

1932

Organolead compounds

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ORGANIC COMPOUNDS

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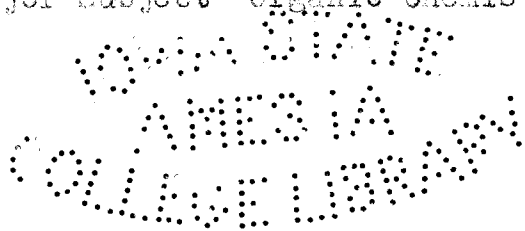
Edmund E. Towne

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A Thesis Submitted to the Graduate Faculty
for the degree of

DOCTOR OF PHILOSOPHY

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A. THE PREFERENTIAL CLEAVAGE OF RADICALS FROM UNSYMMETRICAL
ORGANOLEAD COMPOUNDS. A STUDY OF THE RELATIVE
LABILITIES OF ORGANIC RADICALS

INTRODUCTION

Many reactions have been used to determine the relative negativity or lability of organic radicals. Lability or negativity series of radicals based on these various reactions are not always in agreement and quite often agree only in a general way. This is to be expected when we consider the many factors such as experimental conditions, reagents and the intra-molecular forces that may influence the results obtained by the various methods.

A method based on the preferential cleavage of radicals from unsymmetrical organometallic compounds is perhaps the most direct and at the same time is, in general, the most applicable. The results obtained by this method are apparently the same whether unsymmetrical mercury, tin or lead compounds are used. However, the nature of the splitting agent has an effect for anomalous results are obtained in the case of the benzyl group when halogens are used as the splitting agent (1). This particular anomaly does not occur when hydrogen chloride is used and is probably due to substitution or oxidation which

(1) These results are described in more detail with original references under "Discussion of the Cleavage Method".

precedes splitting. (The cleavage of a few $R_2SnR_2^1$ and $R_2PbR_2^1$ compounds with hydrogen chloride splits off one R and one R^1 group when R and R^1 are of nearly the same negativity.)

Because of this abnormal behavior of halogens, the present study of the cleavage of unsymmetrical organolead compounds containing unsaturated radicals has been carried out using hydrogen chloride as the splitting agent.

Examination of the results of cleavage of organic radicals from unsymmetrical organometallic compounds has shown that the group or groups removed first are those which are generally considered the most negative or labile.

Thus aromatic radicals are split off before aliphatic radicals. The position that aliphatic unsaturated radicals will occupy in the general lability series (aromatic, aliphatic, unsaturated aliphatic) is not known (2). It was pointed out many years ago, however, that the negativity of radicals (hydrocarbon radicals containing other elements as substituents for the most part) was directly dependent on their degree of unsaturation (3).

In a study of the preferential cleavage of some phenyl-thienyl-, phenyl-furyl- and thienyl-furyl-lead compounds, the result of which is published elsewhere (4), it has been shown

- (2) Austin, J. Am. Chem. Soc., 53, 3514 (1931), has shown that triphenyl-allyl-lead is split by hydrogen bromide to give triphenyl-lead bromide.
- (3) Heinrich, Ber., 32, 688 (1899).
- (4) Gilman and Towne, Rec. trav. chim., 51, Nov. (1932).

that the relative lability or negativity of these radicals increases in the order: phenyl, thienyl, furyl. It was also pointed out that these facts could be correlated with the increasing degree of aromaticity exhibited by the hydrocarbons from which these radicals are derived, that is, benzene, thiophene and furan. Since any definition or consideration of aromaticity involves a conception of unsaturated linkages, a number of unsaturated radicals other than aromatic have been studied.

The present investigation is concerned with the cleavage of some unsymmetrical lead compounds containing unsaturated aliphatic radicals in order to determine to what extent an ethylenic double bond and its position with respect to the carbon-lead linkage influences the lability or negativity of a radical. For this purpose lead compounds containing the allyl-, beta-styryl- and (buten-3-yl)-lead linkage were investigated.

The splitting of triphenyl-allyl-lead, triphenyl-beta-styryl-lead and triphenyl-(buten-3-yl)-lead (5) with hydrogen chloride showed that allyl and beta-styryl radicals were removed before phenyl while the phenyl radical is split off before the buten-3-yl radical.

- (5) The names of these mixed organolead compounds may be written more correctly without hyphens but for the sake of clarity they are used to denote a metal-carbon linkage when following the name of a radical. Thus triphenyl-allyl-lead is usually written triphenylallyllead.

This anomalous cleavage of the allyl radical was not entirely unexpected. The extreme lability of this type of radical is well known. von Braun and Kohler (6) have pointed out the labile nature of allyl and cinnamyl radicals in their weak linkages to nitrogen, oxygen and the halogens. Physiologically, compounds containing these groups behave quite differently from compounds containing the penten-4-yl ($\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2-$) group. The latter are less toxic and behave like compounds with aliphatic substituents while allyl and cinnamyl groups increase the toxicity of the compounds.

The enhanced activity or lability of groups of the allyl type is demonstrated by the ready coupling of allyl bromide evidenced by the difficulty of the independent preparation of allylmagnesium bromide under ordinary conditions (7), by the rearrangement of allyl phenyl ethers (8), and by the rearrangement of cinnamyl-magnesium chloride (9) and other compounds containing the allylic system of unsaturation. Not as much is known concerning the beta-styryl radical but its linkage to halogen is fairly labile since the preparation of beta-styryl magnesium bromide involves considerable coupling unless special conditions are used (10).

The results of cleavage of these unsaturated lead compounds

- (6) von Braun and Kohler, Ber., 51, 79 (1918).
- (7) Gilman and Mc Clumphy, Bull. soc. chim., 43, 1322 (1928).
- (8) Claisen and Pietze, Ber., 58, 275 (1925).
- (9) Gilman and Harris, J. Am. Chem. Soc., 53, 3541 (1931).
- (10) Gilman and Zoellner, Unpublished work.

indicate that unsaturated radicals of the ethylenic type are more labile than the phenyl radical if the double bond is in the 1,2 or 2,3 position with respect to the lead-carbon linkage (11). However, if the double bond is in the 3,4 position, as is the case with the buten-3-yl radical ($\text{CH}_2=\text{CHCH}_2\text{CH}_2\cdot$) the radical is then less labile than the phenyl radical, that is, behaves as a saturated aliphatic radical in cleavage reactions.

- (11) The part that the unsaturation of the phenyl group plays in labilizing the styryl group can only be determined by investigating the cleavage of other related unsaturated radicals.

DISCUSSION OF THE CLEAVAGE METHOD

The most extensive work on the determination of relative negativity or lability of radicals by the cleavage of organo-metallic compounds is that of Kharasch and coworkers (12). Their work is based on the cleavage of unsymmetrical organo-mercury compounds with hydrogen chloride in alcohol solution. They also check these results by splitting the unsymmetrical compound with mercuric chloride.

They state that in unsymmetrical organomercury compounds the more electronegative group is split off first by hydrogen chloride. These investigators in subsequent work have compiled a rather complete series of radicals in the order of their relative electronegativity (13).

The splitting action of halogen acids on organotin compounds likewise has shown that the more negative radical is split off first.

Ladenburg (14) has shown that with hydrochloric acid triethyl-phenyl-stannane yields triethyl-tin chloride and benzene. Kipping (15) found that the order of removal of groups from mixed stannanes was the same whether he used hydrochloric acid

- (12) Kharasch and Graflin, *J. Am. Chem. Soc.*, 47, 1948 (1925); also see *Science*, 58, 1510 (1923).
- (13) Kharasch and Marker, *J. Am. Chem. Soc.*, 48, 3130 (1926); Kharasch and Reinmuth, *J. Chem. Education*, 5, 404 (1928); *J. Chem. Education*, 8, 1703 (1931); Kharasch and Flenner, *J. Am. Chem. Soc.*, 54, 674 (1932).
- (14) Ladenburg, *Ber.*, 4, 17 (1871); *Ann.*, 159, 251 (1871).
- (15) Kipping, *J. Chem. Soc.*, 131, 2365 (1928).

or iodine except in the case of the benzyl radical. The benzyl group was split off first from trimethyl-benzyl-stannane (16) and triethyl-benzyl-stannane (17) when halogens were used. The order was reversed with hydrochloric acid, ethyl and methyl groups being removed before the benzyl group.

Thus it is seen that the benzyl radical appears to be less negative than ethyl and methyl radicals when hydrogen chloride is the splitting agent and more negative when halogens are used. With this exception the series of labilities or negativities of radicals does not vary with the splitting agent used. Possibly the halogens are substituted in the benzyl radical or as Kharasch and Flenner (13) point out the halogens may cause oxidation to take place. The investigators who have used the halogens as splitting agents find the splitting products to be a mixture of benzyl bromide and trimethyl-tin bromide as determined by boiling point and molecular weight determinations. Toluene was not identified in reaction with hydrogen chloride.

Bullard and Holden (18) found that with unsymmetrical stannanes of the type, R_2SnR_2 , hydrogen chloride removed one ethyl and one methyl group from dimethyl-diethyl-stannane rather than two methyl groups. Likewise diethyl-di-n-propyl-stannane lost one ethyl and one propyl group. These workers used dry hydrogen chloride on the pure stannane at relatively

- (16) Kraus, C. A. and Bullard, J. Am. Chem. Soc., 48, 2135 (1926).
(17) Kipping and Smith, J. Chem. Soc., 101, 2552 (1912).
(18) Bullard and Holden, J. Am. Chem. Soc., 53, 3150 (1931).

high temperatures and it would be interesting to know whether the order of cleavage is changed by the use of a solvent.

In this connection the cleavage of diphenyl-di-biphenyl-lead is described. The results show that about 52% of the available biphenyl radicals are split off to form diphenyl. The mixture of organolead dichlorides, obtained by splitting, when treated with phenylmagnesium bromide yielded a mixture of phenyl-biphenyl-lead compounds from which was isolated 11.63% of pure tetraphenyl-lead. This shows that the splitting does not involve solely the cleavage of one phenyl and one biphenyl radical from each molecule of diphenyl-di-biphenyl-lead.

The splitting action of halogen acids on unsymmetrical organolead compounds has been investigated by various workers.

The work of Gilman and Jones (19) on the splitting of some phenyl-alpha-naphthyl- and phenyl-benzyl-lead compounds showed the order of increasing lability or negativity of these radicals to be: benzyl, phenyl, alpha-naphthyl. The reaction was carried out in chloroform when R_2PbR^2 compounds were split and in benzene in the case of $R_2PbR_2^2$ compounds; the latter reaction was quantitative. Their work shows the cleavage of unsymmetrical organolead compounds to be a satisfactory method for the determination of the relative lability or negativity of organic radicals.

- (19) Jones, H. L., The Relative Labilities of Radicals Attached to Lead in Organolead Compounds. Unpublished Thesis, Iowa State College, Ames, Iowa, 1929.

Möller and Pfeiffer (20) found that hydrogen chloride preferentially removed aryl before alkyl groups in unsymmetrical alkyl-aryl-lead compounds. Goddard and Goddard (21) confirmed this result by splitting similar compounds with thallic chloride. Grüttner (22) split diphenyl-dicyclohexyl-lead with hydrogen chloride and hydrogen bromide and obtained dicyclohexyl-lead dihalides.

Likewise Hurd and Austin (23) and Austin (24) using a variety of unsymmetrical organolead compounds have shown that concentrated mineral acids (HBr, HCl and HNO₃) remove aryl before alkyl groups. They point out that the group having the greatest electron attraction is the controlling factor in splitting reactions, predominating the influence of the relative number of R and R' groups present in a lead molecule. Thus, with tri-*o*-tolyl-phenyl-lead and triethyl-phenyl-lead the *o*-tolyl and phenyl groups are removed first respectively.

Since this thesis concerns the action of hydrogen chloride on organolead compounds, a review of the action of the halogens on organometallic compounds would be out of place but for the fact that a negativity series of radicals based on the splitting action of either reagent is almost identical.

- (20) Möller and Pfeiffer, Ber., 49, 2441 (1916).
- (21) Goddard and Goddard, J. Chem. Soc., 121, 482 (1922).
- (22) Grüttner, Ber., 47, 3257 (1914).
- (23) Hurd and Austin, J. Am. Chem. Soc., 53, 1543 (1931).
- (24) Austin, J. Am. Chem. Soc., 53, 1548 (1931).

As pointed out by Kharasch and Flenner (13) these two series of radicals differ only when two radicals are of nearly the same negativity or oxidation and substitution reactions of the halogens come into play.

In a comprehensive study of the actions of halogens on organolead compounds, Grüttner and Krause and their coworkers and others have drawn the following conclusions regarding the relative ease of splitting of various groups:

1. The lightest group is removed first from mixed alkyl lead compounds if in primary attachment to lead. A secondary group is removed more readily than a primary group (25).

2. Aryl radicals are removed before alkyl in mixed aryl-alkyl-lead compounds (20, 26).

3. The heavier aryl group is split off first from mixed aryllead compounds (27).

4. The group of which there is the largest number is removed first from an organolead compound (28, 29).

5. The electron attraction or negativity or lability of a group has more influence than the relative number of R and R' groups present in an organolead compound (23, 24).

These conclusions require examination in view of more recent investigations. Conclusion one and two hold as stated

(25) Grüttner and Krause, Ber., 50, 202, 278 (1917).

(26) Grüttner and Grüttner, Ber., 51, 1294 (1918).

(27) Krause and Schlöttig, Ber., 58, 427 (1925).

(28) Grüttner and Krause, Ber., 49, 1125 (1916).

(29) Calingaert, Chem. Reviews, 2, 43 (1925).

in all known cases. The conclusion that the heavier aryl radical is split off first from mixed aryl-lead compounds needs modification. It was, no doubt, a matter of chance that, in the mixed aryl-lead compounds on which this conclusion was based, these compounds all possessed more negative groups which at the same time were heavier than the phenyl or other radical to which they were compared. The furyl radical is an aryl group which is lighter than phenyl and it was shown to be more negative than the phenyl radical (4). Likewise it is also lighter and at the same time more negative than the thienyl radical.

The workers who originally formulated conclusion four were working with mixed alkyllead compounds and here again it was a matter of chance more than anything else that the compounds under consideration were so constituted as to lead to this conclusion. However, Grüttner and Krause (28) point out an exception in the case of triethyl-methyl-lead where it is the lone methyl group rather than one of the three ethyl groups that is split off. In most cases it has been other writers and workers who have applied this conclusion when speaking of the aromatic series.

Conclusion five is undoubtedly true in all cases.

The above conclusions for the splitting action of halogens and halogen acids on mixed plumbanes are also valid for mixed stannanes as shown by various investigators (14, 15, 16, 17, 30).

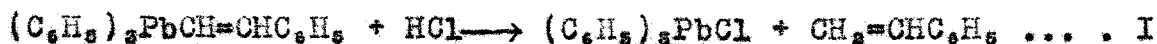
In addition to the halogen acids and halogens, mercuric chloride (31), thallic chloride (16) and silver nitrate (32) have been used as splitting agents for organolead compounds.

This review of the splitting action of hydrogen chloride and halogens on the mixed organometallic compounds of mercury, tin and lead is sufficient to show that the preferential splitting of groups from such compounds presents difficulties that must not be overlooked if conclusions drawn from experimental work are to be valid. In the first place, the splitting action must be as nearly quantitative as possible and the products recovered quantitatively in order to eliminate the possibility that secondary splitting reactions take place concurrently with the main reaction. Secondly, the splitting action must not be preceded by substitution or other reactions so that it may be certain that the group split off is the group originally attached to the metal. The quantitative recovery and identification of the splitting products will determine this satisfactorily. The third point, that we are dealing with pure organometallic compounds, must be determined with all the care that is requisite of any compound to be used in a series of critical chemical reactions.

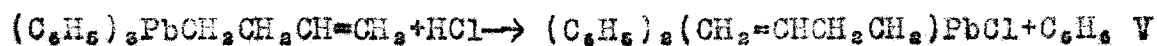
- (30) Grüttner and Krause, Ber., 50, 1802 (1917); Bullard and Robinson, J. Am. Chem. Soc., 49, 1372 (1927); Bullard and Vingee, J. Am. Chem. Soc., 51, 892 (1929); Bullard, J. Am. Chem. Soc., 51, 3065 (1929).
- (31) Challenger, J. Chem. Soc., 125, 864 (1924); Goddard, J. Chem. Soc., 121, 975 (1922).
- (32) Krause and Schmitz, Ber., 52, 2150 (1919).

