# INVESTIGATIONS ON ORGANOLEAD COMPOUNDS IX*. ACYLTRIPHENYLLEAD COMPOUNDS

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SUMMARY

Acyl–lead compounds such as acetyl- and benzoyltriphenyllead were found to be too unstable to be isolated, but (ethoxycarbonyl)- and (dimethylcarbamoyl)-triphenyllead, which were prepared from (triphenylplumbyl)lithium and the appropriate acid halide, proved to be stable.

On warming the acetyl and ethoxycarbonyl derivatives decomposed in different ways, according to the following equations:

$$Ph_3Pb-CO-Me \xrightarrow{50°} [Ph_2Pb] + Ph-CO-Me \tag{1}$$

$$\hookrightarrow \tfrac{1}{3} Ph_6Pb_2 + \tfrac{1}{3} Pb$$

$$Ph_3Pb-CO-OEt \xrightarrow{160°} [Ph_3Pb-OEt] + CO \tag{2}$$

$$\Big|^{Ph_3PbCOOEt} \longrightarrow [Ph_6Pb_2] + (EtO)_2CO$$

$$\hookrightarrow \tfrac{3}{2} Ph_4Pb + \tfrac{1}{2} Pb$$

Some 80% of the decomposition of the carbamoyl derivative, $Ph_3Pb-CO-NMe_2$, at ca. 160° was analogous to that of the acetyl compound (eqn. 1) and the other 20% was analogous to that of the organolead ester (eqn. 2).

Spectral data are discussed.

Acyl–lead compounds containing the $\gtrless Pb-C(O)-$ skeleton were previously unknown[2] because of their general instability. We now describe here the preparation, stability and decomposition of some of these compounds.

RESULTS AND DISCUSSION

*Preparation*

We attempted to prepare acetyltriphenyllead by the reaction between (tri-

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* For Part VIII see ref. 1.

phenylplumbyl)lithium and acetyl chloride in tetrahydrofuran (THF) at $-30°$ :

$$Ph_3PbLi + ClCOCH_3 \rightarrow Ph_3PbCOCH_3 + LiCl$$

We were unable to isolate the desired product, however, because both hydrolytic and non-hydrolytic work-up gave unstable, red to yellow solutions from which metallic lead rapidly separated.* Evidence that acetyltriphenyllead had nevertheless formed, was provided by the NMR spectrum of the mixture. A peak at $\delta$ 2.69 ppm was assigned to the methyl hydrogens of the acetyl group; the coupling with $^{207}Pb$ was 33 Hz. Two other possible components of the reaction mixture, acetyl chloride and acetophenone, absorbed at 2.63 and 2.53 ppm, respectively.

For stable derivatives to exist it seems that the acyl group must be of a special nature. Consequently, reactions of (triphenylplumbyl)lithium with ethyl chloroformate and dimethylcarbamoyl chloride were carried out, and stable colourless derivatives were indeed isolated:

$$Ph_3PbLi + ClCOOEt \rightarrow Ph_3Pb-COOEt + LiCl$$

$$Ph_3PbLi + ClCONMe_2 \rightarrow Ph_3Pb-CONMe_2 + LiCl$$

The ethoxycarbonyl derivative (m.p. 76°) is moderately stable, decomposing only very slowly at room temperature. The dimethylcarbamoyl derivative (m.p. 142–145°) can be stored indefinitely.

*Decomposition*

The decomposition of the unstable acetyltriphenyllead was followed by use of NMR spectroscopy. No decomposition was observed below 0° in one hour or at 20° in 20 min. However, at 50° the $PbCOCH_3$ peak gradually disappeared, and a new peak developed 0.16 ppm towards higher field, at the position of the $CH_3$ proton signal of acetophenone. All the acetyltriphenyllead decomposed within one hour.

