[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE REACTION OF ARYLLITHIUM COMPOUNDS WITH LEAD DICHLORIDE. TRIPHENYLLEADLITHIUM

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The most widely useful method for the preparation of organometallic derivatives of the heavier metals involves the reaction of a more reactive organometallic type, such as a Grignard reagent or an organolithium compound, with a halide of the heavy metal. For example, organomercury or organotin compounds are conveniently prepared by reactions such as

$$2RMgX + HgCl_2 \rightarrow R_2Hg + MgX_2 + MgCl_2$$

$$4RMgX + SnCl_4 \rightarrow R_4Sn + 2MgX_2 + 2MgCl_2$$

Organometallic derivatives of tetravalent lead may be obtained in an analogous manner (1), but the method is not used for preparative purposes because of the relative instability of lead tetrachloride. Fortunately, such organolead compounds are available from the reaction of Grignard reagents with lead dichloride (2) according to the over-all reaction

$$4RMgX + 2PbCl_2 \xrightarrow{\text{Heat}} R_4Pb + Pb + 2MgX_2 + 2MgCl_2 \qquad \textbf{1.}$$

This is the common laboratory method of preparation of tetraarylleads.

The nature of the reaction of Grignard reagents with lead dichloride was studied extensively by Krause and co-workers. They concluded (3) that the steps involved were

$$2RMgX + PbCl_2 \rightarrow R_2Pb + MgX_2 + MgCl_2 \qquad \textbf{2.}$$

$$3R_2Pb \rightarrow R_6Pb_2 + Pb \qquad \textbf{3.}$$

$$2R_6Pb_2 \rightarrow 3R_4Pb + Pb \qquad \textbf{4.}$$

[where, in accordance with later evidence (4), we have written R_6Pb_2 rather than R_3Pb as given by Krause]. It is readily possible to isolate R_6Pb_2 compounds from these reaction mixtures if the heating time is limited, and when heated alone such compounds do undergo further thermal decomposition in accordance with reaction 4 above (5). Of the R_2Pb compounds presumably produced in reaction 2, however, the only two examples which have been isolated are diphenyllead and di-*p*-tolyllead. These were obtained (6) by the reaction of lead chloride with the Grignard reagent at 2°. The yields were only about 4%. At higher temperatures the decomposition was presumably too rapid, and even at 2° most of the product was R_4Pb and R_6Pb_2; whereas at lower temperatures the Grignard reagent essentially did not react with lead chloride.

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Organolithium compounds can be employed, in exactly the same way as Grignard reagents, for the preparation of R_4Pb derivatives (7).

$$4RLi + 2PbCl_2 \rightarrow R_4Pb + Pb + 4LiCl \qquad 5.$$

The RLi compounds, used in this manner, offer no particular advantage over the Grignard reagent except in certain cases where the latter is unavailable (for example, in the preparation of tetra-*p*-dimethylaminophenyllead). However, studies carried out in these laboratories on the synthesis of organolead derivatives show that the RLi compounds can be employed in other ways, and that they represent a very useful tool for the synthesis of symmetrical and unsymmetrical organolead types directly from lead chloride. In a recent communication (8) the preparation of tetramethyllead by the reaction

$$3RLi + PbX_2 + RI \rightarrow R_4Pb + LiI + 2LiX. \qquad 6.$$

was described. The technique employed involved the addition of methyllithium to a mixture of lead iodide and methyl iodide in ether. The product contained no metallic lead, and the yield was 92%. It was found that the Grignard reagent could also be used for the production of tetraalkyllead compounds in an analogous fashion. We have extended this reaction to the aromatic series, and find that tetraphenyllead is similarly available from phenyllithium, lead chloride, and iodobenzene. The procedure represents probably the best method for this preparation, since the time required is several hours less than for the preparation by the customary method [reaction 1 (9)], and the crude product is easier to handle because it is free from the large amount of metallic lead. Experiments were also carried out in which phenylmagnesium bromide was employed in the reaction, but the results were not satisfactory. Some other experiments designed to throw some light on the mechanism and conditions of the reaction are described in the Experimental part. It was previously suggested (8) that the reactions involved were

$$4RLi + 2PbCl_2 \rightarrow R_4Pb + Pb + 4LiCl \qquad 7.$$

$$2RI + Pb \rightarrow R_2PbI_2 \qquad 8.$$

$$2RLi + R_2PbI_2 \rightarrow R_4Pb + 2LiI \qquad 9.$$

This formulation was supported by the observation that the metallic lead which precipitated in the early stages of the reaction was redissolved as the reaction proceeded, leaving finally a clear solution. None of our observations on the reaction conflicts with this formulation.

