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# SYNTHESIS OF ORGANOLEAD COMPOUNDS
## III. PREPARATION AND REACTIONS OF TRIALKYLPLUMBYLMAGNESIUM CHLORIDES*

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## SUMMARY

The preparation, properties, and reactions of trimethylplumbylmagnesium chloride and triethylplumbylmagnesium chloride are described. The complexes are highly reactive and fairly stable intermediates in the reaction of Grignard reagents with lead(II) salts in the presence of alkyl halides to give tetraalkyllead compounds. Some new organolead and silicon-substituted organolead compounds are reported.

## INTRODUCTION

The synthesis of organolead compounds from lead(II) salts has been studied by several investigators in recent years[1,2], and the most widely recommended method to prepare compounds of the type $R_4Pb$ in the laboratory is from the reaction of lead chloride and an organomagnesium or organolithium derivative in ether[3].

$$4\,RM + 2\,PbCl_2 \xrightarrow[\text{ether}]{\text{heat}} R_4Pb + Pb + 4\,MCl \qquad (1)$$

Krause and co-workers[4] concluded after extensive study that the above reaction involved the following steps:

$$2\,RMgX + PbCl_2 \rightarrow R_2Pb + MgX_2 + MgCl_2 \qquad (2)$$

$$3\,R_2Pb \rightarrow R_6Pb_2 + Pb \qquad (3)$$

$$2\,R_6Pb_2 \rightarrow 3\,R_4Pb + Pb \qquad (4)$$

($R_6Pb_2$ has been used rather than $R_3Pb$ as given by Krause). Gilman and co-workers[5,6] reported that organolithium compounds or Grignard reagents react with lead chloride in the presence of alkyl or aryl iodides in ether to give tetraorganolead compounds without formation of by-product lead metal. It was suggested that the reactions in-

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volved were

$$4\,RLi+2\,PbCl_2 \rightarrow R_4Pb+Pb+4\,LiCl \quad (5)$$

$$2\,RI+Pb \rightarrow R_2PbI_2 \quad (6)$$

$$2\,RLi+R_2PbI_2 \rightarrow R_4Pb+2\,LiI \quad (7)$$

This sequence of reactions was supported by the observation that lead metal which precipitated in the early stages of the reaction was redissolved as the reaction proceeded. Based upon the above equations, tetramethyllead was obtained in essentially a quantitative yield by reaction of methyllithium with lead chloride in the presence of methyl iodide. When methylmagnesium chloride or iodide was used in place of the methyllithium the yield of tetramethyllead was in the range of 70 to 80 percent. Willemsen and Van der Kerk[7] have suggested that an intermediate of the type $R_3PbLi$ is formed in the reaction.

Organolead metal compounds ($R_3PbM$) have been known for several years. Both trialkylplumbylsodium and triarylplumbylsodium derivatives[8] have been described in the literature; however, only triarylplumbyllithium compounds have been reported*. The most studied compound of this type is triphenylplumbyllithium which was originally[6] prepared by the reaction of phenyllithium and lead chloride in diethyl ether at −10°. Recently many derivatives of triphenylplumbyllithium have been prepared[9].

The possible existence as an intermediate of a compound of the type $R_3Pb$-MgCl was originally proposed in 1939 by Gilman and Bailie[10] in the reaction of triethyllead chloride and magnesium metal to give tetraethyllead. Since this early proposal no trialkylplumbylmagnesium halide compounds have been reported. The preparation of triarylplumbylmagnesium bromides has been described in the literature by several investigators. In 1961, Glockling, Hooton and Kingston[11] postulated trimesitylplumbylmagnesium bromide to be an intermediate in the reaction of lead bromide and mesitylmagnesium bromide in tetrahydrofuran as solvent. Willemsens and Van der Kerk[12] have described the preparation of triphenylplumbylmagnesium bromide from reaction of lead chloride and phenylmagnesium bromide in tetrahydrofuran or pyridine as solvent. However, Gorsich and Robbins[14] have found that reaction of three moles of vinylmagnesium chloride with one mole of lead chloride in the presence of methyl chloride in tetrahydrofuran as solvent gives trivinylmethyllead in high yields.