Further information on this decomposition was obtained by evaporating the reaction mixture to dryness at $-30°$ in vacuum, then heating the yellow to red residue in an evacuated system to about 50 to 60° and keeping it at that temperature for 10 hours. Gas-chromatographic analysis showed that acetophenone was the sole volatile product, and no acetone or carbon monoxide was detected. The residue consisted of a mixture of hexaphenyldilead and metallic lead. The following scheme accounts for the results:

$$Ph_2Pb-COCH_3 \rightarrow [Ph_2Pb] + PhCOCH_3 \ (87\%)$$
$$\overset{|}{Ph} \overset{\curvearrowright}{\phantom{x}}$$
$$\phantom{xxxxxxxxxx} \rightarrow \tfrac{1}{3} Ph_6Pb_2 \ (88.5\%) + \tfrac{1}{3} Pb \ (64\%)$$

Whereas the migration of a phenyl group from one lead atom to a neighbouring lead atom (1,2 phenyl shift) is quite common in organolead chemistry (see *e.g.* ref. 3), this is the first example of a shift to a neighbouring *carbon* atom.

The decomposition of (ethoxycarbonyl)triphenyllead followed a completely different course. This compound is stable at room temperature and was decomposed by keeping it at 160° for 4 hours. The material balance is illustrated by the following overall equation:

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* A similar result was obtained with benzoyl chloride.

$$4 \ Ph_3PbCOOEt \ \rightarrow \ 3 \ Ph_4Pb + Pb \quad + 2 \ CO \quad + 2 (EtO)_2CO$$
$$95\% \qquad 98.5\% \ \ 88.5\% \ \ 91\%$$

The first step of the mechanism of the decomposition is probably similar to that for corresponding organosilicon compounds[2], *i.e.* ejection of carbon monoxide with formation of triphenyllead ethoxide. In a subsequent reaction the ethoxide reacts with unreacted starting material to give hexaphenyldilead and diethyl carbonate. The resulting hexaphenyldilead is unstable at $160°$ and disproportionates to give tetraphenyllead and metallic lead.

$$Ph_3PbCOOEt \ \rightarrow \ Ph_3PbOEt + CO$$

$$Ph_3PbCOOEt + Ph_3PbOEt \ \rightarrow \ Ph_6Pb_2 + (EtO)_2CO$$

$$2 \ Ph_6Pb_2 \ \rightarrow \ 3 \ Ph_4Pb + Pb$$
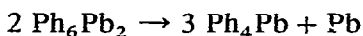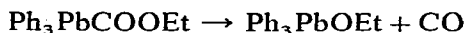
The occurrence of the second step was confirmed by carrying out a reaction between (ethoxycarbonyl)triphenyllead and triphenyllead ethoxide in benzene at room temperature, which did, indeed, give hexaphenyldilead and diethyl carbonate.

The decomposition of (dimethylcarbamoyl)triphenyllead (carried out at $160–180°$ for 4 h in vacuum) followed both pathways, as indicated by the formation of *N,N*-dimethylbenzamide as well as of carbon monoxide and tetramethylurea:

$$4 \ Ph_3PbCONMe_2 \quad \begin{cases} \rightarrow \ 2 \ Ph_4Pb^\star + 2 \ Pb^\star + 4 \ PhCONMe_2 \quad (1) \\ \rightarrow \ 3 \ Ph_4Pb^\star + Pb^\star + CO + (Me_2N)_2CO \quad (2) \end{cases}$$
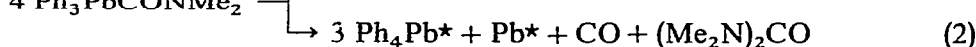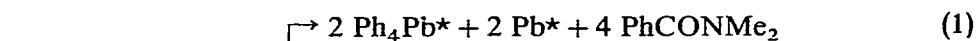
The ratio of the products shows that reaction (1) is 4 times as important as reaction (2).

$$Ph_3PbCONMe_2 \ \rightarrow \ Ph_4Pb + Pb \quad + PhCONMe_2 + (Me_2N)_2CO + CO$$

| | | | | | |
|---|---|---|---|---|---|
| mmoles theor.: 20 | 11 | 9 | 16 | 2 | 2 |
| found: 20 | 11.4 | 8.25 | 11.4 | 2.2 | 2.0 |
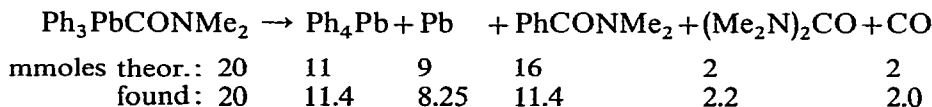
*Spectra*

The pertinent spectra are collected in Table 1.

