

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

## STUDIES OF ORGANIC LEAD COMPOUNDS.

## II. OXIDATION REACTIONS

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RECEIVED JULY 1, 1931

PUBLISHED SEPTEMBER 5, 1931

Up to the present time no tetraalkyl- or aryl lead compound containing a basic or an acidic group has been prepared. In searching for a method of preparing such a compound, oxidation reactions seemed to offer a favorable method of approach in view of the success attained in the oxidation of the tritolylbismuth dichlorides.<sup>2</sup> Since the organic lead compounds are sensitive to acidic reagents, the oxidations were for the most part carried out by means of potassium permanganate in acetone solution. Attempts to oxidize triphenyl-*p*-tolyllead, tri-*o*-tolyllead chloride, tetra-*o*- and *p*-tolyllead in this manner were wholly unsuccessful, only unreacted material was recovered. In the trivalent series tri-*p*- and *o*-tolyllead were oxidized similarly. Although no carboxyl group was produced, the compounds were attacked by the oxidizing reagent. Tri-*p*-tolyllead yielded tri-*p*-tolyllead acetate as the direct reaction product. Presumably tri-*p*-tolyllead hydroxide was first formed and this was converted to the acetate by acetic acid formed from oxidation of the acetone. Tri-*p*-tolyllead acetate was identified by a separate synthesis and by conversion to the corresponding chloride.

Tri-*o*-tolyllead was also attacked by the permanganate in acetone solution but no direct oxidation product could be isolated. The oil obtained was treated in alcoholic solution with hydrochloric or hydrobromic acid and the corresponding tri-*o*-tolyllead halide was obtained. This indicates that tri-*o*-tolyllead hydroxide was formed as an intermediate product here as well as in the analogous case of the para compound.

Since the tolyl compounds failed to yield derivatives containing a carboxyl group, triphenylallyllead was synthesized in the hope that it would be possible to oxidize the double bond in preference to a lead-carbon linkage. Ozonization was first tried but resulted in the elimination of the allyl group. The amorphous product obtained was not characterized but was probably triphenyllead oxide since it could be readily converted to triphenyllead acetate and identified as such.

When triphenylallyllead was oxidized by potassium permanganate in acetone solution two products were obtained. For the most part the allyl group was severed and the triphenyllead hydroxide isolated was identified by converting it to triphenyllead acetate. The second product obtained was found to be 1-triphenyllead-2,3-propanediol,  $(C_6H_5)_3PbCH_2-$

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<sup>2</sup> Supniewski and Adams, *THIS JOURNAL*, **48**, 507 (1926).

$\text{CHOHCH}_2\text{OH}$ , which would result by partial oxidation of the double bond. This is the first organic lead compound containing an alcoholic hydroxyl group to be prepared. It is a white crystalline solid melting at  $124\text{--}125^\circ$ . It is soluble in alcohol and can be recrystallized readily from aqueous alcohol.

In view of the fact that acid reagents sever an aromatic before an aliphatic group in the case of alkyl-aryl lead compounds<sup>3</sup> it was rather surprising that the oxidation of triphenylallyllead resulted in the loss of the allyl group. Consequently this compound as well as the glycol derived from it was treated in alcoholic solution with hydrobromic acid and in each case triphenyllead bromide was obtained in practically quantitative yield. The action of hydrobromic acid to sever the allyl group in preference to a phenyl group may probably be accounted for by the great reactivity of the system  $\text{CH}_2=\text{CH}-\text{CH}_2-$ , but triphenylbenzyllead which contains the same system behaves in the normal manner; a phenyl group is replaced by the action of bromine and the benzyl group is left intact.<sup>4</sup>

Since triphenylallyllead and the glycol derived from it were so sensitive to hydrobromic acid, the oxidation products of triphenylallyllead were treated with acetic acid, which readily converted triphenyllead hydroxide to the acetate, but had no effect on triphenylallyllead under the conditions used in the experiment.

In the course of this investigation some new aryl lead salts were prepared for the purpose of identification of reaction products.

