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INVESTIGATIONS ON ORGANOLEAD COMPOUNDS
IV*. A NEW TYPE OF REDISTRIBUTION REACTION SUITED FOR THE PREPARATION OF PHENYLLEAD TRIACETATE AND DIPHENYLLEAD DIACETATE**

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SUMMARY

The following redistribution has been found to occur in acetic acid at 70° in the presence of a catalytic amount of mercury diacetate:

$$\mathrm{Ph}_n\mathrm{Pb(OAc)}_{4-n} + (n-1)\,\mathrm{Pb(OAc)}_4 \rightarrow n\,\mathrm{PhPb(OAc)}_3 \qquad n = 2\text{–}4$$

It provides a convenient method of preparing phenyllead triacetate.

Diphenyllead diacetate can be analogously obtained from lead tetraacetate and tetraphenyllead, but triphenyllead acetate cannot be prepared in this way. No such redistribution occurs with alkyllead compounds.

INTRODUCTION

Redistribution reactions (eqn. 1) are of great importance in organotin chemistry for the manufacture of organotin halides.

$$n\,\mathrm{R_4Sn} + (4-n)\,\mathrm{SnCl_4} \rightarrow 4\,\mathrm{R}_n\mathrm{SnCl}_{4-n} \qquad n = 1\text{–}3 \tag{1}$$

So far, in organolead chemistry such reactions are not known, probably because lead tetrachloride is not a convenient starting material, being highly unstable and strongly oxidizing. Furthermore, the conditions sometimes may be so drastic that serious decomposition of the organolead products will occur.

In this paper a redistribution reaction is described which constitutes a useful method for the preparation of diphenyllead diacetate and, in particular of phenyllead triacetate.

This latter compound was first described by Panov and Kocheshkov[3] and was prepared by dephenylating diphenyllead diacetate with mercury diacetate in acetic acid at room temperature:

$$\mathrm{Ph_2Pb(OAc)_2} + \mathrm{Hg(OAc)_2} \rightarrow \mathrm{PhPb(OAc)_3} + \mathrm{PhHgOAc} \tag{2}$$

Another method for the preparation of this compound is monophenylation of lead tetraacetate by diphenylmercury[4,5] (eqn. 3),

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* For Part III see ref. 1.

** A patent has been filed[2].

$$Pb(OAc)_4+Ph_2Hg \rightarrow PhPb(OAc)_3+PhHgOAc \qquad (3)$$

resulting in the same products as obtained according to eqn. (2).

RESULTS AND DISCUSSION

We tried the combination of these two methods by starting from lead tetraacetate, diphenyllead diacetate and a catalytic amount of mercury diacetate in acetic acid;

$$Pb(OAc)_4+Ph_2Pb(OAc)_2 \xrightarrow[HOAc]{Hg(OAc)_2} 2\ PhPb(OAc)_3 \qquad (4)$$

A good yield (84%) of phenyllead triacetate was indeed obtained when the two lead compounds were heated for 1–2 days at 70° in acetic acid with 3 mole % of mercury diacetate. Without the catalyst, no trace of phenyllead triacetate was formed. When the reaction period was reduced to two hours the yield dropped to 11%. Raising the temperature was disadvantageous because of extensive decomposition.

Obviously, the mechanism of the reaction is phenyl transfer via mercury from diphenyllead diacetate to lead tetraacetate. Diphenyllead diacetate reacts with mercury diacetate according to eqn. (2) to produce phenylmercury acetate which is thought then to phenylate lead tetraacetate with regeneration of mercury diacetate (eqn. 5).

$$Pb(OAc)_4+PhHgOAc \rightarrow PhPb(OAc)_3+Hg(OAc)_2 \qquad (5)$$

This mechanism is supported by the observation that diphenylmercury also acts as a catalyst.

Higher phenylated lead compounds gave a similar reaction with lead tetraacetate;

$$Ph_3PbOAc+2\ Pb(OAc)_4 \xrightarrow{cat.} 3\ PhPb(OAc)_3 \qquad (6)$$

$$Ph_4Pb+3\ Pb(OAc)_4 \xrightarrow{cat.} 4\ PhPb(OAc)_3 \qquad (7)$$

This result was pleasantly surprising since another reaction was expected to occur preferentially, *viz.*, the elimination of phenyl groups by acetic acid; *e.g.*, triphenyllead acetate in acetic acid is completely converted into diphenyllead diacetate at room temperature within two hours;

$$Ph_3PbOAc+HOAc \rightarrow Ph_2Pb(OAc)_2+C_6H_6 \qquad (8)$$

Another advantage is that tetraphenyllead and triphenyllead acetate are more attractive starting materials. In both cases the catalyst was necessary.

