[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE PREPARATION AND CHEMICAL PROPERTIES OF R_3PbNa COMPOUNDS

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Organolead compounds of the type R_3PbM' (where R = an organic group and M' = an active metal) were first reported in 1939, when the preparation of triphenyllead-sodium by the action of sodium in liquid ammonia on hexaphenyldilead or triphenyllead halides (1, 2) was described. Further investigation (3) showed that lithium, potassium, rubidium, calcium, strontium, or barium would react in similar fashion with hexaphenyldilead; and also that trialkyllead-metal compounds such as triethyllead-lithium could be obtained from trialkyllead chlorides.

These preparations all involved the use of solutions of the metal in liquid ammonia. As the work progressed, it was discovered that the lithium derivatives of the type of triphenyllead-lithium could be obtained also from the reaction of aryllithium solutions with lead dichloride in ether at low temperatures. This line of investigation was followed at some length. The preparation of triaryllead-lithium compounds in this fashion, and applications of such compounds in organolead syntheses, have been discussed in previous papers (4, 5).

Simultaneously, research on the liquid ammonia reactions was also continued, and the present paper describes some further results which have been obtained. Although we have found these reactions to be perhaps somewhat less convenient for preparative purposes than the reactions involving phenyllithium and lead dichloride, they may nevertheless be of value for the preparation of some unsymmetrical organolead compounds. Certain aspects of the cleavage of organolead compounds with metals in liquid ammonia are also of great theoretical interest.

In the investigations mentioned above, the organolead starting materials had been hexaaryldileads (equation 1) or triaryl- or triethyl-lead halides (equation 2). It seemed reasonable to expect that tetraaryl- or tetraalkyl-leads might also react to give the R_3PbNa compound. This we found to be the case. The reaction produced also sodamide (equation 3). The conditions influencing the yield of triphenyllead-sodium from tetraphenyllead, and of triethyllead-sodium from tetraethyllead, were studied in some detail, and optimum conditions were established. In the case of tetraethyllead, use of an ether-liquid ammonia mixed solvent was advantageous.

$$R_3PbPbR_3 + 2Na \xrightarrow{NH_3} 2\ R_3PbNa \tag{1}$$

$$R_3PbCl + 2Na \xrightarrow{NH_3} R_3PbNa + NaCl \tag{2}$$

$$R_4Pb + 2Na + NH_3 \rightarrow R_3PbNa + RH + NaNH_2 \tag{3}$$

Some comparison may now be made of the usefulness of these three methods for the preparation of R_3PbNa compounds. This will of course depend on various considerations, such as the use for which the R_3PbNa compound is desired, and also the availability of the various starting materials. Hexaaryldileads, in general, are prepared at least as readily as the tetraarylleads, and are quite stable. Pure solutions of triphenyllead-sodium are probably best prepared from hexaphenyldilead (equation 1), since there is in this case no by-product. The sodamide which was produced when tetraphenyllead was used caused, however, no great difficulty. It could be filtered out or dissolved by addition of ammonium bromide; or, if the R_3PbNa compound was desired for reaction with an alkyl halide, enough excess of the latter could be added to react also with the sodamide. The yields of R_3PbNa compounds are high, no matter what starting material is used. For triethyllead-sodium, the starting material of choice is probably tetraethyllead, since hexaethyldilead is difficult to preserve in a pure state. In this case the sodamide had to be filtered out if its removal was desired. It could not be destroyed by ammonium bromide, because the latter destroyed also much of the trialkyllead-sodium compound. But it should be noted that triethyllead-sodium reacted with alkyl halides much faster than did sodamide, so that removal of sodamide was not important.

The synthetic usefulness of R_3PbM' derivatives lies in the fact that they react with many organic halides according to the equation $R_3PbM' + R'X \rightarrow R_3PbR' + M'X$ (X = halogen, R and R' = organic groups) to produce unsymmetrical organolead compounds in good yield. In order to outline the scope and limitations of this type of reaction with R_3PbNa compounds, such reactions were carried out with a number of organic halides. In general, triethyllead-sodium was found to be much more reactive in this respect than triphenyllead-sodium. The latter reacted with alkyl halides, although a large excess of the halide was required; but it did not react with aromatic halides. Triethyllead-sodium, however, reacted rapidly and completely with primary alkyl halides and also with bromobenzene. With *sec*-butyl bromide, triethyllead-sodium reacted more slowly and gave a lower yield than with the *n*-butyl compound, and with *tert*-butyl bromide no R_3PbR' product resulted