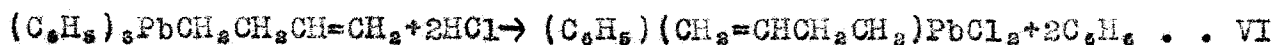
DISCUSSION OF RESULTS

The treatment of triphenyl-beta-styryl-lead and triphenyl-allyl-lead with dry hydrogen chloride in chloroform solution caused the cleavage of the unsaturated group forming styrene and propylene. The other products of the splitting were soluble triphenyl-lead chloride and insoluble diphenyl-lead dichloride. The latter is always formed when an R_3PbR' compound is split with hydrogen chloride unless the reaction is stopped before all of the original compound has been split. The reactions involved are as follows:



Styrene and propylene have been identified and the triphenyl-lead chloride and diphenyl-lead dichloride have been recovered and identified in practically quantitative yields. The cleavage of triphenyl-(buten-3-yl)-lead did not split off the unsaturated group first but gave diphenyl-butenyl-lead, phenyl-butenyl-lead dichloride and benzene according to the following reactions:





No evidence of butylene was obtained in this splitting reaction and benzene was identified in 41% yield. Diphenyl-butenyl-lead chloride was identified by conversion to triphenyl-butenyl-lead with phenylmagnesium bromide. Phenyl-butenyl-lead dichloride is apparently unstable and on analysis was found to have lost its organic constituents leaving inorganic lead chloride.

These results indicate that an unsaturated radical is more labile or negative than a phenyl radical if the double bond is in the 1,2 or 2,3 position from the carbon-lead linkage but less labile or more like an aliphatic radical if the double bond is farther removed from the carbon-lead linkage.

In addition to the cleavage reaction several other characteristics such as physiological properties (6), coupling reactions (7, 10) and rearrangements (8, 9) were mentioned in the Introduction as distinguishing factors between allyl and beta-styryl groups on the one hand and buten-3-yl and penten-4-yl groups on the other.

This would indicate that, in general, ethylene and propylene radicals and their derivatives are more labile or negative radicals than phenyl while buten-3-yl, penten-4-yl and higher homologous unsaturated radicals are less labile or negative than the phenyl group.

These facts go to show that in unsaturated compounds the

lability of the group and its chemical properties are not dependent on the presence of the double bond, but on the position that the double bond occupies with respect to the rest of the molecule.

The cleavage of diphenyl-di-biphenyl-lead gave anomalous results indicating that cleavage proceeds in a heterogeneous manner and undoubtedly means that there is very little difference in the relative lability of phenyl and biphenyl groups.

The isolation of 11% of pure tetraphenyl-lead when the mixture of phenyl-biphenyl-lead dichlorides resulting from cleavage was treated with phenylmagnesium bromide precluded the possibility of the sole cleavage of one phenyl and one biphenyl radical from each molecule of diphenyl-di-biphenyl-lead.

This reaction is described and explained in more detail in the Experimental Part.

EXPERIMENTAL

Apparatus and Procedure

The various Grignard reagents incidental to the preparation of triphenyl-beta-styryl-lead, triphenyl-allyl-lead, triphenyl-butenyl-lead, and diphenyl-di-biphenyl-lead were prepared as follows:

The magnesium, contained in a three-neck, round bottom flask of appropriate size and equipped with a reflux condenser and mercury-seal, mechanical stirrer, was covered with ether and 30-40 drops of the halide added. The ether was refluxed gently, and if reaction did not start in a few minutes, a crystal of iodine was added. As soon as reaction started, the remainder of the halide dissolved in about 6.0 moles of ether was then added dropwise at such a rate as to cause gentle refluxing. After all the halide had been added, the reaction was stirred and heated for fifteen to thirty minutes.

The Grignard reagent was then decanted in a dry nitrogen atmosphere from excess magnesium and aliquots were titrated (33). The Grignard reagent in slight excess was then added from a dropping funnel to an ether suspension of the appropriate organolead halide contained in a flask equipped as described above. In a few cases the organolead halide was added to the Grignard reagent; these cases will be mentioned in the

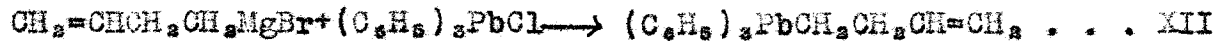
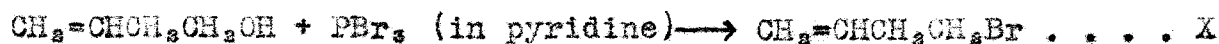
(33) Gilman, Wilkinson, Fishel and Meyers, *J. Am. Chem. Soc.*, 45, 150 (1923). See also Gilman, Zoeliner and Dickey, *ibid.*, 51, 1576 (1929).

detailed account of the various runs. The reaction mixture was then hydrolyzed by pouring into iced ammonium chloride solution and worked up in the customary manner.

In the preparation of triphenyl-allyl-lead, triphenyl-beta-styryl-lead and diphenyl-di-biphenyl-lead the halides for preparing the Grignard reagents were directly available, and the lead compounds were prepared according to the following reactions:



In the preparation of triphenyl-(buten-3-yl)-lead the halide and lead compounds were prepared by the following series of reactions:



Preparation of Triphenyl-beta-styryl-lead (10)

Run 1. To a 200 cc. flask was added 7.3 g. (0.3 atom) of 80-200 mesh magnesium with 30 cc. of anhydrous ether, 35 drops of beta-styryl bromide and a crystal of iodine. The flask was

heated with a micro burner and reaction appeared to start. The remainder of the 18.2 g. (0.1 mole) of halide, diluted with 35 cc. of ether was added from a dropping funnel over a period of two hours, with gentle refluxing over a hot plate. A color test was negative (34) so the reaction had not started in the first place. The reaction mixture was then heated over a hot plate until reaction began, which was quite violent and the solution became dark red in color. After the vigorous reaction had subsided, it was refluxed and stirred for fifteen minutes. An average of two titrations indicated a 49.81% yield of Grignard present (33).

Fourteen and twenty-two hundredths grams (0.03 mole) of triphenyl-lead chloride was added to the solution of beta-styrylmagnesium bromide at one time which caused gentle refluxing. It was then refluxed and stirred for one hour and hydrolyzed. More ether was added and the ether layer filtered from 3 g. of insoluble material. This proved to be impure tetraphenyl-lead contaminated with triphenyl-lead chloride. The 3 g. of product yielded 1 g. of pure tetraphenyl-lead, m. p. 227-8°, soft 225°, which did not depress the melting point of an authentic specimen.

The ether solution when washed and dried and the solvent distilled off, yielded an oil mixed with a sludge of crystals. This was dissolved in alcohol and on filtering an oil came

(34) Gilman and Schulze, J. Am. Chem. Soc., 47, 2002 (1925).

down which crystallized over night. The crude triphenyl-beta-styryl-lead thus obtained weighed 5.5 g. (m. p. 74-80°, soft 67°). Recrystallization from alcohol gave 3 g. of product that melted at 90° to a sludge (clear liquid 110°, soft 85°). It blackened at 150° and decomposed with bubbling at 275°. Another crystallization gave a melting point of 99-100° with decomposition, soft 96°.

A lead analysis (35) was 0.68% low showing the sample to be impure.

The various mother liquors yielded 4.5 g. of a gummy product from which there was obtained 1.5 g. of crude triphenyl-beta-styryl-lead, m. p. 100-10°, soft 90°, and 0.3 g. of 1,4 diphenyl butadiene, melting at 150-1° and giving no lead test.

Run 2. To a 500 cc. flask was added 74.6 g. (0.6 atom) of 30-80 mesh magnesium, 40 cc. of ether, a crystal of iodine and 2 cc. of beta-bromostyrene (redistilled). The reaction mixture was heated several hours without causing reaction, even after 2 cc. more of the halide was added. Over night a brown color developed and when a few drops of halide were added a vigorous reaction ensued. The remainder of the 36.4 g. (0.2 mole) of beta-bromostyrene dissolved in 90 cc. of ether was then added from a dropping funnel over a period of two and one-quarter hours with external heating. The solution was then decanted

(35) Gilman and Robinson, J. Am. Chem. Soc., 50, 1714 (1928).

through glass wool in a stream of dry nitrogen to remove magnesium. Titration gave a 77.30% yield of Grignard.

To the filtered Grignard solution, diluted with 50 cc. of ether, was added in small portions 38 g. (0.0802 mole) of triphenyl-lead chloride over a period of one hour. Addition of the triphenyl-lead chloride caused the solution to reflux. A final color test indicated only a trace of Grignard reagent. It was then refluxed and stirred fifteen minutes and hydrolyzed. An insoluble residue containing some finely divided lead was filtered off and weighed 6.8 g.

The ether layer was dried and the solvent distilled from a water bath. The residue consisted of a gummy solid that was cooled in the ice box for several days when it became more crystalline. These pasty crystals were dried on a porous plate for several days and then weighed 25 g. Recrystallization from 350 cc. of alcohol yielded 12 g. of product, m. p. 105-7°. Continued cooling of this alcohol mother liquor yielded 0.5 g. of 1,4 diphenyl butadiene, m. p. 147-9°, and 0.9 g. of an alcohol insoluble product (m. p. 200-25°, sludge 150°, sinter 140°).

The yield of fairly pure product, m. p. 100-7° was 12 g. or 27.65%.

Several recrystallizations of the 12 g. of crude triphenyl beta-styryl-lead from alcohol gave 8.2 g. or 18.89% of pure product, m. p. 107-9°, and 1 g. of 1,4 diphenyl butadiene.

Anal. Calcd. for $C_{26}H_{22}Pb$: Pb, 38.26%. Found: Pb, 38.11 and 37.97%.

Cleavage of Triphenyl-beta-styryl-lead

A solution of 5.41 g. (0.01 mole) of triphenyl-beta-styryl-lead and 150 cc. of dry chloroform was treated with dry hydrogen chloride for forty minutes, just below the boiling point of chloroform. A precipitate of diphenyl-lead dichloride began to separate from the hot solution at the end of thirty-five minutes.

The reaction was carried out in a 300 cc. Erlenmeyer flask equipped with an inlet tube for hydrogen chloride and a spiral condenser. The flask containing the solution of triphenyl beta-styryl-lead was swept out with a stream of dry nitrogen before passing in the hydrogen chloride.

The diphenyl-lead dichloride was filtered from the chloroform solution and weighed 0.7 g. (16.20%) when oven-dried. When treated with phenylmagnesium bromide it yielded 0.93 g. of crude tetraphenyl lead (m. p. 223-30°, soft 215°, sinter 190°). Digestion with hot alcohol yielded 0.72 g. of pure tetraphenyl lead, m. p. 227-8°, soft 224-6°; a mixed melting point with an authentic specimen (m. p. 227-8°, soft 226°) melted at 227-8°, soft 224-6°. This was an 86.11% yield of pure tetraphenyl-lead.

The chloroform solution from which diphenyl-lead dichloride had been filtered yielded when distilled, 3.8 g.

(80.17%) of triphenyl-lead chloride after digestion with petroleum ether. The melting point of the triphenyl-lead chloride was 205-6°, soft 202-3°, and a mixed melting point with an authentic specimen (m. p. 205-6°, soft 202-3°) was 202-3°, soft 200-1°.

Recrystallization of 3.45 g. of the above triphenyl-lead chloride yielded 2.2 g. of pure triphenyl-lead chloride, m. p. 207-8°; a mixed melting point with an authentic specimen (m. p. 204-5°) was 205-6°. There was also obtained 0.6 g. of crude triphenyl-lead chloride, m. p. 203-5°.

The total yield of phenyl-lead halides was 96.37%.

The petroleum ether solution which contained the other product of cleavage, styrene, was practically all evaporated by suction and decanted from a small amount of solid. The remaining solution evaporated spontaneously and about 0.15 g. of an orange colored liquid remained which no longer had the odor of petroleum ether. Two boiling point determinations, made by adding a portion of the liquid to a large melting point tube and inverting in the larger tube a small melting point tube, gave boiling points of 145° and 146-7°, respectively. Styrene boils at 146°. The boiling point of toluene made in the same manner was 111°. The styrene became turbid as the temperature approached its boiling point in each case. It readily decolorized a solution of bromine in carbon tetrachloride.

An attempt to prepare dibromostyrene gave a few crystals

but not enough for a reliable melting point determination.

Preparation of Triphenyl-allyl-lead (2)

Run 1. The allylmagnesium bromide (7) was made by adding twenty drops of allyl bromide to 14.59 g. (0.6 atom) of 80 mesh magnesium and 50 cc. of ether in a 500 cc. flask. Gentle heating sufficed to start the reaction and the remainder of the halide, (24.2 g. or 0.2 mole) in 200 cc. of anhydrous ether was added from a dropping funnel over a period of three hours. The reaction mixture was heated fifteen minutes after spontaneous refluxing ceased.

The allylmagnesium bromide solution was decanted in an inert atmosphere to a dropping funnel. The Grignard reagent was then added dropwise over a period of one hour to a suspension of 18.96 g. (0.04 mole) of triphenyl-lead chloride in 100 cc. of anhydrous ether contained in a 500 cc. flask. Addition of the allylmagnesium bromide caused gentle refluxing and the suspension changed in appearance and gradually dissolved. After reaction ceased it was refluxed for fifteen minutes when a color test for Grignard reagent was positive.

The reaction mixture was hydrolyzed and the ether layer was separated and dried. The solvent was distilled from a water bath which left a liquid layer still containing some ether. Addition of alcohol precipitated the triphenyl-allyl-lead as a cream white, crystalline body, m. p. 72-5°, soft 70°. Recrystallization from alcohol yielded 13.60 g. of pure product, m. p. 74-6°, soft 73°. The mother liquors yielded

2.20 g. more of material which was a total yield of 82.42% of recrystallized product, based on triphenyl-lead chloride. Triphenyl-allyl-lead forms beautiful fluffy crystals having a slight lemon yellow color.

Run 2. A crystal of iodine and 30-40 drops of the halide were added to a suspension of 21.90 g. (0.9 atom) of 30-80 mesh magnesium in 50 cc. of ether. The reaction started in a few minutes when warmed and the remainder of the halide (36.3 g. or 0.3 mole total) in 200 cc. of anhydrous ether was added over a period of two hours. The solution was decanted from excess magnesium in an inert atmosphere of nitrogen and was titrated giving a 60% yield of Grignard.

To the decanted solution of allylmagnesium bromide contained in a 500 cc. flask was added over a period of one hour 48.3 g. (0.102 mole) of triphenyl-lead chloride. It was then refluxed for about one hour when a color test was still positive.

The reaction mixture was hydrolyzed and the dried ether layer distilled, yielding a crude white solid. This was treated with 50 cc. of alcohol, filtered and washed with alcohol and yielded 33.30 g. of dried product melting at 70-1° and decomposing with blackening at 183-5°. This is a 68.10% yield of crude product based on the triphenyl-lead chloride used. Recrystallization from 350 cc. of alcohol yielded 27.4 g. of triphenyl-allyl-lead (m. p. 73°) which is a

56.03% yield.

Attempted Preparation of Diphenyl-diallyl-lead

Allylmagnesium chloride was prepared from 29.18 g. (1.2 atoms) of 80 mesh magnesium and 30.60 (0.4 mole) of allyl chloride and 400 cc. of anhydrous ether as follows:

The magnesium, contained in a one liter flask was covered with 50 cc. of ether and 30-40 drops of the halide were added. The reaction did not start when heated gently. Fifty more drops of halide and a crystal of iodine were added. The reaction then started vigorously when warmed gently. The remainder of the halide in 350 cc. of ether was added dropwise over a period of one hour at such a rate that moderate refluxing took place. It was stirred and refluxed for thirty minutes after the addition of the halide.

The ether solution of allylmagnesium chloride was siphoned from magnesium into a dropping funnel and titrated. Titration indicated a 43.90% yield of allylmagnesium chloride.

