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INVESTIGATIONS ON ORGANOLEAD COMPOUNDS VI*. TRIPHENYLPLUMBYLSODIUM AND TRIPHENYLPLUMBYLMAGNESIUM HALIDE

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

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SUMMARY

Triphenylplumbylsodium can be prepared from hexaphenyldilead and finely divided sodium in tetrahydrofuran at room temperature while triphenylplumbylmagnesium halide can be conveniently prepared from lead dichloride and phenylmagnesium chloride or bromide in tetrahydrofuran.

These reagents resemble the previously investigated compound triphenylplumbyllithium in many respects. They usually couple readily with reactive halides, but sometimes an exchange reaction is observed. The tendency to exchange increases in the order: $Ph_3PbNa < Ph_3PbLi < Ph_3PbMgX$.

Triphenylplumbylsodium has been previously prepared from triphenyllead chloride or hexaphenyldilead and sodium in liquid ammonia[2,3] and from tetraphenyllead and sodium in liquid ammonia[4]:

$$Ph_3Pb\text{-}PbPh_3 + 2\,Na \rightarrow 2\,Ph_3PbNa$$

$$Ph_4Pb + 2\,Na + NH_3 \rightarrow Ph_3PbNa + NaNH_2 + C_6H_6$$

It couples with reactive halides such as ethyl bromide and benzyl chloride to give Ph_3PbR compounds[2-4], but no reaction occurs with aryl halides[4].

Triphenylplumbylmagnesium halide has not yet been described.

We describe here convenient syntheses of these reagents in tetrahydrofuran and compare their reactions with those of triphenylplumbyllithium[1,5a,6,7].

RESULTS AND DISCUSSION

Preparation of the reagents

Triphenylplumbylsodium. For some purposes tetrahydrofuran is a more convenient and suitable solvent than liquid ammonia, and we have made triphenylplumbylsodium in tetrahydrofuran by a method analogous to that used for triphenylplumbyllithium[1,5b], involving interaction of hexaphenyldilead and sodium. Because

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* For Part V see ref. 1.

the reaction is rather sluggish, the sodium must be very finely divided (sodium sand) if the reaction is to be completed in one night of stirring at room temperature. A dark solution results containing a dark sludge which can be filtered off. A reaction with benzyl chloride gave a yield of 85% of benzyltriphenyllead. Upon storage, initially some more sludge forms, the solution turns lighter, and the concentration may fall by a few percent, but after a few weeks no further decomposition occurs.

Attempts to prepare triphenylplumbylsodium from lead dichloride and phenylsodium (analogous to a preparation of triphenylplumbyllithium[8]) failed. Lead dichloride did not react with phenylsodium prepared[9] from chlorobenzene and sodium in toluene*. When complexing solvents were added, a vigorous reaction set in which destroyed the phenylsodium. (The Gilman test[11] became negative; no phenyl–lead compound could be isolated.)

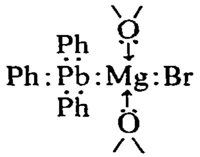
Triphenylplumbylmagnesium chloride and bromide. These reagents are readily prepared in one step from lead dichloride and phenylmagnesium halide in tetrahydrofuran[5c]:

$$PbCl_2+3\ PhMgCl \rightarrow Ph_3PbMgCl+2\ MgCl_2$$

In tetrahydrofuran the compounds are stable, but in diethyl ether the bromide** soon decomposes with formation of metallic lead. In tetrahydrofuran the Gilman test[11] is negative whereas in diethyl ether a positive test is observed. Probably, the reagent partly dissociates:

$$Ph_3PbMgBr \overset{Et_2O}{\rightleftharpoons} Ph_2Pb+PhMgBr$$

This suggests that stability is connected with the solvating (electron-donating) power of the solvent:



$$\begin{array}{c} \mathrm{Ph} \\ \mathrm{Ph:\ddot{P}b:} \\ \mathrm{Ph} \end{array}\!\!\begin{array}{c} \mathrm{O} \\ \downarrow \\ \mathrm{Mg:Br} \\ \uparrow \\ \mathrm{O} \end{array}$$

Because tetrahydrofuran is more electron-donating than diethyl ether, the magnesium atom in the tetrahydrofuran complex is electronically more saturated, and so there is less tendency for the phenyl anion to migrate from lead to magnesium.