The preparation of diphenyllead diacetate by means of this catalytic redistribution reaction proved equally satisfactory:

$$Ph_4Pb+Pb(OAc)_4 \xrightarrow{cat.} 2\ Ph_2Pb(OAc)_2 \qquad (9)$$

$$Ph_4Pb+2\ PhPb(OAc)_3 \xrightarrow{cat.} 3\ Ph_2Pb(OAc)_2 \qquad (10)$$

Reaction (9) gave a 93% yield of diphenyllead diacetate. Whereas the other reactions so far discussed needed 1–2 days for completion, this reaction was complete after two hours. The explanation is that only two, rapid steps are involved:

$$Ph_4Pb + Pb(OAc)_4 \rightarrow Ph_3PbOAc + PhPb(OAc)_3 \quad (11)$$

$$Ph_3PbOAc + PhPb(OAc)_3 \rightarrow 2\ Ph_2Pb(OAc)_2 \quad (12)$$

In all other redistributions step (4), which is much slower, is involved.

Reaction (10) (which is of no practical value) gave a quantitative yield of diphenyllead diacetate within a short period of time [no step (4) involved!]. This was the only case wherein some redistribution occurred *without* catalyst, although the reaction occurred more easily in the presence of the catalyst.

Finally the redistribution between diphenyllead diacetate and tetraphenyllead was investigated. This reaction cannot be studied in acetic acid because of reaction (8). Therefore, the reaction was carried out in toluene/dioxane with phenylmercury acetate and diphenylmercury as catalysts. Thin-layer chromatography did not, however, reveal any formation of triphenyllead acetate in this case.

In the alkyl series the corresponding redistribution reactions do not occur, perhaps because alkyllead triacylates do not exist. An attempt resulted in a vigorous oxidative cleavage of methyl groups from tetramethyllead (even at −60° in toluene).

EXPERIMENTAL

Brown, commercial lead tetraacetate was recrystallized from acetic acid to give pure white crystals which can be handled for short periods of time in the open air without decomposition. The tetraacetate was also prepared from minium (Pb_3O_4)[6].

Tetraphenyllead[7a], triphenyllead acetate [7b] and diphenyllead diacetate[7c] were prepared as earlier described.

The acetic acid used as a solvent contained a trace of formic acid (detected by GLC) which consumed part of the lead tetraacetate (oxidation)*. Therefore excess of lead tetraacetate was used in most experiments.

1. *The redistribution between diphenyllead diacetate and lead tetraacetate*

(*a*). *With catalyst.* A mixture of 11.0 g of lead tetraacetate (25 mmole), 9.6 g of diphenyllead diacetate (20 mmole) and 0.195 g of mercury diacetate (0.6 mmole) was heated in 80 ml of acetic acid for 24 h. The excess of tetraacetate was allowed to crystallize and was filtered off. A few drops of ethylene glycol were added to the filtrate (to destroy the last traces of tetraacetate) until a drop of the solution added to water in a test tube no longer gave a brown coloration (owing to hydrolysis to PbO_2). The filtrate was evaporated to dryness, and the residue was taken up in dry ethyl acetate or diethyl ether. After filtering, 0.5 ml of water was added and this caused the hydrate of phenyllead triacetate to precipitate. Yield 16.15 g (84%). The m.p. showed a large traject of ca. 77–86°**. (Found: C, 30.38; H, 3.40; Pb, 43.24. $C_{12}H_{16}O_7Pb$ calcd.: C, 30.06; H, 3.36 Pb, 43.22%.) The compound performed well in the gelation test ($ArPbX_3$ compounds are active catalysts in the formation of polyurethan foams)[8].

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* Of course the presence of this impurity will decrease the yield of lead tetraacetate prepared from minium[6].

** In the literature[3,5] the m.p. of the water-free product has been reported as 101–102° and 103–105°, respectively. We have not made serious attempts to isolate it water-free in the solid state since the isolation of the hydrate was more convenient.

A good yield (89%) of the triacetate was also obtained with diphenylmercury as catalyst instead of mercury diacetate.

When the reaction period lasted 2 h, the yield was only 11%.

(*b*). *Without catalyst.* In another experiment no catalyst was added. After a 40-h reaction period diphenyllead diacetate was recovered quantitatively. Neither copper diacetate nor silver acetate catalyzed the reaction.

2. *The redistribution between triphenyllead acetate and lead tetraacetate*

(*a*). *With catalyst.* Lead tetraacetate (9.75 g, 22 mmole), 0.195 g of mercury diacetate (0.6 mmole) and 4.95 g of triphenyllead acetate (10 mmole) were subsequently added to 70 ml of acetic acid. The mixture was heated for 2.5 h at room temperature and 40 h at 70°. The small excess of tetraacetate was destroyed by adding ethylene glycol until negative. Work-up as described in 1(*a*) gave 10.8 g of phenyllead triacetate hydrate (75%).