The allylmagnesium chloride was added dropwise to an ether suspension of 17.2 g. (0.04 mole) of diphenyl-lead dichloride which is 46% of the theoretical amount based on the titration value above. After being stirred, the reaction still gave a heavy color test and 13.0 g. (0.03 mole) of additional diphenyl-lead dichloride was added in small portions. A color test was then faint. It was refluxed for forty-five minutes and then stood two hours when a very small

amount of deposited lead made the solution appear grey. ✓

It was then hydrolyzed and the ether layer removed and dried over sodium sulfate. The dried ether solution partially evaporated over night and deposited a reddish amorphous solid which was extracted with ether in a Soxhlet Extractor for five hours. Evaporation of the ether solutions yielded 4.3 g. of a crystalline product, which partially melted at 65-70° to a sludge that still remained at 160°. Recrystallization from alcohol gave 3.20 g. of triphenyl-allyl-lead, m. p. 73-4°. A mixed melting point with an authentic specimen showed no depression.

The ether solution from which the amorphous solid had been filtered was treated with alcohol, but no precipitate formed. The alcohol-ether mixture was concentrated by suction and yielded liquid and resinous portions. The liquid became darker and darker, did not solidify and continued to deposit a resinous, amorphous product.

The remainder of the liquid and these resinous products (8.15 g.) were dissolved in benzene and treated with hydrogen chloride for an hour. The solid product obtained by splitting proved to be mostly lead chloride as it dissolved readily in ammonium acetate and gave a copious test for lead with potassium dichromate. The gaseous products from this hydrogen chloride treatment were passed through bromine water. A brown liquid separated out of the bromine water which was extracted with ether. The dried ether solution on removal of the solvent

yielded a dark brown oil which boiled at 138-9°. Dibromopropane boils at 141.5°. The apparatus used for determining the boiling point of this small amount of material is described under the splitting of triphenyl-beta-styryl-lead. The dibromopropane did not apparently decolorize bromine water although its brown color made observation difficult.

Apparently diphenyl-diallyl-lead is unstable and may rearrange to give triphenyl-allyl-lead. However, it is possible that the diphenyl-lead dichloride used was contaminated with some triphenyl-lead chloride; this is conceivable considering its method of preparation. The 3.20 g. of pure triphenyl-allyl lead obtained above is a 9.43% yield based on the moles of diphenyl-lead dichloride used. It hardly seems plausible that the diphenyl-lead dichloride was contaminated to this extent with triphenyl-lead chloride since the formation of R_3PbR' has not been noticed before in preparing R_2PbR_2' compounds.

Cleavage of Triphenyl-allyl-lead

Run 1. In this run triphenyl-lead chloride and diphenyl-lead dichloride were quantitatively identified as the two solid products resulting from the cleavage.

A solution of 9.58 g. (0.02 mole) of triphenyl-allyl-lead dissolved in 200 cc. of dry chloroform was placed in a 300 cc. Erlenmeyer flask fitted with an inlet tube for hydrogen chloride and an air condenser connected to three 125 cc. Erlenmeyer flasks. The first flask was immersed in an ice bath and the second and third contained bromine water.

Hydrogen chloride was passed slowly through the solution kept at 50-60° for forty-five minutes when diphenyl-lead dichloride began to precipitate. After passing in hydrogen chloride for a short time, the bromine water began to suck back indicating that it was reacting rapidly with a gas. A few oily drops of liquid separated from the bromine water but these were lost in working up.

Filtration of the chloroform solution yielded 1.5 g. (17.4%) of dry diphenyl-lead dichloride. One and four-tenths grams of this diphenyl-lead dichloride when treated with phenylmagnesium bromide yielded 1.2 g. of tetraphenyl-lead which is 77.85% yield. The tetraphenyl-lead melted at 228° and showed no depression when a mixed melting point was made with an authentic specimen.

Evaporation of the chloroform solution yielded 7.35 g. of dry triphenyl-lead chloride (m. p. 207-8° with decomposition to a solid, soft 204°). A mixed melting point with authentic triphenyl-lead chloride (m. p. 206-8°, soft 204° and decomposing to a solid) melted at 207°, soft 203-4° and also decomposing to a solid. The 7.35 g. of triphenyl-lead chloride was a 77.62% yield.

Conversion of 4.74 g. (0.01 mole) of this triphenyl-lead chloride to tetraphenyl-lead by treating with phenylmagnesium bromide in ether yielded 4.5 g. of a crude product which was digested with alcohol and then melted at 228°, soft 224°. This is a 90.91% yield of tetraphenyl-lead. Crystallization

from benzene yielded 4.03 g. of tetraphenyl-lead, m. p. 228° , which is a 81.65% yield of recrystallized product. A mixed melting point with an authentic specimen melted at 228° .

The total yield of phenyl-lead chlorides from this cleavage of triphenyl-allyl-lead was 95.02%.

Run 2. In this run triphenyl-lead chloride and diphenyl-lead dichloride were recovered quantitatively and propylene was identified as dibromopropane.

A solution of 9.59 g. (0.02 mole) of triphenyl-allyl-lead and 350 cc. of dry chloroform was treated with dry hydrogen chloride for one hour at a moderate rate. The temperature was kept just below the boiling point of chloroform throughout the reaction. After thirty minutes, insoluble diphenyl-lead dichloride began to precipitate.

The reaction was carried out in a 500 cc. Erlenmeyer flask equipped with an inlet tube for hydrogen chloride and an outlet tube leading to a catch bottle and thence to two 125 cc. Erlenmeyer flasks containing bromine in carbon tetrachloride.

At first there was no appreciable evidence of much absorption of gas by the bromine solution but toward the end of the run the bromine solution sucked back and eventually all siphoned back into the catch bottle. More bromine solution was added to the Erlenmeyer flasks and the stream of hydrogen chloride was replaced by one of dry nitrogen to remove all the propylene possible from the hot solution.

The bromine solution was treated with aqueous sodium

bisulfite to remove bromine, dried over calcium chloride and the solvent distilled from a water bath. About 5 cc. of residue remained which was distilled from a Claisen flask. Two to three grams of chloroform distilled over first and then 1 g. of liquid boiling at 100-130°. The liquid remaining in the flask boiled at 141-3° and weighed 0.38 g.: $D_{20}^{25} = 1.9084$; $n_D^{20} = 1.5193$. The physical constants given for 1,2 dibromopropane are: b. p. 141.6°; $D_{20}^{20} = 1.9333$; $n_D^{20} = 1.5190$.

The total yield of pure dibromopropane obtained from this cleavage of 0.02 mole of triphenyl-allyl-lead was 0.75 g. or 18.56%.

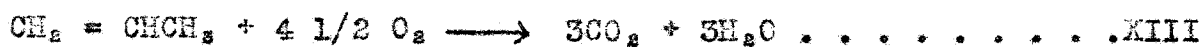
The chloroform solution was filtered from diphenyl-lead dichloride which weighed 1.85 g. (21.41%). Distillation of the chloroform filtrate yielded 6.9 g. (72.86%) of dry triphenyl-lead chloride, m. p. 206-7°, soft 205°. A mixed melting point with an authentic specimen (m. p. 206-7°, soft 205°) melted at 206-7°, soft 204.5°.

The total yield of phenyl-lead chlorides obtained in this cleavage of triphenyl-allyl-lead was 94.27%.

Runs 3, 4, and 5. The results of these cleavage runs of triphenyl-allyl-lead are summarized in Table I. The procedure was the same in Run 1 and 2 except that the gases were collected and then analyzed by the explosion method. Important details of each run are found in footnotes to the table.

The results of these explosion analyses were not satisfactory. This may possibly be due to the appreciable

solubility of propylene in water. However, in Run 4 Explosion I and II were made with gas measured over mercury and the volume of carbon dioxide and the contraction observed were not in the correct ratio according to the equation,



The volume of carbon dioxide according to the equation is three and the contraction is two and five-tenths volumes (5.5 minus 3) for each volume of propylene burned. The ratio of carbon dioxide to contraction actually obtained was 3 volumes to 2.8 volumes.

The results of explosion of the propylene mixtures from Runs 3, 4 and 5 are tabulated in Table II although they seem to have little significance. The values in column eight represent the volume of unsaturated gas exploded as calculated from the contraction and volume of carbon dioxide actually observed. The values in column nine represent the number of carbon atoms present in an unsaturated gas of the formula, C_nH_{2n} , calculated on the basis of the values in column eight.

In no case did the volume of propylene measured by absorption check the value calculated from the contraction and volume of carbon dioxide actually measured.

Table I

Cleavage of Triphenyl-allyl-lead

Run	$(C_6H_5)_3PbCH_2CH=CH_2$			$(C_6H_5)_3PbCl$		$(C_6H_5)_3PbCl_2$		cc. $CH_2CH=CH_2$	$CH_2BrCHBrCH_2$
	moles:	Temp:	Time	moles :	%	moles :	%	STP:the :% un- : or :sat.	b. p.
1	0.02	50°	45	0.0155	77.6	0.0035	17.40	- : - : -	----
2	0.02	50°	60	0.0148	73.9	0.0043	21.41	- : - : -	141-143°
3	0.02	50°	60	0.0017	8.45	0.0177	88.54	(a): : 874:448 :30.00	(b) 132-135°
4	0.01	26°	120	----	---	0.0086	88.19	(c) (d): : 302:224 :55.20	----
5	0.01	26°	60	----	---	0.0096	95.84	: : 340:224 :43.90	(b) 147-149°

- (a) Carbon dioxide was passed through the solution before, during and after cleavage with hydrogen chloride. The gas was collected over 40% potassium hydroxide and on standing the volume of gas increased. This may have been due to some chloroform that collected in the absorption bulb over the mercury. The volume of gas collected was 1050 cc. at 36° and 737.8 mm. The vapor pressure was taken as one-half that of water.
- (b) This product was obtained from the bromine water used to determine the per cent of propylene present. It may not be pure dibromopropane since bromine water contains other substances than bromine.
- (c) A small amount of chloroform solution of triphenyl-allyl-lead was lost in introducing it into the reaction flask. The yield of diphenyl-lead dichloride (88.19%) indicates 0.009 moles of triphenyl-allyl-lead was actually used.
- (d) The gas was collected over water saturated with hydrogen chloride.

Table II

Analysis of Propylene by Explosion

Cleavage Run	Explosion Run	cc. gas used	cc. propylene by absorption	cc. O ₂	cc. con- traction	cc. CO ₂	cc. $\frac{2c-CO_2}{2}$	No. of carbons in formula of unsat. gas $N = \frac{CO_2}{V}$
3	III	14.4	4.32	92.0	11.4	17.0	2.90	5.86
3	IV	18.0	5.40	99.0	15.5	21.5	4.75	4.52
3	V	17.6	5.28	90.4	14.2	23.8	2.30	10.40
3	VI	19.0	5.70	91.2	15.8	22.8	4.40	5.20
4	I	10.4	5.74	87.4	13.6	14.4	6.40	2.25
4	II	15.6	8.61	92.6	21.9	23.7	10.05	2.36
4	III	13.4	6.18	74.6	16.2	18.2	9.10	2.00
5	I	12.2	5.36	80.5	19.1	10.4	13.90	0.75
5	II	17.7	7.77	77.0	22.5	20.6	12.20	1.70
5	III	15.4	6.76	75.6	19.2	14.0	12.20	1.12
5	IV	17.8	7.81	74.4	20.8	21.0	10.30	2.04
5	V	20.3	8.91	86.2	23.1	23.6	11.30	2.10

Preparation of Buten-1-ol-4, $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{OH}$

This unsaturated alcohol has been prepared in small yields by Demjanoff (36) and Wagner (37). Better yields were obtained by Pariselle (38), Zelinka (39), Grischkewitch and Trochimowski (40) and Juvala (41). These latter workers prepared buten-1-ol-4 by treating magnesium and trioxymethylene with allyl bromide.

Following the directions of Juvala a 13.75% yield of crude buten-1-ol-4, b. p. 95-120°, was obtained in a preliminary run as follows:

A solution of 60.5 g. (0.5 mole) of allyl bromide in 50 cc. of anhydrous ether was added dropwise over a period of twelve hours to a suspension of 15 g. of trioxymethylene, 13.4 g. (0.55 atom) of 80 mesh magnesium and 50 cc. of ether contained in a 500 cc. flask. The reaction mixture was heated and stirred for four and one-half hours and then worked up as described by Juvala. He obtained a 47% yield of crude product in a similar one mole run.

In a second preliminary run 20 g. of trioxymethylene when heated with 0.5 mole allylmagnesium bromide (7) (80% Grignard by titration) gave 24.13% of crude buten-1-ol-4, b. p. 95-120°.

- (36) Demjanoff, J. Russ. Phys. Chem. Soc., 24, 346 (1892).
- (37) Wagner, Ber., 27, 2437 (1894).
- (38) Pariselle, Ann. chim. phys., (8), 24, 315 (1911).
- (39) Zelinka, Monatsh., 35, 1507 (1914).
- (40) Grischkewitch and Trochimowski, J. Russ. Phys. Chem. Soc., 48, 891 (1916).
- (41) Juvala, Ber., 63, 1989 (1930).

This gave 8.9 g. or a 15.45% yield of buten-1-ol-4, b. p. 111-16°, when dried and redistilled.

Run 1. The use of gaseous formaldehyde with allylmagnesium bromide gave 43% yield of pure buten-1-ol-4 (43). One mole of allylmagnesium bromide (titrating 78% Grignard) which had been decanted from magnesium was treated while stirred with gaseous formaldehyde until a color test was negative. The formaldehyde was prepared (43) by heating 50 g. of trioxymethylene in a 500 cc. round bottom flask in an oil bath at 180-200°. The flask was fitted with an inlet tube for dry nitrogen and a large outlet tube leading to the reaction flask.

The reaction mixture was hydrolyzed by pouring into cracked ice and then adding an excess of 20% sulfuric acid. The acid layer was steam distilled until 2300 cc. of distillate collected. This distillate was saturated with potassium carbonate and extracted four times with ether. This ether portion was combined with the original ether layer and the whole dried over potassium carbonate and the solvent distilled from a water bath. The residue was fractionated yielding 3.2 g. of

- (42) Ger. pat., 554,310 (C. A., 26, 5101 (1932)), report the reaction of ethylene oxide with allylmagnesium bromide but the procedure appears to be a combination of the Grignard and Barbier reactions. The reaction of gaseous formaldehyde with allylmagnesium halides has not been reported; Gilman and Woolley obtained a 65% yield of buten-1-ol-4 by this method.
- (43) "Organic Syntheses", John Wiley and Sons, Inc., New York, 1932, Collective Vol. I, p. 182.

product boiling below 95° , 33.18 g. of crude buten-1-ol-4 boiling at $95-125^{\circ}$, and 2.27 g. of product boiling at $125-85^{\circ}$. The 33.18 g. of crude buten-1-ol-4 was a 59% yield based on the 78% of allylmagnesium bromide actually present.

The first and second fractions when dried over barium oxide and again fractionated yielding 24.25 g. or 43.15% of buten-1-ol-4 boiling at $111-16^{\circ}$. There was also obtained 1.1 g. of product, b. p. $95-111^{\circ}$, 2.1 g. of product, b. p. $116-25^{\circ}$, and 2.27 g. of product, b. p. $125-85^{\circ}$ all of which were not fractionated again.

Preparation of Buten-3-yl Bromide, $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{Br}$

This halide was prepared according to the directions of Juvala (38) as follows:

A solution of 3.56 g. (0.045 mole) of pyridine and 14.4 g. (0.2 mole) of buten-1-ol-4 was added from a dropping funnel to a 150 cc. distilling flask containing 21.7 g. (0.08 mole) of phosphorus tribromide. The reaction mixture was shaken throughout the addition which required one hour. The reaction mixture was distilled and the distillate neutralized with 20% potassium hydroxide, and the layer of bromide was washed three times with water and dried over calcium chloride. Distillation yielded 12.5 g. (46.33%) of crude butenyl bromide boiling at $97-114^{\circ}$. This crude product was washed twice with water and dried over calcium chloride and when distilled yielded 7.75 g. of product boiling at $97-99.5^{\circ}$. This is a 28.72% yield of pure buten-3-yl bromide.

A second run similar to the first yielded 4.7 g. of pure butenyl bromide, b. p. 96-8°, refractive index, n_D^{25} 1.4586.

This halide has also been prepared by Pariselle (38) and Zelinka (39) in rather poor yields. The use of pyridine prevents to a great extent, addition to the double bond.

Preparation of Buten-3-yl-magnesium Bromide, $CH_2=CHCH_2CH_2MgBr$

von Braun and Deutsch (44) have prepared this Grignard reagent from 1,2,4-tribromobutane according to Reaction XIV. The reaction of magnesium with buten-3-yl bromide has not been previously reported.