In organotin chemistry a related phenomenon has recently been observed[12]. Triphenylstannylmagnesium bromide, solvated by triethylamine or diethyl ether, is converted to a dimeric diphenylstannylene/phenylmagnesium bromide complex upon removing the coordinating solvent:

$$2\ Ph_3SnMgBr\cdot Et_3N \rightarrow [Ph_2Sn\cdot PhMgBr]_2+2\ Et_3N\uparrow$$

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* Similarly, we found that *ether-free* phenylmagnesium bromide (prepared from bromobenzene and magnesium in decalin[10]) did not react with lead dichloride.

** The stability of the *chloride* in diethyl ether was not investigated since phenylmagnesium chloride cannot be prepared directly in this solvent.

Reactions

Hydrolysis. Triphenylplumbylsodium and -magnesium halide completely hydrolyze to lead oxide and benzene (analogous to the hydrolysis of triphenylplumbyllithium[1,5d]):

$$\mathrm{Ph_3PbM^{\star} + 2\,H_2O \rightarrow PbO + MOH + 3\,C_6H_6}$$

With the sodium reagent a characteristic transient orange-red colour is perceptible which disappears within 2 hours stirring. The magnesium reagent gives a much shorter-lived intermediate, the red colour vanishing within a few seconds. The red species is possibly diphenyllead. This red coloration is useful as a test for triphenylplumbyl–metal reagents.

During hydrolysis no triphenyllead hydride is formed since no Pb–H absorption in the 1800 cm^{-1} region of the infrared spectrum is observed.

Reactions with organic halides. We studied the reactions of the lead–sodium and lead–magnesium reagents with a few organic halides to determine the scope of the coupling reaction, which is of synthetic interest:

$$\mathrm{Ph_3PbM + RX \rightarrow Ph_3PbR + MX}$$

The sodium reagent readily couples with reactive halides such as ethyl bromide and benzyl chloride[2–4]. With butyl chloride the reaction at room temperature is much slower, being complete after standing overnight. Carbon tetrachloride gives either (trichloromethyl)triphenyllead[5e] or tetrakis(triphenylplumbyl)methane[5e,6], depending on the ratio of the reactants:

$$\mathrm{Ph_3PbNa + CCl_4 \rightarrow Ph_3PbCCl_3 + NaCl}$$
$$\mathrm{4\,Ph_3PbNa + CCl_4 \rightarrow (Ph_3Pb)_4C + 4\,NaCl}$$

All these results strongly resemble those of triphenylplumbyllithium. However, triphenylplumbylsodium couples with ethyl chloroacetate whereas the lithium analogue gives rise to exchange with formation of hexaphenyldilead[5f]. This suggests that the sodium derivative is an even better coupling reagent than the lithium compound.

The reactions of the magnesium reagent with organic halides are quite similar to those of the sodium reagent. The reaction with butyl chloride is still slower, not yet being complete after standing overnight at room temperature followed by 3 hours at 50°. Triphenylplumbylmagnesium halide is more liable to exchange reactions than the lithium and sodium analogue, as is illustrated by the reaction with carbon tetrachloride (mole ratio 4/1), from which the main product was hexaphenyldilead (exchange product, 49%) and only 10% of the 1/1 coupling product, (trichloromethyl)-triphenyllead, was isolated.

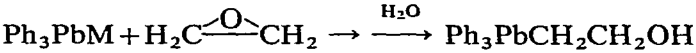
The triphenylplumbyl-metal reagents react with 1,2-dihaloethanes to give hexaphenyldilead and ethylene in almost quantitative yields e.g.:

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

This provides an attractive new method for the preparation of hexaphenyldilead. (For a more detailed discussion of this reaction see Part VII of this series[13].)

★ M means Na or MgX throughout this paper.

Other reactions. The reaction of both the lead–metal reagents with ethylene oxide takes the expected route[5g,7], giving (2-hydroxyethyl)triphenyllead in good yield:



$$\mathrm{Ph_3PbM + H_2C}\overset{O}{\text{—}}\mathrm{CH_2} \rightarrow \xrightarrow{\mathrm{H_2O}} \mathrm{Ph_3PbCH_2CH_2OH}$$

Triphenylplumbylsodium does not react with benzophenone when kept 14 hours at 50° (as has also been observed for the lithium analogue[14]). If benzyl chloride is subsequently added, a yield of 84% of benzyltriphenyllead is obtained. This explains why triphenylplumbyl–metal compounds do not respond to the Gilman test[11], which is based on the formation of a dye upon addition of an organometallic reagent to the CO bond of *p,p′*-bis(dimethylamino)benzophenone.

