

## INVESTIGATIONS ON ORGANOLEAD COMPOUNDS

I. A NOVEL RED ORGANOLEAD COMPOUND\*.  
A REINVESTIGATION OF KRAUSE'S RED DIPHENYLLEAD

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## INTRODUCTION

Highly coloured lead compounds in which the colour is intrinsically linked with the presence of lead are comparatively rare. Among inorganic lead compounds the fiery red minium ("red lead") is, of course, the best known example.

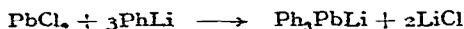
Two red organolead compounds have been mentioned in the literature: Krause and Reissaus<sup>1</sup> described red-coloured diphenyllead and di-*p*-tolyllead which were obtained from lead dichloride and the appropriate Grignard reagents. Later workers<sup>2,3,4,5</sup> could not repeat this work. At the end of this paper we will return to these compounds.

Intense brown-red colours have been observed frequently in organolead chemistry\*\* upon reacting lead dichloride with Grignard or organolithium reagents. The substances causing these colours—thought to be diorganoleads—are very unstable and could not be isolated. They disproportionate spontaneously into metallic lead and the yellow-coloured hexaorganodileads, or even further into the colourless tetraorganoleads.

In this paper we describe a red organolead compound of a novel type which emerged from an investigation of the properties and reactions of triphenylplumbyl-lithium,  $\text{Ph}_3\text{PbLi}$ : viz. tetrakis(triphenylplumbyl)lead,  $(\text{Ph}_3\text{Pb})_4\text{Pb}$ .

## PREPARATION AND STRUCTURE

Triphenylplumbyl-lithium was prepared according to Gilman *et al.*<sup>4</sup> from lead dichloride and three equivalents of phenyllithium in diethyl ether in an atmosphere of dry nitrogen at about  $-10^\circ\text{C}$ :

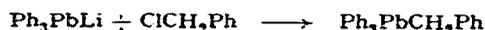


Triphenylplumbyl-lithium is soluble in tetrahydrofuran<sup>9</sup> but insoluble in ether. That the required compound had indeed precipitated under the reaction conditions

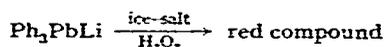
\* Presented in part at the XIXth International Congress of Pure and Applied Chemistry, London, 1963.

\*\* For reviews on organolead chemistry see refs. 6, 7 and 8.

employed was proved by sucking off the supernatant solvent and reacting the residue ( $\text{Ph}_3\text{PbLi} \div \text{LiCl}$ ) with benzyl chloride. A nearly quantitative yield of benzyltriphenyllead was obtained:



By chance, we observed that crude triphenylplumbyllithium, freed from ether by sucking off the supernatant liquid followed by vacuum-drying, upon exposure to air, changed rapidly at its surface into a red substance. Subsequently, it was found that this phenomenon is due to simultaneous hydrolysis and oxidation at low temperature. Finally, the red compound was prepared conveniently by treating vacuum-dried triphenylplumbyllithium with an ice-salt mixture containing a small amount of hydrogen peroxide:



After extraction of the reaction mixture with chloroform and concentration of the chloroform solution at low temperature, a crystalline red solid was obtained. Recrystallization from chloroform yielded a pure substance. The analyses point to the empirical formula  $\text{Ph}_{1.2}\text{Pb}_3$ . The yield was usually about 30% based on lead dichloride.

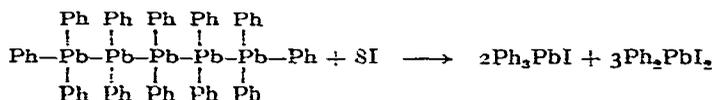
The compound is insoluble in alcohol and petroleum ether but dissolves readily in chloroform and benzene. The pure substance is rather unstable; in air within a few days a substantial amount of decomposition to hexaphenyldilead and lead oxide occurs. Under nitrogen decomposition proceeds more slowly, hexaphenyldilead and lead being formed. In solution the compound is still less stable, in particular in polar solvents; in acetone the colour disappears within a few seconds. For this reason the removal of ether from triphenylplumbyllithium before the hydrolysis-oxidation reaction is essential.

