

INVESTIGATIONS ON ORGANOLEAD COMPOUNDS

II*. THE REACTION OF TRIPHENYLPLUMBYLLITHIUM WITH SMALL-RING HETEROCYCLES: FUNCTIONALLY SUBSTITUTED ORGANOLEAD COMPOUNDS

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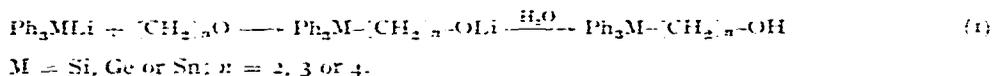
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INTRODUCTION

General methods for the preparation of functionally substituted organometallic compounds are not available in organometallic chemistry because in many cases rupture of the metal-carbon bonds occurs. In Group IV organometallic chemistry the element-carbon bond weakens when going from carbon to lead. Therefore, in this Group the preparation of functionally substituted compounds is least developed for lead.

An elegant method developed by Gilman *et al.*²⁻⁷ for the preparation of certain functionally substituted organic Group IV derivatives, is the ring opening of saturated small-ring oxygen heterocycles by triphenylmetallithium:

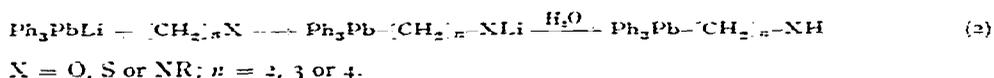


Thus, reactions of triphenylsilyllithium with epoxides², trimethylene oxide³ and tetrahydrofuran⁴ occur according to eqn. (1). In the last case a higher reaction temperature is required, indicating that the reaction is aided by strain in the heterocyclic ring. The reaction of triphenylgermyllithium with tetrahydrofuran⁵ and of triphenylstannylithium with ethylene oxide^{6,7} and with epichlorohydrin⁷ have also been described. No corresponding reactions in organolead chemistry or attempts to extend this reaction to other small-ring heterocycles have been reported.

We now report reactions of triphenylplumbyllithium with a number of reactive heterocycles, which resulted in the ready preparation of a series of new, functionally substituted organolead compounds.

PROCEDURE

The reaction



* For Part I see ref. 1.

was carried out as follows. A solution of triphenylplumbyllithium in tetrahydrofuran was added dropwise to a solution of the heterocycle at about -60° and the reaction mixture was allowed to come slowly to room temperature. Neutralization with glacial acetic acid, followed by the addition of ice and diethyl ether, gave two clear colourless layers (with the product in the organic layer) if the reaction had taken the expected course.

If the reaction had failed to run satisfactorily this was apparent from the formation of metallic lead during the reaction (pointing to decomposition of triphenylplumbyllithium) or from the occurrence, after hydrolysis, of a transient red colour (hydrolysis-oxidation of unreacted triphenylplumbyllithium; *cf. ref. 1*).

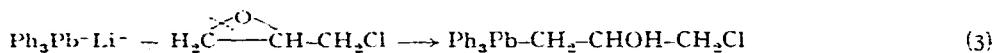
PRODUCTS

From three-membered rings

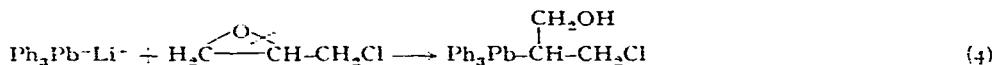
Three-membered rings containing oxygen or sulphur reacted satisfactorily with triphenylplumbyllithium. Thus, ethylene oxide gave (2-hydroxyethyl)triphenyllead and ethylene sulphide yielded (2-mercaptoethyl)triphenyllead. The latter compound is light-sensitive and in day-light turns black within a few days, probably because of the formation of lead sulphide, and was different from an authentic sample of triphenyllead ethyl sulphide⁸, Ph_3PbSEt . This observation furnishes additional structural evidence and, moreover, indicates the absence of secondary rearrangement.

