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INVESTIGATIONS ON ORGANOLEAD COMPOUNDS
VII*. THE PREPARATION OF HEXAARYLDILEADS**

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SUMMARY

Hexaaryldilead compounds have been prepared in high yield from lead dichloride, arylmagnesium halides and 1,2-dichloro- or 1,2-dibromoethane:

$$2\ PbCl_2 + 6\ ArMgX \rightarrow 2\ Ar_3PbMgX + 4\ MgClX$$

$$2\ Ar_3PbMgX + XCH_2CH_2X \rightarrow Ar_6Pb_2 + 2\ MgX_2 + H_2C{=}CH_2\uparrow$$

Ar = phenyl, *o*- *m*- and *p*-tolyl, *p*-methoxyphenyl, and 1- and 2-naphthyl

A mechanism for this reaction is proposed.

INTRODUCTION

Hexaaryldilead compounds, $Ar_3Pb{-}PbAr_3$ have previously been prepared from lead dichloride and arylmagnesium halides in ether solvents. It is generally assumed that in these reactions diarylleads exist as unstable intermediates which readily disproportionate into hexaaryldileads and metallic lead[2]:

$$PbCl_2 + 2\ ArMgCl \rightarrow Ar_2Pb + 2\ MgCl_2 \quad (1)$$

$$3\ Ar_2Pb \rightarrow Ar_6Pb_2 + Pb \quad (2)$$

In 1919 Krause and coworkers reported the first hexaaryldilead compounds, *viz.* hexa-2,5-xylyldilead[3], which was followed a few years later by the preparation of the phenyl derivative[4] in a yield of 40%. Recently, we slightly modified Krause's procedure for preparing hexaphenyldilead, but in no case could we obtain yields better than 75% [based on eqns. (1) and (2)][2,5]. Hexa-*o*-tolyldilead[4] has been prepared in 50% yield, the *m*-derivative[6] in 38% yield, and the *p*-derivative[4] in 50% yield. Hexa-1-naphthyldilead[7] could only be made in a yield not exceeding 10% (we obtained a similar result with this method[8]). Hexa-2-naphthyldilead has not previously been made.

Hexaaryldileads are important intermediates in the preparation of other aryllead compounds, *e.g.* oxidative cleavage of the lead–lead bond of hexaphenyldilead

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* For Part VI see ref. 1.

** A patent has been applied for.

results in the formation of triphenyllead salts without loss of phenyl groups[5]. However, disadvantages of the above method of preparation of hexaaryldileads (eqns. 1 and 2) are the moderate to low yields and the formation of metallic lead. In this paper we report on a new method, also starting from lead dichloride and Grignard reagents, which gives nearly quantitative yields without formation of metallic lead.

RESULTS AND DISCUSSION

Preparation of hexaphenyldilead

Bindschadler[9] has briefly reported that triphenylplumbylsodium reacted with 1,2-dibromoethane to give hexaphenyldilead in good yield. On the other hand, Gorth and Henry[10] isolated tetraphenyllead in 70% from a reaction between triphenylplumbyllithium and 1,2-dibromoethane. We have confirmed the result of Bindschadler.

$$2\,Ph_3PbNa + BrCH_2CH_2Br \;\begin{cases} \rightarrow Ph_6Ph_2 + H_2C{=}CH_2 + 2\,NaBr & (3) \\ \not\rightarrow Ph_3Pb{-}CH_2CH_2{-}PbPh_3 + 2\,NaBr & (4) \end{cases}$$

Since this reaction was aimed at the preparation of ethylenebis(triphenyllead), at first the result was disappointing, the more so because the sodium reagent had been prepared from hexaphenyldilead[1]. On the other hand, the corresponding magnesium reagent can be prepared directly from lead dichloride and phenylmagnesium chloride[1] in a 1/3 ratio, and this reagent thus looked very attractive for the preparation of hexaphenyldilead, particularly since 1,2-dichloroethane could be used instead of the bromo analogue:

$$2\,Ph_3PbMgCl + ClCH_2CH_2Cl \rightarrow Ph_6Pb_2 + H_2C{=}CH_2\uparrow + 2\,MgCl_2 \tag{5}$$

Yields of *ca.* 95% were in fact, obtained from this reaction. At room temperature the reaction is rather slow and requires at least 5 hours stirring. The presence of excess phenylmagnesium chloride (used in the preparation of the lead–magnesium reagent) is not harmful. It does not seem to react with 1,2-dichloroethane, as shown by a positive Gilman test[11] at the end of the reaction after standing overnight or 2 h of reflux.