Another way in which organolithium compounds can be employed for organolead syntheses is in reactions in which triphenylleadlithium, $(C_6H_5)_3PbLi$, is an intermediate. The reactions mentioned in our discussion above were all carried out near the refluxing temperature of ether. Continuing our studies, we investigated the reaction of phenyllithium with lead chloride in ether at low temperatures, near −10°, and found that under these conditions, lead chloride reacts with three equivalents of the RLi compound to give triphenylleadlithium

$$3C_6H_5Li + PbCl_2 \xrightarrow{\text{Ether, } -10°} (C_6H_5)_3PbLi + 2LiCl \qquad 10.$$

That such a reaction could occur was indicated previously (10). The triphenylleadlithium can then be reacted, without isolation, with an RX compound (X = halogen).

$$(C_6H_5)_3PbLi + RX \rightarrow (C_6H_5)_3PbR + LiX \qquad 11.$$

Thus unsymmetrical organolead types can be prepared from lead chloride in one process, and the preparations proceed smoothly and give good yields in appropriate cases. The R_3PbM' derivatives (M' = an active metal), such as triphenylleadsodium, have always been prepared previously by treating R_4Pb, R_6Pb_2, or R_3PbCl compounds with sodium in liquid ammonia (5a, 11). This procedure, however, requires the previous preparation of the organolead starting material. By the present method we proceed directly from lead chloride, and the technique is more convenient.

The reaction of lead chloride with phenyllithium in ether at low temperature proceeds in two stages, distinguishable by color phenomena and by other methods, as described below. Our investigations of the chemistry involved lead us to believe that these stages are as represented by the reactions

$$2C_6H_5Li + PbCl_2 \xrightarrow{-10°} (C_6H_5)_2Pb + 2LiCl \text{ (irreversible)} \qquad 12.$$

$$(C_6H_5)_2Pb + C_6H_5Li \rightleftarrows (C_6H_5)_3PbLi \text{ (reversible)} \qquad 13.$$

We therefore regard the triphenylleadlithium preparations as an equilibrium system, containing $(C_6H_5)_3PbLi$ and C_6H_5Li, as indicated in reaction 13. Carbonation experiments and other observations support this point of view. Qualitative observations indicate that in the case of the phenyl compound, and in the concentrations at which we have worked, the equilibrium at −10° is displaced at least 80% toward $(C_6H_5)_3PbLi$.

EXPERIMENTAL

The aryllithium solutions were prepared as in the following example: To 6 g. (0.86 g.-atom) of lithium metal, cut into small pieces and stirred continuously in 250 ml. of dry ether, there was added a solution of 62.8 g. (0.40 mole) of bromobenzene in 100 ml. of ether, at such a rate that steady refluxing was maintained throughout the addition. After the reaction was completed, the stirring was stopped and the solid was allowed to settle. The clear solution was then decanted through glass wool, under nitrogen, into a calibrated dropping-funnel. For standardization, 2-ml. aliquots of the RLi solution were pipetted into water and the resulting solution was titrated with 0.1 *N* sulfuric acid, using phenolphthalein (or, in the case of *p*-dimethylaminophenyllithium, thymol blue) as indicator. The yields were always between 90 and 95%, so that the solutions were approximately 1 *M*.

In reactions involving organolithium compounds, the preparation of the RLi solution and all subsequent operations up to the hydrolysis were carried out in an atmosphere of dry nitrogen.

The lead chloride was ordinary reagent grade material.

In the experiments involving lead chloride we employed a glass stirrer with a heavy shaft and a semicircular glass blade which fit closely the contour of the bottom of the flask. Efficient stirring is an important point in the technique, because otherwise the dense lead chloride settles to the bottom of the flask and clumps together, causing the reactions to proceed irregularly.

