867. *Mesityl and Phenyl Derivatives of Lead.*

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Lead chloride or bromide reacts rapidly with phenyl-lithium or phenyl- or mesityl-magnesium bromide in tetrahydrofuran at $-40°$. Deeply coloured solutions result which involve equilibrium mixtures, $PbAr_2 + ArLi(MgX) \rightleftharpoons Ar_3Pb{\cdot}Li(MgX)$. Evidence is presented that diaryl-leads are rapidly hydrolysed even at low temperatures, giving a basic lead bromide. Bromination studies indicate that dimesityl-lead is produced by carbonation of $(Mesityl)_3Pb{\cdot}MgBr$.

The isolation of diphenyl- and di-*p*-tolyl-lead was reported by Krause and Reissaus[1] in 1922. They treated anhydrous lead chloride with ethereal phenylmagnesium bromide at +2° and obtained a deep red-brown solution from which, after hydrolysis at 0°, they isolated diphenyl-lead by extraction into benzene and precipitation with ethanol. Diphenyl-lead obtained in this way (4—5% yield) is described as a blood-red, air-sensitive, amorphous powder which is decolorised when heated above 100° and is monomeric in benzene solution. More recently Gilman and his co-workers[2] investigated the apparently analogous reaction between lead chloride and phenyl-lithium in ether. They obtained evidence for the equilibrium, $Ph_3Pb{\cdot}Li \rightleftharpoons PbPh_2 + PhLi$, based on the appearance of a positive Gilman colour test when more than 2·8 moles of phenyl-lithium were used per mole of lead chloride. Hydrolysis of such solutions (which might have been expected to produce diphenyl-lead) gave a heavy yellow precipitate and a red or yellow ether solution. Attempts to isolate diphenyl-lead were unsuccessful. In contrast to the deep red solutions (presumably of diphenyl-lead) obtained by Krause and Reissaus, Gilman *et al.* found that using two moles of phenyl-lithium and one of lead chloride in ether at $-10°$ led to a yellow solution that gave a negative colour test, deposited lead when boiled, and on hydrolysis afforded hexaphenyldilead in 79% yield:

$$PbCl_2 + 2PhLi \xrightarrow[-10^\circ]{Et_2O} PbPh_2 \xrightarrow{Reflux} Pb + Pb_2Ph_6$$

Solutions of triphenyl-leadlithium in boiling ether were, by contrast, stable.

We have made further studies on the reaction of lead halides with both Grignard and aryl-lithium reagents with a view to obtaining diphenyl- and dimesityl-lead. Our attempts

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[1] Krause and Reissaus, *Ber.*, 1922, **55**, 888.

[2] Gilman, Summers, and Leeper, *J. Org. Chem.*, 1952, **17**, 630.

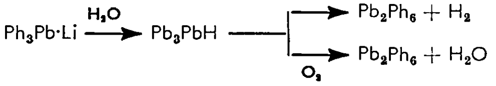
to repeat the work of Krause and Reissaus have been unsuccessful: we find that hydrolysis, at 0°, of the deeply coloured ether solutions containing diphenyl-lead results in discharge of the colour.

Reactions of Lead Chloride and Bromide with Phenyl-lithium.—The reaction of lead chloride with phenyl-lithium in ether is reported [2] as being slow below —10°. In contrast, with tetrahydrofuran as solvent, the reaction is rapid even at —40°, giving yellow-green solutions, and does not involve separation of lead. When either 2 or 3 moles of phenyl-lithium were used per mole of lead bromide hydrolysis then gave a copious dense yellow precipitate (cf. ref. 2) which we have characterised as lead oxide bromide [$3PbO,PbBr_2(1—3H_2O)$] contaminated with 1—2% of hexaphenyldilead. No diphenyl-lead is isolable in either case, even after hydrolysis at —30°. This behaviour is compatible with the equilibrium suggested by Gilman *et al.*, but also implies that diphenyl-lead is itself highly susceptible to hydrolysis (Krause and Reissaus claimed that they isolated diphenyl-lead *after* hydrolysis of reaction mixtures):

$$Ph_3Pb{\cdot}Li \rightleftharpoons PbPh_2 + PhLi \xrightarrow{H_2O} LiOH + C_6H_6 + Pb(OH)_2$$

If lead hydroxide is suspended in a tetrahydrofuran solution of magnesium bromide and the mixture subsequently hydrolysed, a basic lead bromide is isolated.