We wish to report the results of our work which was undertaken to further investigate the preparation of organolead compounds without formation of by-product lead metal[15]. In this paper are described the preparation and properties of two trialkylplumbylmagnesium chloride compounds. This work has led to a general method of synthesis of symmetrical and unsymmetrical organolead compounds as well as di-lead and silicon–lead intermetallic compounds which is especially suitable for laboratory preparations.

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* Willemsens and Van der Kerk[13] have reported the preparation of tetrabutyllead from reaction of lead chloride, n-butyl bromide and butyllithium which probably involves a trialkylplumbyllithium derivative as an intermediate.

## DISCUSSION

Reaction of three moles of ethylmagnesium chloride or methylmagnesium chloride with one mole of lead(II) chloride or lead(II) acetate in tetrahydrofuran gives greenish-brown and homogeneous solutions containing triethylplumbylmagnesium chloride and trimethylplumbylmagnesium chloride respectively. The equations involved in formation of the complexes are:

$$2\,RMgCl + PbX_2 \xrightarrow{THF} R_2Pb + MgCl_2 + MgX_2 \qquad (8)$$

$$R_2Pb + RMgCl \xrightarrow{THF} R_3PbMgCl \qquad (9)$$

In the preparation of the trialkylplumbylmagnesium chloride it is necessary to add the lead salt to the Grignard reagent in order to prevent formation of lead metal. The formation of lead under these conditions is undoubtedly due to disproportionation of the dialkyllead intermediate formed according to eqn. (3) above when excess Grignard is not available to react immediately to form the relatively stable trialkylplumbylmagnesium chloride complex. Further support for eqns. (8) and (9) is found in the observation that similar results are obtained regardless of the lead salt used, *i.e.*, complexes prepared from lead chloride and lead acetate are identical in appearance and equally high yields of derivatives are obtained.

Eqn. (9) above is not written as an equilibrium even though it is possible that the complex trialkylplumbylmagnesium chlorides exist in equilibrium with dialkyllead and the corresponding Grignard reagent. However, this equilibrium was ruled out because of the instability of dialkyllead compounds under the conditions used to study these complexes. Willemsens and Van der Kerk[16] have discounted a similar equilibrium for triphenylplumbyllithium.

Triethylplumbylmagnesium chloride and trimethylplumbylmagnesium chloride were characterized by reaction with several alkyl halides and (chloromethyl)trimethylsilane.

$$R_3PbMgCl + R'Cl \xrightarrow{THF} R_3R'Pb + MgCl_2 \qquad (10)$$

Table 1 lists the yields of several derivatives, along with molecular weights of some

TABLE 1

REACTIONS OF TRIALKYLPLUMBYLMAGNESIUM CHLORIDES

| $R_3PbMgCl$ | Reactant | Product | Yield (%) | Molecular weight | |
|---|---|---|---|---|---|
| | | | | Calcd. | Found |
| $(C_2H_5)_3PbMgCl$ | $C_2H_5Cl$ | $(C_2H_5)_4Pb$ | 90 | | |
| $(C_2H_5)_3PbMgCl$ | $CH_3Cl$ | $(C_2H_5)_3(CH_3)Pb$ | 89 | | |
| $(C_2H_5)_3PbMgCl$ | $(CH_3)_3SiCH_2Cl$ | $(C_2H_5)_3Pb–CH_2–Si(CH_3)_3$ | 73 | 381 | 394 |
| $(C_2H_5)_3PbMgCl$ | $CH_2Cl_2$ | $[(C_2H_5)_3Pb]_2CH_2$ | 81 | 603 | 620 |
| $(CH_3)_3PbMgCl$ | $CH_3Cl$ | $(CH_3)_4Pb$ | 95 | | |
| $(CH_3)_3PbMgCl$ | $C_2H_5Cl$ | $(CH_3)_3(C_2H_5)Pb$ | 78 | | |
| $(CH_3)_3PbMgCl$ | $(CH_3)_3SiCH_2Cl$ | $(CH_3)_3Pb–CH_2–Si(CH_3)_3$ | 70 | 339 | 362 |
| $(CH_3)_3PbMgCl$ | $CH_2Cl_2$ | $[(CH_3)_3Pb]_2CH_2$ | 80 | 518 | 550 |

new organolead compounds, indicating them to be monomeric as expected. The high yields are indicative of the high reactivity of trialkylplumbylmagnesium chlorides. In similar reactions involving trialkylstannyllithium compounds the yields are substantially lower[17]. (Trimethylplumbyl)(trimethylsilyl)methane, which was prepared in this investigation by reaction of trimethylplumbylmagnesium chloride and (chloromethyl)trimethylsilane, was prepared earlier by Schmidbaur[18] by reaction of [(trimethylsilyl)methyl]magnesium chloride with trimethyllead chloride.