EXPERIMENTS ON REACTION 6

Preparation of tetraphenyllead. The phenyllithium solution prepared from 126 g. (0.80 mole) of bromobenzene, in the concentration indicated above, was added slowly with stirring to a mixture of 69.5 g. (0.25 mole) of $PbCl_2$, 56 g. (0.25 mole plus 10%) of iodobenzene, and 200 ml. of ether, at such a rate that gentle refluxing occurred. No cooling was necessary; the reaction was not vigorous. An occasional trace of bright yellow color, and an occasional trace of gray, were noted; but in the main the reaction mixture remained white. After addition was complete, the mixture was refluxed for two hours, with no change in appearance. It was then cooled in an ice-bath, water was added cautiously, and the precipitate was filtered with suction. The white residue was dried in air, then extracted for 24 hours in a Soxhlet extractor with 350 ml. of chloroform. Filtration of the chloroform gave 103 g. (80%, based on reaction 6) of tetraphenyllead, m.p. 227–229°.

The preparation was repeated several times, always with the same result, and with yields always close to 80%.

When the reaction was carried out as above, except that the refluxing time was decreased to 15 minutes, the yield of tetraphenyllead was only 32%, and 46% of the iodobenzene was recovered from the ether layer.

Use of bromobenzene. The reaction was carried out as above except that 39.2 g. (0.25 mole) of bromobenzene was substituted for the iodobenzene. As the phenyllithium was added, there developed at first an orange color, after which the solution darkened, giving finally a deep black suspension of metallic lead. These are the same phenomena which occur when tetraphenyllead is prepared by the customary method (reaction 5), with no phenyl halide present. During the two hours' refluxing the color lightened somewhat. The final yield of tetraphenyllead was 32 g. (25% based on reaction 6), and 18 g. (46%) of the bromobenzene was recovered.

Use of phenylmagnesium bromide. The Grignard reagent prepared from 156 g. (1 mole) of bromobenzene and 29.3 g. (1 g.-atom) of magnesium in 350 ml. of ether was added slowly to a stirred mixture of 93 g. (0.30 mole) of $PbCl_2$ and 68 g. (0.30 mole) of iodobenzene in 350 ml. of toluene. The phenomena observed were the fleeting orange color, followed by the deep black precipitate of metallic lead, as in the customary preparation. The black mixture was refluxed for five hours, then hydrolyzed and worked up. The yield of tetraphenyllead was 63.5 g., which is 37% based on reaction 6, or 74% based on reaction 5 [compare the 83% reported for the customary preparation (9)].

In a check experiment, only ether was used as solvent and the refluxing time was limited to two hours. The yield was 34%, based on reaction 6.

Use of a deficiency of phenyllithium. In one experiment, 0.100 mole of phenyllithium in 95 ml. of ether was added dropwise to a stirred mixture of 13.9 g. (0.050 mole) of $PbCl_2$ and 10.2 g. (0.050 mole) of iodobenzene in 40 ml. of ether, and the mixture was then refluxed. Color Test I (12) became negative after one hour. The mixture was cooled, hydrolyzed with saturated aqueous ammonium chloride, and worked up. The only organolead product obtained was 15.1 g. of tetraphenyllead, or 88% based on reaction 6 and calculated from the phenyllithium actually present. There was recovered 3.1 g. (0.015 mole) of iodobenzene; the excess present on the basis of reaction 6 was 0.017 mole.

In another experiment, only 0.050 mole of phenyllithium in 47 ml. of ether was used, with 0.050 mole of $PbCl_2$ and 0.050 mole of iodobenzene. The yield of tetraphenyllead was 73%, calculated as before. Again, no other organolead product was found.

Metallic lead. The result (8) regarding the redissolution of metallic lead was checked for the phenyl compounds. To 11.1 g. (0.040 mole) of $PbCl_2$ in 30 ml. of ether, stirred and cooled to −10° in ice-salt, there was added 0.080 mole of phenyllithium in 76 ml. of ether. This gives a preparation which is essentially diphenyllead, as described below. Color Test I was negative. The yellow mixture was now refluxed for one hour to precipitate metallic lead. The result finally was a black suspension in a light brown liquid. To this mixture, at room temperature, was added 0.040 mole more of phenyllithium and 0.040 mole, plus 10%, of iodobenzene, and stirring was continued. The mixture became white, and considerable refluxing occurred. Although some gray color remained and not all the lead dissolved, hydrolysis and working up of the mixture gave 16.2 g. of tetraphenyllead (78% based on reaction 6, or essentially the same yield as when the preparation was carried out directly).

