

clusion that the two theoretically possible *dl*-1,2-dihydroxybutyric acids have melting points of 73.5–74.5 and 81.5°.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

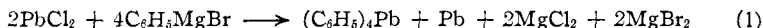
## THE PREPARATION OF TETRAPHENYL LEAD<sup>1</sup>

BY HENRY GILMAN AND JACK ROBINSON

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There are, at present, two general methods for the preparation of tetraphenyl lead. One, by Polis,<sup>2</sup> is the protracted heating of an ethyl acetate solution of bromobenzene with sodium-lead alloy. The other, by Pfeiffer and Truskier,<sup>3</sup> is commonly represented by the following reaction.<sup>4</sup>



The method using the Grignard reagent has been widely employed<sup>5</sup> because of its greater convenience and better yields. In connection with the application of organolead compounds as antiknock reagents and in the treatment of cancer and some plant diseases, tetraphenyl lead is being used as one of the types for the preparation of variously substituted derivatives. The present study reports the effect of various factors on the yield of tetraphenyl lead as prepared by the Grignard reaction. Using Pfeiffer and Truskier's technique we have not succeeded in equaling their yields. However, the quantity of phenylmagnesium bromide required to give a yield that closely approximates theirs has been significantly decreased below that which they used. Our present maximum yield of about 50% points strongly to a series of reactions more complex than that illustrated in Reaction (1). Experiments have shown that lead chloride cannot be effectively replaced by lead bromide, lead iodide or lead dioxide in this method of preparation. It is possible that better yields may be realized by treating the phenylmagnesium bromide with zinc chloride prior to the addition of lead chloride. Such a method, involving the intermediate formation of organozinc compounds, has been

<sup>1</sup> A preliminary report was read at the meeting of the Iowa Academy of Sciences held at Iowa City on May 6, 1927.

<sup>2</sup> Polis, *Ber.*, **20**, 717 (1887).

<sup>3</sup> Pfeiffer and Truskier, *Ber.*, **37**, 1125 (1904).

<sup>4</sup> A recent excellent survey of organolead compounds has been made by Calingaert, *Chem. Reviews*, **2**, 43 (1925).

<sup>5</sup> (a) Hofmann and Wöfl, *Ber.*, **40**, 2425 (1907). (b) Möller and Pfeiffer, *Ber.*, **49**, 2443 (1916). (c) Jones and Werner, *THIS JOURNAL*, **40**, 1257 (1918). (d) Krause and Schmitz, *Ber.*, **52**, 2165 (1919). (e) von Hevesy and Zechmeister, *Ber.*, **53**, 410 (1920). (f) Richards, King and Hall, *THIS JOURNAL*, **48**, 1530 (1926). (g) Ebert, *Ion*, **2**, 277 (1910). (h) Staehling, *Compt. rend.*, **157**, 1430 (1913). (i) Dillon, Clarke and Hinchy, *Sci. Proc. Roy. Dublin Soc.*, **17**, 53 (1922).

used in the preparation of some other organometallic compounds. Probably the optimal conditions described here for the preparation of tetraphenyl lead cannot be used without some variations in the preparation of other tetra-aryl lead compounds, for Krause and Schmitz<sup>5d</sup> have found that the quantity of "unsaturated" organolead compound increases with more complex radicals like that present in *p*-xylylmagnesium bromide.

### Experimental Part

The following directions give the optimum yield, and they incorporate the more desirable features suggested by a limited study of several factors.

Phenylmagnesium bromide is prepared in a three-necked flask from 12.15 g. (0.5 mole) of magnesium, 78.5 g. (0.5 mole) of bromobenzene and 200 cc. of anhydrous ether. When the Grignard reagent has been prepared in the customary manner,<sup>6</sup> there is added 400 cc. of benzene which has been dried by standing for a few days over sodium. To this solution is added, in one lot, 63 g. (0.23 mole) of finely divided lead chloride,<sup>7</sup> and the mixture is refluxed, while being continuously stirred, for eight hours.