*Infrared.* The IR spectra of acetyltriphenyllead and (dimethylcarbamoyl)-triphenyllead showed a slight bathochromic shift of the carbonyl stretching frequency relative to the carbon analogues, but this shift was far less than has been observed in the corresponding silicon derivatives[2,4]. However, $\nu(CO)$ of (ethoxycarbonyl)-triphenyllead was shifted by about the same amount as in the silicon analogue.

*Ultraviolet.* We were unable to obtain useful UV spectra of our Pb–CO compounds; *e.g.*, a cyclohexane solution of the carbamoyl compound (0.74 mg in 25 ml) started absorbing at 300 nm, and this steadily increased to total absorption at 220 nm. The THF solution of acetyltriphenyllead was yellow-coloured, but this may be due to an impurity ($Ph_2Pb$?) in the (triphenylplumbyl)lithium used as a starting material; no colour change was noticed when the acetyl chloride was added to the lithium reagent.

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$\star$ Generated by disproportionation of diphenyllead (unstable $\geqslant 0°$) and hexaphenyldilead (unstable $\geqslant 80°$), respectively.

TABLE I

IR AND NMR SPECTRA OF ACYLTRIPHENYLLEAD COMPOUNDS AND SOME REFERENCE COMPOUNDS

| Compound | IR, $v(CO)$ $(cm^{-1})$ | NMR, $\delta(Me)$ (ppm) |
|---|---|---|
| $Ph_3PbCOCH_3$ | 1694 | 2.69 (THF); $J$ 33 Hz |
| $Ph_3CCOCH_3$ | 1710 (ref. 2) | 2.01 ($CCl_4$) (ref. 2) |
| $Ph_3SiCOCH_3$ | 1644 (ref. 2) | 2.30 ($CCl_4$) (ref. 2) |
| $ClCOCH_3$ | 1807 | 2.63 (THF) |
| $PhCOCH_3$ | 1675 | 2.53 (THF), 2.59 ($CDCl_3$) |
| $CH_3COCH_3$ | 1725 | 2.14 (THF), 2.06 ($CDCl_3$) |
| | | |
| $Ph_3PbCOOEt$ | 1678 | |
| $Me_3CCOOEt$ | 1730 | |
| $R_3SiCOOEt$ | 1680 (ref. 6) | |
| | | |
| $Ph_3PbCONMe_2$ | 1615 | 2.94, 2.98 ($CCl_4$); $J$ 4, 11 Hz[a] |
| $Me_3CCONMe_2$ | 1620 (ref. 4) | Coalesc. at $-12°$ (ref. 4) |
| $Me_3SiCONMe_2$ | 1560 (ref. 4) | Coalesc. at $55-60°$ (ref. 4) |
| $MeCONMe_2$ | | 2.83, 3.01 ($CCl_4$) |

[a] After coalescence at ca. 55° $J$ 7.5 Hz.

The IR and UV spectra of these compounds do not show the several interesting features observed for the corresponding silicon compounds[2,5], so that the conclusions drawn for the organosilicon compounds may not apply to the organolead compounds.

*Nuclear magnetic resonance.* The chemical shift of the methyl hydrogens in acetyltriphenyllead ($\delta$ 2.69 ppm) is at rather low field, close to chemical shifts of acyl groups bearing electron-withdrawing groups such as chlorine (2.63) and phenyl (2.53 ppm). However, this is not unusual since the presence of triphenyllead groups in the vicinity of hydrogen atoms causes a marked shift of these hydrogens to lower field[1]; e.g., $\delta(Me)$ of $Ph_3PbCH_2CH_3$ at 1.66 ppm, $\delta(Me)$ of $(Ph_3Pb)_2CHCH_3$ at 2.37 ppm[7].

The coupling of $^{207}Pb$ with the methyl hydrogens of acetyltriphenyllead, 33 Hz, is surprisingly low; the corresponding coupling in ethyltriphenyllead is 168 Hz[7]. Warner and Noltes[8] have recently found a similarly low coupling in (1,1-dichloroethyl)triphenyllead (60 Hz).

