

On pyrolysis, lead tetrabenzoate and lead tetraacetate give rise to benzoic acid and lead dibenzoate and acetic acid and lead diacetate, respectively.

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

## STUDIES OF ORGANIC LEAD COMPOUNDS.

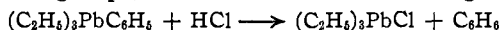
### I. ACTION OF ACIDS ON LEAD ARYLS

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In the study of the severing action of mineral acids or halogens on mixed alkyl-aryl or mixed aryl lead compounds, there appear to be two factors which determine the group that is removed. Almost invariably one of the groups of which there is the largest number is removed first.<sup>2</sup> As has been shown in a previous paper,<sup>3</sup> the electron attraction of the group in question is an even more determining factor, superseding the effect of the predominance of one of the groups, as is seen from the following example



In general, aromatic groups are replaced before aliphatic<sup>4</sup> and in the aromatic series (in contrast to the aliphatic) the heaviest group is replaced first.<sup>5</sup>

In these replacement reactions it is usually possible to replace one or two groups as desired. The removal of three groups to leave a single lead-carbon linkage in the molecule has never been accomplished. The reactions of a compound in which both the electron attraction and predominance of groups worked together should, therefore, prove to be interesting. Phenyltri-*o*-tolyllead was selected as being such a compound; the three *o*-tolyl groups have a greater electron attraction than the phenyl group.

Actually, the reactions of phenyltri-*o*-tolyllead show the strong tendency of organo-lead compounds to retain at least two lead-carbon linkages. Hydrobromic acid removed either one or two *o*-tolyl groups of phenyltri-*o*-tolyllead according to the concentration of the hydrobromic acid used. Nitric acid exerted a similar selective action: phenyltri-*o*-tolyllead in chloroform solution yielded phenyl-*o*-tolyllead dinitrate when treated with nitric acid. Even when the phenyltri-*o*-tolyllead was added to boiling concentrated nitric acid, phenyl-*o*-tolyllead dinitrate and di-*o*-tolyllead dinitrate were produced, but no single lead-carbon linkage was established.

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<sup>2</sup> Grüttner and Krause, *Ber.*, **49**, 1128 (1916).

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

<sup>4</sup> Möller and Pfeiffer, *Ber.*, **49**, 2441 (1916); Grüttner and Grüttner, *ibid.*, **51**, 1294 (1918).

<sup>5</sup> Krause and Schlöttig, *ibid.*, **58**, 427 (1925).

The production of a mixture of products from the latter reaction is not without precedent. Triphenyl-*p*-phenetyllead yields an analogous mixture of products when treated with silver nitrate.<sup>6</sup>

In connection with the above study several interesting reactions were encountered. Tetra-*o*-tolyllead (which cannot be prepared directly from the Grignard reagent and lead chloride) was prepared by heating tri-*o*-tolyllead in xylene for twenty-four hours. The reaction is similar to the action of heat on triphenyllead.<sup>7</sup>

Attempts to prepare tri-*o*-tolyllead bromide by the action of bromine on tri-*o*-tolyllead at low temperatures were unsuccessful, probably due to the insolubility of the tri-*o*-tolyllead. The action of bromine on tri-*o*-tolyllead at room temperature yielded di-*o*-tolyllead dibromide.

The action of hydrobromic acid on tri-*o*-tolyllead yielded the tri-*o*-tolyllead bromide desired for the synthesis of phenyltri-*o*-tolyllead. This is a new type of synthesis of triaryl lead halides and should prove to be useful in other similar cases. The reaction also takes place in the aliphatic series,<sup>8</sup> but is not of importance as a method of synthesis of trialkyl lead halides.

Since the iodimetric method for the determination of lead in organo-lead compounds<sup>9</sup> did not appear to be suitable for this study and a volumetric method was desirable, the molybdate method for lead was adapted to the analysis of aryl lead compounds.

