*Journal of Organometallic Chemistry*
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

# INVESTIGATIONS ON ORGANOLEAD COMPOUNDS
## VIII*. REACTIONS OF (TRIORGANOPLUMBYL)METAL REAGENTS WITH POLYCHLOROMETHANES; TETRAKIS(TRIPHENYLPLUMBYL)METHANE AND RELATED COMPOUNDS**

L. C. WILLEMSENS AND G. J. M. VAN DER KERK
*Institute for Organic Chemistry TNO, Utrecht (The Netherlands)*

(Received February 11th, 1970)

## SUMMARY

Triphenylplumbyllithium couples readily in tetrahydrofuran with carbon tetrachloride, chloroform and dichloromethane to produce the following compounds in good yields: $(Ph_3Pb)_4C$, $(Ph_3Pb)_2CCl_2$, $Ph_3PbCCl_3$, $(Ph_3Pb)_3CH$, $Ph_3PbCHCl_2$, and $(Ph_3Pb)_2CH_2$. The structure of $(Ph_3Pb)_4C$ was confirmed by converting it into $(Ph_2PbBr)_4C$.

Similarly $(Me_3Pb)_4C$ was prepared from trimethylplumbylsodium and carbon tetrabromide in liquid ammonia.

The reaction of triphenylsilyllithium, $Ph_3SiLi$, with polyhalomethanes has been reported[4] to give mainly hexaphenyldisilane along with several other products. The complexity of the reaction has been explained by assuming that three kinds of reactions operate simultaneously, *viz.* (1) lithium–halogen coupling; (2) lithium–halogen exchange; and (3) metalation.

$$Ph_3SiLi + RX \rightarrow Ph_3SiR + LiX \tag{1}$$

$$Ph_3SiLi + RX \rightarrow Ph_3SiX + RLi \tag{2}$$

$$Ph_3SiLi + R_2CHX \rightarrow Ph_3SiH + R_2CLiX \tag{3}$$

The hexaphenyldisilane is formed by means of an exchange reaction (2) followed by a coupling reaction (1) of the triphenylchlorosilane formed with unreacted triphenylsilyllithium.

We have studied the analogous reaction of triphenylplumbyllithium with the chlorinated methanes: methyl chloride, dichloromethane, chloroform and carbon tetrachloride. In contrast to the reactions with triphenylsilyllithium[4] the coupling reaction was found to take place almost exclusively. (In one instance exchange also occurred, but only to a small extent.) This is fortunate because only the coupling leads to new organolead compounds.

---

* For Part VII see ref. 1.

** Partly described in dissertation[2] of L. C. Willemsens, Utrecht 1965. For a preliminary note see ref. 3.

Thus, carbon tetrachloride with an excess of triphenylplumbyllithium gave the fully triphenylplumbyl-substituted methane derivative, tetrakis(triphenylplumbyl)-methane, $(Ph_3Pb)_4C$, in a yield of about 65%. For an organolead derivative the compound is exceedingly stable (obviously due to its high symmetry); it sharply decomposes at 292–294°. Its ease of formation is surprising but its existence was quite unexpected. At first sight it seemed sterically impossible to connect four big triphenyllead groups with one carbon atom. The compound has been further characterized by its reaction with bromine (8 atoms per molecule), resulting in the elimination of 4 phenyl groups. The compound isolated shows analytical values and a molecular weight consistent with the formula $(Ph_2PbBr)_4C$, and its structure has been confirmed by X-ray analysis[5].

As a by-product in the synthesis of $(Ph_3Pb)_4C$, tris(triphenylplumbyl)methane, $(Ph_3Pb)_3CH$, was isolated in a yield of about 20%. The compound is formed, probably by a lithium–chlorine exchange, from the intermediate $(Ph_3Pb)_3CCl$.

Similarly, reactions with chloroform, methylene chloride and methyl chloride gave fair yields of the corresponding triphenylplumbyl-substituted methanes, $(Ph_3Pb)_3CH$, $(Ph_3Pb)_2CH_2$ and $Ph_3PbCH_3$ respectively, all stable compounds with sharp melting points.