With 1,2-dibromoethane the reaction is much faster, being complete within half a minute after the addition of this reagent. In this case excess of phenylmagnesium *bromide* gave rise to tetraphenyllead in addition to hexaphenyldilead, *viz.* when the reaction mixture was hydrolyzed after a reaction period of 30 *minutes*; however, when the reaction period was only *half a minute*, solely hexaphenyldilead was isolated. This proves that tetraphenyllead is formed in a secondary reaction of hexaphenyldilead with phenylmagnesium *bromide*[5]. Remarkably enough, phenylmagnesium *chloride* did not react with hexaphenyldilead under these conditions. This difference in reactivity between the chloride and the bromide was further demonstrated by the following reactions:

$$PbCl_2 + 4\,PhMgCl \rightarrow Ph_3PbMgCl + PhMgCl + 2\,MgCl_2$$

$$\xrightarrow[\text{2h reflux}]{ClCH_2CH_2Cl} Ph_6Pb_2\ (86\%) \tag{6}$$

$$\begin{tikzcd}
\mathrm{PbCl_2 + 4\,PhMgBr} \arrow[r] & \mathrm{Ph_3PbMgBr + PhMgBr + 2\,MgClBr} \arrow[d, "\mathrm{ClCH_2CH_2Cl}", "\text{2h reflux}"'] \\
 & \mathrm{Ph_6Pb_2} \arrow[d, "\mathrm{PhMgBr}"] \\
 & \mathrm{Ph_3PbMgBr + Ph_4Pb\ (80\%)} \arrow[uu, bend left]
\end{tikzcd} \qquad (7)$$

Mechanistic evidence

The following experiments and considerations throw light on the mechanism of the formation of hexaphenyldilead.

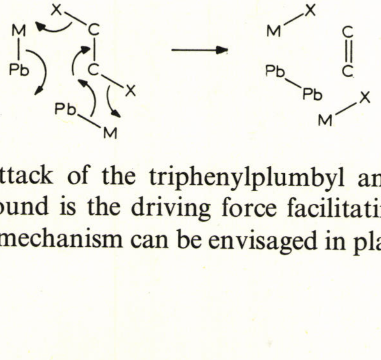
The occurrence of triphenyllead chloride as an intermediate (generated by an elimination or exchange reaction) is eliminated by the following evidence. As stated above, the presence of excess phenylmagnesium chloride does not affect the yield of hexaphenyldilead. Thus, if triphenyllead chloride were an intermediate, it would have to react exclusively with (triphenylplumbyl)magnesium chloride (to give hexaphenyldilead) and not with phenylmagnesium chloride (which would give tetraphenyllead). However, when triphenyllead chloride (1 mole) was added slowly to a 1/1 mixture of (triphenylplumbyl)magnesium chloride and phenylmagnesium chloride (1 mole each) 44% of it was converted into hexaphenyldilead, and 53% into tetraphenyllead:

$$\begin{tikzcd}
 & \mathrm{Ph_6Pb_2 + MgCl_2} \\
\begin{matrix}\mathrm{Ph_3PbMgCl}\\ +\\ \mathrm{PhMgCl}\end{matrix} + \mathrm{Ph_3PbCl} \arrow[ur, "44\%"] \arrow[dr, "53\%"'] & \\
 & \mathrm{Ph_4Pb + MgCl_2}
\end{tikzcd} \qquad (8)$$

Interesting results were obtained in the reaction of (triphenylplumbyl)magnesium halide with *cis*- and *trans*-1,2-dibromocyclohexane. The *trans* compound reacted rapidly to give 89% hexaphenyldilead, but the *cis* analogue hardly reacted. This proves that bromine atoms are only readily eliminated when in the *trans* position.