The NMR spectrum of (dimethylcarbamoyl)triphenyllead contains two separate peaks (at $\delta$ 2.94 and 2.98 ppm in $CCl_4$) as is usual in dimethylamides owing to restricted rotation around the C(O)–N bond. Small peaks close to the methyl peaks may be attributed to couplings with $^{207}Pb$: $^4J[^{207}Pb-C(O)-N-CH_3]$ is 4 and 11 Hz, respectively. The peaks coalesce at ca. 55° (at about the same temperature as Peddle and Walsingham[4] have found for $Me_3SiCONMe_2$), and the coupling becomes 7.5 Hz (measured at 90°).

EXPERIMENTAL

THF was distilled from lithium aluminium hydride and stored under nitrogen. (Triphenylplumbyl)lithium was prepared from hexaphenyldilead and lithium in

THF[9]. Commercially supplied acyl chlorides were used, but acetyl chloride was freshly distilled from quinoline. Reactions were carried out under nitrogen.

## Preparations

*Acetyltriphenyllead (attempted)*. To a solution of 16.6 mmole (triphenyl-plumbyl)lithium in 30 ml THF 1.4g acetyl chloride (17.8 mmole) was added at $-30°$. After stirring for $1\frac{1}{2}$ h at $-15°$ the mixture was poured onto ice/salt plus chloroform ($-15°$). The red chloroform phase was separated as rapidly as possible and dried over sodium sulphate. Concentration in vacuum gave 0.4 g triphenyllead chloride (0.8 mmole). Addition of light petroleum (40–60°) gave a precipitate of 3.2 g hexaphenyl-dilead (3.6 mmole, 7.2 mg-atom Pb). The filtrate was evaporated to dryness. The yellow residue (4.5 g) soon turned black.

In another experiment the reaction mixture was *not* hydrolyzed, but concentrated in vacuum at low temperature to a small volume. The residue was extracted with pre-cooled chloroform. On concentration the yellow-orange extract turned turbid and metallic lead subsequently separated.

*Benzoyltriphenyllead (attempted)*. A solution of 2.4 g benzoyl chloride (16.8 mmole) in 10 ml THF was added to a solution of 16.8 mmole (triphenylplumbyl)-lithium in 25 ml THF at $-30°$. The resulting dark-red solution was evaporated to dryness in vacuum. Addition of benzene to the residue caused immediate separation of metallic lead.

*(Ethoxycarbonyl)triphenyllead*. Ethyl chloroformate (3.8 g, 35 mmole) was added at $-70°$ to a solution of 29.6 mmole (triphenylplumbyl)lithium in 50 ml THF. After stirring for $4\frac{1}{2}$ h at $-40°$ 10 ml water were slowly added at $-40°$. A thick precipitate formed. The mixture was poured into 200 ml chloroform, pre-chilled to $-20°$, and sodium sulphate was added to take up the water. The filtrate was evaporated to dryness. The residue completely dissolved in diethyl ether. Concentration in vacuum gave 11.3 g of product. Further concentration of the mother liquor gave an additional crop of 2.2 g. Total yield 13.5 g (89 %). After recrystallization twice from diethyl ether, the m.p. was 76°. (Found: C, 49.62; H, 4.17; Pb, 40.27. $C_{21}H_{20}O_2Pb$ calcd.: C, 49.30; H, 3.95; Pb, 40.50%.)

*(Dimethylcarbamoyl)triphenyllead*. A solution of 1.8 g dimethylcarbamoyl chloride (16.8 mmole) in 10 ml THF was added to a solution of 16.8 mmole (triphenyl-plumbyl)lithium in THF at $-30°$. The temperature slightly rose. After $2\frac{1}{2}$ h stirring at room temperature, the reaction mixture was poured onto ice and extracted with chloroform. The extract was dried on sodium sulphate, filtered and evaporated to dryness. The residue was dissolved in diethyl ether. Ethanol was added just until crystallization started. Evaporation gave more crystals (7.2 g, 14.1 mmole, 84%). Successive recrystallizations from diethyl ether and benzene/hexane 1/1 gave a product of m.p. 142–145° (with slight decomposition). (Found: Pb, 40.36; mol. wt. osmom. in benzene, 538. $C_{21}H_{21}NOPb$ calcd.: Pb, 40.58%; mol. wt., 511.)