Buten-3-yl-magnesium bromide was prepared in 75.00% yield using the directions of Gilman and McGlumphy (7) for allyl-magnesium bromide, and in quantitative yield using the standard conditions of Gilman, Zoellner and Dickey, (45) according to Reaction XV.



Run 1. A suspension of 3.7 g. (0.15 atom) of 80 mesh magnesium and 10 cc. of anhydrous ether in a 200 cc. flask was heated with a crystal of iodine and 10 drops of buten-3-yl

- (44) von Braun and Deutsch, Ber., 44, 3699 (1911).
(45) Gilman, Zoellner and Dickey, J. Am. Chem. Soc., 51, 1576 (1929).

bromide. Reaction began at once and the remainder of the halide (6.85 g. or 0.0507 mole, total) in 40 cc. of ether was then added over a period of one hour while the reaction was stirred. After spontaneous refluxing ceased, the reaction mixture was stirred and heated over a hot plate for fifteen minutes. A color test was positive and titration showed a 75.22% yield of Grignard present.

Run 2. Using the standard conditions of Gilman, Zoellner and Dickey (45), 3.37 g. (0.025 mole) of buten-3-yl bromide and 0.59 g. (0.028 atom) of magnesium turnings and 30 cc. of ether gave a quantitative yield of Grignard when titrated.

Carbonation of Buten-3-yl-magnesium Bromide

The Grignard reagent prepared in Run 2 was decanted from magnesium in an inert atmosphere into a 200 cc. flask and was carbonated in the usual manner (46) at -2° or lower. Hydrolysis was effected with dilute hydrochloric acid and the ether layer was extracted with 10% sodium hydroxide. Acidification, and extraction of the acid layer with ether yielded upon evaporation of the solvent, 1 g. of product. This was distilled giving 0.5 g. of allyl acetic acid, $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{COOH}$, boiling at $185-7^{\circ}$ by the melting point tube method. Bromine in carbon tetrachloride converted this acid to 3,4 dibromovaleric

(46) Gilman and Parker, J. Am. Chem. Soc., 46, 2816 (1924).

acid (47), m. p. 54-55°. Recrystallization from a mixture of ligroin and carbon disulfide yielded a pure product, m. p. 57-8°.

Preparation of Triphenyl-(buten-3-yl)-lead, $(C_6H_5)_3PbCH_2CH_2CH=CH_2$

The buten-3-yl-magnesium bromide from Run 1 was decanted from magnesium in an inert atmosphere to a dropping funnel. It was then added dropwise to a suspension of 9.47 g. (0.02 mole) of triphenyl-lead chloride in 20 cc. of ether. Reaction ensued and after three-fourths of the Grignard solution was added the triphenyl lead chloride had gone into solution but a color test was negative. The remainder of the Grignard solution was added and the reaction mixture was refluxed over a hot plate for fifteen minutes when a color test was still negative.

The reaction mixture was hydrolyzed by pouring into iced ammonium chloride solution. The ether layer was separated and filtered from a small amount of white insoluble product and dried over calcium chloride. The ether was distilled from a water bath and yielded 9.5 g. of a white solid melting to a cloudy liquid at 85°, (clear 95°, sinter 75°). This is a 96.35% yield of crude product based on the triphenyl-lead chloride used. Two recrystallizations from alcohol raised the melting point to 90-2° but the liquid was cloudy and became clear at 118°. By dissolving the product melting at 90-2° in petroleum

(47) Messerschmidt, Ann., 208, 100 (1881).

ether (b. p. 30-30°) and evaporating the solvent, constant melting triphenyl-(buten-3-yl)-lead was obtained, m. p. 84-6°. It is a white solid not affected by sunlight.

Anal. Calcd. for $C_{22}H_{22}Pb$: Pb, 42.01%. Found: Pb, 41.78 and 41.87%.

Cleavage of Triphenyl-(buten-3-yl)-lead

Run 1. A solution of 2.47 g. (0.005 mole) of triphenyl-(buten-3-yl)-lead and 70 cc. of dry chloroform was placed in a 150 cc. Erlenmeyer flask equipped with an inlet tube for hydrogen chloride and an outlet tube leading through a safety flask to two flasks containing 2% bromine in carbon tetrachloride. The solution was kept at 40-45° and dry hydrogen chloride from a generator was passed slowly through the solution for one hour after the flask had been swept out with dry nitrogen. After thirty minutes a flocculent, white precipitate began to form.

The solution of bromine in carbon tetrachloride showed no decolorization and did not suck back as it does when an unsaturated gas is being absorbed.

This insoluble product was filtered from the chloroform solution and dried and weighed 0.79 g. which is a 38.72% yield. It had no melting point but showed slight sintering at about 220° and gave a test for lead when treated with ammonium acetate and potassium dichromate.

It may well be that a compound like phenyl-butenyl-lead dichloride is decomposed by ammonium acetate or decomposes

spontaneously to give lead chloride. Sixty-five hundredths gram of the product was washed with ammonium acetate then with alcohol and finally with ether in the hope of removing lead chloride. It seemed that the ether removed a considerable amount of the product but only a trace of product was recovered from the ether. After this treatment there remained only 0.1 g. of product which was treated with phenylmagnesium bromide but the only product isolated was a very small amount of diphenyl melting at 66° and showing no depression with an authentic specimen. Fourteen hundredths gram of the original product when extracted with ether yielded a small amount of triphenyl-butenyl-lead melting with decomposition at $127-30^{\circ}$.

The chloroform filtrate from the splitting reaction gave no rapid decolorization of potassium permanganate solution as a solution of butylene should. The chloroform was distilled on a water bath leaving 1.15 g. of diphenyl-butenyl-lead chloride which is a 51.11% yield. It melted with decomposition at $133-5^{\circ}$ and turned brown at 216° and black at $220-5^{\circ}$. Recrystallization from alcohol gave 0.85 g. of product melting with decomposition at $134-5^{\circ}$ and the mother liquors yielded 0.13 g. of product melting with decomposition at 130° .

The diphenyl-butenyl-lead chloride was dried in a vacuum desiccator over phosphorus pentachloride and analyzed for chlorine.

Anal. Calcd. for $C_{16}H_{17}ClPb$: Cl, 7.85%. Found: Cl, 7.72 and 7.79%.

Sixty-three hundredths gram of the diphenyl-butenyl-lead chloride was treated with a dilute solution of phenylmagnesium bromide. The reaction mixture when hydrolyzed yielded a somewhat gummy solid melting at 80-85° to a sludge, all clear by 135° and blackening at 215-220°. The product was dissolved in petroleum ether and filtered from a trace of insoluble product. Evaporation of the petroleum ether yielded 0.2 g. of triphenyl-butenyl-lead melting at 84-6°. A mixed melting point with an authentic specimen of triphenyl-butenyl-lead (m. p. 81-2°) melted at 82-3°. This is a 29.16% yield of recrystallized product. The actual yield of product would be much higher since considerable difficulty was encountered in working it up.

The chloroform distillate containing the benzene resulting from the cleavage of triphenyl-butenyl-lead was added to a mixture of 12 cc. of concentrated sulfuric acid and 6 cc. of fuming nitric acid contained in a 200 cc. round bottom flask equipped with a reflux condenser. It was refluxed one and one-half hours and when cool was poured into cold water. The chloroform layer was dried over potassium carbonate and the solvent distilled yielding crude dinitro-benzene. This was recrystallized from alcohol and yielded 0.37 g. of dinitro-benzene, m. p. 88-9°. A mixed melting point with an authentic sample (m. p. 90°) melted at 90°. The mother liquors yielded 0.08 g. of crude product, m. p. 60-5°. This is a total yield of 41.67% of dinitrobenzene based on the amount of benzene

produced by the splitting of 0.005 moles of triphenyl-butenyl-lead into 51.11% of diphenyl-butenyl-lead chloride and 38.72% of phenyl-butenyl-lead dichloride.

Run 2. Hydrogen chloride was passed slowly through a solution of 1.17 g. (0.0024 mole) of triphenyl-butenyl-lead in 40 cc. of dry chloroform which was kept just below the boiling point of chloroform throughout the reaction. The hydrogen chloride was passed through the solution for forty-five minutes and a white precipitate began to form after thirty minutes. The reaction was carried out in a 125 cc. Erlenmeyer flask equipped with an inlet tube for the hydrogen chloride and an outlet tube leading through a catch bottle to a flask containing a few drops of 2% bromine in carbon tetrachloride. This dilute solution of bromine was light orange in color but leading the products of cleavage through this solution showed no decolorization. A control solution of bromine in carbon tetrachloride of the same strength as above was immediately decolorized by a drop or two of amylene.

Evidently there is no measurable cleavage of the butenyl group from lead.

The chloroform solution was filtered from the precipitate of insoluble dichloride which weighed 0.76 g. and is a 77.87% yield, calculated as phenyl-butenyl-lead. This product gave no lead test when treated with ammonium acetate and potassium dichromate for about thirty seconds but gradually a yellow precipitate of lead dichromate formed. A water suspension of

the product gave a lead test immediately.

Extraction of the phenyl-butenyl-lead dichloride with ether yielded 0.1 g. of diphenyl-butenyl-lead chloride melting with decomposition at 132-4°. A mixed melting point with an authentic specimen showed no depression of the melting point.

The ether washed, supposed phenyl-butenyl-lead dichloride obtained in this cleavage run was analyzed for chlorine.

Anal. Calcd. for $C_{10}H_{12}Cl_2Pb$: Cl, 17.31%; Calcd. for $PbCl_2$: Cl, 25.52%. Found: Cl, 22.43%.

This 22.43% chlorine corresponds to a mixture of 62.36% of lead chloride and 37.64% of phenyl-butenyl-lead dichloride.

In order to convert any phenyl-butenyl-lead to triphenyl-butenyl-lead 0.4 g. of the dichloride was treated with an ether solution of phenylmagnesium bromide; the solution became brown and then black as in the reaction of lead chloride with phenylmagnesium bromide. It was refluxed gently for fifteen minutes and yielded triphenyl-lead decomposing at 150-5°. When worked up this product was extracted with alcohol to remove any triphenyl-butenyl-lead that might be present, but the only product recovered from the alcohol was diphenyl, m. p. 69-70°, which did not depress the melting point of an authentic specimen. Although there wasn't any appreciable triphenyl-butenyl-lead formed unless alcohol failed to remove it from the triphenyl-lead, a sample of the dichloride did decolorize a very dilute bromine solution; similar samples of authentic lead chloride

and diphenyl-lead dichloride did not.

There is no question that originally the dichloride obtained by cleavage was phenyl-butenyl-lead dichloride since under all ordinary conditions diphenyl-lead dichloride does not decompose to lead chloride. It must, however, lose its organic constituent rather readily. A similar instability of an R_2PbCl_2 compound was observed in the preparation of dithienyl-lead dichloride (4) although several mixed alkyl lead dichlorides have been described and are apparently stable (48).

Evaporation of the chloroform solution from which the dichloride was filtered yielded 0.05 g. of diphenyl-butenyl-lead, m. p. $129\text{--}32^\circ$. This is a 4.63% yield.

The total yield of solid products (lead chloride and diphenyl-butenyl-lead) obtained in this cleavage run was 82.5% (49).

Preparation of Diphenyl-di-biphenyl-lead, $(C_6H_5)_2Pb(C_6H_4C_6H_5)_2$

This compound was made from para-phenyl phenylmagnesium bromide and diphenyl-lead dichloride in the following manner:

Run 1. A solution of 46.6 g. (0.2 mole) of para-bromo-diphenyl and 200 cc. of ether was treated with 5.6 g. (0.23 atom) of magnesium turnings in a 500 cc. flask. Heat or activated catalyst (50) did not start the reaction so one

(48) Grüttner and Krause, Ber., 50, 209 (1917).

(49) If the per cent of dichloride obtained by cleavage is calculated as lead chloride, the total per cent of cleavage products is 118.63%.

half of the ether was distilled off. Reaction then began immediately when warmed with a crystal of iodine. It was heated for seven and one-half hours and the reaction mixture turned reddish brown toward the end. One hundred cubic centimeters of ether were added and two aliquots of the solution titrated; the yield of Grignard was 70.47%.

Addition of 19 g. (0.04 mole) of diphenyl-lead dichloride to the p-phenyl phenylmagnesium bromide left a faint color test after the reaction was stirred and refluxed for thirty minutes. The solution was hydrolyzed and the ether layer filtered from an insoluble residue. Partial evaporation of the ether yielded 0.5 g. of a product softening from 165-230° but still partly solid. The ether solution yielded a gummy residue which was treated with 50 cc. of cold alcohol and the resulting semi-crystalline product was dried on a porous plate. The crude diphenyl-di-biphenyl-lead softened at 110-18° and melted to a clear liquid at 123°, yield 13 g. or 48.70%.

Recrystallization from four parts of alcohol and one part of benzene and then from chloroform by adding alcohol yielded 5.2 g. (19.50%), of fairly pure diphenyl-di-biphenyl-lead, m. p. 131-3°, soft 129°.

A second run was made in the same manner from 0.06 mole

- (50) Gilman, Peterson and Schulze, *Rec. trav. chim.*, 47, 19 (1928); Gilman and Heck, *Bull. soc. chim.*, 45, 250 (1929).

of p-phenyl phenylmagnesium bromide in benzene-ether solution and 8.6 g. (0.02 mole) of diphenyl-lead dichloride. The yield of crude product was 9.5 g. or 71.21%. Two recrystallizations from two parts of alcohol and one part of benzene and then a recrystallization from chloroform and alcohol yielded a constant melting product, m. p. 154-5°. This sample of diphenyl-di-biphenyl-lead was analyzed.

Anal. Calcd. for $C_{36}H_{28}Pb$: Pb, 51.06. Found: Pb, 30.76 and 30.76%.

Two runs of diphenyl-di-biphenyl-lead were made using p-phenyl phenyllithium but the products could not be crystallized to give anything but gummy residue. This is in accord with the results obtained by Austin when the organolithium compound was in excess (51).

Cleavage of Diphenyl-di-biphenyl-lead

A preliminary run was made by passing hydrogen chloride through a benzene solution of 0.5 g. (0.00075 mole) of diphenyl di-biphenyl-lead for ten minutes yielding 0.06 g. of pure diphenyl which is a 26% yield. There was also obtained a mixture of phenyl-biphenyl-lead dichlorides. This product yielded 0.1 g. (20.00%) of rather crude tetraphenyl-lead, m. p. 220°, soft 205°, when treated with phenylmagnesium bromide. This indicates that the cleavage of diphenyl-di-

(51) Austin, J. Am. Chem. Soc., 54, 3726 (1932).

biphenyl-lead proceeds by at least two different reactions simultaneously.

Run 1. A solution of 6.67 g. (0.01 mole) of diphenyl-di-biphenyl-lead in 150 cc. of benzene was treated with hydrogen chloride for thirty minutes just below the boiling point of the solution. The white precipitate began to form after ten minutes. This was filtered off and the filtrate treated with hydrogen chloride for another thirty minutes and again filtered.

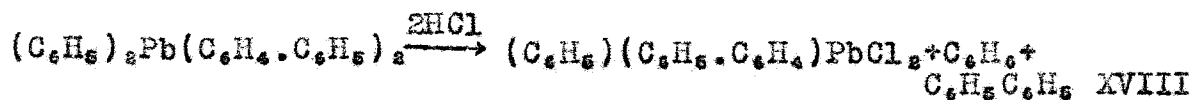
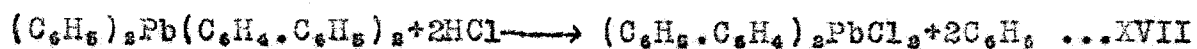
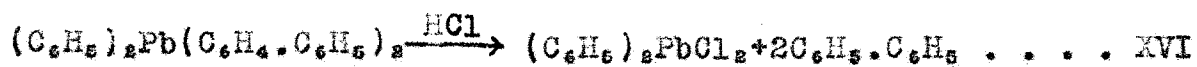
The dry insoluble dichloride weighed 4.37 g. which is a quantitative yield. The 4.37 g. of product was treated with phenylmagnesium bromide and yielded 3.75 g. of crude product, m. p. 220°, soft 200°, sinter 160°. Digestion with alcohol and recrystallization from benzene twice gave 0.6 g. of pure tetraphenyl-lead, m. p. 227-8°, which is a 11.06% yield. The remainder of the product consisted of 0.57 g. of a more soluble portion, m. p. 125-8°, soft 115°, which is probably impure diphenyl-di-biphenyl-lead although recrystallization did not give a sharper melting point. The less soluble portion, (0.8 g.) melted at 190-225°, soft, 126°, and is undoubtedly very impure tetraphenyl-lead.