This is in agreement with Winkler's results on the stereospecific reaction of phenyllithium with *meso*- and DL-2,3-dibromobutane[12], in which *trans*- and *cis*-2-butene are formed respectively. On the other hand, Winkler's reactions yielded 80% bromobenzene, whereas in our case the triphenyllead halide did not even occur as an intermediate (see above). This may be a consequence of the generally observed nucleophilic attack of the phenyl anion at halogen, whereas the triphenylplumbyl anion prefers to attack at carbon. [Compare the usual *exchange* reactions of organolithium reagents with the *coupling* reactions of (triphenylplumbyl)metal reagents with organic halides[1].]

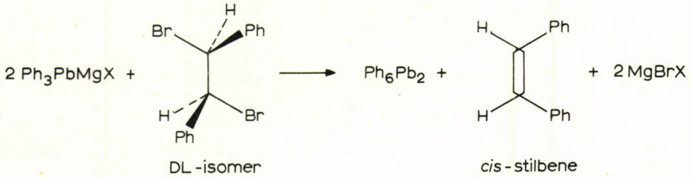
In view of the evidence obtained the following mechanism is suggested:



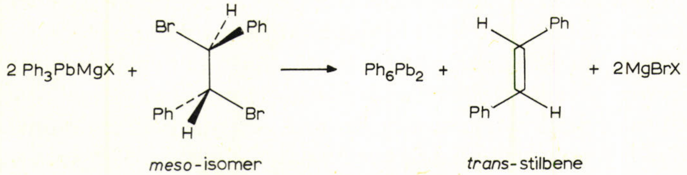
(9)

The attack of the triphenylplumbyl anion on the carbon atom of the 1,2-dihalo compound is the driving force facilitating the elimination of the halogen atoms. A chain mechanism can be envisaged in place of a cyclic mechanism.

The *trans* elimination was further corroborated by reacting (triphenylplumbyl)-magnesium halide with α,α′-dibromobibenzyl: the DL isomer yielded 78% *cis*-stilbene (plus 21% *trans*-stilbene), whereas the *meso* isomer gave exclusively *trans*-stilbene (98%):



(10)



(11)

Preparation of other hexaaryldileads

The new method proved to be very satisfactory for the preparation of other hexaaryldileads (see Tables 1 and 2). In particular the naphthyl derivatives, which previously were almost inaccessible, were obtained in excellent yield. Because of the higher reaction velocity mostly 1,2-dibromoethane was used. Excess Grignard reagent was avoided and the reaction mixtures were hydrolyzed with ice as soon as evolution of heat had ceased; otherwise the hexa derivative sometimes slowly decomposed under the reaction conditions to give tetraaryllead, as was found for the 2-naphthyl derivative.

Hexa-1-naphthyldilead differs greatly from the other hexaaryldileads prepared in being practically insoluble in all solvents tried and decomposing at a markedly higher temperature (*ca.* 280°).

TABLE 1

PREPARATION OF HEXAARYLDILEADS FROM (TRIARYLPLUMBYL)MAGNESIUM HALIDES (Ar_3PbMgX) AND EXCESS OF 1,2-DIHALOETHANES ($X'CH_2CH_2X'$) IN TETRAHYDROFURAN

Reactants			Reaction period (h)	Product	Yield (%)	Lit. yield (%)[b]	M.p. (°C) *ca.*	Recrystn. solvent
Ar[a]	X	X′						
Ph	Cl	Cl	20	Ph_6Pb_2	95	75(ref. 5)	155 dec.	$CHCl_3$/EtOH
o-Tol	Cl	Br	3	*o*-Tol_6Pb_2	77	50(ref. 4)	230 dec.	$CHCl_3$
m-Tol	Br	Br	0.3	*m*-Tol_6Pb_2	75	38(ref. 6)	109	MeCOMe
p-Tol	Br	Br	0.15	*p*-Tol_6Pb_2	99	50(ref. 4)	244 dec.	$CHCl_3$/EtOH
p-An	Br	Br	0.15	*p*-An_6Pb_2	78	57(ref. 7)	196 dec.	$CHCl_3$/EtOH
1-Np	Br	Br	20	1-Np_6Pb_2	98	10(ref. 7)	280 dec.	*m*-$C_6H_4Cl_2$
2-Np	Br	Br	0.3	2-Np_6Pb_2	83		200 dec.	$CHCl_3$/EtOH

[a] Ar=aryl; Tol=tolyl; An=anisyl, $MeOC_6H_4$; Np=naphthyl. [b] Based on: $3\ PbCl_2+6\ ArMgX \rightarrow Ar_6Pb_2+Pb+6\ MgX_2$.

