. (0.0003 mole) of (benz[*a*]anthracen-7-yl)triphenyllead, a white precipitate formed. This was filtered and dried to give 0.12 g. (92%) of diphenyllead dichloride, identified by conversion to tetraphenyllead and by mixed melting point. The chloroform was evaporated from the benz[*a*]anthracene produced in the hydrogen chloride cleavage and 0.07 g. (quantitative) of the hydrocarbon was recovered and identified by mixed melting point.

Bis(benz[a]anthracen-7-yl)diphenyllead. To the butyllithium prepared in 40 cc. of absolute ether from 3 g. (0.022 mole) of *n*-butyl bromide and 0.033 g. (0.048 g.-atom) of lithium was added 2.5 g. (0.0081 mole) of 7-bromobenz[*a*]anthracene. The mixture was stirred 2 minutes and then 1.75 g. (0.004 mole) of diphenyllead dichloride was added. Stirring was continued for 10 minutes before hydrolyzing with water. The resultant mixture was filtered and the solid extracted with benzene. Concentration of the benzene and addition of ethanol to the residue caused small, slightly yellow needles of bis(benz[*a*]anthracen-7-yl)diphenyllead to form; yield, 0.3 g. (3.6%); m.p. 295–296° with some decomposition.

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

Attempted nitration of tetraphenyllead. Powdered tetraphenyllead was slowly added to 45 cc. of fuming nitric acid and 35 cc. of concentrated sulfuric acid at −50°. Under these particular conditions, the reaction yielded only lead sulfate, nitrobenzene, and unchanged tetraphenyllead.

Nitration of diphenyllead dichloride. Diphenyllead dichloride, treated in a similar manner, evolved chlorine and formed a paste. After standing overnight it was poured upon ice, the solid filtered, washed with water, and air-dried. The product analyzed 33.34% lead. $(m\text{-}NO_2C_6H_4)_2PbCl_2$ contains 39.65% lead; $(m\text{-}NO_2C_6H_4)_2Pb(NO_3)_2$, 36.00; $(C_6H_5)_2Pb(NO_3)_2$, 42.68.

Di-m-nitrophenyllead dichloride. Diphenyllead dinitrate (17) was converted to di-*m*-nitrophenyllead dinitrate as directed (3), except that a bath temperature of −50° allowed faster addition.

To a solution of 10 g. (0.02 mole) of di-*m*-nitrophenyllead dinitrate in 200 cc. of boiling water was added 2.9 g. (0.05 mole) of sodium chloride in 100 cc. of water. A white precipitate formed. The mixture was cooled, filtered, and washed with water. The di-*m*-nitrophenyllead dichloride weighed 10.1 g. (97%). It was ethanol-soluble, and crystallized from ethyl acetate in small colorless plates which sublimed at 250° and decomposed at 285–288°.

Anal. Calc'd for $C_{12}H_8Cl_2NO_4Pb$: Pb, 39.65; N, 5.36.
Found: Pb, 39.33; N, 5.35.

Di-m-nitrophenyllead diiodide. The preparation was similar to that used for the dichloride. The diiodide was a bright yellow crystalline material which decomposed about 135°. Like diphenyllead diiodide it tended to decompose upon attempted recrystallization, but to a lesser extent.

Anal. Calc'd for $C_{12}H_8I_2N_2O_4Pb$: Pb, 29.36. Found: Pb, 30.05.

Triphenyllead nitrate. To a solution of 1 g. (0.0022 mole) of triphenyllead hydroxide in 30 cc. of hot ethanol was added 0.5 cc. of concentrated nitric acid in 10 cc. of ethanol. After evaporating to a small volume on a steam-plate, cooling caused a mass of colorless needles to form. The product was filtered, washed with a little ethanol, and air-dried. It sintered with some decomposition at 220–225°.

Anal. Calc'd for $C_{18}H_{15}NO_3Pb$: Pb, 41.40. Found: Pb, 41.07.

When concentrated sulfuric acid was added to the analytical sample it burst into flames and evolved considerable smoke.

Nitration of triphenyllead nitrate. The general procedure used in nitration of diphenyllead dinitrate was followed. The precipitated tri-*m*-nitrophenyllead nitrate from the diluted nitration solution was filtered, washed with water, air-dried, and extracted with ethyl acetate.

Anal. Calc'd for $C_{18}H_{12}N_4O_9Pb$: Pb, 32.44. Found: Pb, 32.45.