### Experimental Part

**Analytical.**—A method for the analysis of lead in aryl lead compounds which has given satisfactory results has been worked out as follows. The compound was first decomposed with nitric and sulfuric acid as described by Gilman and Robinson.<sup>10</sup> After the lead sulfate stood for an hour with aqueous alcohol mixture, the solution was decanted through a filter and the residue was washed five times by decantation using 10-cc. portions of 1% sulfuric acid. Boiling ammonium acetate solution (15–20 cc.) was then poured through the filter paper into the beaker containing the precipitate. The filter paper was washed with boiling water containing ammonium acetate, the solution was diluted to 100 cc. and titrated hot with standard ammonium molybdate, using tannic acid as the indicator.<sup>11</sup> Inasmuch as a definite concentration of ammonium molybdate must be present to give the color reaction with the indicator, a blank determination should be made. The ammonium molybdate should be restandardized occasionally. This method gave satisfactory results with known tri-*o*-tolyllead and so was used in all of the analyses given in this paper. Analyses for bromine in the organo-lead salts were made as described by Grüttner.<sup>12</sup>

<sup>6</sup> Krause and Schmitz, *Ber.*, **52**, 2151 (1919).

<sup>7</sup> Krause and Reissaus, *ibid.*, **55**, 896 (1922).

<sup>8</sup> Midgley, Hochwalt and Calingaert, *THIS JOURNAL*, **45**, 1822 (1923).

<sup>9</sup> Calingaert, *Chem. Reviews*, **2**, 78 (1925).

<sup>10</sup> Gilman and Robinson, *THIS JOURNAL*, **50**, 1715 (1928).

<sup>11</sup> Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1924, 6th ed., Vol. II, p. 618.

<sup>12</sup> Grüttner, *Ber.*, **51**, 1301 (1918).

**Tri-*o*-tolyllead.**—This compound has been previously prepared by Krause and Reissaus<sup>13</sup> and their directions were followed with some modification. To one mole of *o*-tolylmagnesium bromide in 400 cc. of ether, 1500 cc. of benzene and 150 g. of lead chloride were added and the whole was refluxed and stirred for five and one-half hours. The mixture was cooled and decomposed with iced ammonium chloride solution and then filtered with suction. Tri-*o*-tolyllead was extracted from the dried sludge with hot toluene. The benzene-ether layer separated from the water in the above filtrate was distilled and yielded an additional amount of product. The total yield of tri-*o*-tolyllead was 87 g. or 51% of the theoretical amount based on the *o*-bromotoluene used.

**Tetra-*o*-tolyllead.**—The preparation of this compound was carried out by refluxing 5 g. of tri-*o*-tolyllead in 130 cc. of xylene for twenty-four hours. A black precipitate of metallic lead was filtered, and refluxing again for nineteen hours did not induce further precipitation of lead. The solution was filtered again to remove a small amount of yellowish-brown precipitate and the xylene was evaporated. Recrystallization of the residue from acetone yielded 1 g. of original material (insoluble in hot acetone) and 2 g. of tetra-*o*-tolyllead. The compound was recrystallized from acetone or alcohol and melted at 201–202°.

*Anal.* Calcd. for (C<sub>7</sub>H<sub>7</sub>)<sub>4</sub>Pb: Pb, 36.26. Found: Pb, 36.10, 36.07.

**Phenyltri-*o*-tolyllead.**—This compound was prepared by the general method described by Krause and Schmitz.<sup>14</sup> Eighteen grams (0.032 mole) of tri-*o*-tolyllead bromide was added in small portions to 0.2 mole of phenylmagnesium bromide contained in 300 cc. of ether and the mixture was stirred and refluxed for three hours. The mixture was decomposed with iced ammonium chloride solution and filtered to remove some crude phenyltri-*o*-tolyllead. The ether was separated and evaporated and the residue was added to the crude phenyltri-*o*-tolyllead obtained by filtration. The combined crude products were recrystallized from acetone or benzene, which yielded 16 g. of phenyltri-*o*-tolyllead. The pure compound melted at 161–162°.

*Anal.* Calcd. for (C<sub>7</sub>H<sub>7</sub>)<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)Pb: Pb, 37.17. Found: Pb, 37.10, 37.13.

**Aryl Lead Salts.**—The properties of these compounds are given in Table I. The experimental conditions of the reactions varied and are recorded for each salt.