The nitrogen-containing three-membered rings, ethylenimine and *N*-butylethylenimine, did not react with triphenylplumbyllithium. Even in a sealed Carius tube at 115° only slight decomposition of triphenylplumbyllithium was observed (separation of a small amount of metallic lead). No lithium-hydrogen exchange was observed in the reaction with ethylenimine but this is not unexpected in view of the stability of triphenylplumbylalkali compounds in liquid ammonia⁹. Acylated ethylenimines, however, reacted smoothly in the expected way, producing [2-(acylamino)-ethyl]triphenyllead compounds. Probably acylation weakens the carbon-nitrogen bonds in ethylenimine (acidification of ethylenimine causes rapid polymerization with ring opening), thus allowing ring opening by triphenylplumbyllithium.

Substituted ethylene oxides also reacted in the expected way. Thus, epichlorohydrin (1-chloro-2,3-epoxypropane) produced (3-chloro-2-hydroxypropyl)triphenyllead. Formally, two products can be formed depending on which C-O bond is split by triphenylplumbyllithium:



or



NMR data proved that only the linear product (eqn. 3) had been isolated. A doublet at 2.4 ppm ($J = 4$ cps) (becoming a singlet in the presence of a catalytic amount of trifluoroacetic acid) could be assigned to the hydrogen atom of a secondary OH group; the primary OH group of the branched product (eqn. 4) should have caused a triplet. For attempts to obtain chemical evidence see the section: DEGRADATION REACTIONS.

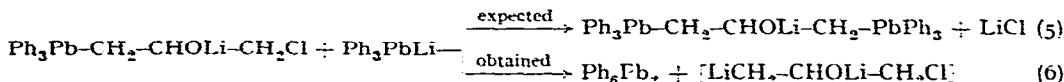
TABLE I
FUNCTIONALLY SUBSTITUTED ORGANOLEAD COMPOUNDS PREPARED

Starting heterocycle	Reaction product	Solvent for recrystallization	Yield ^a	M.p.	Analyses	Element	Found	Calcd.
					Formula			
	$\text{Ph}_3\text{Pb}-\text{CH}_2-\text{CH}_2\text{OH}$	petr. ether (60-80°)	91	72°	$\text{C}_{20}\text{H}_{30}\text{OPb}$	C	49.35	49.68
						H	4.26	4.16
						Pb	44.98	44.85
	$\text{Ph}_3\text{Pb}-\text{CH}_2-\text{CH}_2\text{SH}^b$	diethyl ether	90	104-106°	$\text{C}_{20}\text{H}_{30}\text{PbS}$	Pb	41.61	41.47
	$\text{Ph}_3\text{Pb}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{Ac}$	benzene	90	113°	$\text{C}_{23}\text{H}_{33}\text{NOPb}$	N	4.74	4.67
						Pb	39.13	39.49
	$\text{Ph}_3\text{Pb}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{Bz}^c$	benzene	67	130-138°	$\text{C}_{27}\text{H}_{35}\text{NOPb}$	N	4.39	4.40
						Pb	35.24	35.31
	$\text{Ph}_3\text{Pb}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2\text{Cl}$	petr. ether (60-80°)	96	93-91°	$\text{C}_{21}\text{H}_{31}\text{ClOPb}$	C	47.96	47.40
						H	3.95	3.98
						Pb	38.99	38.91
	$\text{Ph}_3\text{Pb}-\text{CH}_2-\text{CH}_2-\text{OH}$	hexane	89	99°	$\text{C}_{21}\text{H}_{32}\text{OPb}$	C	47.96	47.49
						H	3.95	3.98
						Pb	41.47	41.61
	$\text{HO}(\text{Ph})_2\text{Pb}-\text{CH}_2-\text{CH}_2-\text{COO}-\text{C}_6\text{H}_5^d$	d	76	20-210°	$\text{C}_{35}\text{H}_{43}\text{O}_2\text{Pb}_2$	C	40.88	41.00
						H	3.49	3.36
						Pb	47.40	47.15
	$\text{Ph}_3\text{Pb}-\text{CH}_2-\text{CH}_2-\text{COOMe}^e$	ethanol	95	52-5°	$\text{C}_{22}\text{H}_{32}\text{O}_2\text{Pb}$	C	50.33	50.27
						H	4.10	4.22
						Pb	39.48	39.43

^a Yields are based on the yield of benzyltriphenyllead in the reaction of triphenylmethyllead with benzyl chloride. ^b Mol. wt. found 535, calcd. 500. ^c In the infrared spectrum a -NH-CO- absorption is present. ^d Dissolved in aqueous alcoholic base and precipitated with acetic acid. ^e Obtained upon rapid treatment of the acidified reaction mixture with diazomethane.