Their NMR spectra show a marked shift of the resonance of the methyl H atoms towards lower field as hydrogen atoms are replaced by triphenyllead groups.

Reversed procedures, *i.e.* addition of triphenylplumbyllithium to an excess of a chloro methane at $-60°$, yielded in case of carbon tetrachloride and chloroform the expected products $Ph_3PbCCl_3$ and $Ph_3PbCHCl_2$, respectively. In case of methylene chloride only $(Ph_3Pb)_2CH_2$ could be isolated, in spite of several attempts to obtain $Ph_3PbCH_2Cl$ as well. It seems that the latter compound is so reactive that its further reaction with triphenylplumbyllithium cannot be prevented.

Whereas at $-60°$ addition of triphenylplumbyllithium to an excess carbon tetrachloride results in the formation of $Ph_3PbCCl_3$, at room temperature the disubstituted product, $(Ph_3Pb)_2CCl_2$, is formed. Clearly, at room temperature the primary product, $Ph_3PbCCl_3$, is very reactive and reacts further with triphenylplumbyllithium even though carbon tetrachloride is present in excess.

Attempts to prepare $(Ph_3Pb)_3CCl$ and $(Ph_3Pb)_2CHCl$ failed, again because of further reaction with triphenylplumbyllithium. Thus, all compounds of the type $(Ph_3Pb)_xCH_yCl_z$ ($x+y+z=4$, $x$ is 1 to 4, $y$ 0 to 3, $z$ 0 to 3) could be prepared according to the above method except the three containing one chlorine atom ($z=1$). The seven compounds prepared are listed in Table 1.

The compound $(Me_3Pb)_4C$ was similarly prepared from trimethylplumbylsodium[7] and carbon tetrabromide in liquid ammonia. This compound could not be prepared from carbon tetrachloride. Neither could the analogous ethyl compound, $(Et_3Pb)_4C$, be obtained from treatment of triethylplumbylsodium with carbon tetrachloride or carbon tetrabromide. $(Me_3Pb)_4C$ is a snow-white sublimable substance, decomposing at about 220° without melting. For NMR see Experimental.

## EXPERIMENTAL

### *The reaction of triphenylplumbyllithium with polychloromethanes*

The reaction with carbon tetrachloride is fully described here; reactions with

TABLE 1

PRODUCTS FROM TRIPHENYLPLUMBYLLITHIUM AND POLYCHLOROMETHANES

| Compound | Yield (%) | Solvent for recrystallization | M.p. (°C) | Analyses (%) | | | NMR[a] | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Found | Calcd. | δ | J |
| $(Ph_3Pb)_4C$[b] | 61[c] | Chlorobenzene/ acetone | 292–294 | C | 49.61 | 49.65 | | |
| | | | | H | 3.49 | 3.42 | | |
| | | | | Pb | 46.95 | 46.93 | | |
| $(Ph_3Pb)_3CH$ | 66 | Acetone/ ethanol 70/30 | 167–168 | C | 49.78 | 49.72 | 3.49 | 70 |
| | | | | H | 3.72 | 3.49 | | |
| | | | | Pb | 46.66 | 46.79 | | |
| | | | | Mol. wt.[e] | 1370 | 1328 | | |
| $(Ph_3Pb)_2CH_2$ | 72 | Acetone/ ethanol 70/30 | 94–95 | C | 49.50 | 49.87 | 2.15 | 60.5 |
| | | | | H | 3.77 | 3.62 | | |
| | | | | Pb | 46.34 | 46.51 | | |
| | | | | Mol. wt.[e] | 884 | 891 | | |
| $Ph_3PbCH_3$ | 75 | Ethanol | 61–62[d] | Pb | 45.81 | 45.68 | 1.26 | 67 |
| | | | | Mol. wt.[e] | 480 | 453 | | |
| $(Ph_3Pb)_2CCl_2$ | 80 | THF | 207–208 | Cl | 7.49 | 7.39 | | |
| | | | | Pb | 43.00 | 43.17 | | |
| | | | | Mol. wt.[e] | 983 | 959 | | |
| $Ph_3PbCHCl_2$ | 75 | Ethanol | 124–125 | C | 43.77 | 43.68 | 6.10 | 61 |
| | | | | H | 3.16 | 3.09 | | |
| | | | | Cl | 13.68 | 13.57 | | |
| | | | | Pb | 39.75 | 39.66 | | |
| | | | | Mol. wt.[e] | 532 | 522 | | |
| $Ph_3PbCCl_3$ | 92 | Benzene | 172–173 | Cl | 19.04 | 19.10 | | |
| | | | | Pb | 37.01 | 37.20 | | |
| | | | | Mol. wt.[e] | 546 | 556 | | |