$$(CH_3)_3SiCH_2MgCl + (CH_3)_3PbCl \rightarrow (CH_3)_3Pb\text{–}CH_2\text{–}Si(CH_3)_3 + MgCl_2 \qquad (11)$$

The properties of the silicon-substituted organolead compound thus prepared are consistent with those found in this investigation.

The reactions described in the experimental section were carried out in two steps to give the tetraalkyllead compounds, *i.e.*, the complexes were prepared and then reacted with an organic chloride to give the expected product. These reactions can be carried out in one step to give equally high yields of tetraalkyllead compounds.

$$3\,RMgCl + R'Cl + PbX_2 \xrightarrow[\text{THF}]{5°} R_3R'Pb + 2\,MgCl_2 + MgX_2$$

In this manner the lead salt is added to a solution containing both Grignard reagent and an organic halide.

Trialkylplumbylmagnesium chlorides form readily in tetrahydrofuran, but the reactivity of Grignard reagents toward lead(II) chloride in diethyl ether is not nearly as great in formation of these complexes. In fact, there was no indication that a complex was formed in diethyl ether. The enhanced stability in the more basic tetrahydrofuran is probably related to the increase in solvating power of the medium.

Table 2 contains a tabulation of the observed chemical shifts and spin–spin coupling constants of the new organolead compounds. The peak areas were in the expected ratio for each of the reported compounds. The internal chemical shifts of methyl and methylene groups in the ethyllead compounds were zero, the same as for tetraethyllead[19]. The spectrum of (trimethylplumbyl)(trimethylsilyl)methane agrees with that reported previously by Schmidbaur[18].

TABLE 2

PROTON MAGNETIC SPECTRA DATA[a]

| Compound | $\tau$ | | | $J(^{207}Pb\text{–}H)$ (Hz)[b] | | |
|---|---|---|---|---|---|---|
| | $R_3Pb$ | $MCH_2Pb$ | $CH_3Si$ | $PbCH_2(M)$ | PbCH | $PbCCH_3$ |
| $[(CH_3)_3Pb]_2CH_2$ | 9.28 | 8.68 | | 58.0 | 59.0 | |
| $(CH_3)_3SiCH_2Pb(CH_3)_3$ | 9.23 | 9.57 | | 87.5 | 59.0 | |
| $[(C_2H_5)_3Pb]_2CH_2$ | 8.56 | 8.93 | 9.97 | 48.0 | 41.5 | 134.0 |
| $(C_2H_5)_3PbCH_2Si(CH_3)_3$ | 8.52 | 9.72 | 10.0 | 70.0 | 43.0 | 135.0 |

[a] The spectra were taken in 20% carbon tetrachloride solutions with TMS as an internal standard. [b] Lead has 21.11% natural abundance of its isotope $^{207}Pb$ of spin $\frac{1}{2}$.

The trimethylplumbylmagnesium chloride prepared is a relatively stable complex. After storage in a refrigerator for twenty-four hours at 5°, a 95 percent yield of tetramethyllead was obtained when the complex was treated with methyl chloride, indicating little or no decomposition. However, when the complex was stored for two hours at ambient temperature (26°C) before reaction with methyl chloride, an 85 percent yield of tetramethyllead was obtained. This indicates some decomposition, as evidenced also by formation of a small amount of lead metal.

The greenish-brown color obtained for tetrahydrofuran solutions of the trialkylplumbylmagnesium chloride complexes seems to be a characteristic color for solutions of compounds of the type $R_3M-M'$. Trialkylstannyllithium[19] solutions as well as triarylplumbylmagnesium chloride[11] solutions exhibit this same color.

## EXPERIMENTAL

All reactions were carried out under a nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride before use. Anhydrous lead(II) acetate was obtained by heating the trihydrate at 110° for several hours under a vacuum or removal of the water of hydration by azeotropic distillation with toluene.