As in the case of the reactions of Grignard reagents with epoxides¹⁰ and of organotin hydrides with unsaturated compounds¹¹, steric factors seem to dominate in determining the course of these reactions. Electronically the branched structure would be expected, but sterically the linear structure is favoured.

Reaction of two moles of triphenylplumbyllithium with one mole of epichlorohydrin did not give $\text{Ph}_3\text{Pb}-\text{CH}_2-\text{CHOH}-\text{CH}_2-\text{PbPh}_3$. Instead, the second mole of triphenylplumbyllithium cleaved the 1:1 addition product:

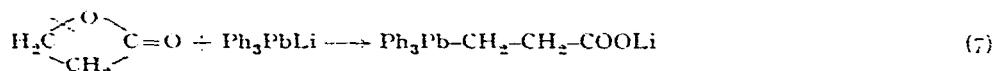


A 75 % yield of hexaphenyldilead was obtained based on eqn. (6).

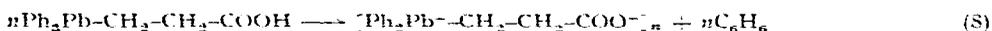
From four-membered rings

Trimethylene oxide reacted smoothly with triphenylplumbyllithium to give (3-hydroxypropyl)triphenyllead. Surprisingly, trimethylene sulphide did not react at room temperature: at elevated temperatures only an impure oil could be obtained. Because it is difficult to obtain, trimethylenimine was not investigated, but in view of the inertness of ethylenimine and trimethylene sulphide, it will probably not react.

The reaction with β -propiolactone was interesting:



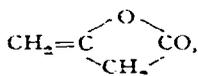
The product isolated after acidification with one equivalent of acetic acid resulted from elimination of benzene from the expected (2-carboxyethyl)triphenyllead*:



The compound shows polymeric properties and is soluble only in dilute alcoholic-aqueous base, from which it precipitates upon neutralization with acetic acid.

That (2-carboxyethyl)triphenyllead was the primary reaction product, was proved as follows. After completion of the reaction, double the amount of acetic acid was added at -60° (to ensure that all of the reaction product was in the acid form), immediately followed by addition of an excess of an ethereal solution of diazomethane. Treatment with water, and extraction with ether, gave the methyl ester, [2-(methoxycarbonyl)ethyl]triphenyllead, $\text{Ph}_3\text{Pb}-\text{CH}_2-\text{CH}_2-\text{COOMe}$ (83 %).

Ketene dimer, of which the most probable structure is



caused decomposition of triphenylplumbyllithium (lead separation). Possibly it reacted in the form of one of its tautomers.

* The corresponding organotin compound shows similar behaviour¹².

Attempts with five-membered rings

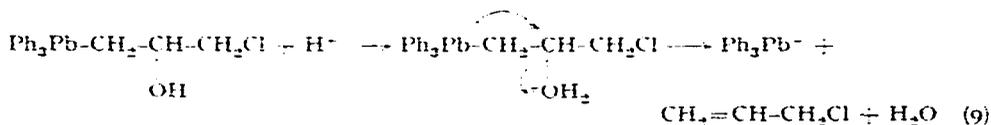
Triphenylplumbyllithium did not react with five-membered heterocycles (*e.g.* tetrahydrofuran), even when heated for 6 hours at 115° in a Carius tube. Treatment of such a reaction mixture with benzyl chloride gave the same yield of benzyltriphenyllead as without any preheating. Incidentally, the experiment gives evidence for the remarkable thermal stability of triphenylplumbyllithium and for the somewhat lower reactivity of the reagent compared with the corresponding silicon⁴ and germanium⁵ derivatives, which have been reported to give (4-hydroxybutyl)triphenylmetal derivatives with tetrahydrofuran.