TABLE I  
ARYL SALTS OF LEAD

| Aryl lead salts                                 | Yield, % | M. p., °C. | Formula  | Lead, % |       | Bromine, %        |       |
|---|----------|------------|--|---------|-------|-------------------|-------|
|   |          |            |  | Calcd.  | Found | Calcd.            | Found |
| Tri- <i>o</i> -tolyl bromide                    | 64       | 129–130    | (C <sub>7</sub> H <sub>7</sub> ) <sub>3</sub> PbBr   | 36.98   | 36.85 | 14.26             | 14.23 |
|   |          |            |  |         | 36.92 |                   | 14.32 |
| Phenyl <i>di-o</i> -tolyl bromide               | 93       | 117–118    | (C <sub>6</sub> H <sub>5</sub> )(C <sub>7</sub> H <sub>7</sub> ) <sub>2</sub> PbBr                                   | 37.93   | 37.84 | 14.63             | 14.59 |
|   |          |            |  |         | 37.90 |                   | 14.58 |
| Di- <i>o</i> -tolyl dibromide                   | 35       | 150–151    | (C <sub>7</sub> H <sub>7</sub> ) <sub>2</sub> PbBr <sub>2</sub>  | 37.73   | 37.63 | 29.10             | 29.18 |
|   |          |            |  |         | 37.43 |                   | 29.18 |
| Phenyl- <i>o</i> -tolyl di-bromide              | 44       | 116–117    | (C <sub>6</sub> H <sub>5</sub> )(C <sub>7</sub> H <sub>7</sub> )PbBr <sub>2</sub>                                    | 38.72   | 38.56 | 29.87             | 29.54 |
|   |          |            |  |         | 38.43 |                   | 29.78 |
| Phenyl- <i>o</i> -tolyllead dinitrate dihydrate | 69–93    | .....      | (C <sub>6</sub> H <sub>5</sub> )(C <sub>7</sub> H <sub>7</sub> )Pb(NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O | 38.71   | 38.70 | 6.73 <sup>a</sup> | 6.59  |
|   |          |            |  |         | 38.24 |                   | 6.79  |

<sup>a</sup> H<sub>2</sub>O.

**Tri-*o*-tolyllead Bromide.**—This compound was prepared by placing 8 g. of tri-*o*-tolyllead, 150 cc. of chloroform and 9 cc. of 40% hydrobromic acid in a 200-cc. round-

<sup>13</sup> Krause and Reissaus, *Ber.*, **55**, 901 (1922).

<sup>14</sup> Krause and Schmitz, *ibid.*, **52**, 2152 (1919).

bottomed flask and shaking on a mechanical shaker for two to three hours. The mixture was filtered to remove any unreacted material and lead bromide and the chloroform separated and evaporated. The residue was recrystallized from alcohol. The product of two such reactions usually yielded 4 g. of unreacted material and 6 g. of tri-*o*-tolyllead bromide.

**Di-*o*-tolyllead Dibromide.**—(A) Five grams of tri-*o*-tolyllead, 150 cc. of chloroform and 10 cc. of 40% hydrobromic acid were shaken in a mechanical shaker for two hours. A clear solution resulted. The residue obtained by evaporation of the chloroform was recrystallized from alcohol. This yielded 2 g. of a mixture of tri-*o*-tolyllead bromide and di-*o*-tolyllead dibromide. Consecutive recrystallizations from aqueous alcohol and from ligroin yielded one g. of the di-*o*-tolyllead dibromide.

(B) Five grams of tri-*o*-tolyllead was dissolved and suspended in 200 cc. of chloroform. A 10% solution of bromine in chloroform was then added dropwise with stirring until the bromine color no longer disappeared. The solution was filtered to remove lead bromide and was then evaporated. Recrystallization from alcohol yielded 2 g. of di-*o*-tolyllead dibromide.

**Phenyldi-*o*-tolyllead Bromide.**—Six grams of phenyltri-*o*-tolyllead, 100 cc. of chloroform and 6 cc. of 40% hydrobromic acid were refluxed and stirred for forty-five minutes. The chloroform was separated and evaporated and the residue extracted first with a mixture of hot ligroin and absolute alcohol and then with hot alcohol. This yielded 5.5 g. of phenyldi-*o*-tolyllead bromide which was recrystallized from alcohol.

**Phenyl-*o*-tolyllead Dibromide.**—To a solution of 3.5 g. of phenyltri-*o*-tolyllead in 100 cc. of chloroform, 10 cc. of 40% hydrobromic acid was added and the mixture was refluxed and stirred rapidly for ninety minutes. Another 10 cc. of 40% hydrobromic acid was then added and the reaction continued for ninety minutes longer. The chloroform was separated and evaporated and the residue was recrystallized from aqueous alcohol, which yielded 1.5 g. of phenyl-*o*-tolyllead dibromide.