EXPERIMENTS ON REACTIONS 10 AND 11

Preparation of triphenylleadlithium from lead chloride in ether. This preparation is carried out simply by adding phenyllithium solution, in the concentration indicated above, to dry, finely powdered lead chloride, stirred and cooled in ether at −10°. For instance, 0.120 mole of phenyllithium in about 110 ml. of ether is added, over a period of about one hour, to 11.1 g. (0.040 mole) of $PbCl_2$ in 30 ml. of ether contained in a 500-ml. three-neck flask equipped with stirrer, reflux condenser, and dropping-funnel. The preparation has been repeated many times, using quantities of lead chloride up to 0.1 mole. Larger runs cause no trouble if cooling and stirring are efficient. If however, due to heat of reaction or to any other cause, the internal temperature rises locally much above that indicated, some decomposition with deposition of lead will take place. The phenomena which occur during the preparation are as follows (these observations were all repeated carefully on four different runs): After addition of the first 5 or 10 ml. of phenyllithium there develops in the mixture a bright yellow color, which we believe to be due to diphenyllead, formed by reaction 12. As addition proceeds at about the rate indicated above this yellow or orange-yellow color persists. If the phenyllithium is added more rapidly, the color will disappear, due to the using up of the diphenyllead by reaction 13. If addition of phenyllithium is then stopped for a few minutes, the yellow color returns. However, the rate of addition of the phenyllithium is not a critical point, and apparently does not affect the result of the reaction except insofar as it affects the temperature. Color Test I remains negative up to about 2.8 equivalents of phenyllithium per mole of $PbCl_2$. Between 2.8 and 3.0 equivalents the Color Test becomes positive, indicating the presence of a detectable amount of phenyllithium as such. At the same time, the yellow color disappears and does not return. The final preparation is a suspension of a grayishwhite, dense solid in a slightly yellowish solution.

As already stated, the yellow intermediate is believed to be diphenyllead in some form. The evidence for this belief will be given below. In the only reported isolation (6) of diphenllead, however, the material is described as blood-red. The reason for the discrepancy is not clear at this time. The product of Krause and Reissaus (6) was well characterized. It is possible that the variations in color of the preparations reflect some variation in state, such as a different degree of polymerization, for instance. Transient blood-red colorations, were in fact not uncommon when our triphenylleadlithium preparations were hydrolyzed, but the characteristic color was yellow.

Reaction of triphenylleadlithium with benzyl chloride. To triphenylleadlithium, prepared as above from 0.040 mole of lead chloride and 0.120 mole of phenyllithium in ether, there was added rapidly, still in the cold, a solution of 6.1 g. (0.04 mole plus 20%) of benzyl chloride in 20 ml. of ether, and the mixture was refluxed for 1.5 hours. The grayish-white suspension took on the pure white color of lithium chloride. The mixture was cooled in an ice-bath and hydrolyzed by addition of aqueous ammonium chloride. The ether layer was separated, washed with water, dried over Drierite, and the ether removed on a water-bath. The solid residue (20.6 g.) was extracted with 150 ml. of hot 95% ethanol. The extract, on cooling, gave 14.7 g. (69%) of triphenylbenzyllead, m.p. 91–93° (lit., 93°), identified by mixture m.p. with an authentic sample (13).

Heat stability. The yellow product believed to be diphenyllead was found to be unstable on heating. As described above, when the reaction was carried out using only two equivalents of phenyllithium per mole of $PbCl_2$, and when the yellow mixture thus obtained was warmed to room temperature and refluxed, the same rapid darkening resulted as in the case of an ordinary tetraphenyllead preparation, and after one hour, there was a dense, black precipitate of metallic lead. Hydrolysis of the mixture and working up now gave 79% of hexaphenyldilead, as indicated by the Krause formulation (reaction 3).

Because of this decomposition, therefore, it is necessary to maintain the low temperature past the diphenyllead stage. However, the final product at the triphenylleadlithium stage is apparently stable to heat. In one experiment, triphenylleadlithium was prepared as above, in the cold, and the mixture was then refluxed for two hours with stirring. There was no deposition of lead or other visible change. In another experiment, triphenylleadlithium was prepared from 0.040 mole of $PbCl_2$, and to the mixture, 150 ml. of dry toluene was added. This mixture was then refluxed for five hours, with little visible change. The mixture was cooled, 6.1 g. of benzyl chloride was added, and the preparation of triphenylbenzyllead was carried out as above, to give a 65% yield. The residue of metallic lead produced on hydrolysis was filtered out, and weighed only 0.3 g.

