[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE PREPARATION OF TRIPHENYL LEAD CHLORIDE AND DIPHENYL LEAD DICHLORIDE

BY HENRY GILMAN AND JACK D. ROBINSON

RECEIVED JUNE 1, 1929 PUBLISHED OCTOBER 5, 1929

Introduction

In connection with studies on organolead compounds a need was felt for a satisfactory method for the preparation of triaryl lead chlorides and diaryl lead dichlorides. We selected the chlorides in preference to the other halides for three reasons: first, the chlorides are more stable than the bromides and iodides; second, they are less expensive than the other halides, assuming that all of them can be prepared in approximately equal yields; and, third, there is no essential difference in reactivity between the several halides in our particular studies.

Triphenyl lead halide, $(C_6H_5)_3PbX$, and diphenyl lead dihalide, $(C_6H_5)_2PbX_2$, have generally been prepared from tetraphenyl lead, $(C_6H_5)_4Pb$, which is obtainable in satisfactory yield from the reaction between lead chloride and phenylmagnesium bromide.[1] Triphenyl lead bromide has been prepared in excellent yields by Grüttner[2] from tetraphenyl lead and the bromine addition compound of pyridine, at low temperatures obtained with solid carbon dioxide. Objections to this method are the expense of pyridine and the inconvenience of using solid carbon dioxide. Krause and Reissaus[3] prepared triphenyl lead iodide by adding a dilute solution of iodine to triphenyl lead. Krause and Pohland[4] prepared triphenyl lead fluoride by double decomposition of potassium fluoride with triphenyl lead bromide, and Krause and Schlöttig[5] prepared triphenyl lead chloride by treating phenylmagnesium bromide with a slight excess of lead chloride. They also observed that triphenyl lead chloride could be obtained in 75% yield by heating tetraphenyl lead with four equivalents of ammonium chloride at 170–180° for twelve hours. This method, however, only gives satisfactory yields with small quantities of compound and is valueless with mixed aryl lead chlorides because of their thermal instability. The method most generally used has been that of Grüttner.[2]

The first diphenyl lead dihalide was prepared by Polis,[6] who obtained diphenyl lead di-iodide from a chloroform solution of tetraphenyl lead and iodine. Later[7] he prepared the corresponding bromide and chloride

---

[1] Gilman and Robinson, THIS JOURNAL, **49**, 2315 (1927).

[2] Grüttner, *Ber.*, **51**, 1298 (1918).

[3] Krause and Reissaus, *ibid.*, **55**, 888 (1922).

[4] Krause and Pohland, *ibid.*, **55**, 1282 (1922).

[5] Krause and Schlöttig, *ibid.*, **58**, 427 (1925).

[6] Polis, *ibid.*, **20**, 716 (1887).

[7] Polis, *ibid.*, **20**, 3331 (1887); see, also, Pfeiffer and co-workers, *ibid.*, **37**, 1125 (1904); **49**, 2445 (1916).

in like manner using bromine and chlorine. Werner and Pfeiffer[8] incidentally obtained some diphenyl lead dichloride in searching for an addition compound of tetraphenyl lead and hydrogen chloride. Goddard, Ashley and Evans[9] obtained the dichloride from a reaction between tetraphenyl lead and a miscellany of inorganic chlorides. The method most generally used has been that of Polis.[6,7]

The methods described at this time involve the following reactions

$$(C_6H_5)_4Pb + HCl \longrightarrow (C_6H_5)_3PbCl + C_6H_6 \qquad (I)$$
$$(C_6H_5)_3PbCl + HCl \longrightarrow (C_6H_5)_2PbCl_2 + C_6H_6 \qquad (II)$$

These reactions are in agreement with Werner and Pfeiffer's[8] observations that hydrogen chloride reacts with tetraphenyl lead in a dry chloroform solution. Polis,[6] on the other hand, reported that concentrated hydrochloric acid does not react with tetraphenyl lead until heated in a tube at 230°, and then lead chloride results.

In our preparation of triphenyl lead chloride, the hydrogen chloride was bubbled into a warm chloroform solution of tetraphenyl lead until crystals of diphenyl lead dichloride formed. The formation of this insoluble dichloride is an excellent end-point, and the yields are distinctly satisfactory (about 75%). The diphenyl lead dichloride was prepared in practically quantitative yields by merely saturating a benzene solution of tetraphenyl lead with hydrogen chloride.