The isolation of small quantities of hexaphenyldilead without simultaneous production of metallic lead could be accounted for by the hydrolysis of undissociated triphenyl-lead-lithium followed by thermal decomposition or oxidation of the hydride:



$$Ph_3Pb{\cdot}Li \xrightarrow{H_2O} Pb_3PbH \longrightarrow \begin{cases} \longrightarrow Pb_2Ph_6 + H_2 \\ \xrightarrow[O_2]{} Pb_2Ph_6 + H_2O \end{cases}$$

Hydrolysis of triphenyl-leadlithium in a vacuum apparatus failed to produce hydrogen, and hexaphenyldilead was isolated in 1·4% yield without exposure to air. Much higher yields (~20%) of hexaphenyldilead result if air is not excluded.

When equimolar ratios of phenyl-lithium (or phenylmagnesium bromide) and lead bromide are used in tetrahydrofuran, about half of the lead bromide remains undissolved after the Gilman colour test becomes negative, and treatment of the filtrate with benzyl chloride leads to benzyltriphenyl-lead in 28% yield based on " soluble " lead. Thus we consider that the initial reaction, $PbBr_2 + PhLi \longrightarrow PhPbBr + LiBr$, is slow and that phenyl-lead bromide (which may be soluble in tetrahydrofuran) reacts rapidly to give diphenyl-lead. Moreover, the isolation of benzyltriphenyl-lead under these conditions points to there being triphenyl-leadlithium in equilibrium with diphenyl-lead even when equimolar ratios of phenyl-lithium to lead bromide are initially involved.

Reactions of Lead Bromide with Phenylmagnesium Bromide.—In contrast to reactions involving phenyl-lithium, lead bromide and phenylmagnesium bromide show more distinct colour changes in tetrahydrofuran:

$$PbBr_2 \xrightarrow[\text{1 mol.}]{PhMgBr} \text{Yellow solution} \xrightarrow[\text{1 mol.}]{PhMgBr} \text{Red solution} \xrightarrow[\text{1—3 mol.}]{PhMgBr} \text{Red-brown solution}$$

If the red-brown solutions resulting from an excess of phenylmagnesium bromide are hydrolysed or treated with anhydrous ethanol, the red colour returns momentarily and is followed by the precipitation of a basic lead bromide. Only traces of hexaphenyldilead are produced on hydrolysis, and over 90% of the lead appears as the basic bromide. Removal of tetrahydrofuran from the red solution (2 mol. of PhMgBr) and extraction with methylene chloride gave an orange-red solid which decomposed (giving lead) at room temperature and was sensitive to both air and water. This material contained lead, magnesium, and bromine, and is probably a mixture of $PbPh_2$, $Ph_3Pb{\cdot}MgBr$, and $MgBr_2$–tetrahydrofuran.

Reactions of Lead Bromide with Mesitylmagnesium Bromide.—Some of the difficulties encountered in our attempts to isolate diphenyl-lead result from thermal instability, and the reaction of mesitylmagnesium bromide, which showed analogous colour changes and behaviour on hydrolysis, led to considerably more stable products. For example, lead bromide may be heated under reflux in tetrahydrofuran for 4 hr. with a large excess of mesitylmagnesium bromide without separation of metallic lead; more prolonged heating results in the formation of lead and tetramesityl-lead. As in reactions involving phenylmagnesium bromide, these observations are compatible with an equilibrium between dimesityl-lead and trimesityl-leadmagnesium bromide. Failure to isolate more than traces of organolead compounds on treatment with water again points to rapid hydrolysis of mesityl groups.

We have attempted to displace the equilibrium in favour of dimesityl-lead by reaction of trimesityl-leadmagnesium bromide with reagents milder than water. Dry ethanol causes immediate discharge of the colour, but addition of pure carbon dioxide results in intensification of the red colour. Attempts to isolate pure dimesityl-lead from these deep red solutions have not been successful owing to the similar solubility properties of magnesium bromide–tetrahydrofuran complexes. That carbon dioxide does displace the equilibrium, giving dimesityl-lead, $(\text{Mesityl})_3\text{Pb}\cdot\text{MgBr} \rightleftharpoons \text{Pb}(\text{Mesityl})_2 + \text{MesitylMgBr} \xrightarrow{CO_2} C_6H_2Me_3\cdot CO_2MgBr + \text{Pb}(\text{Mesityl})_2$, is inferred from comparative bromination experiments. Reaction mixtures corresponding in composition to $(\text{Mesityl})_3\text{Pb}\cdot\text{MgBr}$ on bromination at a low temperature gave trimesityl-lead bromide, whilst under identical conditions dimesityl-lead dibromide is produced by bromination of the deep red material obtained after reaction with carbon dioxide.

EXPERIMENTAL

Lead analyses were carried out by Saunders and Stacey's method.[3] M. p.s are corrected. All reactions were carried out in an atmosphere of dry oxygen-free nitrogen.