(*b*). *Without catalyst.* In another experiment 13.3 g of lead tetraacetate (30 mmole) and 4.95 g of triphenyllead acetate (10 mmole) were heated without catalyst in 45 ml of acetic acid for 2 h at 40° followed by 40 h at 70°. After concentrating and cooling lead tetraacetate crystallized out and was filtered off (8.85 g 20.1 mmole). The filtrate was treated with ethylene glycol (to destroy the remainder of the lead tetraacetate) and evaporated to dryness. The residue was extracted with 80 ml of dry diethyl ether. No precipitate of hydrate formed upon wetting the extract with water. The residue was further extracted with chloroform to leave 2.75 g of lead diacetate (8.5 mmole). The extracts were combined and evaporated to dryness to give 4.85 g of diphenyllead diacetate (10.1 mmole). Total lead recovery 38.6 mmole (96.5%).

3. *The redistribution between tetraphenyllead and lead tetraacetate*

(*a*). *Reactant ratio* 1 : 3, *producing phenyllead triacetate.* Tetraphenyllead (5.15 g, 10 mmole), 17.7 g of lead tetraacetate (40 mmole, 10 mmole excess) and 0.286 g of mercury diacetate (0.9 mmole) were heated for 24 h at 70° in 70 ml of acetic acid. Work-up gave 16.9 g of product (88.5%).

(*b*). *Reactant ratio* 1 : 1, *producing diphenyllead diacetate.* Similarly, 5.15 g of tetraphenyllead (10 mmole), 4.45 g of lead tetraacetate (10 mmole) and 0.095 g of mercury diacetate (0.3 mmole) were heated at 70° with stirring in 40 ml of acetic acid (frozen out twice to reduce the amount of formic acid). After 2.5 h all tetraphenyllead had dissolved. After heating for another 2 h, the mixture was worked up to give 8.9 g of diphenyllead diacetate (93%) and traces of phenyllead triacetate hydrate and lead diacetate.

4. *The redistribution between tetraphenyllead and phenyllead triacetate hydrate*

(*a*). *With catalyst.* Tetraphenyllead (7.6 g, 15 mmole, 50% excess), 9.6 g of phenyllead triacetate hydrate (20 mmole), 0.195 g of mercury diacetate (0.6 mmole) and 2 g of acetic anhydride (20 mmole; to account for the hydrate water, possibly not necessary) were subsequently added to 60 ml of acetic acid. After 1 h stirring at 70°, nearly all of the tetraphenyllead had dissolved, and the solution showed a negative test for phenyllead triacetate with phenothiazine[7d]. Work-up gave 16.8 g of diphenyllead diacetate (100%), m.p. *ca.* 210°.

(*b*). *Without catalyst.* Expt. 4(*a*) was repeated, however, without catalyst.

After 2 h the mixture was still strongly positive for phenyllead triacetate. Unreacted tetraphenyllead (0.6 g, 1.2 mmole) was filtered off. The filtrate was evaporated to dryness in vacuum. The residue was thoroughly extracted with dry diethyl ether to leave 13.5 g of diphenyllead diacetate (28.2 mmole). The ethereal extract was concentrated and treated with water, whereupon 2.2 g of hydrate precipitated (4.6 mmole). Total lead recovery 34.0 mmole (97%).

5. *Attempted redistribution between tetraphenyllead and diphenyllead diacetate*

Tetraphenyllead (5.15 g, 10 mmole), 4.8 g of diphenyllead diacetate (10 mmole) and 0.106 g of diphenylmercury (0.3 mmole) were added to 125 ml of dry toluene. No reaction was observed at 75° and at reflux. This was demonstrated by the absence of triphenyllead acetate in a thin-layer chromatogram (Kodak silica gel sheet; benzene/acetic acid 9/1; spray with 0.1% dithizone solution in chloroform; Ph_3PbX causes a yellow spot at R_f *ca.* 0.65, Ph_2PbX_2 a red spot at *ca.* 0.50). A reaction was not observed either, when phenylmercury acetate or diphenylmercury were added as catalysts, or when toluene was partly replaced by dry peroxide-free dioxane.

Attempted redistribution between tetramethyllead and lead tetraacetate

A mixture (16.9 g) of tetramethyllead and toluene (Octel Corp., London., 80/20 w/w, 50 mmole of tetramethyllead), 0.9 g of mercury diacetate (3 mmole) and 25 ml of acetic acid in 150 ml of toluene was chilled to −60°. Lead tetraacetate (22.1 g, 50 mmole) was added in small portions with magnetic stirring in about 15 min. At the end the test for lead tetraacetate was negative. The mixture was evaporated to dryness, and the residue was dissolved in water. Thin-layer chromatography revealed the presence of di- and trimethyllead salt. Addition of sulphuric acid (4 *N*) gave 13.2 g of lead sulphate (43.7 mmole, 87% based on lead tetraacetate). (Dimethyllead diacetate under similar conditions did not give a precipitate with sulphuric acid.) Consequently, lead tetraacetate had been reduced instead of methylated.

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