The yield of crude diphenyl resulting from the cleavage was 1.65 g. or 53.57%. When recrystallized from alcohol there was 1.3 g. or 42.21% pure diphenyl as shown by a mixed melting point determination.

Run 2. A chloroform solution of 1.33 g. (0.002 mole) of diphenyl-di-biphenyl-lead was treated with hydrogen chloride for one and three-quarters hours just below the boiling point of the solution. The insoluble organolead dihalide when filtered off weighed 0.84 g. It gave a slight lead test when washed with ammonium acetate, so it was washed several times with the latter and then with alcohol and ether. When dry it weighed 0.58 g. and was analyzed for lead. The per cent of lead for the three possible organolead dihalides that might result from cleavage are: diphenyl-lead dichloride, 47.95%; di-biphenyl-lead dichloride, 35.47%; phenyl-biphenyl-lead dichloride, 40.77%; a mixture of the first and second, 41.71%.

Anal. Found: Pb, 40.68%.

This per cent of lead corresponds most closely to phenyl-biphenyl-lead dichloride but could have just as well resulted from the right mixture of di-biphenyl-lead dichloride and diphenyl-lead dichloride. The cleavage of diphenyl-di-biphenyl-lead may conceivably proceed in three ways, according to the following reactions:



Considering the amount of diphenyl obtained in the cleavage of diphenyl-di-biphenyl-lead, the following conclusions may be made:

- (1) If cleavage proceeds according to reaction XVIII, no tetraphenyl-lead should have been obtained when the phenyl-biphenyl-lead dichloride was treated with phenylmagnesium bromide (precluding, of course, the rearrangement of triphenyl-biphenyl-lead to tetraphenyl-lead). Eleven and six hundredths per cent of pure tetraphenyl-lead was obtained.
- (2) If only the first and second reactions take place, they must proceed simultaneously and at about the same rate to account for the 53% of diphenyl obtained.
- (3) If all three reactions take place simultaneously, then the second reaction must proceed at a greater rate or to a greater extent than the first and third reactions to account for the approximately 53% of diphenyl obtained.

Work in progress on the cleavage of triphenyl-biphenyl-lead, not ready for presentation as yet, may throw light on this anomalous cleavage. The phenyl and biphenyl radicals are probably of very nearly the same lability or negatively thus accounting for these results.

SUMMARY

Three unsymmetrical organolead compounds containing unsaturated groups have been split with hydrogen chloride. The result of this splitting shows that the relative lability or negativity of an ethylene radical is not conditioned by the presence of a double bond but rather by its position within the radical.

The cleavage of triphenyl-beta-styryl-lead, triphenyl-allyl-lead and triphenyl-buten-3-yl-lead shows the order of decreasing relative lability or negativity of the radicals involved to be: (allyl, beta-styryl), phenyl, buten-3-yl. Thus, the cleavage reaction confirms the extreme lability of the allyl radical and of the beta-styryl radical to a lesser degree in other chemical and physiological reactions. The decreased lability of buten-3-yl radical, evidenced by the results of cleavage, is further shown by the smooth reaction of magnesium with buten-3-yl bromide to give a quantitative yield of Grignard reagent under ordinary conditions in the manner of saturated aliphatic halides.

It is pointed out that in determining the relative negativity or lability of radicals by the cleavage method certain compounds, such as diphenyl-di-biphenyl-lead which contain radicals of about the same lability, are split in a heterogenous manner.

B. THE INTRODUCTION OF WATER SOLUBLE GROUPS INTO
ORGANOLEAD COMPOUNDS

INTRODUCTION

The preparation of organolead compounds containing solubilizing groups is of interest both from a practical and a theoretical point of view. The interest in water soluble organolead compounds results directly from the recent discovery of certain physiological properties which lead compounds have in general. It has been found that lead in any form has a pronounced deleterious effect on the growth of certain tissues and cells and this toxic effect is especially pronounced in rapidly growing cells such as embryos and reproductive germ cells (1).

Since cancer tissue likewise consists of rapidly growing cells, it was hoped that the toxic effect of lead could be utilized therapeutically in the cure and alleviation of cancer. During the early stages of lead therapy in cancer it was soon found that the general insolubility of lead compounds and the slight difference between the therapeutic and toxic dose would be important drawbacks to any widespread use of lead. Despite this, Bell (2) in England and Ullmann (3) in this country have

- (1) Bell, Lancet, 203, 1005 (1922); 206, 267 (1924); 209, 1003 (1925).
- (2) Bell, Lancet, 210, 537 (1926).
- (3) Ullmann, Radiology, 8, 461 (1927).

reported quite favorably on the results obtained in many advanced cases of cancer by the use of colloidal preparations of lead and lead salts. However, it is also true that other investigators have not reported so favorably, but this may in some cases be due to inferior preparations or faulty administration.

The advantage which organolead compounds would have over inorganic preparations because of their greater fat solubility and consequent ease of penetrating cancer tissue has been pointed out (4). This point loses some of its attractiveness in view of the extreme sensitiveness of organolead compounds to acids. Since the usual method of injection is intravenously, the acidity of the blood may convert the original organolead compound into a form that is more toxic and at the same time less soluble.

It would seem that in order to have pronounced superiority an organolead compound must be preferentially absorbed by the cancer tissue or else be directly injected into the diseased tissue. Otherwise it would find its way to all of the organs and the consequent severe lead poisoning would counteract to a greater or lesser degree the beneficial effect in retarding growth or alleviating pain.

Numerous investigators have studied the toxicity of

(4) Bischoff, Maxwell, Evans and Nuzum, J. Pharmacol., 34, 85 (1928).

organolead compounds and their effect on cancer tissue in animals (4). Buck and Kumro have studied the effect of a number of organolead compounds on animals. They find tetramethyl-lead to be the least toxic of the compounds investigated and point out that these compounds affect other tissues as well as the cancer tissue (5).

Krause (6) has investigated the beneficial effects of certain organolead compounds on cancer in mice and finds that several compounds, especially tri-n-propyl-lead fluoride, have prophylactic and curative value.

Gilman and Gruhzt (7) have found several organic salts of triethyl-lead hydroxide to be quite toxic when tested on rats.

Experimentally the introduction of water solubilizing groups such as hydroxyl, carboxyl and amino into organolead compounds presents certain difficulties which are due to the peculiar properties of these compounds. These difficulties hinge primarily on, (a) the extreme sensitiveness of the carbon-lead linkage to acidic and to extremely electropositive reagents; (b) the inertness of halogens in Grignard formation when attached through a phenyl or other group to lead and, (c) the inability of organolead halides, such as R_2PbX , to couple in reactions such as the malonic ester and acetoacetic ester

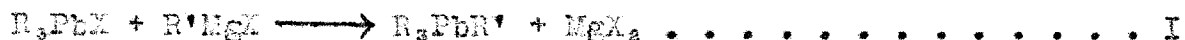
(5) Buck and Kumro, J. Pharmacol., 38, 161 (1930).

(6) Krause, Ber., 62, 135 (1929).

(7) Gilman and Gruhzt, J. Pharmacol., 41, 1 (1931).

condensation.

Practically the only method available for the preparation of mixed organolead compounds is the reaction of organolead halides with the Grignard reagent. The reactions proceed smoothly as follows:



However, the introduced R' group cannot contain a functional group having an active hydrogen since the Grignard reagent would react with this hydrogen.

The analogous use of organolithium compounds is successful if there is not an excess of the lithium compound present (8). In the experimental part of this thesis it is shown that the coupling of organolithium compounds with organolead mono-halides proceeds much better than with the dihalides.

Organo-sodium compounds have been used very little in coupling reactions with organolead halides because they cause decomposition of the lead compound (9). In this connection Schlenk and Holtz (10) have prepared impure ethylsodium by the reaction of sodium on tetraethyl-lead. Likewise, Foster (11) has found that the reaction of triphenyl-lead chloride

- (8) Austin, J. Am. Chem. Soc., 53, 3726 (1932).
- (9) Kraus and Sessions, J. Am. Chem. Soc., 47, 2366 (1925).
- (10) Schlenk and Holtz, Ber., 50, 262 (1917).
- (11) Private communication.

with sodium in liquid ammonia causes decomposition of the lead compound rather than forming triphenyl-lead sodium. However, Calingaert (12) has prepared trivalent lead compounds by this reaction and it may well be that under the proper conditions an unstable R_3PbNa compound can exist.

The preparation of a compound of the type, R_3PbNa , would make available a method for preparing mixed organolead compounds that has been used successfully with germanium and tin compounds. The reactions proceed in liquid ammonia as follows:



Further evidence for the decomposition of the lead-carbon linkage by electropositive groups is presented in this thesis in the reaction of magnesium on triethyl-lead bromide. This probably involves the electropositive $MgBr$ group and the intermediate formation of $(C_2H_5)_3PbMgBr$, although postulation of the latter is not essential in explaining the formation of ethylmagnesium bromide that occurs. Ethylmagnesium bromide might form from the reaction of the $MgBr$ group with an ethyl group that was removed from lead directly or it may utilize ethyl groups that were liberated in the spontaneous conversion

(12) Chem. Reviews, 2, 43 (1925).

of triethyl-lead to tetraethyl-lead.

The coupling of organolead halides with the sodium compound of malonic ester and acetoacetic ester did not give evidence of the formation of an organolead ester (13).

It should be borne in mind that in any coupling reaction the products formed depend entirely on the relative attraction which the groups involved have for each other and for themselves. Thus in the following reaction:



it may be expected to proceed as written if triethyl-lead groups and trimethyl-tin groups have more attraction for each other than the trimethyl-tin and triethyl-lead groups have for themselves. If the latter is the case, hexamethyl-di-stannane and hexaethyl-di-plumbane would be the products formed.

The preparation of organolead compounds containing a carboxyl group attached to carbon has been attempted by preparing the Grignard reagent of an organolead halide in which the halogen is one or more carbons removed from lead. Grüttner and Krause (14) have reported the preparation of the Grignard reagent of triethyl-5-bromoamyl-lead. Gilman and Robinson (13) did not obtain a Grignard reagent with this compound however.

(13) Robinson, Jack D., Organolead Compounds, Unpublished Thesis, Iowa State College, Ames, Iowa, 1929.

(14) Gruttner and Krause, Ber., 49, 2666 (1916).

Gilman and Robinson have attempted to prepare the Grignard reagent of triphenyl-para-bromophenyl-lead with no success (13).

In spite of the difficulty of introducing solubilizing groups into organolead compounds, certain functional groups have been introduced. Vörländer (15) nitrated tetraphenyl-lead and obtained m-dinitro-diphenyl-lead dinitrate. Austin (16) has prepared 1-(diphenyl-lead)-2,3-propanediol, $(C_6H_5)_2PbCH_2CH(OH)CH_2OH$, by the oxidation of triphenyl-allyl-lead. Gilman and Robinson (13) oxidized triethyl-allyl-lead but obtained no acidic compounds from the reaction. Austin has also prepared several organolead compounds containing dimethyl-amino-lead groups (17).

The reaction of copper-bronze with some double salts of diazonium compounds and lead salts is reported in this thesis in an attempt to prepare some substituted organolead compounds. This method, although successful with the analogous mercury complexes, does not work with the diazonium-lead complexes. Numerous coupling reactions were also carried out between organolead halides and alpha-halogen esters and other compounds. One of these, using sodium as a coupling agent, gave some promise as a means of introducing solubilizing groups into organolead compounds.

(15) Vörländer, Ber., 58, 1893 (1925).

(16) Austin, J. Am. Chem. Soc., 53, 3514 (1931).

(17) Austin, J. Am. Chem. Soc., 54, 3726 (1932).

The preparation of a number of organolead compounds incidental to the work of this thesis is also described. In this connection the mechanism of the reaction of lead chloride on phenylmagnesium bromide in the preparation of tetraphenyllead is discussed. It has been found that by extreme care in working up all products of the reaction, the yield of tetraphenyllead is materially increased. The procedure used also gives appreciable quantities of triphenyllead bromide thus increasing the total yield of phenyllead products obtained.

EXPERIMENTAL

Some Organic Complexes of Lead Salts with
Diazonium Compounds and with Amines

Discussion

Many complexes of diazonium compounds with inorganic salts are known. The more common are those of mercury, gold, tin and platinum salts although diazonium complexes of bismuth and antimony salts are also known. Sakellarios (18) has described the complex salt of plumbic chloride with benzene-diazonium chloride.

Nesmejanow (19) and Nesmejanow and Kahn (20) have shown that the aryldiazonium chloride complexes with mercuric chloride can be converted by copper to arylmercuric chlorides according to Reaction VI. If ammonium hydroxide (21) is used with the copper, diaryl mercurials are obtained by Reaction VII. They report a 32% yield of phenylmercuric chloride and smaller yields of para-hydroxy phenylmercuric chloride, di-para-iodo-phenylmercury and other substituted mercurials.



- (18) Sakellarios, Ber., 56, 2536 (1923).
- (19) Nesmejanow, Ber., 69, 1010 (1929).
- (20) Nesmejanow and Kahn, Ber., 69, 1018 (1929).
- (21) Hein and Wagler, Ber., 58, 1499 (1925).

This unique preparation of substituted organomercury compounds, if successful with lead compounds, would furnish a ready means of preparing organolead compounds containing solubilizing groups. The double salts of benzenediazonium chloride and para-tolyldiazonium chloride with lead chloride have been prepared for the first time, but their decomposition with copper gave no evidence that an organolead compound was formed. Other metals than copper and other diazonium salts than the chloride were tried but the results were negative in every case (22).

Because of the instability of the complexes, particularly toward water, it was impossible to completely free them from lead chloride and consequently the analyses for lead are high.

The double salt of plumbic chloride with benzenediazonium chloride (18) was prepared and treated with copper in acetone but no organolead compound was obtained.

In a survey of the literature many references to organic complexes with lead salts were found. The following articles contain many leading references, (23, 24, 25, 26, 27, 28).

- (22) The traces of lead found by extraction with organic solvents is undoubtedly due to slight solubility of lead halides or the complexes in the solvents.
- (23) Mosnier, *Ann. chim. phys.*, (7), 12, 388 (1897).
- (24) Matthews, *J. Am. Chem. Soc.*, 20, 832 (1898).
- (25) Mandal, *Ber.*, 54, 703 (1921).
- (26) Byrkit and Dehn, *J. Am. Chem. Soc.*, 51, 1167 (1929).
- (27) Lum, *Pharm. J.*, 122, 149, 321 (1929).
- (28) Griess, *Ann.*, 137, 39 (1866).

Preparation of $C_6H_5N_2Cl.PbCl_2$ (Run 2, Table I)

The procedure of Nesmejanow (19, 20) for the corresponding mercury complex was followed in preparing the benzenediazonium lead-chloride complex. Several runs were made and in the first of these no complex salt was obtained since it was decomposed by the water used in washing. All of the runs are summarized in Table I.

A solution of 46.5 g. (0.5 mole) of aniline in 150 cc. of concentrated hydrochloric acid was cooled and 150 g. of cracked ice added. Diazotization was effected by adding a concentrated water solution of 38 g. of sodium nitrite while stirred vigorously. The solution of benzenediazonium chloride was added with mechanical stirring to a liter beaker containing 69.5 g. (0.25 mole) of lead chloride suspended in 69.5 g. of concentrated hydrochloric acid and 75 g. of cracked ice. After a few minutes a pale yellowish, curdy precipitate filled the beaker.

It was filtered by suction and washed with cold alcohol and then with cold ether. The air dried product weighed 85 g. which is an 81.20% yield. The complex thus obtained was fluffy and yellowish but became paler. It dissolved in hot water with a neutral reaction, evolved an aromatic odor and gave a lead test. The product did not melt but exploded with a puff when heated on a spatula.

Anal. Calcd. for $C_6H_5N_2Cl_3Pb$: Pb, 49.51. Found: Pb, 52.45 and 52.44%.