After one-month's storage there was considerable decomposition. It partly dissolved in glacial acetic acid; the residue dissolved in ammonium acetate solution and gave a heavy precipitate with sodium chromate solution, indicating inorganic lead.

Nitration of triphenyllead chloride. The general procedure used in nitration of diphenyllead dinitrate was followed. There was a 98% recovery of material analyzing 27.9% lead instead of the expected 32.44%.

Triethyllead chloride with diazomethane and diazoethane. Equimolecular quantities of the materials in benzene failed to react after standing overnight at room temperature.

Halogenoesters and lead powder. The lead powder (MD 105, Metals Disintegrating Co., Elizabeth, N. J.; 70% less than 15 microns) was refluxed directly with ethyl α-bromopropionate, bromomethyl acetate, or ethyl bromoacetate. After periods up to 12 hours the esters were recovered unchanged.

Reactions in liquid ammonia between $(R_3Pb)_2$ and several metals, derivatized with benzyl chloride. In a typical run, a 250-cc. three-necked flask fitted with a stirrer was charged with 2.19 g. (0.0025 mole) of hexaphenyldilead and 150 cc. of liquid ammonia. While this mixture was stirred, 0.035 g. (0.005 g. atom) of lithium was slowly added. The solution was stirred for 5 minutes after the addition was completed and then 1 cc. (excess) of benzyl chloride was introduced dropwise.

Evaporation of the ammonia left a residue which was extracted with ether. The ether solution was evaporated and the residue washed with 10 cc. of alcohol. There remained 1.9 g. (72%) of benzyltriphenyllead, m.p. 91–92°.

Reaction in liquid ammonia between 0.1 mole of triethyllead chloride and 0.2 g.-atom of lithium, after derivatizing with benzyl chloride and working up as above, yielded 40% benzyltriethyllead, b.p. 147–151° (13 mm.).

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

Reactions in liquid ammonia between R_2PbX_2 and several metals. In a typical procedure, to 3.99 g. (0.01 mole) of diphenyllead difluoride suspended in 200 cc. of liquid ammonia in a three-necked flask, was slowly added 0.4 g. (0.01 g.-atom) of calcium. The suspension was stirred and a deep red coloration was noticed about each piece of metal. At times the whole suspension took on a momentary reddish-brown color; but when about half of the metal had been added, the ammonia solution became blue and remained so. The ammonia was evaporated and the whitish residue extracted with chloroform. Fractional crystallization of the solution gave crops of tetraphenyllead and hexaphenyldilead.

Attempts to prepare compounds of the type $R_2R'PbPbR'R_2$. (a) *sym-Diphenyltetracyclohexyldilead.* Dicyclohexyldiphenyllead (prepared in 65% yield from diphenyllead dichloride and cyclohexylmagnesium bromide) was dissolved in petroleum ether (b.p. 28–38°) and a slow stream of hydrogen chloride was passed in. Too rapid addition cleaved two phenyl groups. The precipitate was filtered and recrystallized from chloroform to yield dicyclohexylphenyllead chloride; sintered 195°, decomposed 205°.

Anal. Calc'd for $C_{18}H_{27}ClPb$: Pb, 42.63. Found: Pb, 42.58.

To a suspension of 9.76 g. (0.02 mole) of dicyclohexylphenyllead chloride in 350 cc. of liquid ammonia was slowly added 0.46 g. (0.2 g.-atom) of sodium, producing a deep red solution. Evaporation and chloroform extraction of the residue gave a red solution, extremely light sensitive. Low temperature evaporation in the dark still destroyed the color. Analysis of the supposed *sym*-tetracyclohexyldiphenyldilead indicated a different product.

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

(b) *sym-Diethyltetraphenyldilead.* Slowly bubbling hydrogen chloride into a petroleum ether (b.p. 28–38°) solution of ethyltriphenyllead precipitated diphenylethyllead chloride in 81% yield. Recrystallized from alcohol, it sintered at 142° and decomposed at 146–147°.

Anal. Calc'd for $C_{14}H_{15}ClPb$: Pb, 48.70. Found: Pb, 48.37.

No particular color changes were noticed when 4.25 g. (0.01 mole) of diphenylethyllead chloride suspended in 250 cc. of liquid ammonia was treated with 0.23 g. (0.01 g.-atom) of sodium. Evaporation and chloroform extraction of the residue gave a yellowish solution which could not be concentrated without decomposition taking place.