The instability of the compound seriously hampered the exact determination of its molecular weight. Finally, however, we succeeded in performing some osmometric experiments at 25° in chloroform. Values were found of about 1760 (calculated 1961). Probably some decomposition took place during the measurement.

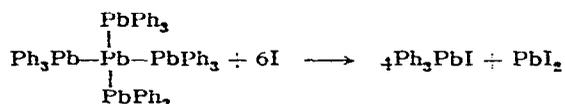
An important further step in the determination of the structure of the red compound was an iodination experiment. A solution of the compound in chloroform was titrated with iodine at about -60° till the colour of the iodine was just perceptible in the solution. Though the equivalence point could not be established exactly owing to the formation of a precipitate (lead diiodide), the experiment gave a sufficiently informative value. The amount of iodine consumed appeared to be 6-8 atoms per mole of red compound. When less iodine was added not all of the red compound was converted. This may be seen as an indication that roughly 6 atoms of iodine per molecule are required in order to obtain the first stable reaction products.

Quite surprisingly it was found that the iodination product consisted of triphenyllead iodide and lead diiodide. At that time a mixture of triphenyllead iodide and diphenyllead diiodide was expected since the compound was presumed to have a linear structure (see following equation). Using thin-layer chromatography, the absence of diphenyllead diiodide in the reaction mixture could, however, be established with certainty. Likewise, the possibility could be ruled out that diphenyllead diiodide

had been formed but had disappeared in some secondary reaction, since diphenyllead diiodide proved to be stable under the prevailing reaction conditions.



The amount of triphenyllead iodide isolated (nearly four moles per mole of  $\text{Ph}_{12}\text{Pb}_5$  when six atoms of iodine were used) pointed to a highly branched structure in which all triphenyllead groups are already present: tetrakis(triphenylplumbyl)lead (or dodecaphenylneopentaplumbane):



Triphenyllead iodide and lead diiodide were isolated in amounts of 92 and 93% respectively, based on this reaction equation.

The symmetry of the molecule may explain its relatively high stability (organically-substituted lead chains of more than two lead atoms are not yet known). This consideration also explains why exactly five lead atoms are present in the molecule; if the structure were linear, it would be difficult to explain why only the molecule with five lead atoms should be formed.

We have obtained the red compound in yet another slightly different way. Lead dichloride was reacted at about  $-10^\circ$  with two equivalents of phenylmagnesium bromide in ether. After 1 h stirring at  $-10^\circ$ , the Gilman Test<sup>9</sup> was only faintly positive, showing that nearly all the Grignard reagent had been consumed. At that time a little metallic lead had separated owing to the instability of diphenyllead, which easily disproportionates into lead and hexaphenyldilead (this is part of the normal procedure for the preparation of hexaphenyldilead). After evaporating the ether *in vacuo*, a dark-coloured paste remained. Treatment of this paste with ice-salt containing a small amount of hydrogen peroxide yielded a substantial amount of the red substance. Rigorous exclusion of oxidation resulted only in the hydrolysis of diphenyllead into lead oxide and benzene.

This explains why so often red-coloured solutions have been reported in the preparation of hexaphenyldilead. The required hydrolysis of the reaction mixture by adding ice may cause some oxidation of unconverted diphenyllead to our red compound by traces of oxygen. Isolation has never been achieved under these conditions because of the instability of the red compound in ethereal medium. (Only Krause<sup>1</sup> isolated a red substance which he described as diphenyllead.)