Table I
Diazonium Complexes with Lead Salts

Run	Diazonium Compound	Moles	Lead Salt	Moles	Complex Formed	Moles	Yield %	Lead Found	Lead Calcd.
1	$C_6H_5N_2Cl$	0.25	$PbCl_2$	0.25	$C_6H_5N_2Cl \cdot PbCl_2$	0.20	79.20	61.33	49.51
2	$C_6H_5N_2Cl$	0.50	$PbCl_2$	0.25	$C_6H_5N_2Cl \cdot PbCl_2$	0.204	81.20	52.45	49.51
3	$C_6H_5N_2Cl$	0.75	$PbCl_2$	0.25	$C_6H_5N_2Cl \cdot PbCl_2$	0.204	81.20	57.20	49.51
4	$C_6H_5N_2Cl$	0.25	$PbBr_2$	0.125	$C_6H_5N_2Cl \cdot PbCl_2$	0.091	72.80	---	---
5	$p-CH_3C_6H_4N_2Cl$	0.25	$PbCl_2$	0.125	$p-CH_3C_6H_4N_2Cl \cdot PbCl_2$	0.100	79.50	53.30	47.88
6	$p-CH_3C_6H_4N_2Cl$	0.25	$PbCl_2$	0.125	$p-CH_3C_6H_4N_2Cl \cdot PbCl_2$	0.109	87.00	51.08	43.88
7	$p-CH_3C_6H_4N_2Cl$	1.00	$PbCO_3$	0.500	$p-CH_3C_6H_4N_2Cl \cdot PbCl_2$	0.453	91.00	47.09	47.88
8	$p-CH_3C_6H_4N_2Cl$	1.00	$PbCl_2$	0.500	$p-CH_3C_6H_4N_2Cl \cdot PbCl_2$	0.409	87.00	49.91	47.88
9	$C_6H_5N_2Cl$	0.10	$PbCl_4$	0.050	$(C_6H_5N_2Cl)_7(PbCl_4)_2$	0.017	34.00	24.05	24.32
10	$C_6H_5N_2Cl$	0.60	$PbCl_4$	0.300	$(C_6H_5N_2Cl)_7(PbCl_4)_2$	0.071	23.67	---	---
11	$C_6H_5N_2Cl$	0.60	$PbCl_4$	0.300	$(C_6H_5N_2Cl)_7(PbCl_4)_2$	0.083	27.67	---	---

Reaction of $C_6H_5N_2Cl \cdot PbCl_2$ with Copper in Acetone (Run 2, Table II)

The benzenediazonium chloride complex with lead chloride, prepared as described above, was treated with copper in acetone (13) as follows:

A suspension of 85 g. (0.203 mole) of $C_6H_5N_2Cl \cdot PbCl_2$ in 250 cc. of acetone was treated with 20 g. of copper-bronze powder. Reaction began very slowly but became vigorous after fifteen minutes, and had to be cooled to prevent too vigorous reaction; the reaction was stirred throughout. The reaction mixture was filtered and the residue extracted four times with benzene and washed with ether. The acetone and benzene and ether portions were combined and the solvents distilled from a water bath. The remaining liquid was filtered from a small amount of residue and fractionated. It yielded a considerable amount of benzene, b. p. 78-80°, 6 g. of product, b. p. 83-105° and 8 g. of chlorobenzene, b. p. 128-9°. This is a 31% yield of chlorobenzene. The small amount of residue obtained by distilling off the solvents gave no test for lead. Neither did any of the residues from distillation contain lead. The 83-105° boiling product gave a halogen test and proved to be a mixture of benzene and chlorobenzene. None of the liquid portions gave a lead test.

Reaction of $C_6H_5N_2Cl \cdot PbCl_2$ with Copper in Acetone and Ammonium Hydroxide (Run 3, Table II)

A suspension of 40 g. (0.096 mole) of the double salt prepared in Run 3, Table I in 200 cc. of dry acetone was stirred with 32 g. of copper-bronze powder. Two hundred cubic centimeters of 25% ammonium hydroxide were added and the mixture stood twelve hours. The reaction mixture was filtered from the residue and the filtrate was washed and dried and yielded 3 g. of crude chlorobenzene, b. p. 120-33°. No lead test was obtained in the filtrate or residues. The original residue was extracted with benzene for six hours and distillation of the benzene gave a trace of residue giving a faint lead test.

Reaction of $C_6H_5N_2Cl.PbCl_2$ with Zinc in Acetone (Run 4, Table II)

A suspension of 15 g. (0.04 mole) of the double salt from Run 3, Table I, in 75 cc. of acetone was treated with 6.3 g. (0.1 atom) of zinc (29). The zinc reacted mildly and a gas was evolved as the solution became warm and turned brown. The reaction mixture was worked up as in the previous run and yielded 2.5 g. of crude chlorobenzene, b. p. 125-30°. The slight amount of residue from the distillation of solvents gave a faint lead test.

Reaction of $C_6H_5N_2Cl.PbCl_2$ with Zinc in 20% Sodium Hydroxide

(29) Zinc and other metals were used instead of copper in the hope that they might work better than the copper-bronze.

Table II

Reaction of Diazonium with Metals

Run	Diazonium Complex	Moles	Reagent	Product	b. p.	Moles	Test for lead in Products
1	$C_6H_5N_2Cl \cdot PbCl_2$	0.120	Copper-bronze	C_6H_5Cl	105-30°	0.090	Negative
2	$C_6H_5N_2Cl \cdot PbCl_2$	0.200	Copper-bronze	C_6H_5Cl	129°	0.071	Negative
3	$C_6H_5N_2Cl \cdot PbCl_2$	0.960	Copper-bronze	C_6H_5Cl	120-33°	0.027	Trace
4	$C_6H_5N_2Cl \cdot PbCl_2$	0.040	Copper-bronze	C_6H_5Cl	125-30°	0.022	Trace
5	$C_6H_5N_2Cl \cdot PbCl_2$	0.091	Copper-bronze	C_6H_5Cl	100-20°	0.009	Negative
6	$p-CH_3C_6H_4N_2Cl \cdot PbCl_2$	0.070	Copper-bronze	$p-CH_3C_6H_4Cl$	150-60°	0.016	Negative
7	$p-CH_3C_6H_4N_2Cl \cdot PbCl_2$	0.090	Zinc	---	---	--	Trace
8	$p-CH_3C_6H_4N_2Cl \cdot PbCl_2$	0.100	Tin	---	---	--	Trace
9	$p-CH_3C_6H_4N_2Cl \cdot PbCl_2$	0.100	Aluminum	p,p' ditolyl	(m.p.) 115°	--	Negative
10	$p-CH_3C_6H_4N_2Cl \cdot PbCl_2$	0.100	CuOH	p,p' ditolyl	(m.p.) 121-23°	--	Negative
11	$p-CH_3C_6H_4N_2Cl \cdot PbCl_2$	0.050	Sodium	---	---	--	Trace
12	$p-CH_3C_6H_4N_2Cl \cdot PbCl_2$	0.100	Sodium	---	---	--	Trace
13	$p-CH_3C_6H_4N_2Cl \cdot PbCl_2$	---	NaOH (20%)	solid residue	---	--	Positive Trace
14	$(C_6H_5N_2Cl)_7(PbCl_4)_2$	---	Copper-bronze	trace of	(m.p.) 60-65°	--	Negative
15	$(C_6H_5N_2Cl)_7(PbCl_4)_2$	---	Copper-bronze	C_6H_5Cl etc.	130°	0.090	Negative
16	$(C_6H_5N_2Cl)_7(PbCl_4)_2$	---	Copper-bronze	C_6H_5Cl etc.	135-55°	0.100	Negative

(Run 5, Table II)

A suspension of 38 g. (0.091 mole) of the double salt from Run 4, Table I, in 150 cc. of 20% sodium hydroxide was treated with 12 g. of powdered zinc and a trace of copper-bronze powder. Much heat was evolved and the reaction mixture turned black. Working up the reaction products yielded 1 g. of product, b. p. 100-20° testing for halogen. No lead test was obtained in any of the extracted products.

Preparation of p-CH₃C₆H₄N₂Cl.PbCl₂ (Run 7, Table I)

Several runs of the p-tolyldiazonium chloride-lead chloride complex were made of which the following run is typical. The other runs are included in Table I.

A solution of 142.5 g. (1 mole) of p-toluidine hydrochloride in 560 cc. of concentrated hydrochloric acid was cooled in an ice-salt mixture and treated with 560 g. of cracked ice. The cooled solution was diazotized with a slight excess of the calculated amount (69 g. or 1 mole) of a concentrated solution of sodium nitrite. The p-tolyldiazonium chloride solution was filtered and added with mechanical stirring to 139 g. (0.5 mole) of lead chloride suspended in 250 cc. of concentrated hydrochloric acid. (The lead chloride was prepared from 133.5 g. (0.5 mole) of lead carbonate and concentrated hydrochloric acid). Addition of the diazonium solution caused the formation of a flocculent precipitate and stirring was continued for forty minutes.

The filtered complex was washed with cold alcohol and cold ether. It formed faint pink, feathery crystals and decomposed with a puff at 129°. In another run the complex decomposed at 133-4°. The complex was analyzed for lead.

Anal. Calcd. for $C_7H_7N_2Cl_2Pb$: Pb, 47.86%. Found: Pb, 46.98 and 47.20%.

Reaction of $p-CH_3C_6H_4N_2Cl.PbCl_2$ with Copper in Acetone and Ammonium Hydroxide (Run 6, Table II)

A suspension of 30 g. (0.07 mole) of the double salt from Run 5, Table I in 200 cc. of acetone was treated with 25 g. of copper-bronze powder. No reaction occurred for fifteen minutes and then the evolution of gas became vigorous but very little heat was evolved. It stood some time and 200 cc. of 25% ammonium hydroxide was added to the reaction mixture which then stood for some time and was shaken frequently.

Filtration and extraction of both the filtrate and the residue yielded 2 g. (22%) of crude p-chlorotoluene, b. p. 150-60° but no test for lead was obtained in any of the extracted materials.

Reaction of $p-CH_3C_6H_4N_2Cl.PbCl_2$ with Different Metals in Various Solvents

The double salt of p-tolyldiazonium chloride with lead chloride was treated with the following metals as in the copper run above, and the results are tabulated in Table II.

It was hoped that these metals might be more effective than the copper-bronze, but they were not.

- Run (7) Zinc + ammonium hydroxide in acetone.
- Run (8) Tin + ammonium hydroxide in acetone with heat.
- Run (9) Aluminum+ammonium hydroxide in acetone with heat.
- Run (10) Cuprous Hydroxide+ammonium hydroxide in acetone.
- Run (11) Sodium in acetone.
- Run (12) Sodium in ethyl acetate.
- Run (13) Sodium hydroxide (20%).

In Runs 7, 8, 11, 12 and 13 slight tests for lead were given by the residues obtained when the solvents used to extract the original solution and residues were evaporated. The tests were so faint that it is not probable that they are due to the formation of an organic lead compound but rather to slight extraction either of lead chloride or the diazonium-lead chloride complex.

Runs 9 and 10 yielded small amounts of di-p-tolyl, melting at 121° when purified.

Preparation of $(C_6H_5N_2Cl)_7(PbCl_4)_2$ (Run 9, Table I) (18)

Three runs were made of which the following is typical.

The lead tetrachloride was prepared by dissolving 13.35 g. (0.05 mole) of lead carbonate in 300 cc. of concentrated hydrochloric acid and leading chlorine into this solution cooled in ice. The chlorine was bubbled through until all the lead chloride dissolved. Excess chlorine in the solution was removed by bubbling dry nitrogen through the mixture for about a minute.

The acid solution of lead tetrachloride was treated with

a solution of benzenediazonium chloride prepared from 9.3 g. (0.1 mole) of pure aniline, 60 cc. of hydrochloric acid, 100 g. of ice and 6.9 g. of sodium nitrite. A yellow precipitate appeared immediately which was suspended throughout the solution. It stood two hours in an ice-salt mixture and was filtered by suction and washed with three portions of ice-cold alcohol followed by three portions of ice-cold ether. The air dried product weighed 32 g. and stood in a vacuum desiccator for twelve hours when it weighed 28.5 g.; the yield based on $(C_6H_5N_2Cl)_2PbCl_4$ as the formula of the complex is 90%. However, analysis indicates the formula to be $(C_6H_5N_2Cl)_7.(PbCl_4)_2$; this gives a yield of 34.00%, based on the lead tetrachloride theoretically present.

Anal. Calcd. for $C_{42}H_{35}N_{14}Cl_{15}Pb_2$: Pb, 24.32. Found: Pb, 24.01 and 24.09%.

Sakellarios (18) analyzed his product and found it to have the following formula, $(C_6H_5N_2Cl)_2.PbCl_4$.

Reaction of $(C_6H_5N_2Cl)_7.(PbCl_4)_2$ with Copper in Acetone (Run 14, Table II)

A suspension of 12.6 g. (0.02 mole) of the benzenediazonium chloride complex with lead tetrachloride in 50 cc. of acetone was treated with 7 g. of copper. Evolution of nitrogen began immediately and the flask had to be cooled to prevent too vigorous reaction and it was shaken throughout the reaction. It stood overnight and the residue was

filtered from the acetone. The residue was extracted with ether and the ether and acetone combined and distilled from a water bath. A small amount of residual liquid and green solid gave no test for lead.

The other runs summarized in Table II yielded chlorobenzene and other halogen compounds but no product containing lead. Another run like the above carried out in carbon tetrachloride instead of acetone gave no products soluble in organic solvent that contained lead.

Benzenediazonium Chloride-Tetraphenyl-lead Complex

The diazonium solution from 37.2 g. (0.4 mole) of aniline, 120 cc. of hydrochloric acid, 120 g. of cracked ice and 26 g. (0.4 mole) of sodium nitrite in 75 cc. of water was added slowly with mechanical stirring to a suspension of 51.5 g. (0.1 mole) of tetraphenyl-lead in 400 cc. of 15% sodium hydroxide. A yellowish orange fluffy precipitate formed after part of the benzenediazonium chloride was added and became more and more stiff. After complete addition the solid product completely filled the one liter beaker. It was filtered by suction and dried. Alcohol and ether decomposed the complex leaving tetraphenyl-lead, m. p. 223°, and a red solution. Water apparently had no effect on the complex unless heated to its boiling point when a black residue rose to the top. The product burned on a spatula with slight explosiveness and decomposed vigorously when treated with

sulfuric acid. The yield of the complex was 75 g. which was 81% based on the formula below and the tetraphenyl-lead used. Analysis indicates the formula of the complex to be $(C_6H_5N_2Cl)((C_6H_5)_4Pb)$.

Anal. Calcd. for $C_{42}H_{35}N_2Cl_3Pb$: Pb, 22.11. Found: Pb, 22.47 and 22.68%.

On standing several days the complex decomposed into its components and 46 g. (89.32%) of tetraphenyl-lead melting at 224° was recovered.

Preparation of Aniline-Lead Acetate, $C_6H_5NH_2 \cdot Pb(C_2H_3O_2)_2$

Aniline combined with lead acetate to give a salt having the composition $C_6H_5NH_2 \cdot Pb(C_2H_3O_2)_2$. It melted and decomposed at 204° in one run and at 208° in another. Dimethylaniline did not give a salt; the original lead acetate being recovered apparently. Lead chloride, bromide and nitrate combined with aniline but the products were not as stable as that of aniline and lead acetate.

Two runs of the aniline-lead acetate complex were made and the following procedure was used.

A solution of 16 g. (0.042 mole) of lead acetate trihydrate in 80 cc. of water containing a few drops of acetic acid was treated with 9.3 g. (0.1 mole) of pure aniline. After standing a short time a mass of silky, white crystals separated out. They were filtered, washed with water and dried, yielding 9.7 g. of product which was a 45.36% yield. The crystals

decomposed at 204°, sintering at 195°. The melting point of those from the second run was 208°.

Some of this solid was diazotized with sodium nitrite in hydrochloric acid. No lead chloride precipitated but potassium dichromate gave a yellow precipitate.

The lead acetate salt of aniline, m. p. 208°, was boiled with water for sometime and solidified on cooling. This melted at 209° and a mixed melting point with the original compound melted at 208-10°. The lead acetate hydrate used to prepare the aniline salt melted at 65-70°.

Anal. Calcd. for $C_{10}H_{13}O_4NPb$: Pb, 49.55. Found: Pb, 49.74 and 50.29%.

