

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

REACTIONS OF SOME ORGANIC LEAD COMPOUNDS¹

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Many cases exist to show that in the reaction of mineral acids with aryl-alkyl-metal compounds, the aryl group is more readily severed than the alkyl group. Such, for example, is the case with diphenyldiethyllead,² triphenylalkyllead³ (where alkyl represents methyl, ethyl or cyclohexyl), phenylmethylmercury,⁴ triphenylbenzyltin⁵ and others. On the basis of such evidence, arguments have been advanced that the preferential removal of aryl signifies that aryl groups possess a greater electron attraction than alkyl groups. Although electron attraction is probably the determining factor in compounds like ArHgR or Ar_2PbR_2 , with such a compound as Ar_3PbR it might be said that the greater supply of Ar groups is the determining factor. In fact, Calingaert⁶ has stated: "It is also worth mentioning that, in (lead) compounds containing different organic radicals, the halogen exerts a very decided selective action, reacting almost invariably with one of the groups of which there is the larger number."

Phenyltriethyllead, therefore, presents an interesting case. With the preponderance of ethyl groups, it might be expected that ethyl, rather than phenyl, should be removed first. With electron attraction as the determining factor the reverse might be expected. Actually, it has been found that hydrochloric acid reacts to cause preferential scission of phenyl to yield benzene and triethyllead chloride. Benzene was identified as *m*-dinitrobenzene. With nitric acid and phenyltriethyllead, the reaction product is diethyllead dinitrate, $\text{Et}_2\text{Pb}(\text{NO}_3)_2$. This dinitrate, hitherto unprepared, was also made by the action of nitric acid on tetraethyllead.

These reactions are best carried out in the presence of chloroform. When undiluted, they are difficult to control. Diethyllead dinitrate is a water-soluble salt which was found to be about 79% ionized in tenth molar solution. Conditions were determined for preparing triethyllead nitrate from tetraethyllead. This nitrate rapidly reacts further to yield the dinitrate. Further interaction apparently yields lead nitrate rather than such a substance as ethyllead trinitrate.

Pyrolysis of Lead Compounds.—It is known that in the pyrolysis of

¹ This investigation was made possible by the help of Mr. Thomas Midgley, Jr., and Mr. E. W. Webb of the Ethyl Gasoline Corporation, which is gratefully acknowledged. Original manuscript received July 30, 1930.

² Moeller and Pfeiffer, *Ber.*, **49**, 2441 (1916).

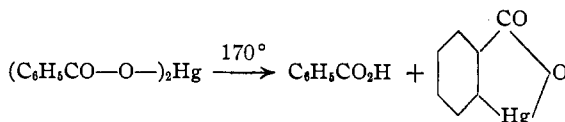
³ Krause and Schlöttig, *ibid.*, **58**, 427 (1925).

⁴ Kharasch and Marker, *THIS JOURNAL*, **48**, 3139 (1926).

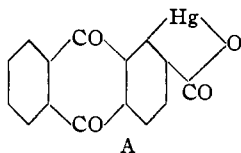
⁵ Bullard, *ibid.*, **51**, 3065 (1929).

⁶ Calingaert, *Chem. Reviews*, **2**, 52 (1925).

mercuric benzoate,⁷ benzoic acid is eliminated and a carbon-to-mercury union is established



Mercuric 1,2-anthraquinonedicarboxylate⁸ has been found to behave similarly, giving the anhydro hydroxymercuri compound, A, when it was heated at 235°.



Since a C-Hg linkage was established in these reactions, it was of interest to see if a carbon-to-lead linkage could be established by an analogous process, namely, by the pyrolysis of lead tetrabenzoate.

We prepared the latter by interaction of lead tetraacetate and benzoic acid, a reaction which has recently been described by Criegee.⁹

The pyrolysis of lead tetrabenzoate was always accompanied by a mild explosion. Possibly this could have been avoided by the use of an inert medium, but this was not tried. Although benzoic acid was detached it is not exactly clear how this occurs for no evidence was found for tetravalent lead in the residue. This residue was completely soluble in dilute sodium hydroxide solution and no lead dioxide was formed thereby. Lead dibenzoate was the only lead compound identified. Had such a compound as $(\text{C}_6\text{H}_4\text{CO}_2)_2\text{Pb}$ been found, (1) the action of bromine on the residue should have yielded *o*-bromobenzoic acid, but no positive evidence for this could be obtained; (2) sodium hydroxide solution should have yielded ortho $(\text{HO})_2\text{Pb}(\text{C}_6\text{H}_4\text{CO}_2\text{Na})_2$ which would have behaved quite differently from the Pb^{++} ions actually found.