If the equilibrium indicated by equation 13 exists, then it might be expected that the preparations at any stage might be unstable on heating, due to the presence of diphenyllead from the equilibrium. This was not, however, the result obtained. It is possible that the equilibrium lies ordinarily very far to the right as written. The higher temperatures involved in these experiments may also cause a shift in the position of the equilibrium.

Carbonation of triphenylleadlithium. Triphenylleadlithium was prepared from 11.1 g. (0.040 mole) of $PbCl_2$ and 0.120 mole of phenyllithium. Color Test I was positive, and the mixture was gray-white. Stirring was continued while gaseous CO_2 was passed over the mixture, still cooled in ice, for five hours. The yellow color gradually reappeared and deepened to an orange-brown shade. Hydrolysis with water gave much yellow precipitate, which was filtered out. The water layer of the filtrate was separated and washed out again with ether, and the ether layers were washed again with 5% aqueous sodium hydroxide. The combined aqueous extracts were acidified with dilute nitric acid, and extracted with ether. Evaporation of the ether, after drying, left 2.4 g. of benzoic acid, m.p. 115–121°, which, after one recrystallization from water, melted at 120–121° and showed no m.p. depression with an authentic sample. This is 0.020 mole of benzoic acid, or 49% based on the 0.040 mole of phenyllithium present in excess of that necessary to form diphenyllead. The experiment was repeated, and gave 2.7 g. (0.022 mole), or 55%, of benzoic acid.

In another case, 0.040 mole of $PbCl_2$ was treated with only 0.104 mole of phenyllithium or 2.6 equivalents. Color Test I was negative, and the mixture was yellow. Carbonation as above gave 1.3 g. (0.011 mole) of benzoic acid, or 44% based on the 0.024 mole of phenyllithium available. Finally a mixture was carbonated at the diphenyllead stage, obtained from 0.040 mole of $PbCl_2$ and 0.080 mole of phenyllithium. No benzoic acid was found. This indicates that under these conditions diphenyllead does not react with CO_2 to give benzoic acid, so that the latter must come from the phenyllithium component of reaction 13.

Reaction of triphenylleadlithium with other alkyl halides. Other RX compounds containing reactive or moderately reactive halogen reacted with triphenylleadlithium smoothly according to reaction 11. The reactions were carried out essentially as described above for triphenylbenzyllead. From *n*-propyl bromide, triphenyl-*n*-propyllead, m.p. 68–69°, was obtained in 58% yield.

Anal. Calc'd for $C_{21}H_{22}Pb$: Pb, 43.0. Found: Pb, 42.7.

Ethyl iodide gave triphenylethyllead, m.p. 48–50°, in 45% yield. It was identified by mixed m.p. with an authentic specimen,[2] and by lead analysis.

Anal. Calc'd for $C_{20}H_{20}Pb$: Pb, 44.3. Found: Pb, 44.0.

Reaction of other aryllithium compounds with lead chloride in the cold. *p*-Tolyllithium reacted like phenyllithium, and the intermediate diaryllead stage was the same yellow color. The final mixture presented the same grayish-white appearance. Derivatization

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[2] Sample prepared by J. D. Robinson.

with benzyl chloride gave 65% of tri-*p*-tolylbenzyllead, m.p. 81–83°, identified by mixture m.p. with an authentic sample (5a). In the case of *o*-tolyllithium, the diaryllead intermediate was deep brick red.

p-Dimethylaminophenyllithum reacted only very slowly. When an ether solution of this lithium compound was added to 11.1 g. (0.040 mole) of $PbCl_2$ in ether at −10°, Color Test I became positive with the first few ml. of the organolithium solution. Two equivalents (0.080 mole) of the RLi compound were added, and the mixture was stirred in the cold for five hours, and finally refluxed for 60 hours before the color test became negative. Upon addition of the first portions of the RLi solution the mixture became a deep violet-blue in color, so that visual observation could not detect whether a colored intermediate, or metallic lead, was produced. This deep violet color is characteristic of some reactions involving this lithium compound. Small samples withdrawn and hydrolyzed with water, however, showed no lead, and there was apparently gradually built up in the mixture an orange-red intermediate.