The high yields of the monochloride and of the dichloride make it possible to prepare the corresponding other halides in either of two ways. First, the following metathetical reactions can be used

$$R_3PbX + NaX' \longrightarrow R_3PbX' + NaX \qquad (III)$$
$$R_2PbX_2 + 2NaX' \longrightarrow R_2PbX_2' + 2NaX \qquad (IV)$$

These reactions are readily carried out in dilute alcoholic solutions.[2,4,10] A second indirect method, and the one which is generally recommended, involves the following reactions[11]

$$R_3PbX + NaOH \longrightarrow R_3PbOH + NaX \qquad (V)$$
$$R_3PbOH + HX' \longrightarrow R_3PbX' + H_2O \qquad (VI)$$

The unusual smoothness of the reactions described at this time has recommended them not only for synthetic purposes (for the preparation of aryl lead halides in general) but also for studies in progress on the relative electronegativities of organic radicals.

---

[8] Werner and Pfeiffer, *Z. anorg. Chem.*, **17**, 82 (1898).

[9] Goddard, Ashley and Evans, *J. Chem. Soc.*, **121**, 256, 978 (1922).

[10] Calingaert, *Chem. Reviews*, **2**, 43 (1925).

[11] It is probable that the bromides can be prepared in equally good yields after the methods described here for the preparation of the chlorides, that is, from tetraphenyl lead and hydrogen bromide. The hydrogen chloride method also gives excellent yields of the tin mono- and dichlorides. Also, alkyl lead mono- and dichlorides can be prepared in the same high yields as the corresponding aryl halides.

Experimental Part

The following directions are typical of a series of experiments carried out by us.

Triphenyl Lead Chloride.—20.2 g. (0.04 mole) of tetraphenyl lead is dissolved in 300 cc. of boiling chloroform and hydrogen chloride is then bubbled through the solution, which is kept near its boiling point (or it may be refluxed gently) by the application of heat. After about fifteen minutes (depending on the rate of flow of gas) a precipitate of shiny plates of diphenyl lead dichloride starts to form and the stream of gas is quickly shut off. This precipitate resembles greatly a precipitate of mercurous chloride, and is not to be confused with a flocculent precipitate that may form if the tetraphenyl lead is impure or if the gas is introduced very rapidly. The flocculent precipitate need not be removed if it forms, inasmuch as the precipitate of diphenyl lead dichloride is very readily recognized even in the presence of the flocks. After the entry of hydrogen chloride has been terminated, the solution is boiled to complete the reaction with any dissolved hydrogen chloride and the solution is then filtered. The quantity of diphenyl lead dichloride obtained by this filtration is 1.5–2.0%.

The chloroform is removed from the clear solution by distillation from a water-bath. The residue when extracted with two 200-cc. portions of hot alcohol leaves the unaltered tetraphenyl lead (about 20%). The alcohol extract yields the pure triphenyl lead chloride (about 75% yield). Approximately the same ratio of products was obtained from a run starting with 56.7 g. (0.11 mole) of tetraphenyl lead.

Diphenyl Lead Dichloride.—An excess of hydrogen chloride is run into a solution of 51.5 g. (0.1 mole) of tetraphenyl lead in 500 cc. of benzene warmed to about 50°. The flask may be open or closed, but one advantage of a closed system is that it gives an indication of the stage of the reaction from the rate at which the gas is being absorbed. The end of the reaction is not readily determined inasmuch as the hydrogen chloride is very slowly absorbed even when the reaction appears to be completed. A better way is to filter the shiny plates of diphenyl lead dichloride when the reaction appears to be at an end and then pass more hydrogen chloride into the hot filtrate.[12] If there is no additional precipitate the reaction is done. Only a very small quantity of lead chloride forms even after prolonged treatment with hydrogen chloride.[12] The yield is 42.2 g. or 98.5%.

Summary

Triphenyl lead chloride and diphenyl lead dichloride may be prepared in high yields by the action of hydrogen chloride on tetraphenyl lead.

AMES, IOWA

---

[12] The mixture should be filtered hot in order to avoid precipitation of any unaltered tetraphenyl lead. Tetraphenyl lead and triphenyl lead chloride are readily soluble in hot benzene.