Chemistry

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Abstract

Full Text

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STUDY OF THE ELEMENTOXANE BOND. PLUMBOXANES

High-molecular-weight organosilicon compounds with a siloxane bond have acquired great practical importance. Investigations of the nearest organoelement analogues of silicon—organogermanium[^1] and organotin compounds[^2]—with the aim of studying the El—O—El bond began only in recent years. In the present work a method is described for the synthesis of compounds with a plumboxane bond, which, as we have shown, is also applicable to other elements[^3]. In studying the methods of synthesis and the properties of compounds of the type Ar_2PbX_2[^4] and $ArPbX_3$[^5] (where Ar is an aromatic radical, and X is the residue of an organic acid), we noted their insufficient stability toward moisture; on storage in air the melting point decreases, and impurities appear that are insoluble in organic solvents. During recrystallization, even of a freshly prepared product, it is necessary to add several drops of acid to prevent hydrolysis.

In the presence of water, a considerable part of the organolead salt is already hydrolyzed. For example, from a solution of diphenyllead diacetate in a mixture of acetone with water, 15–20% of the substance gradually separates in the form $(C_6H_5)_2Pb(OH) \cdot OCOCH_3$. In the hydrolysis of $Ar_2Pb(OCOR)_2$ in the presence of a diazoalkane, the reaction proceeds with formation of a plumboxane bond. In this way we have for the first time synthesized compounds with a plumboxane bond containing residues of an organic acid as terminal groups:

$$2(C_6H_5)_2Pb(OCOCH_3)_2 + 2H_2O + 2CH_2N_2 \rightarrow 2CH_3COOCH_3 + 2N_2$$

$$+\ CH_3COO \begin{array}{c} C_6H_5 \\ | \\ -\ Pb \\ | \\ C_6H_5 \end{array} - O - \begin{array}{c} C_6H_5 \\ | \\ Pb\ - \\ | \\ C_6H_5 \end{array} OCOCH_3$$

According to our experiments, the reaction proceeds most smoothly in acetone. A few minutes after adding, to a solution of $Ar_2Pb(OCOCH_3)_2$ in acetone–water, 1–2 ml of diazoalkane in ether, tetra-phenyldiplumboxane diacetate begins to

crystallize from the reaction mixture. With an excess of diazomethane the yield is almost quantitative. Tetraphenyldiplumboxane diisobutyrate was obtained in 72% yield by the same method.

Hydrolysis of the organolead salt is the first stage of the process. When dry solvents are used, the reaction does not occur. It is enough to add to the reaction mixture an equivalent, or preferably a somewhat larger, amount of water, and diazomethane begins rapidly to decolorize. The diazoalkane itself does not participate in the structure of the final reaction product (the same products were obtained with diazoethane and diazobutane). The diazoalkane binds the acid formed during hydrolysis and thus prevents the reverse reaction. Indeed, on heating with organic acids the plumboxane bond is cleaved (with formation of the initial $Ar_2Pb(OOCR)_2$). The analytical results given in the experimental section and the molecular weights found (from the depression of the freezing point of stilbene) leave no doubt as to the formula of the compounds obtained.

Experimental Part

I. Action of diazoalkanes on diphenyllead diacetate. Diazomethane. To a solution of 2.88 g (0.006 mol) of diphenyllead diacetate in 150 ml of dry acetone, with stirring, several drops (about 0.1 ml, 0.006 mol) of water are added, and then, in portions over 6 min, 0.504 g (0.012 mol) of diazomethane in 14 ml of ether. The diazomethane is rapidly decolorized, and gas is evolved. If the solvents contain water in an amount sufficient for hydrolysis, its additional introduction is unnecessary. After the addition of approximately 2 mol of diazomethane per mole of organolead salt, the yellow color of the solution persists for a considerable time. Several minutes after the start of the reaction the first crystals of precipitate appear on the walls of the flask. After several hours it is filtered off, washed with acetone, and dried in vacuo. Yield 2.06 g (96%); m.p. 218–219° (with decomposition).

Found, %: C 39.41; 39.42; H 3.01; 3.06; Pb 48.40; 48.48
$C_{28}H_{26}O_5Pb_2$. Calculated, %: C 39.23; H 3.04; Pb 48.39

Mol. wt. found 863, calculated 856.4.

In a mixture of benzene with acetone the reaction proceeds more slowly, and the yield decreases. Thus, from 1.922 g (0.004 mol) of diphenyllead diacetate in 100 ml of acetone and 0.336 g (0.008 mol) of diazomethane in 20 ml of benzene, 1.35 g (80%) of product is obtained, m.p. 218–219° (with decomposition).