Preparation of tetra-p-dimethylaminophenyllead. Because of the behavior described above, it is not readily possible in the case of the *p*-dimethylaminophenyl compound to distinguish the stages in the reaction or to demonstrate one distinct mechanism. However, tetra-*p*-dimethylaminophenyllead was desired for other work, and a method was therefore developed empirically by which it could be obtained in good yields in small batches. The technique used resembled that of reference (8) (reaction 6), but we do not believe that the mechanism can be the same, since free lead does not appear to be developed on heating the intermediate in this case. A solution of 0.120 mole of *p*-dimethylaminophenyllithium in ether was added over a period of 1.5 hours to a mixture of 11.1 g. (0.040 mole) of $PbCl_2$ and 10.9 g. (0.040 mole plus 10%) of *p*-iododimethylaniline (14) in 32 ml. of ether, stirred and refluxed under nitrogen. Refluxing was continued for 24 hours. Color Test I was weak, but still positive. The mixture was poured into ice-water, and the precipitate was filtered off with suction. The residue was placed in a flash and washed, by decantation, first with 95% alcohol and then with petroleum ether (b.p. 60–67°), and finally collected on a filter. The nearly white powder remaining was dissolved in 300 ml. of benzene, boiled with charcoal, and filtered hot. To the warm filtrate was added 500 ml. of petroleum ether, and the solution was cooled, finally in the refrigerator, to give 17.4 g. (63%, based on reaction 6) of white crystals, m.p. 187–189°.

Anal. Calc'd for $C_{28}H_{40}N_4Pb$: Pb, 30.1. Found: Pb, 29.9.

This material was previously prepared by Austin (7) from the lithium compound in 17% yield, based on reaction 5.

In other preparations on the same scale, two hours' refluxing gave only 20% yield; five hours' refluxing gave 27%.

In a run using 45.9 g. (0.16 mole) of $PbCl_2$, with 24 hours' refluxing, the yield was 23%. Apparently, for a run of this size, a much longer reflux time would be necessary.

Hydrolysis experiments. Hydrolysis of various reaction mixtures obtained from phenyllithium and $PbCl_2$ at −10°, whether at a stage corresponding to diphenyllead or to triphenylleadlithium, gave no reproducible products. There was always obtained a heavy yellow precipitate and a deep yellow to red coloration in the ether. The precipitate was in part organic, but undoubtedly contained inorganic material, and was not completely soluble in organic solvents. Whether the hydrolysis was conducted under nitrogen or not made no apparent difference. Ether or benzene extracts, on storage even under nitrogen, continued for several days to deposit more yellowish precipitate. It was thought that, since the intermediate obtained from *p*-dimethylaminophenyllithium was indicated by the experiments above to be quite unreactive, it might be possible in this case to obtain a well-defined product corresponding to a diaryllead. The experiment is described in detail, since it is a good example of the indefinite behavior of the materials obtained in such experiments, including those with phenyllithium. A solution of 0.120 mole of *p*-dimethylaminophenyllithium was added to 11.1 g. (0.040 mole) of $PbCl_2$ in 30 ml. of ether and the mixture was refluxed with stirring for 40 hours. The solid was allowed to settle and liquid was decanted off into a separatory-funnel and then added, under nitrogen, to ice-water. There resulted 6.0 g. of a bright orange-red precipitate, which did not change in appearance on exposure to air. The dry powder was washed three times by decantation with ether. The residue contained nitrogen (and no halogen), and the Pb content was near that calculated for di-*p*-dimethylaminophenyllead.

Anal. Calc'd for $C_{16}H_{20}N_2Pb$: Pb, 46.3. Found: Pb, 49.3.

The material could not be purified without change. One gram of it was extracted with 150 ml. of hot benzene, and to the warm filtrate there was added 160 ml. of petroleum ether. The solution, on cooling to room temperature, deposited 0.3 g. of microcrystalline material of a clear deep brick-red color. However, the Pb content was now considerably lower.

Anal. Found: Pb, 39.2.