The mode of formation of the red compound is still obscure. Intermediates may be either diphenyllead or triphenyllead hydride or even both. The former intermediate may originate from triphenylplumbyllithium, which, it has been suggested in the literature<sup>4</sup>, is in equilibrium with diphenyllead and phenyllithium. The latter intermediate may come from hydrolysis of triphenylplumbyllithium. Another possibility is that triphenylplumbyllithium reacts with bivalent inorganic lead (a de-

composition product) to give  $(\text{Ph}_3\text{Pb})_2\text{Pb}$  which disproportionates directly into  $(\text{Ph}_2\text{Pb})_4\text{Pb}$  and Pb. For such reactions see ref. 10.

For a discussion of the absorption spectra see ref. 11. Absorption maxima were observed at 444 and 358  $m\mu$  ( $\log \epsilon$  4.40 and 4.63 resp. in benzene).

The *p*-tolyl analogue tetrakis(tri-*p*-tolylplumbyl)lead was also obtained. However, owing to difficult separation from the by-product hexa-*p*-tolylidilead, the analyses were not satisfactory. The compound looked slightly more stable than the phenyl derivative. Absorption maxima were observed at 448  $m\mu$  ( $\log \epsilon$  4.38) and 365  $m\mu$  ( $\log \epsilon$  4.63).

#### KRAUSE'S DIPHENYLLEAD

As we have already stated, Krause and Reissaus<sup>1</sup> have also described a red organolead compound, which they presumed to be diphenyllead. They prepared this compound from lead dichloride and phenylmagnesium bromide in ether at 2°. After hydrolysis the reaction mixture was treated with benzene, hexaphenyldilead was allowed to crystallize from the benzene layer, and diphenyllead was precipitated by dropping the red filtrate into alcohol.

A strong point against the possible isolation of diphenyllead in this way is that Glockling *et al.*<sup>5</sup> have shown that the initial reaction product of lead dichloride and phenylmagnesium bromide—believed to be diphenyllead—is hydrolyzed by water, yielding lead oxide and benzene. We also found that hydrolysis of the above reaction mixture instantaneously yielded lead oxide without any appearance of a red colour if the hydrolysis was carried out in an atmosphere of pure nitrogen with oxygen-free water. If diphenyllead is so hydrolytically sensitive, it seems unlikely that it can be isolated from a hydrolyzed reaction mixture.

It is possible that in Krause's experiments some tetrakis(triphenylplumbyl)lead had been formed through oxidation (e.g. by traces of oxygen in the water). Due to its instability in ether this compound must have been contaminated with hexaphenyldilead and other decomposition products.

#### EXPERIMENTAL

##### *Triphenylplumbyllithium*<sup>2</sup>

$\text{PbCl}_2$  (5.6 g, 0.02 mole) were placed in a three-necked 250 ml round-bottomed flask. After flushing with pure nitrogen, 50 ml of anhydrous ether were introduced and the reaction flask was chilled in a dry ice-acetone bath. Then 0.06 mole of PhLi (dissolved in 75 ml of ether) was added at once and the temperature was allowed to rise to about  $-10^\circ$  under magnetic stirring. Stirring was continued for one hour at  $-10^\circ$ . After the greyish-white mixture of  $\text{Ph}_3\text{PbLi}$  and LiCl had settled the slightly yellow-coloured supernatant liquid, which contained practically no lead, was sucked off. The residue was used as such for further experiments without isolating the triphenylplumbyllithium.

##### *Benzyltriphenyllead*<sup>2</sup>

Benzyl chloride (5 g, excess) in 75 ml of anhydrous ether was added with stirring to the ether-moist mixture of  $\text{Ph}_3\text{PbLi}$  and LiCl mentioned above. After 2 h stirring at

$-10^{\circ}$ , the mixture was refluxed for 2 h. Hydrolysis yielded two nearly colourless layers without precipitate. The ethereal layer was dried over anhydrous sodium sulphate. After filtration the ether was evaporated and the residue was recrystallized from ethyl alcohol; yield 9.3 g (89 %) of  $\text{Ph}_3\text{PbCH}_2\text{Ph}$ , m.p.  $91-93^{\circ}$ .