A very small amount of an unidentified by-product was obtained from this reaction. The compound is less soluble than the phenyl-*o*-tolyllead dibromide. It was recrystallized twice from alcohol and melted at 232° with decomposition. That the compound was not phenyllead tribromide was shown by analysis.

*Anal.* Calcd. for (C<sub>6</sub>H<sub>5</sub>)PbBr<sub>2</sub>: Br, 45.75. Found: Br, 29.86.

**Phenyl-*o*-tolyllead Dinitrate Dihydrate.**—Three grams of phenyltri-*o*-tolyllead was dissolved in 100 cc. of petroleum ether (b. p. 65–110°) (chloroform was used in some reactions) and was stirred and refluxed for one hour during the slow addition of 7 cc. of nitric acid (sp. gr. 1.42). The insoluble product was filtered and weighed 2.0 g. It was recrystallized from water acidified with nitric acid.

Two grams of the above lead compound was dissolved in water and added to an aqueous solution of 3 g. of sodium bromide. The precipitate was filtered and recrystallized from aqueous alcohol, yield, 1.5 g. After three recrystallizations from aqueous alcohol the compound was pure and it was shown to be phenyl-*o*-tolyllead dibromide by a melting point and mixed melting point determination. About 0.2 g. of a substance which melted at 220–225° with decomposition was obtained as a by-product. This was less soluble than the main product and was undoubtedly identical with the by-product obtained above in the reaction of phenyltri-*o*-tolyllead and hydrobromic acid.

A more vigorous reaction was tried by adding 5 g. of phenyltri-*o*-tolyllead to 40 cc. of boiling nitric acid (sp. gr. 1.42). After the addition, the solution was cooled and filtered on a sintered glass funnel. Two such runs yielded 9 g. of crude product. This was recrystallized three times from water acidified with nitric acid, but the substance was not analytically pure. Three grams of the dinitrate was converted to the bromide as above; yield, 1.3 g. Repeated recrystallization from aqueous alcohol yielded two

products. The larger and more soluble fraction was shown to be phenyl-*o*-tolyl lead dibromide by a melting point and mixed melting point. The smaller less soluble fraction was not obtained entirely pure after five recrystallizations. It melted at 144–145° and a mixed melting point with di-*o*-tolyllead dibromide indicated its identity with that substance. The di-*o*-tolyllead dibromide isolated from this reaction turned purple on exposure to light, a phenomenon not observed with the pure compound.

The author wishes to express his appreciation to Professor C. S. Marvel for his many helpful suggestions.

### Summary

1. The strong tendency of organo-lead compounds to retain at least two lead-carbon linkages has been further demonstrated by the action of nitric and hydrobromic acids on phenyltri-*o*-tolyllead.

2. A new method for the preparation of certain triaryl lead halides has been described.

3. A new volumetric method for the determination of lead in aryl lead compounds has been developed.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

## THE REACTIONS OF SOME CARBONYL COMPOUNDS WITH PHENYLHYDRAZINE

BY L. CHAS. RAIFORD AND WILBUR T. DADDOW

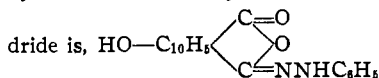
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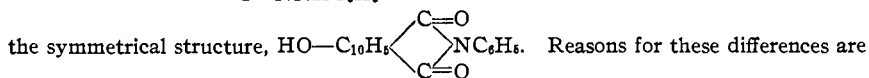
The interaction of phenylhydrazine with a carbonyl group joined directly to carbon and hydrogen (aldehydic) or to carbon and carbon (ketonic) is well known; but instances of this reaction are rare when the radical is situated between other elements. It is true that hydrazones corresponding to the last-named group of carbonyl compounds are known, but they are usually prepared by some method other than the direct<sup>1</sup> one indicated above.

The carbonyl radical in formanilide is bound directly to hydrogen and to nitrogen. A compound said to represent the hydrazone theoretically derivable from formanilide was prepared by Zwingenberger and Walther<sup>2</sup>

<sup>1</sup> The structure assigned by Anselm and Zuckmayer [*Ber.*, 32, 3294 (1899)] to the hydrazone obtained by direct action of phenylhydrazine on hydroxynaphthalic anhydride is,



In the same paper the anilide is represented by



the symmetrical structure, Reasons for these differences are not given, which raises a question regarding the first structure.

<sup>2</sup> Zwingenberger and Walther, *J. prakt. Chem.*, [2] 57, 223 (1898).