TABLE 2

ANALYTICAL DATA OF THE HEXAARYLDILEADS PREPARED

Ar_6Pb_2	Analyses, found (calcd.) (%)					
	C		H		Pb	
o-Tol_6Pb_2	52.28	(52.48)	4.49	(4.41)	43.22	(43.11)
m-Tol_6Pb_2[a]	52.52	(52.48)	4.48	(4.41)	43.18	(43.11)
p-Tol_6Pb_2	52.57	(52.48)	4.45	(4.41)	43.01	(43.11)
p-An_6Pb_2	47.88	(47.72)	3.96	(4.00)	39.29	(39.20)
1-Np_6Pb_2	61.03	(61.21)	3.77	(3.60)	34.81	(35.19)
2-Np_6Pb_2	60.82	(61.21)	3.66	(3.60)	35.10	(35.19)

[a] Mol. wt. osmometrically found in benzene 934, calcd. 961.

EXPERIMENTAL PART

General

All reactions were carried out under nitrogen as a precautionary measure. The tetrahydrofuran used had been distilled from lithium aluminium hydride and stored under nitrogen. The Grignard reagents were prepared in the usual manner from magnesium turnings and the corresponding organic halide in tetrahydrofuran; sometimes the reaction was started by adding a few drops of 1,2-dibromoethane. The concentration was determined by a double titration technique[13]; the yields were about 90%.

Reactions of (triphenylplumbyl)magnesium halides with 1,2-dihalo compounds

(a). With 1,2-dichloroethane. Preparation of hexaphenyldilead. To a solution of 300 mmole phenylmagnesium chloride in 150 ml tetrahydrofuran under nitrogen, lead dichloride (27.8 g, 100 mmole) was added in small portions with stirring at 5°, and the mixture was subsequently gently warmed to about 30° to dissolve all lead dichloride. The mixture gave a negative (or very weakly positive) Gilman test[11] which showed that (nearly) all the Grignard reagent had reacted. 1,2-Dichloroethane (19.8 g, 200 mmole) was added at once at room temperature. The mixture slowly thickened, with formation of a cream-coloured precipitate. After standing overnight, the mixture was poured onto ice, carefully neutralized with acetic acid and extracted with chloroform. The dried (Na_2SO_4) extract was evaporated to dryness. The residue gave a clear solution in the minimum amount of cold chloroform (*ca.* 150 ml), which showed that the material was essentially free of tetraphenyllead. About 150 ml 96% ethanol was added to precipitate hexaphenyldilead (41.4 g, 47.5 mmole, 95%). On the Kofler hot stage it melted at about 170° rapidly followed by blackening and solidification, a behaviour which is typical for hexaphenyldilead.

When 400 mmole phenylmagnesium chloride was used (thus leaving 100 mmole unreacted), the reaction mixture showed a positive Gilman test even after standing overnight in presence of an excess of 1,2-dichloroethane. Hydrolytic work-up gave 41.2 g hexaphenyldilead (47 mmole, 94%). When the same reaction mixture after the addition of 1,2-dichloroethane was refluxed for 2 h (Gilman test remained positive), 86% hexaphenyldilead and 6% tetraphenyllead were obtained after the usual work-up.

When the lead–magnesium reagent was prepared from lead dichloride and an excess of phenylmagnesium *bromide* (thus leaving 100 mmole PhMgBr unreacted), the Gilman test was negative after reflux for 2 h with excess 1,2-dichloroethane. The products isolated after the usual work-up were 14% hexaphenyldilead and 80% tetraphenyllead.