EXPERIMENTAL

Reaction of tetraphenyllead with sodium. Sodium, 0.022 g.-atom (10% excess), was dissolved in 75 ml. of liquid ammonia, and this solution was forced over by nitrogen pressure into a stirred suspension of 5.15 g. (0.01 mole) of tetraphenyllead in 100 ml. of dry ether. After six minutes, there was added 5 ml. (0.056 mole) of ethyl bromide in 10 ml. of ether. The ammonia was allowed to evaporate, the ether was removed, and the residue was extracted with hot methanol followed by hot benzene. Triphenylethyllead was obtained from the methanol, and was recrystallized from fresh solvent. Tetraphenyllead was isolated from the benzene, and was recrystallized from chloroform. These compounds were identified by mixture m.p.'s with authentic specimens. The residue from the extraction was dissolved in ammonium acetate, and the inorganic lead was determined as chromate. There was obtained 83% of triphenylethyllead, 5% of recovered tetraphenyllead, and 6% of inorganic lead. Another similar experiment (reaction time five minutes) gave 82% of triphenylethyllead.

The procedure described above represents the optimum conditions. Other conditions for the cleavage gave lower yields. When the concentrations used were 0.022 g.-atom of sodium in 15 ml. of liquid ammonia and 5.15 g. of tetraphenyllead in 20 ml. of ether, the yield of triphenylethyllead was 68%, of recovered tetraphenyllead 13%, and of inorganic lead 13%. When the reaction was carried out as above except that the time and temperature were one hour and −70°, respectively, the yield of triphenylethyllead was 47%. When reactions were carried out according to the optimum procedure except that the time of reaction was varied from one minute to two or three hours, there was little difference in yield. As a matter of convenience, five to ten minutes was the time usually allowed for reaction. Use of a large excess of sodium caused some diminution in yield, but a small excess did no harm. It was therefore possible to carry out the reaction by adding sodium metal, in small pieces, directly to a stirred mixture of tetraphenyllead, ether, and liquid ammonia in the proportions given above.

Besides triphenyllead and recovered tetraphenyllead, the benzene and sodamide shown in equation 3 were identified among the products of the reaction. Benzene (b.p. 76–78°) was isolated, in 50% yield, by refractionation of the ethereal distillate from one run. It was identified as *m*-dinitrobenzene. The sodamide precipitated as the reactions progressed. If not removed, it reacted with alkyl halides faster than did triphenyllead-sodium. Thus in one experiment 0.23 g. (0.01 g.-atom) of sodium was added to a suspension of 2.57 g. (0.005 mole) of tetraphenyllead in 150 ml. of liquid ammonia, and after six minutes there was added 0.7 g. (0.0055 mole, 10% excess) of benzyl chloride. Working up of the mixture gave 7% yield of triphenylbenzyllead (m.p. 90–91°), 6% of tetraphenyllead, and 74% of inorganic lead. In another similar experiment, the solution was filtered through sintered glass before the benzyl chloride was added. The yield of triphenylbenzyllead in this case was 70%. In a third experiment, there was added 0.54 g. (0.0055 mole, 10% excess) of ammonium bromide, previous to the addition of the benzyl chloride. The yield of triphenylbenzyllead was 80%. However, use of a large excess of ammonium bromide was not permissible. When triphenyllead-sodium was prepared as above, and 0.98 g. (0.01 mole) of ammonium bromide was then introduced and allowed to react for one minute before addition of the benzyl chloride, the yield was reduced to 24% of triphenylbenzyllead, plus 43% of inorganic lead and 0.37 g. of a mixture of tetraphenyllead and hexaphenyldilead.

Reaction of tetraethyllead with sodium. To a solution of 6.4 g. (0.02 mole) of tetraethyllead in 50 ml. of ether there was added 0.92 g. (0.04 g.-atom) of sodium in solution in 150 ml. of liquid ammonia. After six minutes, there was added 5.48 g. (0.04 mole) of *n*-butyl bromide in 20 ml. of ether. The ammonia was allowed to evaporate, and the ether solution was washed with water, dilute hydrochloric acid, dilute sodium bicarbonate, and water. The solution was dried, the ether was removed, and the residue was distilled to isolate triethyl-*n*-butyllead, b.p. 81–83°/5 mm., n_D^{20} 1.5112, d_4^{20} 1.5283. Yields of triethyl-*n*-butyllead varied from 91 to 95%.