Found, %: Pb 48.15; 48.08.

The substance obtained was analyzed without additional purification. It can be dissolved in chloroform and, by slow addition of ether or acetone, the crystalline precipitate can be obtained again. The melting point rises to 221–222° (with decomposition); repeated reprecipitation is unnecessary.

Diazoethane. The reaction proceeds similarly to the preceding one. From 1.44 g (0.003 mol) of diphenyllead diacetate in 75 ml of acetone and 0.336 g (0.006 mol) of diazoethane in ether, 1 g (77%) of substance is obtained, m.p. 219° (with decomposition).

Found, %: Pb 48.27.

0.7 g of the substance is dissolved in 6 ml of chloroform, and 50 ml of acetone is added to the solution in portions. 0.37 g of crystalline precipitate is obtained, m.p. 221°. A mixed sample with the product obtained in the preceding experiment gives no depression of the melting point.

Found, %: Pb 48.03.

Diazobutane. The reaction proceeds analogously to the preceding ones. From 3.58 g (0.0075 mol) of diphenyllead diacetate in 175 ml of acetone and 1.26 g (0.015 mol) of diazobutane in 20 ml of ether (added over 15 min), 2 g (62%) of substance is obtained, m.p. 217-218°. (The last 3-4 ml of diazobutane do not decolorize over the course of 24 h.) 1.8 g of the substance is dissolved in chloroform and, if necessary, filtered; 45 ml of dry ether is added to the filtrate. 1 g is obtained, m.p. 222°. No depression of the melting point is observed with products obtained using diazomethane and diazoethane.

Found, %: Pb 48.01.

Tetraphenyldiplumboxane diacetate is insoluble in acetone, alcohol, and petroleum ether; in the cold it is sparingly soluble in dichloroethane and readily soluble in chloroform.

II. Action of diazoalkanes on diphenyllead diisobutyrate. Diazomethane. To a solution of 3.1 g (0.006 mol) of diphenyllead diisobutyrate in 40 ml of acetone with several drops

water are added portionwise 0.252 g (0.006 mole) of diazomethane in 8 ml of ether, which is rapidly decolorized. After an hour the precipitate is filtered off and washed with acetone. This gives 1.9 g (72%) of a substance with decomp. temp. 240°.

$C_{32}H_{34}O_5Pb_2$.	Found, %: C 42.37; 42.39; H 3.77; 3.79; Pb 45.37; 45.39
	Calculated, %: C 42.03; H 3.73; Pb 45.41

Mol. wt. found 850, calculated 912.4.

The yield increases if an excess of diazomethane is used (until its decolorization ceases). Thus, from 5.35 g (0.01 mole) of diphenyllead diisobutyrate in 60 ml of acetone and 0.84 g (0.02 mole) of diazomethane in 30 ml of ether, 3.55 g (78%) of a substance with the same decomp. temp. is obtained.

Found, %: Pb 45.60.

III. **Hydrolysis of diphenyllead diacetate.** 1 g of diphenyllead diacetate is dissolved in 50 ml of acetone, 8 ml of water is added dropwise (until a slight turbidity appears), and the mixture is left for 24 hours. The precipitate that separates is isolated, washed with acetone, and dried. Yield 0.2 g (22%); it decomposes without melting.

$C_{14}H_{14}O_3Pb$.	Found, %: C 38.37; 38.34; H 3.35; 3.40; Pb 47.90; 47.85
	Calculated, %: C 38.43; H 3.23; Pb 47.36

Mol. wt. found 430, calculated 437.5.

Plumboxane compounds, on treatment with organic acids, are converted into compounds $Ar_2Pb(OOCR)_2$. Thus, 0.458 g (0.0005 mole) of tetraphenyldiplumboxane diisobutyrate is dissolved in 5 ml of benzene acidified with 0.132 g (0.001 mole + 50% excess) of isobutyric acid. The solvent is evaporated by half, diluted twofold with hexane, and cooled with ice. This gives 0.4 g (75%) of diphenyllead diisobutyrate with m.p. 204°. Diphenyllead diisobutyrate has m.p. 204-205° (4). A mixed sample gives no depression of the melting point.

$C_{20}H_{24}O_4Pb$.	Found, %: Pb 38.25
	Calculated, %: Pb 38.68

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Note: Figure translations are in progress. See original paper for figures.