[a] Varian HA-100; in $CS_2$; chemical shift (δ) of methyl hydrogen atoms in ppm from TMS; coupling (J) between $^{207}Pb$ and these H atoms in Hz. [b] Too insoluble to determine molecular weight. [c] In addition 21% of $(Ph_3Pb)_3CH$ (the second compound) was isolated. [d] No melting point depression with an authentic sample; lit. m.p. 60°. [e] Osmometrically in benzene.

chloroform and methylene dichloride were carried out similarly. For yields, solvents for recrystallization, melting points and analyses see Table 1.

(*a*). *With excess of triphenylplumbyllithium: tetrakis(triphenylplumbyl)methane.* To a solution of about 0.1 mole of triphenylplumbyllithium[8] in tetrahydrofuran under nitrogen at −65° was added at once with stirring 3079 mg of pure carbon tetrachloride (0.02 mole). The solution was allowed to rise to room temperature. At about −35° a precipitate started to form. The mixture was refluxed for 2 h. The mixture was treated with ice. The precipitate was filtered off, washed with tetrahydrofuran and after drying it was extracted with chloroform in a Soxhlet apparatus. The crystals separating from the extract were dissolved in 250 ml of hot chlorobenzene and precipitated with 250 ml of acetone to give 21.4 g (61%) of $(Ph_3Pb)_4C$. From the mother liquor of the extract small amounts of tetraphenyllead and triphenyllead chloride were isolated. The tetrahydrofuran phase, after drying and concentration, gave 5.65 g (21%) of $(Ph_3Pb)_3CH$ (mol. wt., Pb analysis and mixt. m.p.).

(*b*). *With excess of carbon tetrachloride at* −60° : *(trichloromethyl)triphenyllead.* A solution of 10 ml of pure carbon tetrachloride in 25 ml of dry tetrahydrofuran was placed under nitrogen and cooled to −70°. A solution of 0.014 mole of triphenylplumbyllithium in 50 ml of tetrahydrofuran was added (temperature $< -40°$). The mixture was stirred for 2 h at −40° and then allowed to rise to room temperature. After stirring for half an hour, the brownish, yellow solution turned slightly turbid. The mixture was treated with ice, neutralized with 0.25 g of glacial acetic acid and extracted with chloroform. The yellow chloroform solution was dried over sodium sulphate and concentrated: 10.7 g (92%) of $Ph_3PbCCl_3$ crystallized out. The compound was recrystallized from 150 ml of benzene.

(*c*). *Excess of carbon tetrachloride at room temperature*: *bis(triphenylplumbyl)-dichloromethane.* The reaction was carried out as described in (*b*), except that the triphenylplumbyllithium was added dropwise at room temperature. From the chloroform extract $(Ph_3Pb)_2CCl_2$ crystallized upon concentrating. The compound was recrystallized from tetrahydrofuran in the dark. Yield 80%.

*Bromination of tetrakis(triphenylplumbyl)methane*

$(Ph_3Pb)_4C$ (1.766 g, 0.001 mole) was dissolved in 200 ml of chloroform, and 25.1 ml of 0.319 *N* (0.008 g-atom) bromine solution in chloroform was added at once at about −40°. The volume was reduced to 15 ml. Ethanol (100 ml) was added and the solution left overnight in a refrigerator. The yellow crystals were filtered off and sucked dry. Yield 87% of $(Ph_2PbBr)_4C$, dec. 197–198°. (Found: Br, 17.87; Pb, 46.47; mol. wt. osmom. in methylene chloride, 1690. $C_{49}H_{40}Br_4Pb_4$ calcd.: Br, 17.98; Pb, 46.43%; mol. wt., 1777.)