This reaction was less affected by temperature. At −70°, with a three-minute reaction time, a 95% yield was obtained. There was, however, a pronounced solvent effect. When liquid ammonia alone was used, the yield was 80%. Use of toluene-liquid ammonia mixed solvent gave 88% yield. The ether-liquid ammonia solvent, as described above, gave the best result.

The sodamide formed in the reaction could be filtered out, as before. Use of ammonium bromide for removal of sodamide was not permissible in this case. To a solution of triethyllead-sodium prepared from 12.9 g. (0.04 mole) of tetraethyllead in 50 ml. of ether and 1.84 g. (0.08 g.-atom) of sodium of 50 ml. of liquid ammonia, there was added 3.92 g. (0.04 mole) of ammonium bromide. Thirty seconds later, 11.0 g. (0.08 mole) of *n*-butyl bromide was introduced. The resulting yield of triethyl-*n*-butyllead was 57%, plus 41% of inorganic lead. The most satisfactory procedure was not to remove the sodamide, but to add sufficient *n*-butyl bromide to react with it. It was not necessary to use two full equivalents of the halide; use of 1.5 equivalents gave 90% yield or better of triethyl-*n*-butyllead.

Reactions of triphenyllead-sodium with organic halides. Triphenyllead-sodium was prepared as above, and reactions were attempted with *p*-chlorotoluene, *p*-bromotoluene, *p*-iodotoluene, methyl *p*-bromobenzoate, *p*-iodonitrobenzene, and 2,4-dinitrochlorobenzene. Times allowed for reaction varied from 24 to 36 hours. No R_3PbR' products could be isolated from any of these attempts, except that the reaction with *p*-iodotoluene yielded about 5% of impure triphenyl-*p*-tolyllead.

The reactions of triphenyllead-sodium with a large excess of ethyl bromide to give triphenylethyllead (83%), or with benzyl chloride to give triphenylbenzyllead (80%) have been described above.

Reactions of triethyllead-sodium with organic halides. The reaction with *n*-butyl bromide has already been described. Reactions with other halides were carried out similarly, and the products were worked up in the usual manner.

sec-Butyl bromide, 41.1 g. (0.030 mole) and the triethyllead-sodium obtained from 49.4 g. (0.15 mole) of tetraethyllead reacted to give 43.2 g. (82%) of triethyl-*sec*-butyllead, b.p. 108–109°/15 mm., n_D^{20} 1.5190, d_4^{20} 1.5318. The alkyl halide was added rapidly, but the color of the ether-liquid ammonia solution did not fade rapidly, and ebullition was less vigorous than when *n*-butyl bromide was used. The time allowed for the reaction was ten minutes.

When *tert*-butyl bromide (11.0 g., 0.08 mole; tetraethyllead 12.9 g., 0.04 mole) was used, no triethyl-*tert*-butyllead could be isolated. The only product identified was tetraethyllead, 4 g. In another experiment the *tert*-butyl bromide was allowed to react for four hours, under nitrogen, at the temperature of an acetone-solid carbon dioxide mixture. Again the only product isolated was tetraethyllead (9.7 g., 30%).

Benzyl chloride did not react well with triethyllead-sodium. Stilbene (identified by mixture m.p.) was produced, and the highest yield of triethylbenzyllead was 10%.

Iodobenzene, in a 0.1-mole run, gave 5.6 g. (15%) of triethylphenyllead, b.p. 127–131°/7 mm., n_D^{20} 1.5532, plus about 13 g. of tetraethyllead. Bromobenzene gave 77% of triethylphenyllead, b.p. 137–140°/13 mm., n_D^{20} 1.5752, d_4^{21} 1.5915. Four hours was allowed for the latter reaction.

In a 0.15-mole run, 23 g. (0.3 mole) of allyl chloride gave 36.2 g. (72%) of triethylallyllead, b.p. 85–86°/8 mm., n_D^{22} 1.5410, d_4^{23} 1.6056.

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SUMMARY

Triphenyllead-sodium was prepared from tetraphenyllead and sodium in liquid ammonia, and triethyllead-sodium was prepared similarly. A discussion of the relative merits of the known methods for the preparation of these substances is given. Triphenyllead-sodium reacted with active alkyl halides such as benzyl chloride, but not with inactive halides such as aromatic halogen compounds. Triethyllead-sodium was considerably more reactive.

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