Lead Chloride and Phenyl-lithium.—(*a*) Lead chloride (12·5 g., 0·045 mole) was added in several portions during 30 min. to a stirred, deep red solution of phenyl-lithium (0·092 mole) in tetrahydrofuran (150 c.c.) at −60°. At −40° the solution changed rapidly to a yellowish-green, and the Gilman colour test (Michler's ketone) became negative. A sample of this solution deposited lead at room temperature. After being stirred overnight at −78° the mixture was hydrolysed at −30° by aqueous tetrahydrofuran, and extracted with benzene. Filtration gave a yellow solid (12 g.) shown by *X*-ray examination to be a mixture of basic lead chloride and bromide. The yellow benzene extract gave a yellow solid (2 g.) from which hexaphenyldilead (0·4 g., 3%), m. p. 155° (decomp.), was isolated by crystallisation from benzene–ethanol (Found: C, 49·6; H, 3·7. Calc. for $C_{36}H_{30}Pb_2$: C, 49·3; H, 3·5%).

(*b*) Lead chloride (25·75 g., 0·0925 mole) was added to phenyl-lithium (0·09 mole) in tetrahydrofuran (150 c.c.) as described under (*a*). Filtration at −60° gave unchanged lead chloride (13 g., 0·0466 mole). Benzyl chloride (4·2 g., 0·033 mole) was added to the filtrate in 10 min., then the solution was allowed to reach room temperature, and finally it was heated under reflux for 1·5 hr. The resulting mixture, which contained metallic lead, was hydrolysed and filtered in air. Extraction of the solid residue with hot ethanol gave benzyltriphenyl-lead (3·9 g.), m. p. and mixed m. p. 92·5°. Extraction with hot benzene gave tetraphenyl-lead (3·2 g.), m. p. and mixed m. p. 223°. Lead oxide chloride and bromide were also formed. Addition of benzyl chloride to the solution resulting from 2 mol. of phenyl-lithium and 1 mol. of lead chloride at $< -25°$ gave no benzyltriphenyl-lead, and unchanged benzyl chloride was isolated.

Lead Bromide and Phenyl-lithium in Ether.—Lead bromide (12·2 g., 0·033 mole) was added to phenyl-lithium (0·1 mole) in ether (100 c.c.), and the mixture stirred vigorously at −20° for 2 hr. The pale yellow filtrate was connected to a vacuum apparatus, degassed, and hydrolysed by condensing a water–tetrahydrofuran mixture on the solution which was then allowed to attain room temperature. No hydrogen was produced. The ether solution from the hydrolysis was washed with water and filtered under nitrogen. The residue yielded hexaphenyldilead

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[3] Saunders and Stacey, *J.*, 1949, 919.

(0·2 g.) and biphenyl (0·1 g.), oxygen being rigorously excluded at all stages. The solid that was precipitated on hydrolysis was free from organic material; its X-ray powder photograph corresponded to a lead oxide bromide, $3PbO,PbBr_2(1—3H_2O)$.

A comparable experiment in which the isolation procedure after hydrolysis was carried out in air led to the isolation of hexaphenyldilead in 20% yield.

Lead Bromide and Phenylmagnesium Bromide.—(*a*) Phenylmagnesium bromide (0·15 mole) in tetrahydrofuran (120 c.c.) was added to a stirred suspension of lead bromide (18·55 g., 0·05 mole) in tetrahydrofuran (50 c.c.) at $-20°$. Addition of 2 equiv. of phenylmagnesium bromide gave a deep red solution which became yellowish-brown on addition of the third equivalent of Grignard reagent. The mixture was heated to $-10°$ and hydrolysed by dropwise addition of water, which resulted in the momentary return of the deep red colour, followed by precipitation of lead hydroxide bromide (14 g., 92%). In a similar experiment with equimolar ratios of phenylmagnesium bromide and lead bromide a sample of the resulting orange-red solution decomposed, giving lead at room temperature. Hydrolysis again gave lead hydroxide bromide and a trace (~0·1 g.) of hexaphenyldilead.

(*b*) Phenylmagnesium bromide (0·162 mole) in tetrahydrofuran (150 c.c.) was added to lead bromide (0·0545 mole) in tetrahydrofuran (100 c.c.) at $-20°$, and benzyl chloride (0·053 mole) was added slowly. The mixture was allowed to warm to room temperature and refluxed overnight. Metallic lead (3·6 g., 32%) was separated and the filtrate treated with benzene and water. Extraction of the white precipitate with chloroform gave tetraphenyl-lead (6 g.), the residue being lead hydroxide bromide (0·9 g.). The benzene solution was evaporated and extraction of the residue with ethanol gave benzyltriphenyl-lead (2·5 g.) and tetraphenyl-lead (1·0 g.).