Lead acetate and acetic acid, but no other compounds, were noted when lead tetraacetate was decomposed at 190°.

Experimental Part

Triethyllead chloride was prepared from tetraethyllead¹⁰ and concd. hydrochloric acid by the method of Browne and Reid.¹¹ It, in turn, was added in portions to an ether solution of phenylmagnesium bromide. Phenyltriethyllead was thus prepared by the method of Grüttner and Grüttner.¹² They recorded its boiling point as 136° at 13 mm.

⁷ Dimroth, *Ber.*, **35**, 2870 (1902).

⁸ Whitmore and Carnahan, *THIS JOURNAL*, **51**, 856 (1929).

⁹ Criegee, *Ann.*, **481**, 284 (1930).

¹⁰ A generous supply of this material was donated by the Ethyl Gasoline Corporation.

¹¹ Browne and Reid, *THIS JOURNAL*, **49**, 836 (1927). Gilman and Robinson, *ibid.*, **52**, 1975 (1930) describe a preparation using tetraethyllead, ether and hydrogen chloride.

¹² Grüttner and Grüttner, *Ber.*, **51**, 1296 (1918).

Tetraethyllead and Nitric Acid.—One hundred grams of tetraethyllead and 350 cc. of chloroform were placed in a 3-necked flask and 28 cc. of concd. nitric acid was added drop by drop into the boiling solution. Then it was refluxed for one and one-half hours. At the start of the reflux period a heavy liquid layer, presumably a mixture of triethyl- and diethyllead nitrates, appeared. This gradually became solid as the reaction progressed. The solid was filtered while hot. About 50 g. of impure diethyllead dinitrate was collected on the filter. It was identified by conversion into diethyllead dichloride by dissolving it in methanol and adding concd. hydrochloric acid. The mixture was filtered from lead chloride and the filtrate concentrated. The diethyllead dichloride which precipitated was washed with ether, dried and analyzed.

Anal. Calcd. for $(C_2H_5)_2PbCl_2$: Pb, 61.5; Cl, 21.1. Found: Pb, 61.3; Cl, 20.8.

The filtrate, on cooling, gave a small precipitation of a salt analyzing 60–61% of lead which was evidently triethyllead nitrate for the most part. The calcd. Pb in $(C_2H_5)_3PbNO_3$ is 58.1%, and in $(C_2H_5)_2Pb(NO_3)_2$ is 53.2%. Some lead nitrate was also in it. The same substance was found to precipitate at the beginning of the reaction if it was chilled.

Phenyltriethyllead and Nitric Acid.—Three cc. of nitric acid was added to a solution of 8 g. of phenyltriethyllead in 100 cc. of chloroform. A liquid layer formed. The solution was refluxed for fifteen minutes, filtered hot and the filtrate cooled. The 1.3 g. of crystalline diethyllead dinitrate which appeared was collected. Another 0.9 g. was obtained by extracting the residue from the first filtration. These crystals were soluble in water and the solution gave no test for lead ion with potassium dichromate solution.

Anal. Calcd. for $(C_6H_5)_2Pb(NO_3)_2$: Pb, 53.2. Calcd. for $(C_6H_5)(C_2H_5)Pb(NO_3)_2$: Pb, 47.3. Found: Pb, 53.1, 52.9.

Fractionation of the chloroform solution gave a fraction which contained benzene. Thus, nitration of this fraction yielded *m*-dinitrobenzene which melted at 88°. A mixed melting point determination with an authentic specimen of *m. p.* 90°, was 89°.

Conversion of the dinitrate into the dichloride was effected in the manner previously described with the dinitrate from tetraethyllead.

Reaction without Diluents.—Small yields of diethyllead dinitrate which analyzed 53.0% of lead were obtained when 0.9 cc. of nitric acid (sp. gr. 1.4) was dropped onto 2 g. of phenyltriethyllead at room temperature. Far better yields were obtained when solvents were employed, and of these chloroform appeared to give better results than benzene or ether.

Dissociation of Diethyllead Dinitrate.—The apparent molecular weight of this salt was determined by the freezing point method, using water as the solvent. In two experiments, these findings were 150.9 and 150.0, whereas the true molecular weight of $(C_2H_5)_2Pb(NO_3)_2$ is 389.

