INVESTIGATIONS ON ORGANOLEAD COMPOUNDS

III*. THE REACTION OF ORGANOLEAD COMPOUNDS WITH KETENE. (TRIPHENYLPLUMBYL)ACETIC ANHYDRIDE

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The reaction of organometallic compounds with ketene has been shown to result in some cases in insertion of the ketene molecule into the organometallic compound, *e.g.*:

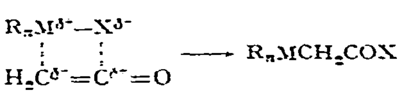
$$Et_3SnOMe + CH_2{=}C{=}O \longrightarrow Et_3SnCH_2COOMe \qquad \text{(ref. 2, } cf. \text{ ref. 3)}$$

$$Et_2Sn(OEt)_2 + 2CH_2{=}C{=}O \longrightarrow Et_2Sn(CH_2COOEt)_2 \qquad \text{(ref. 4)}$$

$$Me_3SiNHBu + CH_2{=}C{=}O \longrightarrow Me_3SiCH_2CONHBu \qquad \text{(ref. 5)}$$

$$Hg(OAc)_2 + 2CH_2{=}C{=}O + 2EtOH \longrightarrow Hg(CH_2COOEt)_2 + 2HOAc \qquad \text{(ref. 6)}$$

These reactions thus give rise to the formation of metal–carbon bonds and constitute a welcome addition to the few methods known for the preparation of β-functionally substituted organometallic derivatives. This reaction can be understood in terms of the unusual charge distribution assumed by the polarized ketene molecule[7]: $H_2C^{\delta-} = C^{\delta+} = O$. Interaction with polar compounds induces this charge distribution and, subsequently, the positively charged metal atom in the organometallic compound forms a bond with the negatively charged carbon atom of the ketene molecule:



$$\begin{array}{l} R_nM^{\delta+}{-}X^{\delta-} \\ \;\vdots \qquad \vdots \\ H_2C^{\delta-}{=}C^{\delta+}{=}O \end{array} \longrightarrow R_nMCH_2COX$$

In our search for useful methods for the preparation of functionally substituted organolead compounds, we decided to study the application of this reaction in organolead chemistry.

The reaction was carried out by passing excess of ketene through the suspension or solution of an organolead compound in diethyl ether or absolute ethanol at about 10°. So far the reaction has been successful in two cases only: (*a*) with triphenyllead hydroxide in diethyl ether and (*b*) with triphenyllead acetate in ethanol. No reaction occurred in either solvent with triethyllead acetate, trimethyllead ethoxide, triphenyl-

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[*] For Part II see ref. 1.

lead chloride, diphenyllead oxide, diphenyllead diacetate and hexaphenyldilead. Lead tetraacetate oxidized the ketene.

Reaction (*a*) produced in 85 % yield (triphenylplumbyl)acetic anhydride, the first known organolead compound of this type:

$$2Ph_3PbOH + 4CH_2{=}C{=}O \longrightarrow (Ph_3PbCH_2CO)_2O + Ac_2O$$

Its formation can be understood by assuming initial formation of the free acid which is then converted into the anhydride by the excess of ketene. The structure is based on analysis and molecular weight determination. The compound is readily soluble in chloroform. It is reasonable stable and can be stored for long periods at room temperature in the dark.

Reaction (*b*) gave in 78 % yield ethyl (triphenylplumbyl)acetate:

$$Ph_3PbOAc + CH_2{=}C{=}O + EtOH \longrightarrow Ph_3PbCH_2COOEt + HOAc$$

It was found to be identical with the compound prepared according to Kocheshkov and Aleksandrov[8] through decarboxylation of triphenyllead ethyl malonate:

$$Ph_3PbOCOCH_2COOEt \longrightarrow Ph_3PbCH_2COOEt + CO_2$$

A few reactions of (triphenylplumbyl)acetic anhydride were studied. Attempts to prepare the free acid by hydrolysis of the anhydride failed. It was found that the anhydride-containing group is very rapidly split off by acids: reaction with hydrogen chloride yielded 98.2 % of triphenyllead chloride. Also bromine eliminates this group prior to phenyl groups in contrast with other β-functionally substituted organolead compounds[1] where halogens split off a phenyl group preferably. Upon reaction with alcohol the anhydride resinified, and the expected ester could not be isolated. Reaction with methylmagnesium iodide or lithium aluminium hydride caused elimination of the anhydride-containing group, methyltriphenyllead and hexaphenyldilead, respectively, being the main reaction products.