Reaction of triphenylplumbyllithium with pyrrolidone (γ -butyrolactam) resulted in separation of metallic lead. It is clear that, no strain in the ring being present, the normal reaction of triphenylplumbyllithium with carbonyl compounds takes place⁹.

DEGRADATION REACTIONS

As pointed out two products could theoretically be formed upon reacting triphenylplumbyllithium with epichlorohydrin: viz. $\text{Ph}_3\text{Pb}-\text{CH}_2-\text{CHOH}-\text{CH}_2\text{Cl}$ and/or $\text{Ph}_3\text{Pb}-\text{CH}(\text{CH}_2\text{OH})-\text{CH}_2\text{Cl}$. The NMR spectrum of the isolated product pointed unequivocally to the former structure.

In attempts to obtain chemical evidence for this structure, the reaction product was treated with one equivalent of hydrogen chloride in diethyl ether. The cleavage product was allyl chloride which gives no information about the structure of the original material chlorination of which resulted in elimination of phenyl groups. Here we see a discrepancy between the cleavage by acid and by halogen*. The phenyl group is the more electronegative one and thus primarily elimination of the phenyl group by electrophilic agents is to be expected. The abnormal cleavage by acid may be explained by assuming protonation of the hydroxyl group, followed by an electron shift towards the oxygen atom:



Such a mechanism has been proposed in organosilicon chemistry¹⁴ to explain the ready cleavage of $(\text{Alkyl})_3\text{SiCH}_2\text{X}$ compounds ($\text{X} = -\text{CO}-\text{R}, -\text{CN}, \text{etc.}$). As far as it is known, it has not been recognized in organotin and organolead chemistry that groups such as $-\text{CH}_2-\text{C}(\text{OH})\text{R}_2$, $-\text{CH}_2-\text{CO}-\text{R}$, $-\text{CH}_2-\text{CN}$, may be eliminated more readily than the phenyl group by acids but not by free halogens. Although the initial purpose, the chemical determination of the structure of the epichlorohydrin product, so far has not been attained, the experiment nevertheless has pointed the attention to the different modes of cleavage of certain Group IV compounds by electrophilic reagents.

* The same kind of discrepancy has been observed in the cleavage of (cyanomethyl)triphenyltin: the cyanomethyl group is extremely readily removed from this compound, but iodination causes elimination of a phenyl group¹⁵.

EXPERIMENTAL

Starting materials

The commercially available ethylene oxide, epichlorohydrin, ethylenimine, β -propiolactone, tetrahydrofuran and pyrrolidone were freshly distilled before use.

The remaining heterocycles studied were prepared according to methods described in the literature. Ethylene sulphide¹⁵ was prepared from potassium thiocyanate and ethylene carbonate in a yield of 67 %; b.p. 54–55°, n_D^{20} 1.4958 (reported¹⁵ yield 68–75 %, b.p. 54–54.5°, n_D^{20} 1.4960). *N*-Butylethylenimine¹⁶ was prepared by ring closure of 2-(butylamino)ethanol hydrochloride with chlorosulphonic acid in a yield of 54 %; b.p. 105–108°, n_D^{25} 1.4119 (reported¹⁶ yield 67 %, b.p. 106–108°, n_D^{25} 1.4118). *N*-Acetythylenimine¹⁷ (slightly unstable) was prepared from ethylenimine and ketene; b.p. 41–42.5°/19 mm, n_D^{20} 1.4378 (reported¹⁷ b.p. 42°/20 mm). *N*-Benzoyl-ethylenimine¹⁸ was prepared from ethylenimine and benzoyl chloride in aqueous carbonate in a yield of 82 %; m.p. 5° (reported¹⁸ yield 70 %, m.p. 5°). Trimethylene oxide¹⁹ was obtained by ring closure of 3-chloropropyl acetate with a strong base in a yield of 54 %; b.p. 47–48°; n_D^{20} 1.3905 (reported¹⁹ yield 42–44 %, b.p. 47–48°, n_D^{23} 1.3905). Trimethylene sulphide²⁰ was prepared from 1-bromo-3-chloropropane and thiourea in a yield of 76 %; b.p. 95–96°, n_D^{20} 1.5058 (reported²⁰ yield 53.5 %, b.p. 95°, n_D^{21} 1.5102). Ketene²¹ dimer was prepared by pyrolysis of acetone and dimerization of the ketene formed in a yield of 42 %; b.p. 67–71°/92 mm, n_D^{20} 1.4355 (reported²¹ yield 50–55 %, b.p. 67–69°/92 mm).