Summary

The complex between lead tetrachloride and benzenediazonium chloride was prepared and treated with copper in acetone (18). It was found that similar complexes of lead chloride with benzenediazonium chloride and p-tolyldiazonium chloride could also be prepared. They were treated with copper and other metals in acetone, but in no case was there good evidence that any organolead compound formed. Apparently the lead complexes do not react in the same manner as do the analogous mercury diazonium complexes. Benzenediazonium chloride also formed an unstable complex with tetraphenyl-lead.

A double salt of aniline with lead acetate was also prepared and remained unchanged when heated. Apparently there was no rearrangement of a lead group to the ring.

Some Coupling Reactions of Organolead Halides

Discussion

The introduction of functional or solubilizing groups into organolead compounds cannot in most cases be effected by the reaction of organolead halides with a Grignard reagent because of the reaction of the latter with the functional groups. Because of this fact an attempt has been made to couple organolead halides with a number of halides containing functional groups. The reagents used to effect coupling of the two halides were sodium, magnesium, zinc-copper couple and aluminum chloride.

One reaction that has been tried is that of organolead halides with alpha-halogen esters. No definite coupling products were isolated in this reaction although reaction occurred. Previous work had also given negative results (15) with triethyl-lead chloride, magnesium and alpha-halogen esters.

Using sodium as the coupling agent yielded a very small amount of product in the reaction of ethyl bromoacetate and triethyl-lead bromide. This product was water soluble and for that reason it is unlikely that it was a lead ester.

In the slow reaction between triphenyl-lead chloride, sodium and chlorobenzene, a 22% yield of tetraphenyl-lead was obtained in what is undoubtedly a coupling reaction (30).

(30) Morton and Stevens, J. Am. Chem. Soc., 53, 2244 (1931).

Tetraphenyl-lead might result from the decomposition of triphenyl-lead (formed by the action of sodium on triphenyl-lead chloride) into tetraphenyl-lead and lead (31) but since there was no deposition of lead this mechanism is not plausible. For this reason it is without question a coupling reaction between the two halides involving possibly (but not necessarily) the intermediate formation of an organosodium compound.

The reaction of triethyl-lead bromide with aluminum chloride and benzene caused decomposition of the triethyl-lead bromide but no evidence of triethyl-phenyl-lead was obtained; furthermore, no hydrogen chloride was evolved until the reaction was hydrolyzed.

It appears that sodium may be the most effective coupling reagent but at the same time it provides greater opportunity for heterogeneous coupling and undesirable reactions with the functional group itself.

The investigation of the coupling of alpha-halogen esters with organolead halides led to a study of the reaction of magnesium on triethyl-lead bromide. In this reaction lead is deposited and tetraphenyl-lead is formed together with ethylmagnesium bromide. The ethylmagnesium bromide was first noticed because of the positive Grignard color test which the solution gave and it was identified by making the propion-

(31) Krause and Reissans, Ber., 55, 888 (1922).

anilide derivative with phenyl isocyanate. It should be remembered that these are the final products of the reaction and that it is quite possible that the intermediate compound (triethyl-lead)-magnesium bromide, $(C_2H_5)_3PbMgBr$, is formed. Reaction with benzophenone and analysis of the solution containing the reaction products point to the formation of (triethyl-lead)-magnesium bromide.

The reaction of triethyl-lead bromide and magnesium would be expected to give triethyl-lead and magnesium bromide and the latter with excess magnesium would produce this free group, magnesium bromide ($-MgBr$), (32). The magnesium bromide or the system magnesium, magnesium bromide could then react in one of three ways to form ethylmagnesium bromide:

1. Magnesium bromide combined directly with an ethyl group from triethyl-lead with the formation of very unstable diethyl-lead; the latter decomposed to give lead and triethyl-lead and possibly tetraethyl-lead.

2. The magnesium bromide might combine with triethyl-lead to give (triethyl-lead)-magnesium bromide which slowly decomposes because of its unstable nature to give diethyl-lead and ethylmagnesium bromide.

3. Ethyl bromide is formed and reacts with magnesium to give ethylmagnesium bromide.

(32) Gomberg and Bachmann, J. Am. Chem. Soc., 49, 241 (1927).

The fact that triethyl-lead chloride and triethyl-tin chloride did not react with magnesium lends support to the proposed role that the magnesium bromide plays in this reaction since magnesium and magnesium chloride do not give magnesium chloride (32).

In this connection tetraethyl-lead was shown not to react with magnesium or with the system magnesium, magnesium bromide to give ethylmagnesium bromide.

Preparation of Triethyl-lead Bromide

This compound has been usually prepared by the method of Grüttner and Krause (33) in which a solution of tetraethyl-lead at -75° is treated with bromine.

It has been found that triethyl-lead bromide may be prepared in as high as 85% yield by treating tetraethyl in petroleum ether solution with dry hydrogen bromide. When dry ether is used as a solvent the yield is 68.60% but the product is purer. This method of preparing triethyl-lead bromide is analogous to that of Gilman and Robinson for preparing triethyl-lead chloride (34).

The tetraethyl-lead used in this preparation was obtained by shaking the commercial product with equal volumes of 50% sulfuric acid until the last acid layer is colorless; the

(33) Grüttner and Krause, Ber., 49, 1415 (1916).

(34) Gilman and Robinson, J. Am. Chem. Soc., 51, 3112 (1929).

temperature was kept below 30°. It was then washed with 10% sodium carbonate solution and finally with distilled water and dried over calcium chloride. The dried tetraethyl-lead was then distilled under reduced pressure in an atmosphere of nitrogen.

The hydrogen bromide was generated by adding bromine from a 50 cc. dropping funnel into a 500 cc. suction flask containing a heavy paste of phosphorus, water and sand. The suction flask was equipped with a two-hole stopper for the dropping funnel and for a glass tube leading to the top of the dropping funnel. The hydrogen bromide was passed through a purifying and drying train consisting of several glass tubes (18" x 2") containing phosphorus, naphthalene, and calcium chloride, respectively. The tubes containing phosphorus and naphthalene were made porous by sifting the reagent into tubes filled with glass wool. Numerous runs were made with ether as the solvent of which the following is typical.

Run 1. A solution of 24.25 g. (0.075 mole) of purified tetraethyl-lead and 320 cc. of anhydrous ether was added to a 500 cc. Erlenmeyer flask previously swept out with dry nitrogen and cooled in an ice-salt mixture. (The low temperature is not necessary, but the yields are somewhat better than at room temperature.) Dry hydrogen bromide was bubbled slowly through this solution for an hour. A small amount of

white, flocculent precipitate appeared toward the end of the treatment, together with some granular diethyl-lead dibromide (33). The ether solution was filtered from the latter and the solvent removed either by suction or on a low temperature water bath. The dry residue of pure triethyl-lead bromide melted at 105° and weighed 19.20 g. which is a 68.60% yield.

Run 2. Using petroleum ether as a solvent a solution of 24.25 g. (0.075 mole of tetraethyl-lead in 230 cc. of petroleum ether (b. p. $40-60^{\circ}$) was treated with hydrogen bromide as in Run 1. Triethyl-lead bromide is insoluble in petroleum ether and precipitates immediately. Hydrogen bromide was passed through the solution for twenty minutes and the triethyl-lead bromide filtered off by suction. The filtrate was again treated with hydrogen bromide as before and a second crop of feathery needles was obtained. The total yield was 23.7 g., m. p. $101-4^{\circ}$, which is a 84.40% yield.

A third treatment of the filtrate with hydrogen bromide yielded 4 g. of a non-melting product. This is probably diethyl-lead dibromide contaminated with lead bromide. The preparation of diethyl-lead dibromide is described below.

Reaction of Triethyl-lead Bromide, Ethyl Bromoacetate and Zinc-copper Couple

An ether solution of 7.46 g. (0.02 mole) of triethyl-lead bromide and 3.54 g. (0.02 mole) of ethyl bromoacetate was stirred for six hours with 8 g. of zinc-copper couple; there was no apparent reaction or deposition of lead.

Two grams of a non-melting, ether insoluble product containing lead was obtained from the reaction product besides 2 g. (26.50%) of the original triethyl-lead bromide. No product that might be an organolead ester was isolated.

Reaction of Triethyl-lead Bromide, Ethyl Bromoacetate and Sodium

In the first of the two runs which were carried out, one equivalent of sodium was used, but no coupling product was isolated. In the second run two equivalents of sodium were used and the results were as follows:

A solution of 14.96 g. (0.04 mole) of triethyl-lead bromide, 7.08 g. (0.04 mole) of ethyl bromoacetate and 1.84 g. (0.08 atom) of sodium was stirred intermittently for seventy hours. Working up the ether solution yielded 6 g. (40.00%) of triethyl-lead bromide and 4 g. (56.50%) of impure ethyl bromoacetate. This brown residue in the flask was separated from unreacted sodium and hydrolyzed with ammonium chloride solution. Two grams of material, insoluble in the aqueous solution gave a good lead test and proved to be an inorganic lead salt. The ether extract of the water solution yielded 1 g. of product melting at 110-35°. Recrystallization did not give a sharper melting point.

Reaction of Triethyl-lead Bromide, Benzene and Aluminum Chloride

A suspension of 30 g. (0.225 mole) of aluminum chloride in 30 cc. of benzene was treated slowly with a concentrated

solution of 14.96 g. (0.04 mole) of triethyl-lead bromide in benzene. The solution was stirred for several hours but no hydrogen chloride was evolved. Hydrolysis with 100 cc. of water caused the evolution of hydrogen chloride however. Working up the reaction mixture yielded a mixture of inorganic lead and aluminum salts but no product which might have been triethyl-phenyl-lead. None of the original triethyl-lead bromide was recovered.

Reaction of Triethyl-lead Bromide with Magnesium. Formation of Ethylmagnesium Bromide and Triethyl-lead

Preliminary experiments showed that triethyl-lead bromide reacted readily with magnesium causing refluxing in much the same manner that the formation of a Grignard reagent does. This reaction was accompanied by the deposition of lead and the solution became green in color. On standing for several days the reaction mixture gave a Grignard color test and this was shown to be caused by ethylmagnesium bromide which was identified as its propionanilide derivative. The solution was also found to contain considerable tetraethyl-lead.

Run 1. Identification of Tetraethyl-lead: A suspension of 22.0 g. (0.059 moles) of triethyl-lead bromide, 250 cc. of ether was treated with 4.25 g. (0.177 mole) of magnesium and reaction and refluxing began at once. The reaction was stirred for twenty hours in a nitrogen atmosphere and the solution was a transparent green color and the magnesium had

become very black, due to deposited lead.

The solution was filtered from magnesium and lead and the clear filtrate soon became cloudy and deposited a large amount of magnesium bromide. The filtrate stood for several weeks and deposited more lead and magnesium bromide. The ether solution was decanted from these products and distilled off yielding a reddish liquid which was distilled at reduced pressure. In this way there was obtained 5.5 g. (0.017 mole) of tetraethyl-lead, b. p. 88-95° at 18-21 mm. This is a 40.00% yield assuming the following transformation of triethyl-lead to tetraethyl-lead either before or during distillation:



A petroleum ether solution of 5 g. (0.0155 mole) of this tetraethyl-lead was treated with dry hydrogen bromide for ten minutes. The insoluble triethyl-lead bromide was filtered off and the filtrate again treated with hydrogen bromide for ten minutes. The combined portions of triethyl-lead bromide, m. p. 104-6°, weighed 4 g. which was a 56.80% yield.

Run 2. Identification of Ethylmagnesium Bromide: A solution of 16.2 g. (0.0433 mole) of triethyl-lead bromide in 425 cc. of ether was treated with 4.32 g. (0.177 atom) of fine magnesium-copper alloy (35). Reaction began at once

(35) Gilman, Peterson and Schulze, Rec. trav. chim., 47, 19 (1928).

and it was stirred at room temperature for three hours in a nitrogen atmosphere. There was no Grignard color test so the reaction was allowed to stand for eight days when a color test was positive; it was also positive after five days. A small amount of black residue and some white crystals separated out on the walls of the flask at the surface of the ether.

This transparent green solution (340 cc.) was treated with 2.68 g. (0.0225 mole) of phenyl isocyanate. Addition caused vigorous reaction and the reaction mixture was stirred for a short time and decanted from magnesium. It was hydrolyzed with water and a great deal of heat was evolved. The ether layer was washed and dried and yielded a crude solid, m. p. 93-5° on distillation of the solvent. The product after digestion with petroleum ether weighed 2.6 g. and gave no lead test. It melted at 104-6°. After crystallization from ether it melted at 105-6°. A mixed melting point with authentic propionanilide (m. p. 104-5°) melted at 104-5°, showing the product to be propionanilide.

The propionanilide must have been produced by the reaction of phenyl isocyanate with ethylmagnesium bromide present in the reaction mixture.

The 2.6 g. of propionanilide obtained represents an approximately 17.00% yield of ethylmagnesium bromide based on the total number of moles (0.1299) of ethyl groups present in the original triethyl-lead bromide used.

In another run of magnesium with triethyl-lead bromide the products thus obtained were treated with benzophenone but the results were inconclusive. Benzophenone was recovered in 82.42% yield and a very small amount of product melting with decomposition at 130-47° that could not be purified was obtained. No pure benzopinacol was isolated although this product should result from the reaction of benzophenone with the system magnesium, magnesium bromide. (This system should be present in the reaction mixture unless it is tied up as a complex or as $(C_2H_5)_3Pb-MgBr$.

When tetraethyl-lead was treated with magnesium and also with magnesium and magnesium bromide these reactions gave no color test for a Grignard reagent. This shows that the formation of ethylmagnesium is not occasioned by the tetraethyl-lead which is also a product of the reaction of magnesium on triethyl-lead bromide.

Triethyl-tin Chloride and Magnesium

A solution of triethyl-tin chloride and 200 cc. of ether was treated with 3.6 g. (0.15 atom) of magnesium. The reaction mixture was stirred and refluxed intermittently for a total of eighteen hours and stood without stirring for sixty-six hours. Frequent color tests for Grignard reagent were made but none was found present.

The magnesium did not appear to have reacted but the solution which was colorless in the beginning became faintly green in color.

This result lends further support to the idea that, in the analogous reaction with triethyl-lead bromide, it is the MgBr group which reacts with triphenyl-lead to give ethyl-magnesium bromide since the -MgCl group does not form in ether solution because of the insolubility of magnesium chloride in this solvent (32).

Reaction of Triphenyl-lead Chloride with Magnesium and Ethyl Bromoacetate

An ether-benzene suspension of 150 cc. of solvent and 23.7 g. (0.05 mole) of triphenyl-lead chloride (36) and 8.5 g. (0.05 mole) of ethyl bromoacetate was heated and stirred with 2.4 g. (0.1 atom) of magnesium turnings for six and one-half hours when a reaction began. The reaction proceeded by itself for thirty minutes and then it was again heated and stirred for three more hours. The solution became green and the magnesium black during reaction but did not give a Grignard color test.

The reaction products on working up yielded 3.5 g. or 15.60% of pure tetraphenyl-lead (mixed melting point), 9 g. of inorganic salts and about 10 g. of product softening at 150° and melting from 170-80°. This proved to be a mixture of triphenyl-lead bromide and chloride. No other product was obtained and apparently all the ethyl bromoacetate had

(36) Gilman and Robinson, J. Am. Chem. Soc., 51, 3112 (1929).

been decomposed.

The tetraphenyl-lead was probably formed by the decomposition of triphenyl-lead formed in the reaction and triphenyl-lead bromide would result from the reaction of magnesium bromide on triphenyl-lead chloride.

Reaction of Triphenyl-lead Chloride, Ethyl Chloroacetate and Magnesium

The reaction of 23.7 g. (0.05 mole) of triphenyl-lead chloride and 8.4 g. (0.07 mole) of ethyl chloroacetate in a toluene-ether mixture with 3.65 g. (0.15 atom) of magnesium turnings for twenty hours with stirring and heating gave no indication of the formation of an organolead ester. The solution became green and lead was deposited after heating for thirteen hours; until then no apparent reaction took place.

The only products isolated from the reaction were unchanged triphenyl-lead chloride and a toluene insoluble product containing inorganic lead. No chloroacetate was recovered.

Reaction of Triphenyl-lead Chloride, Chlorobenzene and Sodium.