A similar experiment with equimolar ratios of phenylmagnesium bromide and lead bromide (36·7 g.) with benzyl chloride (5·06 g.) gave unchanged lead bromide (16·7 g.), tetraphenyl-lead (8·5 g.), benzyltriphenyl-lead (1·5 g.), lead (2·5 g.), and lead hydroxide bromide (5·3 g.).

(*c*) Phenylmagnesium bromide (0·1 mole) and lead bromide (18·35 g., 0·05 mole) were stirred in tetrahydrofuran (150 c.c.) at $-25°$ for 3 hr. The solvent was removed *in vacuo* at $-20°$, and dry methylene chloride (100 c.c.) added at $-20°$ to the orange residue. This procedure precipitated some of the magnesium bromide, though the filtrate after removal of methylene chloride at 0° gave an orange-red solid containing lead, magnesium, bromine, and tetrahydrofuran. Addition of benzene produced two layers, one yellow and the other a deep red, each containing both lead and magnesium. The deep red solution on removal of solvent at 0° left a deep red sticky solid which with water gave lead hydroxide bromide and decomposed to a yellow powder in air. No diphenyl-lead was obtained.

Lead Bromide and Mesitylmagnesium Bromide.—(*a*) Mesitylmagnesium bromide (0·093 mole) in tetrahydrofuran (100 c.c.) was added dropwise to a stirred suspension of lead bromide (17·1 g., 0·0465 mole) in tetrahydrofuran at $-25°$ to $-30°$. Each drop of Grignard solution produced a localised deep red colour which rapidly dispersed, giving a uniform pale yellow colour which deepened as the addition proceeded. The final deep red solution was filtered at $-20°$ from unchanged lead bromide (0·9 g.), and the filtrate was hydrolysed with water which discharged the colour and resulted in the precipitation of lead hydroxide bromide, $PbO,PbBr_2,H_2O$ (11 g., 78%).

(*b*) Mesitylmagnesium bromide (0·1 mole) in tetrahydrofuran (100 c.c.) was added to a stirred suspension of lead bromide (0·033 mole) in tetrahydrofuran (100 c.c.) at $-30°$. The Gilman colour test became positive after addition of 2·8 equiv. of Grignard reagent. When the solution was a deep blood-red the third equivalent of Grignard reagent gave a deep red-brown solution. This was poured on a large excess of pure dry solid carbon dioxide and left for 1 hr. at $-30°$. Filtration in nitrogen at $-40°$ gave a deep red solution. A sample of this solution was immediately decolorised on addition of 2 drops of dry ethanol. The main solution was evaporated at $-20°$, giving a deep red glass which was divided into two parts. One part was allowed to decompose in air at room temperature, then the grey product was extracted with carbon tetrachloride, giving *tetramesityl-lead* as a yellow solid, m. p. 242° (decomp.) (Found: C, 62·1; H, 6·2; Pb, 30·3. $C_{36}H_{44}Pb$ requires C, 63·2; H, 6·5; Pb, 30·3%). Tetramesityl-lead is also produced if lead bromide is heated with a large excess of mesitylmagnesium bromide for 2 days. The colourless residue from the carbon tetrachloride extraction was a mixture of magnesium bromide and lead hydroxide bromide. The second part of the glass was dissolved in methylene chloride (150 c.c.), and the deep red solution treated with hexane (50 c.c.) which precipitated some magnesium bromide–tetrahydrofuran complex. Removal of the solvents from the filtrate again gave a red glass (Found: Pb, 11·3; Br, 25·1%).

Dimesityl-lead Dibromide and Trimesityl-lead Bromide.—The reaction between mesitylmagnesium bromide (0·1 mole) and lead bromide (12·2 g., 0·033 mole) was carried out as described above. The filtrate, after carbonation, was concentrated to 100 c.c., then cooled to −50°, and bromine (1·0 g., 5·6 mmoles) in methylene chloride (15 c.c.) was added dropwise. The resulting yellow solution was shaken with sodium hydrogen carbonate solution, washed, and dried. Removal of solvent gave crude *dimesityl-lead dibromide* (1·7 g.), which from carbon tetrachloride–propan-2-ol produced pale yellow crystals, m. p. 198—199° (Found: C, 39·5; H, 3·5; Br, 25·2. $C_{18}H_{22}Br_2Pb$ requires C, 35·7; H, 3·7; Br, 26·4%).

Bromination of trimesityl-leadmagnesium bromide under identical conditions gave *trimesityl-lead bromide*, as colourless needles, m. p. 145—146° [from light petroleum (b. p. 60—80°)] (Found: Br, 11·6. $C_{27}H_{33}BrPb$ requires Br, 12·4%), together with hexamesityldilead.[4]

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[*Received, June 7th,* 1961.]

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[4] Gilman and Bailie, *J. Amer. Chem. Soc.*, 1939, **61**, 731.