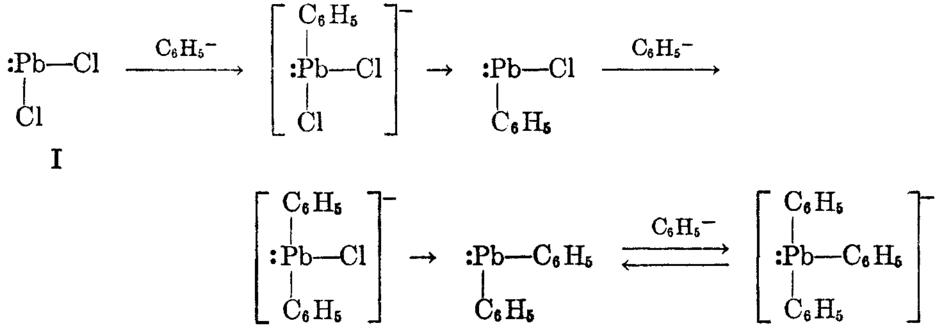
Attempted preparation of $R_2R'R''Pb$ compounds from $PbCl_2$. The next point investigated was whether compounds of this type could be obtained directly from $PbCl_2$, by the use of two different aryllithium compounds in succession. The only known material of this type which is a solid is di-*o*-tolylphenyl-*n*-propyllead (15), and it was therefore chosen for the study. To 11.1 g. (0.040 mole) of $PbCl_2$ in 30 ml. of ether, at −10°, there was added 0.080 mole of *o*-tolyllithium in ether. Color Test I was negative, and the mixture was deep red in color. Then, still at −10°, there was added 0.040 mole of phenyllithium in ether. The color disappeared, and the Color Test became positive. To this preparation was added excess *n*-propyl bromide, and the reaction was completed and worked up as described above for triphenylbenzyllead. The first crop of crystals from ethanol weighed 8.9 g., and melted at 53–79°. Recrystallization from a petroleum ether-methanol mixture gave 4.3 g., melting at 44–92°. The material was apparently a mixture. A consideration of the m.p.'s recorded in the literature, and of the solubility characteristics (the material was completely soluble in petroleum ether) indicated that the mixture could hardly contain tetraaryllead compounds, and probably consisted largely of triaryl-*n*-propylleads. In such a case the least symmetrical compounds of the type $Ar_2Ar'Pb\text{-}n\text{-}C_3H_7$ (Ar = aryl) might be expected to concentrate in the most soluble fractions. The ethanol mother liquor from the first crystallization was therefore concentrated and cooled in the refrigerator. The oil which separated would not crystallize. (The m.p. of the desired compound is 49–50°.)

The experiment was repeated as above, except that the propyl bromide was added beforehand to the reaction mixture. The result was, however, essentially the same.

DISCUSSION

From the results described above, it appears that in the reaction of phenyllithium with lead chloride the key reaction is reaction 12. Although the diphenyllead thus produced is not used as such, it is the intermediate which on the one hand decomposes at higher temperatures, as in the previously reported studies (8), to give metallic lead; and which on the other hand, if the mixture is kept cold, reacts with additional phenyllithium to give triphenylleadlithium. The particular usefulness of the organolithium compounds in the present applications, as compared to the Grignard reagent, lies in the fact that they are active enough to react smoothly with lead chloride at temperatures low enough that decomposition of the diphenyllead does not occur. The lower reactivity found by Krause for the Grignard reagent at such temperatures has been mentioned above.

Since the divalent lead compounds, lead chloride and diphenyllead, are thus involved in these reactions, it is interesting to inquire whether our results can be interpreted in agreement with accepted views of the nature of the divalent state of lead. It appears that this is the case. The divalent states of the Group IV-B elements are regarded as derived from the ground state of the atom, for which in the case of lead the electronic configuration is $6s^26p^2$. The atom is therefore expected to form two p bonds (essentially at right angles), without utilization of the coupled pair of s electrons. This was termed the "inert pair" effect by Sidgwick.[3] Monomolecular lead chloride may therefore be represented essentially as in formula (I) below, and it is seen that, since only six electrons are present around the lead atom, it should be possible for it to accept an electron pair readily. If the organolithium compound is represented as reacting essentially as a phenyl anion, the changes involved may be as follows:

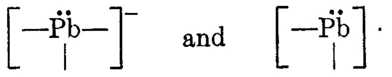


I

$$\underset{\mathrm{Cl}}{:\!\mathrm{Pb{-}Cl}} \xrightarrow{C_6H_5^-} \left[\overset{C_6H_5}{\underset{\mathrm{Cl}}{:\!\mathrm{Pb{-}Cl}}}\right]^- \rightarrow \underset{C_6H_5}{:\!\mathrm{Pb{-}Cl}} \xrightarrow{C_6H_5^-}$$

$$\left[\overset{C_6H_5}{\underset{C_6H_5}{:\!\mathrm{Pb{-}Cl}}}\right]^- \rightarrow \underset{C_6H_5}{:\!\mathrm{Pb}{-}C_6H_5} \overset{C_6H_5^-}{\rightleftarrows} \left[\overset{C_6H_5}{\underset{C_6H_5}{:\!\mathrm{Pb}{-}C_6H_5}}\right]^-$$

This is a formalized representation in that it shows the divalent lead compounds as monomers, whereas they are undoubtedly polymerized; and also in that it represents the organolithium compound as reacting as a simple free anion. In the main, this formulation points out that the occurrence of these reactions is the result essentially of the small energy difference between the two states



$$\left[-\underset{|}{\overset{\cdot\cdot}{\mathrm{Pb}}}-\right]^- \text{ and } \left[-\underset{|}{\overset{\cdot\cdot}{\mathrm{Pb}}}\right]\cdot$$

It is the ready transformations between these two states which lead finally to the desired product. We would clearly expect that the first two steps, involving displacement of chlorine by phenyl, might be essentially irreversible, because of the relatively high stability of chlorine as an anion. In the last step, however, there is no remaining chlorine atom; the groups are all phenyl groups. Elimination of any anionic group at this point, therefore, would simply give back the reactants (diphenyllead and phenyllithium) and the indicated equilibrium would result. The position of this equilibrium would vary according to the nature of the R group. The case would be different when two different organolithium compounds were present in the mixture. There would then be a possibility of interchange of R groups on the lead atom, resulting in a mixture of various types of

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[3] Sidgwick, *The Electronic Theory of Valency*, Oxford, 1927, pp. 178–181. Since Sidgwick's qualitative description of this interesting effect, little theoretical consideration has been given to it, except for some work on carbon. For that element some discussion has been offered concerning the energy difference between the ^3P state derived from this configuration and the ^5S state derived from the $2s2p^3$ configuration which leads to tetravalence. See Ufford, *Phys. Rev.*, **53**, 568 (1938); Long and Norrish, *Proc. Roy. Soc.* (*London*), **A187**, 337 (1946).

organolead intermediates. This is apparently what occurred in our attempts to prepare di-*o*-tolylphenyl-*n*-propyllead.

If these interpretations are valid, then it appears that reaction 13, employing these preparations of triphenylleadlithium in ether, should be a method of preparation of $(C_6H_5)_3PbR$ compounds in general in cases where the halogen in RX is active or moderately active and where the group R does not contain functions which react rapidly with phenyllithium. The desired reaction is favored by the fact that aryllithium compounds in general do not react rapidly with organic halides.

For the synthesis of $R_2R'R''Pb$ compounds directly from lead chloride, however, the method is probably not generally applicable if the above-discussed equilibrium exists. It is still possible that the procedure might be applied in carefully selected cases.

Further studies on applications of these reactions are being carried out.

SUMMARY

An investigation of the nature of the reaction of phenyllithium and other aryllithium compounds with lead chloride under various conditions was undertaken. The purpose of the work was to develop a better understanding of the mechanisms of some of the reactions involved, and to study possible novel synthetic applications of these reactions. It was found that phenyllithium reacts readily with lead chloride at −10° to give triphenylleadlithium, $(C_6H_5)_3PbLi$.

$$3C_6H_5Li + PbCl_2 \rightarrow (C_6H_5)_3PbLi + 2LiCl$$

By treatment of triphenylleadlithium with RX derivatives of appropriate types, $(C_6H_5)_3PbR$ compounds are conveniently prepared from lead chloride in one process. The nature of triphenylleadlithium and the mechanism of its formation are discussed. Some further experiments on the preparation of R_4Pb compounds by a previously reported technique, involving the reaction

$$3RLi + PbCl_2 + RI \rightarrow R_4Pb + 2\,LiCl + LiI$$

are described.

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(5) See for instance (a) GILMAN AND BAILIE, *J. Am. Chem. Soc.*, **61**, 731 (1939); (b) CALINGAERT, SOROOS, AND SHAPIRO, *J. Am. Chem. Soc.*, **64**, 462 (1942).
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