### Experimental Part

**Oxidation with Potassium Permanganate.**—The general method of oxidation was to dissolve or suspend the organic lead compound in acetone and to reflux and stir the solution during the addition of small portions of potassium permanganate. Successive portions were added as soon as the permanganate color disappeared. If the color persisted for about an hour the oxidation was considered to be complete; alcohol was added to decompose the excess permanganate and the solution was filtered and concentrated. The residue was worked up as described separately for each compound. The reaction products and their derivatives were in each case identified by their melting points and mixed melting points with authentic specimens.

**Tri-*p*-tolyllead.**—Ten grams of tri-*p*-tolyllead in 500 cc. of acetone was oxidized by 25 g. of potassium permanganate in five hours. A yield of 6–7 g. of crude product was obtained which after recrystallization from alcohol and from petroleum ether melted at  $162\text{--}163^\circ$ . This was shown to be tri-*p*-tolyllead acetate by analysis for lead and by comparison with the known product. The same product was obtained regardless of whether or not alcohol was added to decompose the excess permanganate. The tri-*p*-tolyllead acetate obtained by the above method was further identified by converting it to tri-*p*-tolyllead chloride. This could be accomplished by treating an alcoholic solution of the acetate with hydrochloric acid or aqueous sodium chloride. The tri-*p*-tolyllead chloride was identified by analysis for lead and chlorine and by a mixed melting point

<sup>3</sup> Hurd and Austin, *THIS JOURNAL*, **53**, 1543 (1931).

<sup>4</sup> Krause and Schlöttig, *Ber.*, **63**, 1384 (1930).

with an authentic specimen. In converting the acetate to the chloride by means of hydrochloric acid, an excess of the acid and prolonged heating gave di-*p*-tolyllead dichloride. This was purified by recrystallization from pyridine, with which it formed a complex. Analysis showed the complex to contain four molecules of pyridine analogous to the compounds described by Pfeiffer, Truskier and Disselkamp.<sup>5</sup>

*Anal.* Calcd. for  $(C_7H_7)PbCl_2 \cdot 4C_5H_5N$ :  $C_5H_5N$ , 40.69. Found:  $C_5H_5N$ , 40.60, 40.59.

The pyridine effloresces slowly when the compound stands in air. The pyridine-free compound was shown to be di-*p*-tolyllead dichloride<sup>6</sup> by analysis for halogen.

**Tri-*o*-tolyllead.**—Ten grams of tri-*o*-tolyllead<sup>7</sup> suspended in 500 cc. of acetone was oxidized by 6 g. of potassium permanganate during the course of four hours. The oily residue was dissolved in alcohol, acidified with hydrochloric or hydrobromic acid and 1–2 g. of crystalline product was obtained. With hydrochloric acid the substance produced melted at 140–141° and was shown to be identical with tri-*o*-tolyllead chloride. Acidification with hydrobromic acid yielded a product which after recrystallization from alcohol and from petroleum ether melted at 126–127° and was identified as tri-*o*-tolyllead bromide.<sup>7</sup>

The manganese dioxide sludge from the first filtration was dissolved with sodium bisulfite solution and filtered. The dried precipitate was extracted with hot toluene and upon evaporation yielded 6 g. of unreacted tri-*o*-tolyllead.

**Triphenylallyllead.**—Five grams of triphenylallyllead was dissolved in a mixture of 250 cc. of acetone and 25 cc. of water and was oxidized in the cold with 3–4 g. of potassium permanganate. Water was added to the concentrated acetone solution and most of the acetone was evaporated. The solution was made alkaline with sodium hydroxide, cooled and filtered. This precipitate constituted the major portion of the reaction product and had no definite melting point; yield, 2–3 g. It was dissolved in hot alcohol and acidification with acetic acid yielded triphenyllead acetate, which was identified as such.

The above alkaline filtrate was concentrated and on cooling yielded 0.7–1.0 g. of a product which after recrystallization from aqueous alcohol melted at 124–125°. Its analysis and properties indicated its identity as 1-triphenyllead-2,3-propanediol.

*Anal.* Calcd. for  $(C_6H_5)_3PbCH_2CHOHCH_2OH$ : Pb, 40.36. Found: Pb, 40.03.

When an alcoholic solution of the glycol was treated with hydrobromic acid, triphenyllead bromide<sup>8</sup> was obtained in practically quantitative yield. It was identical with a known sample of triphenyllead bromide.