#### *Tetrakis(triphenylplumbyl)lead*

(a) *From triphenylplumbyllithium.* The mixture of  $\text{Ph}_3\text{PbLi}$  and  $\text{LiCl}$  described above (again from 5.6 g of  $\text{PbCl}_2$ ) was freed from the last traces of ether by vacuum-drying at room temperature. A crumbling greyish mass remained, which in air slowly turned yellow-red at the surface. An ice-salt mixture ( $\pm 150$  ml, temperature  $-10$  to  $-15^{\circ}$ ) containing 5 ml of 30 %  $\text{H}_2\text{O}_2$  was added at once under vigorous stirring and initial cooling by dry ice-acetone. After all the material had been mixed with the ice-salt mixture, the reaction mass was vigorously stirred for one hour without external cooling. A red product floating on the water was formed from the start but the intensity of the colour deepened with time. Extraction with  $\text{CHCl}_3$  yielded a bright-red solution which rather soon became turbid. This solution was concentrated *in vacuo* during which some decomposition occurred. When the first crystals appeared the solution was filtered through Filtrapid and further concentrated *in vacuo*. The red crystalline substance formed was filtered off (2.5 g, 32 % based on  $\text{PbCl}_2$ ) and recrystallized in a similar way from  $\text{CHCl}_3$ . The lead analyses of six separately prepared samples showed the following percentages: 52.77, 52.99, 53.01, 52.82, 53.04, 52.61 ( $\text{C}_{72}\text{H}_{60}\text{Pb}_5$  calcd.: Pb, 52.82 %).

(b) *From "diphenyllead".* A solution of  $\text{PhMgBr}$  was prepared from 31.4 g of  $\text{PhBr}$  (0.2 mole) and 5.0 g of magnesium (0.2 mole) in 150 ml of anhydrous ether in an atmosphere of pure nitrogen. To this solution (chilled to  $-20^{\circ}$ ) 27.8 g of  $\text{PbCl}_2$  (0.1 mole) were added under vigorous stirring. Stirring was continued for 1 h between  $-15$  and  $-20^{\circ}$ . The mixture rapidly turned intensely dark-brown. Initially, the Gilman test was strongly positive but after one hour it was faint, showing that nearly all of the Grignard reagent had reacted. A small amount of metallic lead had separated. Throughout the reaction the atmosphere of pure nitrogen was maintained. After stirring was stopped, the mixture separated into two layers: the slightly coloured upper layer consists mainly of solvent; the dark-brown lower layer contains most of the lead, probably in the form of diphenyllead. The ether was evaporated *in vacuo* with stirring, whereupon a dark-brown paste remained. This paste was cooled in dry ice-acetone and then stirred with an ice-salt mixture ( $\pm 350$  ml) containing 15 ml of 30 % hydrogen peroxide. Stirring was continued for 1 h. The red compound was extracted with chloroform (in total 500 ml) and the extract dried on anhydrous sodium sulphate and filtered. From the measurement of the extinction value at  $444 \text{ m}\mu$ , an amount of 4.1 g of  $\text{Ph}_{12}\text{Pb}_5$  was calculated to be present (yield 10 %, based on  $\text{PbCl}_2$ ). The solution was concentrated *in vacuo* and worked up as described under (a). Yield 2.2 g of  $\text{Ph}_{12}\text{Pb}_5$ . (Found: C, 44.30; H, 3.07; Pb, 52.79.  $\text{C}_{72}\text{H}_{60}\text{Pb}_5$  calcd.: C, 44.09; H, 3.08; Pb, 52.82 %.)