Triphenylplumbyllithium was prepared by the method of Tamborski *et al.*²² from 100.5 g of hexaphenyldilead (1/8 mole) and 1.8 g of lithium (1/4 g-atom) in 300 ml of tetrahydrofuran in an atmosphere of pure nitrogen*. Care was taken (by working at about –10° and with an equivalent of lithium) that excess of lithium did not attack the triphenylplumbyllithium formed (producing metallic lead). The dark reaction mixture, containing finely divided, very slowly settling, black material (probably metallic lead), was transferred to a storage bottle under nitrogen and the volume added up to 400 ml with tetrahydrofuran. For reactions 25-ml aliquots, theoretically containing 1/64 mole of triphenylplumbyllithium, were used. Reaction of the clear solution with benzyl chloride afforded a yield of 75–90 % of benzyltriphenyllead.

Reactions of triphenylplumbyllithium with small-ring heterocycles

(a) *Standard procedure.* As a typical reaction that with epichlorohydrin is described. To a solution of 1.4 g epichlorohydrin (1/64 mole) in 15 ml tetrahydrofuran was added dropwise 25 ml of the triphenylplumbyllithium solution at –60° with stirring under nitrogen. The reaction was allowed to come to room temperature. After one hour stirring of the clear solution, hydrolysis of a small sample in a test tube produced two colourless layers. The mixture was chilled to about –40° and glacial acetic acid (\approx 1.5 ml) was added dropwise with stirring until neutral to wet pH paper. Slimy lithium acetate precipitated. Cold water and diethyl ether were added, the ethereal layer was separated, dried on sodium sulphate and evaporated to dryness.

* Triphenylplumbyllithium, as prepared in good yield from lead dichloride and phenyllithium²³, also gives satisfactory results in many of the reactions with small-ring heterocycles. However, in running many preparations, it is convenient to have available a stock solution of triphenylplumbyllithium. Moreover in some cases the reversed procedure (addition of the heterocycle to triphenylplumbyllithium) is to be avoided because of possible side-reactions.

The residue was recrystallized from petr. ether (60–80°) to give (3-chloro-2-hydroxypropyl)triphenyllead.

When in another experiment double the amount of triphenylplumbyllithium was added, hexaphenyldilead (76%) and tetraphenyllead (10%) were isolated.

(b) *Reaction with β -propiolactone.* The reaction was carried out as under (a). The mixture was hydrolyzed without prior neutralization. Addition of ether gave an aqueous layer, an ethereal layer and a small amount of viscous oil [probably the lithium salt of (2-carboxyethyl)triphenyllead] which disappeared when 3 ml of acetic acid was added. Evaporation of the dried organic layer gave 7.1 g of a solid residue, which could only partly be dissolved again. Attempts to isolate pure (2-carboxyethyl)triphenyllead failed because of gradual intramolecular elimination of benzene. The residue was refluxed for 1 h in alcohol to complete this elimination. Filtration gave 5.2 g of a product which was dissolved in a mixture of 20 ml of water, 20 ml of alcohol and 0.6 g of sodium hydroxide, 0.7 g of insoluble material being discarded. The yellow solution was decolourized with carbon black. Addition of 0.9 g of acetic acid mixed with 5 ml of water caused precipitation of 4.5 g of $\text{HO}(\text{Ph}_2\text{PbCH}_2\text{CH}_2\text{COO})_3\text{H}$, a polymeric material, decomposing above 240° with blackening.