Sometimes a product melting at 104–105° with decomposition was obtained where the glycol was expected. This was apparently a mixture of the hydroxide with the glycol. It was dissolved in aqueous alcohol and acidified with acetic acid. After cooling to room temperature a high melting precipitate, probably triphenyllead acetate, was filtered and discarded. On cooling in ice or on further concentration of the filtrate the glycol was obtained.

**Miscellaneous.**—Attempts were made to oxidize triphenyl-*p*-tolyllead,<sup>9</sup> tri-*o*-tolyllead chloride, tetra-*p*-tolyllead and tetra-*o*-tolyllead.<sup>7</sup> Samples of from 2.5–5 g. were used in the oxidations and in no case could an organic lead compound other than unreacted material be obtained. The recovery varied from 64–84%.

<sup>5</sup> Pfeiffer, Truskier and Disselkamp, *Ber.*, **49**, 2448 (1916).

<sup>6</sup> Polis, *ibid.*, **21**, 3425 (1888).

<sup>7</sup> Austin, *THIS JOURNAL*, **53**, 1548 (1931).

<sup>8</sup> Grüttner, *Ber.*, **51**, 1300 (1918).

<sup>9</sup> Krause and Schmitz, *ibid.*, **52**, 2153 (1919).

**Preparation of Triphenylallyllead,  $(C_6H_5)_3PbCH_2-CH=CH_2$ .**—The Grignard reagent prepared from 92 g. of allyl bromide, 40 g. of magnesium and 750 cc. of ether was stirred and refluxed for four hours with 57 g. of triphenyllead chloride<sup>10</sup> and then allowed to stand for twelve hours. Decomposition was effected with iced ammonium chloride solution and the ether layer was separated and evaporated. The residue was recrystallized from alcohol and yielded 52 g. of product. Further recrystallization from alcohol yielded pure triphenylallyllead, m. p. 76–77°.

*Anal.* Calcd. for  $(C_6H_5)_3PbC_3H_5$ : Pb, 43.22. Found: Pb, 42.85.

**Ozonization of Triphenylallyllead.**—Triphenylallyllead (2.5 g.) was dissolved in 50 cc. of petroleum ether free of unsaturated compounds and ozonized air or oxygen was passed through for about one hour. About 2 g. of a white precipitate which had no definite melting point separated during the course of the reaction. Attempted decomposition of this product with 3% hydrogen peroxide did not yield an alkali-soluble product. An alcoholic solution of the reaction product was treated with acetic acid, which yielded triphenyllead acetate, identified as such.

**Action of Acids on Triphenylallyllead.**—An alcoholic solution of triphenylallyllead was acidified with hydrobromic acid and boiled for a few minutes. The solution was diluted, cooled and filtered and gave a practically quantitative yield of triphenyllead bromide, identical with a known sample. Acetic acid under similar conditions did not react with triphenylallyllead.

**Preparation of Tetra-*p*-tolyllead.**—Seventeen grams of tri-*p*-tolyllead dissolved in 300 cc. of toluene was refluxed for five hours. The solution was filtered and concentrated and yielded 13 g. of tetra-*p*-tolyllead. Its melting point corresponded to that of the product described by Krause and Reissaus.<sup>11</sup>

**Aryl Lead Salts.**—The properties and analyses of these derivatives are given in Table I. The preparation of each compound is described separately. Petroleum ether called for in the preparations had a boiling point range of 65–110°.

TABLE I  
ARYL LEAD SALTS

Aryl lead salts	Yield, %	M. p., °C.	Formula	Lead, %		Chlorine, %	
				Calcd.	Found	Calcd.	Found
Triphenyllead acetate	63	206–207	$(C_6H_5)_3PbOAc$	41.66	41.55	...	...
Tri- <i>p</i> -tolyllead acetate	76	158–159	$(C_7H_7)_3PbOAc$	38.42	38.30	...	...
Tri- <i>p</i> -tolyllead chloride	70	140–141	$(C_7H_7)_3PbCl$	40.17	40.13	6.87	6.90
Tri- <i>o</i> -tolyllead chloride	58	141–142	$(C_7H_7)_3PbCl$	40.17	40.06	6.87	6.83
Di- <i>o</i> -tolyllead dichloride	75	178–179	$(C_7H_7)_2PbCl_2$	45.02	44.83	15.41	15.43

**Triphenyllead Acetate.**—Six grams of triphenyllead chloride was dissolved in hot alcohol and sodium hydroxide was added until the solution was distinctly alkaline. The solution was diluted somewhat, cooled and filtered and gave five grams of the hydroxide. This was dissolved in hot aqueous alcohol, acidified with acetic acid and on cooling yielded 4 g. of triphenyllead acetate. It was recrystallized from aqueous alcohol and melted at 206–207°.