Data. Subs., 0.8085, 0.4581: H_2O , 20 and 20 g.; moles of the salt per 1000 g. of H_2O , 0.104, 0.059; depression of the freezing point, 0.498°, 0.284°.

From these data, calculation of the percentage ionization of diethyllead dinitrate into three ions gave values of 78.8 and 79.5%, respectively.

Phenyltriethyllead and Hydrochloric Acid.—One hundred cc. of chloroform and 12.7 g. of phenyltriethyllead (b. p. (10 mm.) 128–137°) were put in a reaction flask and 4 cc. of concd. hydrochloric acid was added. The mixture was refluxed for twenty minutes, after which it was carefully fractionated. The last fraction contained benzene. On nitration with nitric and sulfuric acids, it yielded crystals of *m*-dinitrobenzene of melting point 88° and mixed *m. p.* 89° with a known specimen.

The non-volatile residue solidified. It was recrystallized once from alcohol, dried and analyzed for lead and chlorine. The data imply slight contamination with either

diethyllead dichloride or phenyldiethyllead chloride, but they show that the salt represents triethyllead chloride for the most part.

Anal. Calcd. for $(C_2H_5)_3PbCl$: Pb, 62.8; Cl, 10.77. Calcd. for $(C_2H_5)(C_2H_5)_2PbCl$: Pb, 54.8; Cl, 9.4. Found: Pb, 61.7; Cl, 10.69, 10.71.

In another similar reaction of phenyltriethyllead (in chloroform) and hydrochloric acid, a small quantity of material separated from the hot chloroform solution. It was collected on a filter, washed, dried and analyzed. It appeared to be largely diethyllead dichloride.

Anal. Found: Pb, 59.8; Cl, 20.5.

Preparation of Lead Tetrabenzoate.—This compound was synthesized in essentially the manner suggested by Criegee,¹³ but the following details were found to be helpful. A one-liter Claisen flask was arranged for vacuum distillation and a thermometer was placed so that the bulb dipped into the reaction mixture. Five hundred grams of benzoic acid was melted in the flask and then 155 g. of lead tetraacetate was added. Larger quantities could be used if desired. The vacuum of a water pump was used and the heating carried out so that the temperature of the mixture did not exceed 120°. The distillation temperature was from 60–80°. Most of the time the pressure was gradually dropping from 170 to 80 mm., but finally the value was 60 mm. During the course of the distillation, which required one and one-half hours, a yellow precipitate of lead tetrabenzoate separated in the molten benzoic acid. At the conclusion, most of the benzoic acid layer was decanted. This facilitated the separation of the lead tetrabenzoate from benzoic acid. For purification, the lead salt was washed with warm methanol and then with benzene. About 140 g. of the compound was obtained. The product from crystallization from benzene or even from washing with benzene appeared to retain benzene of crystallization.

Colson's observation¹⁴ that lead tetra-salts are decomposed by alcohol was confirmed with lead tetrabenzoate. Thus, when it was boiled with methanol for a short time it went into solution to form the dibenzoate, which crystallized readily on cooling and apparently with methanol of crystallization. After drying for a week in a vacuum desiccator over phosphorus pentoxide, this alcohol was removed and the lead dibenzoate melted at 118–119°. A melting point value of 119–120° was found for lead dibenzoate which was synthesized from lead nitrate and sodium benzoate after similar crystallization from methanol and vacuum drying over phosphorus pentoxide. A mixed melting point of these two samples was 118–119°. These melting points were taken on a Maquenne block. When the usual capillary tube method was used, this lead dibenzoate melted at 107–115° with decomposition.

Anal. Subs., 0.4033, 0.4011: cc. of 0.02957 *M* ammonium molybdate, 30.2, 30.1. Calcd. for $(C_6H_5CO_2)_2Pb$: Pb, 46.1. Found: Pb, 45.9, 46.0.

Curiously, if any of these samples of lead dibenzoate were recrystallized from ethylene dichloride, the melting point was raised about twenty-five degrees. Thus, the value of the 118–119° material was changed to 145–147° (Maquenne block) by this process.

Pyrolysis of Lead Tetrabenzoate.—The pyrolysis was carried out by placing the compound in a 200-cc. round-bottomed flask which was fitted with a long air condenser. The flask was heated slowly with an oil-bath. The decomposition always took place with a mild explosion and was complete in a short time. In four experiments with 10–20 g. samples, the oil-bath temperature when vigorous decomposition occurred was 130, 148, 155 and 170°. The temperature of decomposition seemed to depend somewhat on the rate of heating and somewhat on the benzene which adhered to the compound.