(*b*). *With* 1,2-*dibromoethane*. (Triphenylplumbyl)magnesium halide was prepared as described under (*a*) from 300 mmole phenylmagnesium bromide and 100 mmole lead dichloride in tetrahydrofuran. The mixture gave a weakly positive Gilman test. 1,2-Dibromoethane (28.2 g, 150 mmole) was added at once at about 5°. The colour immediately turned white, and the temperature rose to 25°. About 800 ml gas were evolved (*ca.* 35 mmole or 70%). After half an hour stirring the mixture was worked up as described under (*a*). The crude residue did not dissolve completely in cold chloroform. Filtration gave 1.6 g tetraphenyllead (3.1 mmole, 3%). Precipitation with ethanol yielded 40.5 g hexaphenyldilead (46.2 mmole, 92%).

A similar experiment was carried out using a stoichiometric amount of 1,2-dibromoethane (9.4 g, 50 mmole). The yield of hexaphenyldilead was 41.8 g (47.7 mmole, 95%). The amount of gas evolved was *ca.* 400 ml (*ca.* 17 mmole, *ca.* 35%).

When 100 mmole *excess* phenylmagnesium bromide and excess 1,2-dibromoethane were used for the reaction, hydrolytic work-up after 30 *min* stirring at room temperature gave 42.5 g tetraphenyllead (82.5 mmole, 82.5%) and 6.0 g hexaphenyldilead (6.85 mmole, 14%). However, when the same reaction mixture was hydrolyzed with ice *half a minute* after the addition of 1,2-dibromoethane, exclusively hexaphenyldilead was isolated (42.9 g, 49 mmole, 98%).

(*c*). *With* DL-*α,α′-dibromobibenzyl*. (Triphenylplumbyl)magnesium halide was prepared from 1.4 g lead dichloride (5 mmole) and 15 mmole phenylmagnesium bromide in tetrahydrofuran. DL-α,α′-dibromobibenzyl[14] (0.85 g, 2.5 mmole) was added at once at 5°. After 2½ min the mixture was poured onto ice and extracted with chloroform. After concentration *in vacuo*, ethanol was added, and the precipitated hexaphenyldilead was filtered off (2.1 g, 2.4 mmole, 96%). The filtrate was shown to contain 78% *cis*- and 21% *trans*-stilbene by means of gas chromatography.

(*d*). *With meso-α,α′-dibromobibenzyl. meso*-α,α′-Dibromobibenzyl[15] (8.5 g, 25 mmole) was added at once at 5° to a tetrahydrofuran solution of 50 mmole triphenylplumbylmagnesium halide. The temperature rose to 12°. After 3 h stirring the mixture was poured onto ice and extracted with chloroform. Precipitation with ethanol gave 18.8 g hexaphenyldilead (21.5 mmole, 86%). From the filtrate 4.4 g *trans*-stilbene (24.5 mmole, 98%) was isolated (mixed m.p. 124°).

(*e*). *With trans*-1,2-*dibromocyclohexane*. The reaction of 2.4 g *trans*-1,2-dibromocyclohexane[16] (10 mmole) with 20 mmole (triphenylplumbyl)magnesium halide gave, following hydrolysis after 5 min, 7.8 g hexaphenyldilead (8.9 mmole, 89%).

(*f*). *With cis*-1,2-*dibromocyclohexane*. To 20 mmole triphenylplumbylmagnesium halide, prepared as described under (*b*), in tetrahydrofuran was added at 0° 2.4 g *cis*-1,2-dibromocyclohexane[17] (10 mmole). No heat evolution was observed, and the mixture remained positive for triphenylplumbylmetal reagent[1] after 2½ h stirring at room temperature. Then, the mixture was poured onto ice, neutralized with acetic acid and extracted with chloroform. From the aqueous phase 4.8 g lead sulphate (15.8 mmole, 79%) was precipitated with sulphuric acid. The organic phase, after concentration and addition of ethanol, gave 0.8 g precipitate which proved to consist of 0.5 g hexaphenyldilead (0.6 mmole, 6%) and 0.2 g tetraphenyllead (0.4 mmole, 4%). From the filtrate 2.1 g *cis*-1,2-dibromocyclohexane was recovered (88%).

