CHEMISTRY

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1958

SovietRxiv

Abstract

Full Text

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THE PLUMBATION REACTION

Despite the fact that the reaction of direct introduction of metal atoms into an organic molecule by the action of metal salts has long been known ("mercuration" (^{1})) or was found more recently ("auration" (^{2}), "thallation" (^{3})), until now nothing has been known about a direct reaction of "plumbation."

For this type of reaction, salts of organic acids of metals could be successfully used, as Dimroth showed in mercuration and as one of us, together with V. P. Glushkova, showed in thallation (^{4}). On the other hand, it was well known that thiophene is especially readily subjected to metallation. All this prompted us to carry out an investigation of plumbation on the basis of the interaction between salts of organic acids of tetravalent lead and thiophene.

In developing new methods for the synthesis of organolead compounds (^{5}), including a new class, $ArPbX_3$,* we noted the particular convenience of using lead tetraisobutyrate, which crystallizes well, is sufficiently stable, and is soluble in organic solvents, including thiophene.

Plumbation was observed by us under the following circumstances: when lead tetraisobutyrate was smoothly dissolved in an excess of thiophene, after the mixture had stood for several days at room temperature it was noticed that a sample taken, upon hydrolysis, no longer gave the typical reaction for the presence of a salt of tetravalent lead (a light-yellow precipitate forms). Thus, lead tetraisobutyrate gradually disappears.

Under the conditions described in the experimental part, it is possible to isolate and identify diisobutyrate of di-α-thienyllead in the form of a white crystalline substance, the formation of which may presumably be attributed to the sequence of the following reactions.** Initially, unstable triisobutyrate of thienyllead is formed on the basis of a direct plumbation reaction

$$C_4H_4S+Pb[OOCCH(CH_3)_2]_4 \longrightarrow \alpha\text{-}C_4H_3S{-}Pb[OOCCH(CH_3)_2]_3+(CH_3)_2CHCOOH \quad (I)$$

which then undergoes disproportionation

$$2\,\alpha\text{-}C_4H_3S{-}Pb[OOCCH(CH_3)_2]_3 \longrightarrow (\alpha\text{-}C_4H_3S)_2\,Pb[OOCCH(CH_3)_2]_2 + Pb[OOC{\cdot}CH(CH_3)_2]_4$$
(II)

* Krieg et al. (6), in describing the preparation of compounds of the class $ArPbX_3$ through diarylmercury compounds, did not note that this method had been discovered and published by us almost a year earlier (7).

** Another possible mechanism for the formation of $[C_4H_3S]_2Pb[OOCCH(CH_3)_2]_2$ may be connected with the metallating action of $C_4H_3SPb[OOCCH(CH_3)_2]_3$ toward thiophene.

Analysis, determination of the number of acid groups, and conversion into di-α-thienyllead bismonochloroacetate according to the equation:

$$\left(\begin{matrix}\text{thiophene ring}\\ S\end{matrix}\right)_2 Pb\,[OOCCH(CH_3)_2]_2 + 2CH_2ClCOOH \longrightarrow \left(\begin{matrix}\text{thiophene ring}\\ S\end{matrix}\right)_2 Pb(OOC\cdot CH_2Cl)_2 + 2(C$$
(III)

confirms the formula of the compound.

To determine the position at which lead enters the thiophene molecule, a known diisobutyrate of di-α-thienyllead was obtained from tetra-α-thienyllead (8) by the reaction:

$$\left(\begin{matrix}\text{thiophene ring}\\ S\end{matrix}\right)_4 Pb + 2(CH_3)_2CHCOOH \longrightarrow \left(\begin{matrix}\text{thiophene ring}\\ S\end{matrix}\right)_2 Pb\,[OOCCH(CH_3)_2]_2 + 2\left(\begin{matrix}\text{thiophene ri}\\ S\end{matrix}\right.$$
(IV)

which proved to be identical with the substance obtained by direct plumbation. The "alpha" position of entry, characteristic of thiophene when it is metallated by salts of other metals, is thus also confirmed for lead.