In a second experiment the reaction mixture [obtained from 4.3 g of propiolactone (60 mmole) and 50 ml of triphenylplumbyllithium (theoretically 34.5 mmole)] was acidified at –60° with 4.5 g of acetic acid (75 mmole) (when slimy lithium acetate precipitated), followed rapidly by addition of excess of ethereal diazomethane solution. The mixture was allowed to come to room temperature and treated with water. The dried ethereal layer was evaporated to dryness in vacuo and the residue recrystallized from 100 ml of ethyl alcohol (with treatment with carbon black) to give [2-(methoxycarbonyl)ethyl]triphenyllead, $\text{Ph}_2\text{Pb}-\text{CH}_2-\text{CH}_2-\text{COOMe}$.

(c) *Attempted reaction with tetrahydrofuran.* The clear, brown-yellow solution of triphenylplumbyllithium in tetrahydrofuran (25 ml) was sealed in a Carius tube under nitrogen and shaken for 6 h at 115°. After being cooled to room temperature the tube was opened, no gas pressure appearing to be present. The mixture was now clear yellow with a little black sludge at the bottom. Probably, the colloidal lead had coagulated under these conditions. An excess of benzyl chloride (3.0 g) was added and after 10 min the mixture was hydrolyzed and extracted with chloroform to give 6.8 g of benzyltriphenyllead (82.5%). Direct treatment with benzyl chloride (without heating in a Carius tube) had given 7.2 g of benzyltriphenyllead (87%).

Degradation reactions of (3-chloro-2-hydroxypropyl)triphenyllead

(a) *With hydrogen chloride.* To a solution of 1 g of (3-chloro-2-hydroxypropyl)triphenyllead (1.88 mmole) in 10 ml of dry diethyl ether was added 0.31 ml of 12 N hydrochloric acid (3.72 mmole) and the mixture was shaken for 2 h at room temperature. The precipitate (Ph_2PbCl_2) was centrifuged off and the ethereal solution was dried on sodium carbonate and sodium sulphate. Gas chromatography of this solution revealed allyl chloride and benzene as the only products in the ether.

(b) *Chlorination.* To a stirred solution of 1.005 g of (3-chloro-2-hydroxypropyl)triphenyllead (1.0 mmole) in 5 ml of carbon tetrachloride at –20° was added dropwise 4.5 ml of 1.75 N solution of chlorine (8 mg-atom) in carbon tetrachloride within 2 min. The chlorine reacted immediately and the thick precipitate which formed was centrifuged off. The neutral solution was gas-chromatographed to show chlorobenzene

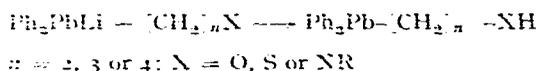
as the only product. The precipitate (820 mg, 96.5 %) was dissolved in 15 ml of ethyl acetate and carefully precipitated twice with 40 ml of petr. ether (40–60°) to give (3-chloro-2-hydroxypropyl)phenyllead dichloride, decomposing at about 135°. (Found: ionic Cl, 15.92. $C_9H_{11}Cl_3OPb$. calcd.: ionic Cl, 15.80 %.)

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SUMMARY

The reactions between triphenylplumbyllithium and small-ring heterocycles have been studied.



The reaction ran successfully with the following heterocycles: ethylene oxide, ethylene sulphide, *N*-acylethylenimines and trimethylene oxide. No reaction occurred with ethylenimine, *N*-butylethylenimine, trimethylene sulphide and tetrahydrofuran. Some substituted rings also reacted in the expected way: epichlorohydrin gave a linear product, $Ph_3Pb-CH_2-CHOH-CH_2Cl$, and β -propiolactone gave primarily $Ph_3Pb-CH_2-CH_2-COOH$, which, however, spontaneously lost one molecule of benzene to give $Ph_2Pb^--CH_2-CH_2-COO^-$; with diazomethane the acid could be trapped as the methyl ester. Ketene dimer and pyrrolidone caused decomposition of triphenylplumbyllithium.

Treatment of the epichlorohydrin product, $Ph_3Pb-CH_2-CHOH-CH_2Cl$, with one equivalent of hydrogen chloride resulted in the elimination of the $-CH_2-CHOH-CH_2Cl$ group; whereas chlorination led merely to elimination of phenyl groups. This discrepancy is explained by assuming that protonation of the hydroxyl group (in case of treatment with hydrogen chloride) facilitates separation of the $-CH_2-CHOH-CH_2Cl$ group.

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