**Tri-*p*-tolyllead Acetate.**—(A) An excess of an aqueous solution of lead acetate was added to 1.5 g. of tri-*p*-tolyllead chloride dissolved in alcohol. The precipitated lead chloride was filtered and the hot filtrate was diluted. On cooling and filtering, 1.2 g. of tri-*p*-tolyllead acetate was obtained which after recrystallization from petroleum ether melted at 161–162°. Petroleum ether adheres strongly to this salt and was removed by heating at 140° in a vacuum for three hours. After this treatment the compound melted at 158–159°.

<sup>10</sup> Gilman and Robinson, *THIS JOURNAL*, **51**, 3112 (1929).

<sup>11</sup> Krause and Reissaus, *Ber.*, **55**, 888 (1922).

(B) By a series of reactions analogous to those described for the preparation of triphenyllead acetate, 1.5 g. of tri-*p*-tolyllead iodide<sup>11</sup> was converted to 0.7 g. of tri-*p*-tolyllead acetate which was recrystallized from petroleum ether and melted at 157–159°.

**Tri-*p*-tolyllead Chloride.**—Six grams of tetra-*p*-tolyllead dissolved in 100 cc. of chloroform was treated with dry hydrogen chloride until a flocculent precipitate of di-*p*-tolyllead dichloride appeared. The solution was filtered and evaporated and the residue was recrystallized from aqueous alcohol. Three grams of unchanged tetra-*p*-tolyllead (insoluble in hot alcohol) and 1.9 g. of tri-*p*-tolyllead chloride was obtained. The halide, after recrystallization from alcohol and then from petroleum ether, melted at 140–141°. For analysis the compound must be recrystallized last from aqueous alcohol or dried thoroughly at 100° in a vacuum to remove strongly adhering solvent.

**Tri-*o*-tolyllead Chloride.**—For the preparation of this compound 3.8 g. of tetra-*o*-tolyllead was dissolved in 250 cc. of petroleum ether and dry hydrogen chloride was passed into the warm solution until a slight precipitate was observed. An excess of hydrogen chloride must be avoided as the reaction proceeds very readily to form di-*o*-tolyllead dichloride. The solution was boiled for a few minutes and then cooled and filtered to remove a small amount of di-*o*-tolyllead dichloride. The filtrate was concentrated and yielded about 2 g. of the desired halide, which was purified by recrystallization from alcohol and then melted at 141–142°.

**Di-*o*-tolyllead Dichloride.**—(A) An excess of dry hydrogen chloride was passed into a solution of 4.6 g. of tetra-*o*-tolyllead in 250 cc. of petroleum ether. The solution was boiled to expel the excess hydrogen chloride and then cooled and filtered. The yield was 2.8 g. of di-*o*-tolyllead dichloride.

(B) Five grams of tri-*o*-tolyllead, 5 cc. of concentrated hydrochloric acid and 150 cc. of chloroform were shaken on a mechanical shaker for four hours. The solution was filtered and concentrated and yielded 1.7 g. of di-*o*-tolyllead dichloride.

In each case the di-*o*-tolyllead dichloride was purified by recrystallization from alcohol and then melted at 178–179°.

The assistance of Professor C. S. Marvel is gratefully acknowledged.

### Summary

Tri-*o*- and *p*-tolyllead were oxidized by potassium permanganate in acetone solution to the corresponding tritolyllead hydroxides. Triphenyl-*p*-tolyllead, tri-*o*-tolyllead chloride, tetra-*o*- and *p*-tolyllead treated in a similar manner did not react.

Ozonization of triphenylallyllead caused the elimination of the allyl group. Permanganate oxidation of triphenylallyllead gave a similar result, but in addition 1-triphenyllead-2,3-propanediol was obtained, produced by oxidation of the double bond in the allyl group.

The action of hydrobromic acid on triphenylallyllead or the glycol derived from it caused the loss of the allyl group and the formation of triphenyllead bromide.