Reaction with double the amount of bromine gave unstable products which could not be characterized.

*Preparation of tetrakis(trimethylplumbyl)methane, $(Me_3Pb)_4C$*

Tetramethyllead (107 g of a 50/50 w/w % mixture with toluene; 0.2 mole) and 50 ml abs. diethyl ether were mixed and chilled under nitrogen to −70°. About 200 ml liquid ammonia was condensed onto the solution.

Small lumps of sodium (8.8. g, 0.38 g-atom) were added just until the blue colour formed by dissolution of the sodium did no longer disappear with formation of trimethylplumbylsodium[7]. Then, 16.5 g carbon tetrabromide (0.05 mole) was added in portions with stirring under nitrogen at about −70°. The greyish solution gradually turned yellow. Substantial heat evolution was observed. At the end 100 ml more diethyl ether was added to keep the mixture stirring. After the ammonia allowing to evaporate, a greenish suspension was left which was hydrolyzed with ice. The mixture was extracted with chloroform. From the aqueous phase plus insoluble material 4.05 g lead sulphate was isolated (6.5%). The extract was dried on sodium sulphate and evaporated to dryness. The residue was recrystallized from acetone to give 39.7 g snow-white $(Me_3Pb)_4C$; yield 78%. The compound sublimed at about 170° (0.1 mm); it decomposed in a sealed glass capillary at about 220° without melting. (Found: C, 15.40; H, 3.76; Pb, 81.42; mol. wt. ebull. in benzene, 1069. $C_{13}H_{36}Pb_4$ calcd.: C, 15.29; H, 3.55; Pb, 81.16%; mol. wt., 1021.) NMR in $CDCl_3$ (Varian HA-100); $\delta$(Me) 0.73 ppm, $J(^{207}Pb\text{–}CH_3)$ 53 Hz.

A similar reaction with carbon tetrachloride gave only hexamethyldilead (yield 61%).

### *Reactions with triethylplumbylsodium*

From several reactions of triethylplumbylsodium with carbon tetrachloride or bromide no ethyl derivative could be isolated. The yellow oils obtained consisted mainly of hexaethyldilead (and possibly some tetraethyllead), and only small amounts of triethyllead bromide were isolated from them.

## ACKNOWLEDGEMENT

This work was sponsored by the International Lead Zinc Research Organization, Inc., New York (Director: Dr. Schrade F. Radtke). We are much indebted to Mr. H. J. H. van der Maas and Mr. G. J. Rotscheid for skilled experimental assistance.

## REFERENCES

1 L. C. WILLEMSENS AND G. J. M. VAN DER KERK, *J. Organometal. Chem.*, 21 (1970) 123.

2 L. C. WILLEMSENS AND G. J. M. VAN DER KERK, *Investigations in the field of organolead chemistry*, Org. Chem. Inst. TNO, Utrecht, ILZRO, New York, 1965, p. 41.

3 L. C. WILLEMSENS AND G. J. M. VAN DER KERK, *Recl. Trav. Chim. Pays-Bas*, 84 (1965) 43.

4 H. GILMAN AND D. AOKI, *J. Organometal. Chem.*, 1 (1964) 449.

5 J. KROON, J. B. HULSCHER AND A. F. PEERDEMAN, *J. Organometal. Chem.*, 23 (1970) 477.

6 E. KRAUSE AND O. SCHLÖTTIG, *Ber.*, 58 (1925) 427.

7 H. GILMAN AND E. BINDSCHADLER, *J. Organometal. Chem.*, 18 (1953) 1675.

8 L. C. WILLEMSENS AND G. J. M. VAN DER KERK, *J. Organometal. Chem.*, 15 (1968) 117.