Preparation of Tetraphenyl-lead

A solution of 14.22 g. (0.03 mole) of triphenyl-lead chloride, 3.39 g. (0.03 mole) of chlorobenzene and 100 cc. of benzene was treated with 1.38 g. (0.06 atom) of sodium. The reactants stood together for five weeks with occasional shaking. The reaction mixture was treated with 100 cc. of alcohol to destroy excess sodium and the solvents were

removed from a water bath.

The residue weighing 17 g., softening at 195° and decomposing at 228°, was crystallized from 400 cc. of alcohol. A residue, insoluble in the alcohol, was crystallized from benzene, yielding 3.5 g. (22.58%) of tetraphenyl-lead. Two and six-tenths grams of sodium chloride insoluble in benzene were also obtained.

The alcohol solution yielded 10 g. of crude triphenyl-lead chloride which melted with decomposition at 200°. Further recrystallization did not increase the purity of the triphenyl-lead chloride.

There was no apparent deposition of lead either before or during the working up of the reaction, so it must be assumed that a coupling reaction took place rather than a conversion of triphenyl-lead to tetraphenyl-lead. Furthermore, if the latter was the case, there should have been evidence of triphenyl-lead (decomposes 155°) since triphenyl-lead does not ordinarily go over to tetraphenyl-lead under these conditions (31).

Preparation of Triphenyl-lead Bromide

Triphenyl-lead bromide was prepared in 58-60% yield by treating tetraphenyl-lead with dry hydrogen bromide in chloroform solution. The yield could be considerably improved by treating with hydrogen bromide until more diphenyl-lead dibromide formed. This is analogous to the method described

by Gilman and Robinson (36) for triphenyl-lead chloride.

A solution of 51.5 g. (0.1 mole) of tetraphenyl-lead and 750 cc. of dry chloroform heated almost to boiling was treated for forty-five minutes with dry hydrogen bromide. (The hydrogen bromide was prepared as in the preparation of triethyl-lead bromide above). The solution was filtered from a trace of silky precipitate of diphenyl-lead dibromide and the chloroform distilled from a water bath. The residue of triphenyl-lead bromide and unreacted tetraphenyl-lead was extracted with two 500 cc. portions of hot alcohol. The insoluble residue, tetraphenyl-lead, weighed 14 g. (27.20% recovery) and melted at 227°. The alcohol solution yielded on cooling and partially distilling, 30 g. (58%) of triphenyl-lead bromide, m. p. 166-8°.

Another one mole run yielded 60% of triphenyl-lead bromide.

Reaction of Triphenyl-lead Bromide, Ethyl Bromoacetate and Magnesium

A solution of 25.9 g. (0.05 mole) of triphenyl-lead bromide and 8.5 g. (0.05 mole) of ethyl bromoacetate was heated for a short time with 2.4 g. (0.1 atom) of magnesium turnings. Reaction began in a few minutes and continued for thirty minutes; it was then refluxed for three hours. The only products isolated from this run were unused triphenyl-lead bromide, tetraphenyl-lead and inorganic salts.

The Preparation of Some Symmetrical and Unsymmetrical
Organolead Compounds

Discussion

The mechanism involved in the formation of symmetrical tetravalent organolead compounds presents an interesting and at the same time perplexing problem.

A consideration of this mechanism involves many factors, to mention only a few of the more important the following will be dealt with.

1. The relative negative or positive nature of the four lead valences in their organic linkages.
2. The relative negativity of the organic groups attached to the lead atom.
3. The tendency of divalent and trivalent compounds to assume a higher, more stable valence configuration.
4. The influence of the relative strength of lead-lead and lead-carbon linkages and the effect of steric hindrance.
5. The effect that different isotopes of lead may have on the formation of organolead compounds.

The amphoteric nature of the lead atom is well illustrated in the type of compounds it forms. With electronegative elements such as chlorine it forms a typically inorganic, stable dichloride and a less stable tetrachloride. When metallic lead is treated in liquid ammonia with the electro-positive element, sodium, it forms the compound Na_4Pb_9 which

is a true salt or electrolyte (37); in the first case lead functions as a positive element and in the latter as a negative element.

Considering the usual methods of preparing compounds in which lead is attached to organic groups it might be assumed that it functions as a negative rather than a positive element in these compounds.

The first method used in preparing symmetrical organolead compounds involved the reaction of an organic halide with sodium-lead alloy (38). If it is assumed that lead functions negatively in such an alloy, and that the reaction proceeds by a coupling of the positive sodium with the negative halogen, then the resulting linkage of the organic radicals to the lead atom should not change its negative state. Even though the formation of organosodium compounds (39) is postulated in this reaction, there is no reason for believing that the now relatively negative organic radical should influence greatly the already negative lead atom.

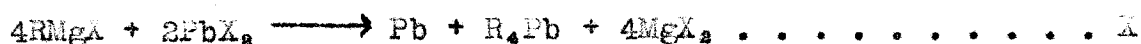
The reaction of sodium-lead alloy on organic halides in the preparation of symmetrical lead compounds may be written:



- (37) Kraus, C.A., Trans. Am. Electrochem. Soc., 45, 175 (1924).
- (38) Löwig, J. prakt. chem., 60, 304 (1853).
- (39) The reaction of an organosodium compound on metallic lead or a sodium-lead alloy has not been studied but it should settle the question as to whether the preparation of organolead compounds by this method involves the formation of an organosodium compound.

Further evidence that this reaction involves lead in the electronegative state is the apparent necessity of having a compound present with the organic halide and sodium-lead alloy that will furnish hydrogen (40, 41). More convincing still is the preparation of organolead compounds by electrolysis at a lead cathode; here the lead is associated with the negative charge and combines with positive groups (42).

The more common method of preparing symmetrical organolead compounds by the reaction of the Grignard reagent on plumbous halides would indicate that the lead atom is perhaps positive (43). The final results of this reaction are usually written as follows,



although the reaction probably proceeds in two or more steps as follows:



- (40) Polis, Ber., 20, 716 3331 (1887); 21, 3425 (1888); Ghira, Gazz. chim. ital., 24, I, 42 (1894).
- (41) Gen. Motors Research Corp., Brit. pat., 216,083.
- (42) Tafel, Ber., 39, 3626 (1907); 44, 323, 337 (1911).
- (43) Pfeiffer and Truskier, Ber., 37, 1125 (1904).

If Reaction XI is assumed to be correct, the divalent lead atom in an R_2Pb compound should be positive since it is furnished by a salt in which lead is positive. Then in Reaction XII one of the three lead atoms is reduced from a positive valence of two to zero valence as it loses its two organic radicals while the lead atoms in the other two R_2Pb molecules are oxidized to a higher valence as they combine with the radicals coming from the first lead atom.

Regardless of whether the lead atom is positive or negative in divalent compounds their tendency to go to compounds of higher valence by inter-molecular oxidation and reduction is spontaneous and rapid.

In unsymmetrical lead compounds such as R_2PbX_2 and R_3PbX it is quite likely that all of the valencies are not exactly the same; cleavage and other reactions indicate this difference. Jones and Werner have also shown that the four valencies of lead in tetra-ethyl- and tetramethyl-lead are not alike because heating with acetic acid gives ethane and alcohol or ester (44).

The influence of different groups on symmetrical organo-lead compounds is pronounced. Tetraphenyl-lead is a relatively stable compound distilling unchanged under reduced pressure at 240° (45). Tetraethyl lead is more sensitive to

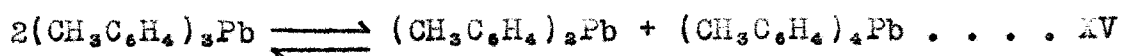
(44) Jones and Werner, J. Am. Chem. Soc., 40, 1257 (1918).

(45) Zechmeister and Csaby, Ber., 60, 1617 (1927).

heat and while it can be distilled in vacuo there is considerable tendency to decompose. Tetrabenzyl-lead (46) and tetranaphthyl-lead have never been prepared in the pure state.

Krause and coworkers have prepared numerous triaryl-lead compounds and in very small yields some deep red diaryl-lead compounds (31, 47, 48). The triaryl-lead compounds were shown to be converted into tetraaryl-lead compounds by heating alone or in solvents. Heating diphenyl-lead caused heterogeneous decomposition but warming with phenylmagnesium bromide gave triphenyl-lead almost quantitatively according to Reaction XII.

When triaryl-lead compounds were treated with bromine in pyridine at low temperature the corresponding triaryl-lead bromide was obtained except in the case of tri-p-tolyl-lead (31). In this case di-p-tolyl-lead dibromide, which decomposed readily, and tetra-p-tolyl-lead were obtained indicating the following equilibrium:



This tendency of di- and trivalent lead compounds to go to a higher valence seems to be general except in cases where steric hindrance may exert an influence. Thus tri-o-tolyl-lead is not converted by heating into tetra-o-tolyl-lead as

- (46) Krause and Schlöttig, Ber., 63, 1381 (1930).
- (47) Krause, Ber., 54, 2060 (1921).
- (48) Krause and Schmitz, Ber., 52, 2165 (1919).

are other triaryl-lead compounds, presumably because of the steric influence of methyl groups close to the lead atom. The only method of preparing tetra-*o*-tolyl-lead is to convert tri-*o*-tolyl-lead to the bromide and to treat this compound with *o*-tolylmagnesium bromide.

It has been suggested that the erratic yields of diphenyl-lead may be due to different isotopes of lead present in samples of lead chloride from different sources (31).

Attempts have been made to separate the isotopes of lead by treating lead chloride with phenylmagnesium bromide and recovering the lead from the tetraphenyl-lead so formed (49). The basis of this method is the greater reactivity of lead chloride containing certain isotopes. The results, however, have not been particularly significant.

Tetraphenyl-lead prepared by means of the Grignard reagent on lead chloride has given about a 50% yield calculated on the basis that one-half of the lead chloride goes to form tetraphenyl-lead (50). Since fairly large quantities of tetraphenyl-lead were needed in these studies, each run was worked up with extreme care in order to determine what became of the other 50% of product theoretically possible.

It was found that the concentrated benzene-ether mother liquor remaining after all the tetraphenyl-lead had been removed contained a relatively large amount of a very soluble

(49) Hofmann and Wölfl, Ber., 40, 2425 (1907).

(50) Gilman and Robinson, J. Am. Chem. Soc., 49, 2315 (1927).

mixture of diphenyl, triphenyl-lead bromide and tetraphenyl-lead. Whether the triphenyl-lead bromide was originally present as such or whether triphenyl-lead, present in these residues, is converted by magnesium bromide or some other product to triphenyl-lead bromide is not known. It is believed, however, that triphenyl-lead bromide was originally present since several runs in which more lead chloride was used gave larger yields of triphenyl-lead bromide.

Krause and Schlöttig have worked up similar residues by treating with alkali and then with hydrochloric acid to obtain triphenyl-lead chloride but they do not give the yields of tetraphenyl-lead or triphenyl-lead chloride (51).

By recovering all the products of this reaction the yield of tetraphenyl-lead has been increased to 61.75% and 5.94% of triphenyl-lead bromide together with 8.00% of diphenyl was obtained. This is a total of 67.69% of phenyl-lead products.

As high as 85% of phenyl-lead products have since been obtained by others (52).

Preparation of Tetraphenyl-lead (50)

Two identical 1.5 mole runs of phenylmagnesium bromide were made in 500 cc. of ether and to each was added 1200 cc. of dry benzene and 181 g. (0.65 mole) of finely pulverized

(51) Krause and Schlöttig, Ber., 58, 427 (1925).

(52) Gilman and Setzer, Unpublished work.

dry lead chloride. The lead chloride was added in several portions quite rapidly. The reaction mixture was refluxed quite vigorously for eight hours.

Hydrolysis was effected by pouring each reaction mixture when cold into a solution of 500 cc. of water, 500 g. of ice and 130 cc. of concentrated hydrochloric acid. After standing some time the hydrolyzed product was filtered by suction. The residue consisted of tetraphenyl-lead and lead and when dry the combined residues from both runs were extracted with several portions of hot benzene. The hot benzene solutions yielded on cooling 193 g. of tetraphenyl-lead, m. p. 227°. This amount together with 14 g. obtained from the mother liquors below represents a 61.75% yield.

The original benzene-ether layer and the benzene used to crystallize the tetraphenyl-lead were evaporated to dryness and the solid product was digested with 400 cc. of alcohol. The insoluble portion (17 g.) gave 14 g. of tetraphenyl when crystallized from benzene.

The alcohol solution was evaporated to dryness yielding 67 g. of product which melted at 100-30°. This product was steam distilled and the distillate yielded 18 g. or 8.00% of pure diphenyl.

The residue not steam distilling was dried and extracted with ether yielding 20 g. of triphenyl-lead bromide, m. p. 162-5°, soft 159°. This is a 5.94% yield of triphenyl-lead

bromide. Crystallization from ether-benzene gave 7.5 g. of product, m. p. 174-5°. A mixed melting point with authentic triphenyl-lead bromide (m. p. 168°) melted at 168-9° showing the product to be triphenyl-lead bromide. The benzene-ether mother liquors yielded 12 g. of triphenyl-lead bromide, m. p. 162-3°.

The total yield of phenyl-lead compounds was 67.69%.

Preparation of Triphenyl-p-anisyl-lead

Triphenyl-p-anisyl-lead was made from p-anisyllithium and triphenyl-lead chloride as follows:

An ether-benzene solution of 0.08 mole of p-anisyl-lithium (53) was added from a dropping funnel to an ether suspension of 18.95 g. (0.04 mole) of triphenyl-lead chloride. Refluxing occurred and the solution was stirred and refluxed thirty minutes after reaction ceased. There was excess lithium compound at the end.

Hydrolysis of the reaction mixture with iced ammonium chloride yielded 10.4 g. (55.40%) of insoluble, crude triphenyl-p-anisyl-lead, m. p. 148-50°. Recrystallization from alcohol gave a constant melting product, m. p. 152° with some decomposition.

Recrystallization of the product above gave 1 g. of tetraphenyl-lead and the ether-benzene solution yielded 9.5 g.

(53) Gilman, Zoellner and Selby, J. Am. Chem. Soc., 54, 1957 (1932). (The reagent used in this run was made by E. A. Zoellner).

of very crude triphenyl-p-anisyl-lead, m. p. 130-50°. Recrystallization did not completely purify this product.

Triphenyl-p-anisyl-lead melts with some decomposition at 152° and crystallizes well from alcohol.

Anal. Calcd. for $C_{22}H_{22}OPb$: Pb, 38.00%, Found: Pb, 38.22 and 38.35%.

Preparation of Diethyl-lead Dibromide

Diethyl-lead dibromide is quite unstable losing its organic constituents rather readily (54). It was found that fairly pure diethyl-lead dibromide could be prepared in the following manner:

A solution of 24.25 g. (0.075 mole) of tetraethyl-lead in 300 cc. of ordinary ether was warmed under reflux as dry hydrogen bromide was passed into the solution for one-half hour. The solution was filtered by suction from 3 g. of insoluble product and in a few minutes the filtrate suddenly deposited a mass of yellow crystals. When dry they weighed 24 g. which is a 75% yield.

Anal. Calcd. for $C_4H_{10}Br_2Pb$: Pb, 48.73%, Br, 37.63%. Found: Pb, 49.19 and 49.16%; Br, 38.41 and 38.42%.

(54) Grüttner and Krause, Ber., 49, 1415 (1916).

SUMMARY

Several attempts to introduce water soluble functional groups into organolead compounds for the purpose of preparing compounds adaptable to cancer therapy have shown little success.

Some new complex salts of benzenediazonium chloride and p-tolyldiazonium chloride with lead chloride have been prepared, but treatment of these complexes with copper-bronze did not form the expected organolead compounds. Neither did the complex salt of lead tetrachloride with benzenediazonium chloride form an organolead compound when treated with copper-bronze.

Numerous coupling reactions of organolead halides with alpha-halogen esters using sodium and magnesium as coupling agents have been carried out. In no case was an organolead ester obtained but sodium caused the coupling of triphenyl-lead chloride and chlorobenzene to form tetraphenyl-lead.

The reaction of magnesium on triethyl-lead bromide in which ethylmagnesium bromide and tetraethyl-lead are formed has been carried out.

Improved yields of tetraphenyl-lead have been obtained in the reaction of lead chloride with phenylmagnesium bromide and the mechanism of this reaction is discussed. The preparation of triphenyl-p-anisyl-lead is described.