Butyltin triiodide. The directions (19) given for the lower members of this series were followed. To 15 g. (0.057 mole) of powdered $KSnCl_3$ (16) in a Carius tube was added 35 cc. (excess) of butyl iodide. After heating 72 hours at 90° the liquid was decanted, the solid extracted with petroleum ether (b.p. 28–38°), and the combined liquids distilled to give 8 g. (25%) of butyltin triiodide, b.p. 154° (5 mm.). It was a clear red liquid which decomposed in a few minutes with deposition of stannous iodide.

Anal. Calc'd for $C_4H_9I_3Sn$: Sn, 21.33. Found: Sn, 21.62.

Tripropyltin bromide and diazoethane. When the tin compound was slowly added to diazoethane there was a vigorous reaction which was controlled by cooling in a low-temperature bath. The product was distilled as a clear liquid, b.p. about 130–135° (3 mm.), which lacked the sharp unpleasant smell of the starting tin compound. Decomposition took place before an analysis could be run, but a qualitative test indicated bromine present.

Tin powder with halogenated compounds. The tin powder used was described as less than 325 mesh (MD 105, Metals Distintegrating Co., Elizabeth, N. J.).

(a) *With ethyl bromoacetate.* In the course of 5.5-hours' refluxing, 5.93 g. (0.05 g.-atom) of tin powder slowly dissolved in 16.7 g. (0.1 mole) of ethyl bromoacetate. Upon cooling, crystals of dicarbethoxymethyltin dibromide formed in the thick black liquid. The material was washed out with ether, recrystallized from benzene; m.p. 139°, yield 3.5 g. (15.5%).

Anal. Calc'd for $C_8H_{14}Br_2O_4Sn$: Sn, 26.22. Found: Sn, 26.22.

(b) *With bromomethyl acetate.* A reaction started as soon as 5.93 g. (0.05 g.-atom) of tin powder was mixed with 15.3 g. (0.1 mole) of bromomethyl acetate. After 5.5-hours' refluxing the mixture gave no crystals upon cooling and decomposed upon distillation using a mercury-vapor pump.

(c) *With phenacyl bromide.* After 4.5-hours' heating, 5.93 g. (0.05 g.-atom) of tin powder had dissolved in 19.9 g. (0.1 mole) of phenacyl bromide. The mixture set to a black glassy solid upon cooling. An attempt to distill using a mercury-vapor pump was unsuccessful.

(d) *With β-bromoethyl acetate.* After 18-hours' heating, 5.93 g. (0.05 g.-atom) of tin powder had dissolved in 16.7 g. (0.1 mole) of the ester. It solidified upon cooling and decomposed in attempted distillation using a mercury-vapor pump.

(e) *With ethyl α-bromopropionate.* After 20-hours' heating in an oil-bath at 150°, 2.95 g. (0.025 g.-atom) of tin powder had dissolved in 20 cc. of the ester. After vacuum-distilling the excess ester, 3 cc. of presumed di-α-carbethoxyethyltin dibromide passed over at about 82–85° (1.5 mm.).

Anal. Calc'd for $C_{10}H_{18}Br_2O_4Sn$: Sn, 23.71. Found: Sn, 23.24.

(f) *With diethyl α-bromosuccinate.* A mixture of 5.93 g. (0.05 g.-atom) of tin powder and 25.3 g. (0.1 mole) of the ester was heated 6 hours in an oil-bath. Vacuum-distillation gave 16 g. of colorless liquid with ester-like odor, b.p. 58–60° (1.5 mm.). Redistillation failed to give a product analyzing near the value of the expected ethyl ester of di-(α-succinic acid)tin dibromide.

Anal. Calc'd for $C_{16}H_{26}Br_2O_8Sn$: Sn, 19.00. Found: Sn, 13.96, 13.87.

(g) *With ethyl dibromomalonate.* Nearly all of 3 g. (0.025 g.-atom) of tin powder had reacted with 25 g. (0.079 mole) of the ester after 15-minutes' heating in an oil-bath at 130°. The product was a dark brown viscous oil which decomposed upon attempted distillation using a mercury-vapor pump.

(h) *With 2-bromopyridine.* After 1.5-hours' refluxing, 12.2 g. (0.104 g.-atom) of tin powder had dissolved in 32.8 g. (0.208 mole) of 2-bromopyridine. The resultant high-melting black glass would not vacuum-distill.