Competitive reactions of (triphenylplumbyl)magnesium halides and phenylmagnesium halides with triphenyllead halides

(*a*). *All halide is chloride.* Lead dichloride (27.8 g, 100 mmole) was added in portions with stirring to 400 mmole phenylmagnesium chloride in 225 ml tetrahydrofuran at *ca.* 5°. After all lead dichloride had dissolved (at 25–30°), the Gilman test was still strongly positive. A solution of 47.4 g triphenyllead chloride (100 mmole) in 200 ml tetrahydrofuran was added slowly with stirring at 5–10° over a period of 25 min. During the addition the mixture slowly turned lighter and a precipitate formed. The Gilman test remained positive. Hydrolytic work-up gave 27.2 g tetraphenyllead (52.8 mmole, 53% based on Ph_3PbCl), 37.6 g hexaphenyldilead (42.7 mmole, 43% based on Ph_3PbCl) and 13.4 g lead sulphate (40.8 mmole, 41%).

In a repeat experiment (starting from Grignard reagent of the same batch) about the same amounts of tetraphenyllead (52.8 mmole, 53%), hexaphenyldilead (44.1 mmole, 44%) and lead sulphate (41.2 mmole, 41%) were isolated.

In a third experiment on a 10 mmole scale, the triphenyllead chloride solution was added at once at 7°. The temperature rose to 17°. One minute after the addition the mixture was poured onto ice. Work-up gave 5.1 g hexaphenyldilead (5.8 mmole, 58%), 1.7 g tetraphenyllead (3.3 mmole, 33%), 0.4 g triphenyllead chloride (0.8 mmole, 8%) and 1.1 g lead sulphate (3.6 mmole, 36%).

(*b*). *All halide is bromide.* Lead dibromide (3.7 g, 10 mmole) was added in portions to 40 mmole phenylmagnesium bromide in 45 ml tetrahydrofuran at 5°. After stirring for 1 h (Gilman test strongly positive), 5.2 g triphenyllead bromide (10 mmole) in 40 ml tetrahydrofuran was added at once. The temperature rose to 11°. Work-up gave 7.5 g hexaphenyldilead (8.6 mmole, 86%) and 0.5 g triphenyllead bromide (1.0 mmole, 10%). No inorganic lead and no tetraphenyllead could be isolated.

Preparation of other hexaaryldilead compounds

The hexaaryldilead compounds listed in Table 1 were prepared from 3 mole part of the relevant arylmagnesium bromide, 1 mole part lead dichloride and 1-1.5 mole part 1,2-dibromoethane (excess) in tetrahydrofuran analogously to the procedure described for hexaphenyldilead. As examples the preparations of hexa-1- and -2-naphthyldilead are described below.

(*a*). *Hexa-*1*-naphthyldilead.* Lead dichloride (27.8 g, 100 mmole) was added in small portions to a well-stirred solution of 300 mmole 1-naphthylmagnesium bromide in *ca.* 600 ml tetrahydrofuran at 0°. After stirring for 1½ h, the Gilman test was very weakly positive. At 0° 27.2 g 1,2-dibromoethane (150 mmole) was added at once. The colour rapidly turned lighter, gas evolved, the temperature rose slightly and the mixture thickened. After 2 h stirring the mixture was poured onto ice, neutralized with acetic acid, filtered, washed with water and ethanol, and sucked dry to give 57.9 g crude product (98.5%). For analytical purpose a small sample was recrystallized from hot *m*-dichlorobenzene (1 g/100 ml).

(*b*). *Hexa-*2*-naphthyldilead.* Lead dichloride (5.6 g, 20 mmole) was added portionwise to 63 mmole 2-naphthylmagnesium bromide in 170 ml tetrahydrofuran.

After the Gilman test had become almost negative, 4 ml 1,2-dibromoethane (8.7 g, 46 mmole) was added at once with ice-bath cooling. Gas evolved. After 20 min stirring the mixture was poured onto ice and extracted with chloroform. Concentration and precipitation with ethanol gave 9.8 g hexa-2-naphthyldilead (8.3 mmole, 83%).

The reaction mixture should be hydrolyzed soon, since in another experiment after standing overnight the main product isolated was the hitherto unknown compound, tetra-2-naphthyllead, yield 75%, m.p. 188° (acetone). (Found: Pb, 29.02. $C_{40}H_{28}Pb$ calcd.: Pb, 28.94%.)

Hexa-2-naphthyldilead is a stable yellow product in the solid state, but in solutions decomposition sometimes occurred, with formation of tetra-2-naphthyllead and metallic lead.

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