## Decomposition

*Acetyltriphenyllead*. A reaction was carried out between 16.6 mmole (triphenyl-plumbyl)lithium and 1.4 g acetyl chloride (17 mmole) in 30 ml THF at $-30°$. The THF was removed as far as possible in high vacuum at $-30°$. A bulb (A) containing the residue was connected via an U-shaped tube with another bulb (B). The system was

evacuated to 0.4 mm. Bulb (B) was placed in dry ice/acetone and the temperature of bulb (A) was allowed to rise slowly to 50–60°. When volatile products no longer distilled over, ethane was admitted. GLC analysis showed no trace of carbon monoxide. The liquid which had distilled over was shown by GLC to consist of THF, benzene and acetophenone (1.75 g, 14.8 mmole, 89%). Work-up of the residue in bulb (A) gave 4.3 g hexaphenyldilead (4.9 mmole) and inorganic lead, isolated as the sulphate (1.1 g, 3.6 mmole). Total lead recovery 81%.

*(Ethoxycarbonyl)triphenyllead.* This compound (5.1 g, 10 mmole) was heated slowly to 160° in an evacuated system. After melting, the material turned red, metallic lead separated, and the mixture solidified. After 4 h heating at 160°, helium was admitted. GLC showed that the gas contained 99 ml carbon monoxide (4.4 mmole, 88%). The system was again evacuated and distillation into the cold trap was continued. The distilled liquid (0.52 g) was shown to be diethyl carbonate (4.4 mmole, 88%) by comparison of IR and GLC characteristics with those of an authentic sample. The residue in bulb(A) gave 3.7 g tetraphenyllead (7.2 mmole, 96%) and 0.75 g lead sulphate (2.5 mmole, 100%).

*(Dimethylcarbamoyl)triphenyllead.* Decomposition of 10.2 g (dimethylcarbamoyl)triphenyllead (20 mmole) as described for the ethoxycarbonyl derivative gave the following products: 5.9 g tetraphenyllead (11.4 mmole), 2.5 g lead sulphate (8.25 mmole), 1.7 g $N,N$-dimethylbenzamide (11.4 mmole), 0.23 g tetramethylurea (2.0 mmole), and 48.5 ml carbon monoxide (2.2 mmole).

*Reaction of (ethoxycarbonyl)triphenyllead with triphenyllead ethoxide*

Triphenyllead chloride (11.8 g, 25 mmole) was stirred for $1\frac{1}{2}$ h with a solution of 27 mmole sodium ethoxide in 100 ml of water-free ethanol. The reaction mixture was evaporated to dryness. The residue was extracted with 50 ml dry benzene under nitrogen. The benzene solution was shown to contain 0.460 $M$ base (by titration with HCl) and 0.456 $M$ Pb. Chloride could not be detected. It was assumed that the sole product was triphenyllead ethoxide, since triphenyllead hydroxide has only a low solubility in benzene. The solution was very sensitive towards moisture.

(Ethoxycarbonyl)triphenyllead (97 mg, 0.19 mmole) was dissolved in 0.7 g dry benzene, and 0.5 ml of the above triphenyllead ethoxide solution was added (0.23 mmole). The temperature rose from 22 to 26°. After 18 h at room temperature, the volatile components were separated from the residue in a vacuum line. GLC showed three peaks, the main one due to benzene, another to diethyl carbonate (same retention time as an authentic sample) and a small due to ethanol. The residue was dissolved in chloroform. Hexaphenyldilead (122 mg, 73%) was precipitated with ethanol.

*Spectra*

*IR.* IR spectra were recorded in KBr on a Grubb–Parsons Spectromaster, except for the low-temperature infrared spectrum of acetyltriphenyllead which was run in THF at $-30°$ on a Perkin–Elmer 337 spectrometer provided with a RIIC VLT-2 variable-temperature cell containing AgCl windows. The wave-length scale was expanded by using an external Hitachi PE 165 recorder. The presence of small negative water vapour bands in the spectra allowed us to calibrate the wave-length scale in a simple way to give an accuracy of $\pm 1$ cm$^{-1}$.

*UV.* UV spectra were recorded on a Cary Model 15 recording spectrophoto-

meter at three concentrations (4, 0.8 and 0.4 mg per 25 ml cyclohexane). Acetyltriphenyllead was measured in THF (ca. $3 \times 10^{-5}$ $M$).

*NMR.* NMR spectra were recorded on a Varian HA-100.

ACKNOWLEDGEMENTS

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