After a short time (during the first 30 minutes) the characteristic blackish precipitate forms and this increases in quantity over the first four hours. At the end of the eight hour period of refluxing, the mixture is cooled, and then hydrolyzed by pouring into iced hydrochloric acid. The whole mixture is filtered through a Büchner funnel, and then the ether-benzene layer is separated from the dilute hydrochloric acid layer. The cake of tetraphenyl lead, lead, etc., is removed from the funnel (for convenience the filter paper may be removed with the filter cake) and transferred to a beaker or an Erlenmeyer flask. Three hundred cc. of benzene is then added to the cake or paste and heated for a minute or two while the benzene solution is boiling. The hot benzene extract is then separated from the sludge and heavier deposit of lead by filtration and decantation through a Büchner funnel.

The filtrate is cooled with tap water to about 20°, and the crystals of tetraphenyl lead that separate are filtered and set aside as one crop of quite pure tetraphenyl lead, melting at 224–225°. The filtrate, consisting essentially of a saturated solution of tetraphenyl lead in benzene, is then added to the original cake or sludge of tetraphenyl lead and lead already once extracted, and the extraction process repeated by heating at the boiling point of the solvent for a minute or two, and then filtering to get the second crop of tetraphenyl lead. This also is quite pure and melts at about 224°.

This process of extraction is twice repeated (making four extractions in all) in order to remove practically all of the tetraphenyl lead. For most purposes the fourth extraction may be omitted, for on cooling to 20° after the fourth extraction very little tetraphenyl lead separates.

The benzene-extraction mother liquors (now of a volume slightly less than 300 cc.) are combined with the ether-benzene layer that was obtained after the hydrolysis of the reaction mixture. The combined solvents are then concentrated to about 100 cc. and, on cooling these liquors, from 6–10 g. of tetraphenyl lead is obtained melting at 224°.

The total yield of tetraphenyl lead obtained in this way is 29 g. or 50%, based on the lead chloride used. It is pure enough for most purposes. Recrystallization from

<sup>6</sup> Gilman and McCracken, *THIS JOURNAL*, **45**, 2462 (1923). Using the general procedures described in this reference, one can count safely on a 90% yield of phenylmagnesium bromide.

<sup>7</sup> The lead chloride used in these studies was taken directly from a stock bottle and was neither pulverized nor dried.

hot benzene gives a product melting at 225°. From 1 to 2 g. of tetraphenyl lead is soluble in 100 g. of benzene at about 20°.

Extraction of the cake or paste may be effected by the use of a Soxhlet apparatus or some modification of it. However, this is not necessary for ordinary purposes. Furthermore, the hot benzene extracts may be filtered conveniently through a Büchner funnel, as stated, without the use of a steam funnel.

Several experiments showed that the yield after refluxing for eight hours is better than that after four, six or twelve hours of refluxing.

The ratio of ether to benzene in the directions given above is about 1 to 2. A lower yield is obtained when two volumes of ether are used to one of benzene.<sup>8</sup> There is practically no change in yield when benzene is replaced by toluene. When the directions of Pfeiffer and Truskier<sup>3</sup> were followed (ether alone as the solvent and an excess of phenylmagnesium bromide) the yield was 43% and not 58.5% as reported by them. This yield of 43% was obtained in one run using the exact amounts of materials recommended by them, as well as in another run twice this size but under the same general conditions.

There is no advantage in using a larger quantity of phenylmagnesium bromide than that stipulated. The directions, therefore, effect a significant saving of RMgX compound.<sup>3</sup> With the quantities finally recommended there is still a slight excess of phenylmagnesium bromide, as is shown by the color test of Gilman and Schulze<sup>9</sup> for RMgX compounds.

It was believed that the yield could be improved by adding the lead chloride in several parts over extended intervals. In this way there was the possibility that the lead chloride would not be so coated with the sludge deposit as to impede reaction with phenylmagnesium bromide. However, there was no improvement in yield when the lead chloride was added in 20 g. portions at either 20 or 30 minute intervals, over that realized when all of the lead chloride was added at one time.

### Summary

Improved directions are given for the preparation of tetraphenyl lead from lead chloride and phenylmagnesium bromide.

AMES, IOWA

<sup>8</sup> Richards, King and Hall (Ref. 5 (f)) found that the substitution of *iso*-amyl ether for ethyl ether was not effective. They also reported that benzene gave more satisfactory yields than ethyl ether.

<sup>9</sup> Gilman and Schulze, *THIS JOURNAL*, **47**, 2002 (1925).