(i) *With 1-chloro-2-iodoethane.* When 17.7 g. (0.149 g.-atom) of tin powder and 42.7 g. (0.224 mole) of 1-chloro-2-iodoethane were refluxed, most of the liquid had disappeared after 5 hours. Upon attempted vacuum-distillation, a small amount of light red liquid distilled at 65–70° (1 mm.) but a heavy coating of stannic iodide indicated much decomposition also took place. The presumed di-β-chloroethyltin diiodide fumed in the air and decomposed leaving an orange solid.

Anal. Calc'd for $C_4H_8Cl_2I_2Sn$: Sn, 23.76. Found: Sn, 25.90.

(j) *With 1-bromo-2-chloroethane.* There was a small amount of an ethanol-soluble oil formed when the reactants were heated 6 hours in a sealed tube at 180°. Complete decomposition occurred in a repeat experiment run 20 hours at 180°.

(k) *With 1-bromo-3-chloropropane.* The reactants were recovered unchanged after heating in an oil-bath at 140° for 72 hours. Decomposition occurred when they were heated 24 hours at 250° in a sealed tube.

Tetra-n-butylgermanium. Anhydrous germanium tetrabromide was prepared according to directions of Laubengayer (14). A general method of preparing R_4Ge compounds (18) was used to prepare tetra-*n*-butylgermanium (80%), b.p. 127–128° (4 mm.).

(a) To 10 g. (0.033 mole) of tetra-*n*-butylgermanium was added 8.38 g. (0.066 g.-atom) of iodine and the mixture warmed on a hot plate for 8 hours. Vacuum-distillation gave 10 g. (69%) of material b.p. 126–128° (4 mm.); same b.p. as starting material but addition of bromine caused evolution of iodine.

(b) To 10 g. (0.033 mole) of tetra-*n*-butylgermanium in 25 cc. of ethylene bromide was added 5.28 g. (0.066 g.-atom) of bromine in 25 cc. of ethylene bromide. After 4 hours refluxing, solvent was distilled, residue shaken with potassium hydroxide solution, extracted with petroleum ether (b.p. 75–115°), dried over sodium sulfate, and distilled at reduced pressure. The oxide had a camphor-like odor.

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

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

Tetra-2-furylgermanium. To a mixture of 20.8 g. (3 g.-atoms) of lithium, 1 l. of ether, and 117 g. (1.5 moles) of furan was slowly added 163 g. (1.5 moles) of ethyl bromide in 200 cc. of ether. The completed reaction was filtered, 500 cc. of benzene was added, the ether was distilled, and 85 g. (0.217 mole) of germanium tetrabromide in 100 cc. of benzene slowly added. After 4 hours refluxing, the liquid layer was separated, the benzene distilled, and the residue vacuum-distilled from an oil-bath. Nothing came over until the oil commenced to smoke, then 20 g. of slightly yellow liquid shot over into the receiver and solidified. It redistilled smoothly at 163° (1 mm.); m.p. 65–80°; Beilstein test negative. After refluxing 3 days in benzene solution and recrystallizing from petroleum ether (b.p. 60–68°), there was 18 g. (24%) of tetra-2-furylgermanium, m.p. 99–100°. Seemingly, the initial product was contaminated with hexafuryldigermanium.

Anal. Calc'd for $C_{16}H_{12}GeO_4$: Ge, 21.07. Found: Ge, 21.04.

In a repeat run, the product exhibited the same superheating observed in the first distillation but then distilled at 163° (1 mm.); m.p. 99–100°; 32% yield.

SUMMARY

1. A number of new organolead compounds have been prepared.

2. Hexaphenyldilead appears to add to the double bond of maleic anhydride.

3. In liquid ammonia reactions: (a). Lithium, sodium, potassium, rubidium, calcium, strontium, and barium converted hexaphenyldilead to $(C_6H_5)_3PbM$ types, which with benzyl chloride gave benzyltriphenyllead in smaller percentages as atomic weight increased within each group. (b). Group II-A metals reacted as though they were monovalent. (c). Diphenyllead dihalides and some Group I-A and II-A metals produced hexaphenyldilead and tetraphenyllead by disproportionation reactions.

4. Diazoethane and tripropyltin bromide reacted to give an unstable product, but diazomethane or diazoethane did not react with triethyllead chloride.

5. Tin powder reacted with some halogenated organic compounds, usually to give a product which could not be isolated in a pure form, but lead powder did not react.

6. Some new organogermanium compounds have been prepared.

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