The proton magnetic resonance spectra were recorded using a Varian Associates A-60 spectrometer. Molecular weights were determined by the differential vapor pressure technique in benzene solution at 37° using a Mechrolab Model 302 vapor pressure osmometer. Tetramethyllead, tetraethyllead and the mixed methylethyllead compounds were identified by gas chromatography. The chromatographs were obtained at 75° on a 4-foot column of 20 percent TCP on Chromosorb W.

The reactions were performed in a 500 ml or 1000 ml three necked round-bottom flask equipped with condenser (Dewar filled with dry ice/acetone) and magnetic or paddle stirrer. The lead salt was added from a 50-ml round-bottom flask connected to the reaction vessel by a short piece of Gooch tubing. The Grignard reagents were prepared from magnesium turnings and a slight excess of the alkyl halide. The excess alkyl halide was then removed by heating at reflux for a few minutes under a nitrogen flush.

The yields of tetramethyllead and trimethylethyllead were determined by iodimetric titration in THF/toluene solution[20]. Lead contents of the new organolead derivatives were determined by reaction with bromine in carbon tetrachloride, destruction with nitric and perchloric acid and titration with EDTA to the endpoint using xylenol orange as indicator.

During the hydrolysis of the reaction mixtures enough dilute HCl was added to solubilize the precipitated magnesium salts.

### 1. *Triethylplumbylmagnesium chloride or trimethylplumbylmagnesium chloride.*

A Grignard solution prepared from 8.0 g (0.33 g-atom) of magnesium and an equivalent amount of methyl chloride or ethyl chloride in 400 ml of THF was treated slowly at 5° with 27.8 g (0.1 mole) of lead (II) chloride. Greenish-brown and homogeneous solutions containing the complexes were obtained. Derivatives of the compounds were prepared as described below.

### 2. *Tetraethyllead*

Triethylplumbylmagnesium chloride was prepared as described above from 4.0 g (0.17 g-atom) of magnesium, an equivalent amount of ethyl chloride and 13.9 g (0.05 mole) of lead(II) chloride in 250 ml of THF. Into this solution was condensed an excess (15 ml) of ethyl chloride at 5°. The ice bath was removed and the mixture was warmed to ambient temperature and stirred for 15 min. The mixture was hydrolyzed with 100 ml of water and the THF was removed by distillation at atmospheric pressure. The heavy organolead product was separated and steam distilled. After drying, 14.4 g (90%) of tetraethyllead was obtained. In a similar experiment, lead(II) acetate was substituted for lead chloride and an 89% yield of tetraethyllead was obtained.

### 3. *Triethylmethyllead*

Triethylplumbylmagnesium chloride was prepared from 8.0 g (0.33 g-atom) of magnesium, an equivalent amount of ethyl chloride, and 27.8 g (0.1 mole) of lead(II) chloride in 400 ml of THF at 5°. An excess (25 ml) of methyl chloride was condensed into the solution. The mixture was warmed to ambient temperature and stirred for 15 min, and hydrolyzed with 200 ml of water. The THF was removed by distillation and the heavy organolead product separated. Steam distillation gave 22.5 g (73%) of triethylmethyllead which contained only a small amount of tetraethyllead. In a similar experiment lead(II) acetate was substituted for lead(II) chloride and an 89% yield of triethylmethyllead was obtained.

### 4. *Bis(triethylplumbyl)methane*

Triethylplumbylmagnesium chloride was prepared from 16.0 g (0.66 g-atom) of magnesium, an equivalent amount of ethyl chloride and 55.6 g (0.2 mole) of lead(II) chloride at 5° in 900 ml of THF. To the solution was added 30 ml (excess) of methylene dichloride. The mixture was stirred at 5° for 15 min, 15 min at ambient temperature, and 10 min at 50°. The greenish-brown color disappeared and a gelatinous precipitate (magnesium chloride/THF etherates) was formed. The mixture was hydrolyzed with 300 ml of water and the THF was removed by distillation. The organolead product was separated and washed several times with water. An attempt was made to vacuum distill the product but considerable decomposition occurred. Purification was achieved by removing the volatile impurities by steam distillation. After separation 48.5 g (81%) of colorless nondistillable product was obtained. (Found: Pb, 68.65. $C_{13}H_{32}Pb_2$ calcd.: Pb, 68.75%.)