EXPERIMENTAL

(Triphenylplumbyl)acetic anhydride

A suspension of 45.5 g of triphenyllead hydroxide[9] (0.1 mole) in 300 ml of anhydrous diethyl ether was placed into a 500-ml three-necked round-bottomed flask provided with magnetic stirrer, thermometer and ketene in- and outlet tubes. Ketene[10] ($\simeq$ 1 mole) was passed through this suspension at about 5° during 2 h with stirring and external cooling in ice–water. The precipitate was filtered off and washed with ether. It proved to be practically pure (triphenylplumbyl)acetic anhydride (41.0 g, yield 84.0 %). For an analytical sample 1.0 g of the compound was dissolved in 5 ml of chloroform and precipitated with 25 ml of petr. ether (40–60°). It decomposed at 100–110°. (Found: C, 48.96; H, 3.59; Pb, 42.43; mol. wt. osmom. in benzene, 1002. $C_{40}H_{34}O_3Pb_2$ calcd.: C, 49.16; H, 3.51; Pb, 42.42 %; mol. wt., 977.)

When the reaction was carried out on a small scale (0.01 mole) in much solvent (100 ml), dissolution of the suspended triphenyllead hydroxide was observed before precipitation of the anhydride.

Ethyl (triphenylplumbyl)acetate

Ketene[10] (3/8 mole) was passed during 45 min through a suspension of 5.0 g of triphenyllead acetate in 25 ml of abs. ethanol at room temperature with stirring and external cooling. After half an hour the acetate had dissolved. The reaction mixture was evaporated to dryness to give 4.9 g of colourless oil which soon solidified. This product was recrystallized from 50 ml of hot petr. ether (60–80°) to give 3.5 g of ethyl (triphenylplumbyl)acetate. The mother liquor on concentrating gave another 0.5 g. The total yield, 4.0 g, is 78 %. M.p. 61–62°; no depression with an authentic sample[8]. (Found: C, 50.53; H, 4.43. $C_{22}H_{22}O_2Pb$ calcd.: C, 50.27; H, 4.22 %.)

Triphenyllead acetate *in ether* did not react with ketene, probably because of its low solubility (0.7 g per l).

Reactions of (triphenylplumbyl)acetic anhydride

(*a*) *With hydrogen chloride*. Dry hydrogen chloride was passed through a solution of 9.8 g of anhydride (0.01 mole) in 80 ml of chloroform at room temperature until a turbidity became perceptible (caused by a further reaction of hydrogen chloride with triphenyllead chloride yielding the completely insoluble diphenyllead dichloride). Concentration of the reaction mixture gave in total 9.3 g of triphenyllead chloride, m.p. 212°; no depression with an authentic sample[11]; yield 98 %.

(*b*) *With bromine*. A solution of 1.952 g of the anhydride (2 mmole) in 35 ml of chloroform was cooled to —40°. At that temperature a solution of 1.28 g of bromine (16 mg-atom) in 10 ml of chloroform was added dropwise with stirring. The bromine reacted immediately and after about half of the solution was added, a precipitate started to form. This was filtered off and proved to be 2.00 g of diphenyllead dibromide (96 %).

(*c*) *With ethanol*. In 25 ml of 96 % alcohol 4.9 g of the anhydride (0.005 mole) was dissolved by boiling for about 20 sec. The cooled solution was put into a refrigerator and after a few hours a tough semi-solid material had separated. The mixture was evaporated to dryness and treated with diethyl ether. The insoluble material (3.0 g) was filtered off and proved to be impure starting material. No product could be extracted from the filtrate with sodium hydroxide or sodium bicarbonate solutions. No ester was obtained from the evaporated ethereal solution.

In a second experiment the anhydride was refluxed for 1 h in ethanol. Evaporation of the reaction mixture gave a glassy residue from which no well-defined products could be isolated.

(*d*) *With methylmagnesium iodide*. The anhydride (9.7 g, 0.01 mole) was added at once at 0° to a solution of methylmagnesium iodide (prepared from 6.9 g of methyl iodide, 0.05 mole, in 50 ml dry ether). The mixture was allowed to come to room temperature with stirring, then refluxed for 10 min, and hydrolyzed with ice. The dried ethereal layer, on concentration, gave 5.2 g of methyltriphenyllead (57.4 %), after recrystallization melting at 62–63° (no depression with an authentic sample[12]).

(*e*) *With lithium aluminium hydride*. A solution of 4.9 g of the anhydride (0.005 mole) in tetrahydrofuran was chilled in a dry ice–acetone bath to about —75°. Lithium aluminium hydride (0.4 g, 0.01 mole) was added at once with mechanical stirring. The mixture turned light-green. After rising slowly to room temperature, the mixture was stirred 1.5 h under reflux, hydrolyzed with 7 ml of water, and the insoluble aluminium salts were filtered off. The filtrate was concentrated to a small volume whereupon 2.2 g of hexaphenyldilead (50 %) crystallized. No further products could be isolated in the pure state.

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SUMMARY

The reaction of ketene with triphenyllead hydroxide in diethyl ether gave (triphenylplumbyl)acetic anhydride, $(Ph_3PbCH_2CO)_2O$, the first anhydride-substituted organolead compound known. The reaction of ketene with triphenyllead acetate in absolute ethanol gave ethyl (triphenylplumbyl)acetate, Ph_3PbCH_2COOEt. A few reactions of the anhydride are described.

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