Thus, the direct introduction into an organic molecule of metals standing in the same row of the periodic system—Au, Hg, Tl, Pb—can be supplemented by the plumbation reaction described here for the first time.

Undoubtedly, there is a considerable slowing of the process in comparison with the rapid mercuration and thallation.

Experimental Part

Plumbation of thiophene. 6 g of lead tetraisobutyrate (8) (previously washed with petroleum ether) are dissolved (rapid, smooth dissolution) in 10 ml of thiophene (a large excess relative to equation I) and left to stand at room temperature. After several days, the test for the starting tetraisobutyrate is already only weakly expressed (a light-yellow precipitate upon addition of water).

After standing for 10 days, 4 ml of absolute alcohol are added to decompose the unreacted lead tetraisobutyrate, and the mixture is left for two days.

The thiophene and alcohol are removed almost to dryness in vacuo at room temperature. The semisolid residue is treated with 5 ml of benzene, filtered from divalent lead diisobutyrate, and the filtrate is diluted with 7.5 ml of hexane.

A white crystalline precipitate separates, m.p. 192° (with decomposition; begins to darken at 186°).

$(C_4H_3S)_2Pb[\,OOCCH(CH_3)_2\,]_2$.	Found % :	Pb 37.70; 38.35
	Calculated % :	Pb 37.85

Number of acid residues: 2.1. When added to concentrated sulfuric acid, the substance decomposes with formation of thiophene (addition of chloroform, then the usual isatin test).

Diisobutyrate of di-α-thienyllead dissolves well in alcohol and acetone, moderately in benzene in the cold and well on heating, and poorly in hexane.

The substance is identical with the diisobutyrate obtained from tetra-α-thienyllead (see below).

Bismonochloroacetate of di-α-thienyllead. 0.55 g of diisobutyrate of di-α-thienyllead, obtained in the preceding experiment, is dissolved at room temperature in 7 ml of benzene acidified with 7 drops of glacial acetic acid. The solution is filtered from turbidity, and to the filtrate is added 0.4 g (twice the theoretical amount according to equation (III)) of a saturated solution of monochloroacetic acid in benzene. The appearing

The white, finely crystalline precipitate is filtered off the next day and washed with benzene. Yield 0.38 g (68%). The substance has m.p. 174° (with decomposition; gradual darkening begins at 165°). The indophenin test for thiophene is positive.

Found, %: Pb 37.40; 37.43; Cl 12.60; 13.00
$(C_4H_3S)_2Pb(OOCCH_2Cl)_2$. Calculated, %: Pb 37.00; Cl 12.66.

Bis(monochloroacetate) of di-α-thienyllead dissolves very poorly, even on heating, in benzene, chloroform, dichloroethane, acetone, and alcohol, and is insoluble in petroleum ether, hexane, and ether.

Diisobutyrate of di-α-thienyllead from tetra-α-thienyllead. 0.82 g of tetra-α-thienyllead, prepared from α-thienylmagnesium bromide and lead chloride (9), is heated on a water bath to 60-70° with 1.5 ml of isobutyric acid. After about half an hour the precipitate dissolves. Heating is continued for another 15 min at the same temperature. A white crystalline precipitate separates from the still-hot solution. For more complete isolation of the product, the reaction mixture is diluted with 1.5 ml of petroleum ether, suction-filtered, and washed with petroleum ether. This gives 0.55 g (67%) of substance with m.p. 192° (with decomposition).

Found, %: Pb 38.05; 37.71.

The number of acid residues is 1.9. The indophenin test for thiophene is positive.

The authentic diisobutyrate of di-α-thienyllead obtained in this way is identical with the diisobutyrate described above on the basis of the plumbination reaction.

The diisobutyrate was converted into bis(monochloroacetate) of di-α-thienyllead; the latter proved, in its properties, to be identical with that described above.

Found, %: Pb 37.22; 37.30; Cl 12.62; 12.53.

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Received
21 VII 1958

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