¹³ Criegee, *Ann.*, **481**, 284 (1930).

¹⁴ Colson, *Compt. rend.*, **136**, 676, 1664 (1903).

Dense white clouds were evolved during the pyrolyses and sublimates of benzoic acid collected on the cooler parts of the flask. The residue was a sticky black gum, soluble in methanol. By slow evaporation and by recrystallization from dilute methanol, lead dibenzoate alone was isolated. A small sample of the residue dissolved almost completely in aqueous sodium hydroxide solution and gave no lead dioxide. Acidification of the alkaline solution with acetic acid, followed by potassium chromate solution, gave a yellow precipitate of lead chromate, indicative of Pb^{++} ion.

The pyrolytic residue was dissolved in chloroform and was apparently held in solution by the small amount of gummy impurity. After a few minutes it precipitated. From a 17-g. run, there was 14 g. of this light gray powder. Some of it was twice recrystallized from ethylene dichloride; m. p. 141–142°. A mixed melting point with lead dibenzoate of melting point 145–147° (from ethylene dichloride) was 143–144° (Maquenne block).

The chloroform filtrate from the first solution of the product was evaporated, leaving a gum. This was treated with hot ligroin (65–110°) and the hydrocarbon decanted and evaporated. This left about 0.3 g. of an oily solid which was shown to be benzoic acid. After crystallization from water and alcohol, it melted at 119–120°.

Three grams of the product from the pyrolysis was dissolved in 100 cc. of ethylene dichloride and treated with bromine (in chloroform) for about one and one-half hours. The excess bromine was evaporated and the solution filtered. Two grams of lead bromide was obtained. The filtrate was given an alkaline wash, the layers separated, and the alkaline solution was poured into cold dilute hydrochloric acid. The precipitate which formed was filtered and recrystallized from water. The first fraction, obtained by cooling slowly to room temperature, melted at 130–132° but there was not enough of this to recrystallize or characterize. After cooling in ice, a fraction of 118–119° was obtained; weight 0.1 g. The third fraction of 0.05 g. precipitated on standing overnight; m. p. 119–120°. The second and third fractions were unmistakably benzoic acid rather than a bromobenzoic acid which might have been formed had there been a C–Pb bond for the bromine to sever.

Pyrolysis of Lead Tetraacetate.—Twenty grams of lead tetraacetate was heated on an oil-bath in a 200-cc. flask which was fitted with a reflux condenser. At a bath temperature of 190°, vigorous decomposition set in. A small portion of the product, after removal from the flask, was found to dissolve completely in water. This gave tests for lead ion (bivalent) with dilute sulfuric acid and with potassium chromate solution.

By ether extracting the contents of the flask, a liquid was obtained on evaporation of the ether which was evidently acetic acid. The residue from the extraction was dissolved in water and filtered. The filter held a trace of black precipitate which was presumably lead dioxide. Almost a quantitative yield of lead diacetate was found in the filtrate. It was twice recrystallized from water, dried for twelve hours at 105°, and then crystallized from absolute alcohol; m. p. 183–187°. An authentic specimen of lead acetate, twice recrystallized from absolute alcohol, melted at 187–189°. A mixed melting point determination was 184–186° (capillary tube).

Summary

Phenyltriethyllead reacts with hydrochloric acid to yield benzene and triethyllead chloride. Further reaction gives the more insoluble dichloride. Both phenyltriethyllead and tetraethyllead react readily with nitric acid to produce diethyllead dinitrate, a salt which reacts metathetically in methanol with hydrochloric acid to give the dichloride. In 0.1 *M* solution, the dinitrate is apparently 79% ionized.

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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STUDIES OF ORGANIC LEAD COMPOUNDS.

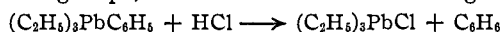
I. ACTION OF ACIDS ON LEAD ARYLS

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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.² As has been shown in a previous paper,³ 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 aliphatic⁴ and in the aromatic series (in contrast to the aliphatic) the heaviest group is replaced first.⁵

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.

¹ National Research Fellow in Chemistry.

² Grüttner and Krause, *Ber.*, **49**, 1128 (1916).

³ Hurd and Austin, *THIS JOURNAL*, **53**, 1543 (1931)

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

⁵ Krause and Schlöttig, *ibid.*, **58**, 427 (1925).