#### *Iodination of tetrakis(triphenylplumbyl)lead*

$(\text{Ph}_3\text{Pb})_4\text{Pb}$  was dissolved in  $\text{CHCl}_3$  and the solution chilled to about  $-60^{\circ}$  in dry ice-acetone. The calculated amount of solid iodine (6 atoms per mole) was added at once with stirring. The iodine dissolved slowly, thus allowing a smooth and regular

supply of iodine to the reaction. The mixture was stirred until all the iodine had been consumed while at the same time the temperature was permitted to rise slowly to room temperature. The precipitated lead diiodide was filtered off and the filtrate was evaporated to dryness to yield a residue of practically pure triphenyllead iodide, m.p.  $138^{\circ}$  (lit.<sup>7</sup>  $138-9^{\circ}$ ). Thin-layer chromatography (in benzene, spray with dithizone) did not show the presence of any diphenyllead diiodide. In a typical experiment 355 mg of the red compound was iodinated in 25 ml of chloroform with 138 mg of iodine to afford 78 mg of  $PbI_2$  (93 %) and 410 mg of  $Ph_3PbI$  (92 %).

#### *Hydrolysis of "diphenyllead"*

"Diphenyllead" was prepared as described above. After the reaction was nearly complete (Gilman Test), cold water, freed from oxygen by boiling, was added dropwise under vigorous stirring and cooling, the temperature carefully being kept below  $-10^{\circ}$ . The thick precipitate was filtered off and extracted with chloroform. The residue did not contain organic matter (flame test). The chloroform extract was concentrated and then diluted with an equal volume of ethanol to precipitate hexaphenyldilead. Only a trace of  $Ph_6Pb_2$  precipitated. In the ethereal layer and in the filtrate only traces of organic lead were present. Therefore nearly all the lead originally present as diphenyllead had been converted into inorganic compounds.

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#### SUMMARY

A red organolead compound of the structure  $(Ph_3Pb)_4Pb$  has been obtained from the simultaneous hydrolysis and oxidation of ether-free triphenylplumbylithium or diphenyllead at low temperatures. Its structure was established by analysis and by an iodination reaction which yielded one mole of lead diiodide and four moles of triphenyllead iodide per mole of  $Ph_{12}Pb_5$ ; no diphenyllead diiodide was formed.

Krause's early report of the isolation of diphenyllead has been critically re-investigated.

#### REFERENCES

- 1 E. KRAUSE AND G. G. REISSAUS, *Ber.*, 55 (1922) 888.
- 2 L. D. APPERSON, *Iowa State Coll. J. Sci.*, 16 (1941) 7.
- 3 K. A. JENSEN AND N. CLAFSON-KAAS, *Z. Anorg. Allgem. Chem.*, 250 (1943) 277.
- 4 H. GILMAN, L. SUMMERS AND R. W. LEEPER, *J. Org. Chem.*, 17 (1952) 630.
- 5 F. GLOCKLING, K. HOGTON AND D. KINGSTON, *J. Chem. Soc.*, (1961) 4405.
- 6 E. KRAUSE AND A. VON GROSSE, *Die Chemie der metall-organischen Verbindungen*, Borntraeger, Berlin, 1937, p. 372-429.
- 7 R. W. LEEPER, L. SUMMERS AND H. GILMAN, *Chem. Rev.*, 54 (1954) 101.
- 8 L. C. WILLEMSSENS, *Organolead Chemistry*, Institute for Organic Chemistry T.N.O., Utrecht, 1964.
- 9 C. TAMBORSKI, F. E. FORD, W. L. LEHN, G. J. MOORE AND E. J. SOLOSKI, *J. Org. Chem.*, 27 (1962) 619.
- 10 L. C. WILLEMSSENS AND G. J. M. VAN DER KERK, *J. Organometal. Chem.*, 2 (1964) 260.
- 11 W. DRENTH, M. J. JANSSEN, G. J. M. VAN DER KERK AND J. A. Vliegenthart, *J. Organometal. Chem.*, 2 (1964) 265.