### 5. *(Triethylplumbyl)(trimethylsilyl)methane*

Triethylplumbylmagnesium chloride was prepared from 16.0 g (0.66 g-atom) of magnesium, an equivalent amount of ethyl chloride and 55.6 g (0.2 mole) of lead(II) chloride at 5° in 900 ml of THF. To the solution was added 25 g (0.2 mole) of (chloromethyl)trimethylsilane. The mixture was warmed to ambient temperature and stirred for 30 min and at 50° for 10 min. The mixture was hydrolyzed with 300 ml of water and the THF was removed by distillation. The organolead product was separated from the aqueous layer and washed several times with water. Vacuum distillation gave 55.3 g (73%) of colorless product boiling at 57–59° (0.5 mm). (Found: Pb, 54.69. $C_{20}H_{26}SiPb$ calcd.: Pb, 54.29%.)

### 6. *Tetramethyllead*

Trimethylplumbylmagnesium chloride was prepared from 4.0 g (0.16 g-atom) of magnesium, an equivalent amount of methyl chloride and 13.9 (0.05 mole) of lead(II) chloride at 5° in 250 ml of THF. Into the solution was condensed 15 ml (excess) of methyl chloride and the solution was warmed to ambient temperature and stirred for 30 min. The mixture was hydrolyzed with 100 ml of water. The organic layer was separated and the aqueous layer was extracted with toluene. The combined organic extracts were diluted to volume in a 500 ml volumetric flask. Titration of the solution showed that 12.5 g (94%) of tetramethyllead was produced in the reaction.

### 7. *Trimethylethyllead*

Trimethylplumbylmagnesium chloride was prepared in 100 ml of THF at 5° from 8.0 g (0.33 g-atom) of magnesium, an equivalent amount of methyl chloride and 33.0 g (0.1 mole) of lead acetate. Into the solution was condensed 25 ml (excess) of ethyl chloride. The mixture was stirred for 30 min at 5° and then warmed to 55° for 10 min. The solution was hydrolyzed with 100 ml of water and two layers were formed. The THF layer was separated from the heavy aqueous layer and the aqueous layer was extracted several times with toluene. The combined organic extracts were diluted to volume in a 500 ml volumetric flask. Titration showed 21.2 g (78%) of trimethylethyllead was present.

### 8. *Bis(trimethylplumbyl)methane*

Trimethylplumbylmagnesium chloride was prepared from 8.0 g (0.33 g-atom) of magnesium, an equivalent amount of methyl chloride and 27.8 g (0.1 mole) of lead(II) chloride at 50° in 400 ml of THF. To the complex was added 15 ml (excess) of methylene dichloride and the mixture was stirred for 30 min at 5°. The ice bath was removed and the reaction mixture was warmed to 50° for 15 min. The greenish-brown color disappeared and a gelatinous precipitate was formed. The mixture was hydrolyzed with 300 ml of water and the THF was removed by distillation. The organolead product was separated from the aqueous layer and washed several times with water. Vacuum distillation gave 21 g (80%) of colorless product boiling at 57–59° (0.3 mm). (Found: Pb, 80.07. $C_7H_{20}Pb_2$ calcd.: Pb, 79.92%.)

### 9. *(Trimethylplumbyl)(trimethylsilyl)methane*

Trimethylplumbylmagnesium chloride was prepared from 8.0 g (0.33 g-atom) of magnesium, an equivalent amount of methyl chloride and 27.8 g (0.1 mole) of lead(II) chloride as described above at 5°. To the solution was added 12.2 g (0.1 mole) of (chloromethyl)trimethylsilane. The ice bath was removed and the solution was warmed to ambient temperature and stirred for 25 min. The greenish-brown color disappeared and a gelatinous precipitate was formed. The mixture was hydrolyzed with 300 ml of water and the THF was removed by distillation. The heavy organolead product was separated from the aqueous layer and washed several times with water. Vacuum distillation gave 23.6 g (70%) of colorless product boiling at 34–35° (0.3 mm). (Found: Pb, 60.83. $C_7H_{20}SiPb$ calcd.: Pb, 61.02%.)

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