Conclusion. When comparing the reactions of triphenylplumbyl–metal reagents with phenyl–metal reagents, the following conclusions can be drawn:

(1) Triphenylplumbyl–metal reagents tend to attack carbon–halogen bonds nucleophilically at the *carbon* atom, thus producing a lead–carbon bond (coupling). On the other hand, phenyl–metal reagents attack the *halogen* atom, thus giving rise to exchange.

(2) The behaviour with respect to the carbonyl group shows a completely different pattern. The triphenylplumbyl anion does not react at all, whereas in this case the phenyl anion attacks at the *carbon* atom.

EXPERIMENTAL PART

Preparation of triphenylplumbylsodium

All operations were under nitrogen.

A clean piece of sodium (2.76 g, 120 mg-atom, 20 mg-atom excess) was melted in 70 ml of dry xylene under nitrogen by heating to *ca.* 110°. After melting the sodium was finely divided by high-speed stirring with a Hershberg stirrer (nichrome wire) while the temperature was slowly lowered. The xylene was replaced by 20 ml of dry tetrahydrofuran. A solution of 43.8 g of hexaphenyldilead (50 mmole) in 150 ml of tetrahydrofuran was added at once. The sodium was slowly attacked and a green turbidity developed. The temperature rose to 30°. After 24 h stirring at room temperature all of the sodium had reacted and a dark mixture resulted. A dark sludge was filtered off under nitrogen over dried Filtrapid (a slow process). The dark-coloured filtrate which was constantly kept under nitrogen was added up to 250 ml with tetrahydrofuran. Aliquots of 25 ml were withdrawn for further reactions.

A reaction of 25 ml with 1.3 g of benzyl chloride (10 mmole) at −40° gave 4.5 g of benzyltriphenyllead (8.5 mmole, 85%), m.p. 93° (mixed m.p.).

Preparation of triphenylplumbylmagnesium halide

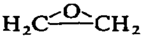
Lead dichloride (5.5 g, 20 mmole) was added with stirring to an ice-cooled solution of 62 mmole of phenylmagnesium chloride in 70 ml of tetrahydrofuran. Stirring was continued at room temperature until all the lead dichloride had dissolved (1–2 h). An almost clear, yellow to brown solution resulted.

A reaction with 3 g of benzyl chloride (24 mmole) at 0° gave 9 g of benzyltriphenyllead (17 mmole, 85% based on $PbCl_2$), m.p. 93°.

The bromide was prepared similarly.

TABLE 1

REACTIONS OF TRIPHENYLPLUMBYLSODIUM AND TRIPHENYLPLUMBYLMAGNESIUM CHLORIDE

Reactant	Product	Yield (%)		M.p. (°C)	Ph_3PbLi ref.
		$-Na$[a]	$-MgCl$		
H_2O	PbO	100	97		1, 5d
	C_6H_6				
$PhCH_2Cl$	Ph_3PbCH_2Ph	100[a]	85	93	1, 5c
BuCl	Ph_3PbBu	91	71	48–49	[b]
	PbO	0	17		
CCl_4	Ph_3PbCCl_3	87		172–173	5e
$\frac{1}{4}$ CCl_4	$(Ph_3Pb)_4C$	51	0	289–291 (dec.)	5e, 6
	Ph_6Pb_2	0	49		
	Ph_3PbCCl_3	0	10	172–173	
	Not characterized	?	32		
$ClCH_2COOEt$	Ph_3PbCH_2COOEt	82	0	59–62	5f
	Ph_6Pb_2	0	82		
$ClCH_2CH_2COOEt$	Ph_6Pb_2	27			5f
	PbO	52			
$ClCH_2CH_2Cl$	Ph_6Pb_2 (see ref. 13)		94		
$BrCH_2CH_2Br$	Ph_6Pb_2 (see ref. 13)	89	88		[c]
 $H_2C\overset{O}{—}CH_2$	$Ph_3PbCH_2CH_2OH$	98	82		5g, 7
PhCOPh	No reaction				[d]

[a] Yields are based on the yield of benzyltriphenyllead (=100%). [b] Triphenylplumbyllithium reacts slowly with butyl chloride to give 100% butyltriphenyllead[14]. [c] Gorth and Henry[15] obtained a 70% yield of tetraphenyllead. [d] Neither did triphenylplumbyllithium react with benzophenone[14].

Reactions

The procedures followed were the same as described for reactions of triphenylplumbyllithium. They are summarized in Table 1. For literature see Table 1, last column.

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