

can then further react with guaiacol, for example, to give C_6-C_3 and $C_6-C_6-C_6$ systems.

The probable existence of two types of $C_6-C_6-C_6$ systems is postulated, namely, one from the cyclic diketone and one from benzoquinone. It is regarded as more probable that the $C_6-C_6-C_6$ systems form the true basic lignin building units present in wood. Action of acids results in cleavage of these to give very reactive C_6-C_3 types which then undergo, to a greater or lesser extent, polymerization-condensation reactions under the influence of the extractant to yield water-insoluble "extracted" lignins.

3. On the basis of the new experimental evidence it seems likely that there are present four types of "lignin" in wood, corresponding to: (a) the simple C_6-C_3 unit; (b) the simple $C_6-C_6-C_6$ unit; (c) reversible polymers of (a) and (b); (d) irreversible polymers of (a) and (b).

4. "Extracted" lignins correspond to Types (c) and (d).

5. The marked difference existing between spruce and maple woods in regard to the amounts of extractable, water-soluble, "ethanolysis" products points to a fundamental difference between the lignin constituents of soft and hard woods, and is explainable on the assumption of the inability of the syringyl building units present only in hard woods to undergo condensation to *irreversible* condensation polymers.

6. The suggestion is put forward that tannins and pigments originate in the plant as a result of a series of related condensation reactions between phenols and a C_6-C_3 unit, the latter arising from condensation reactions between methyl glyoxal and a phenol.

7. The possibility that the lignin building-unit may be formed in the plant through the agency of a "carboligase enzyme" reaction from vanillin and acetaldehyde is pointed out.

MONTREAL, CANADA

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Relative Reactivities of Organometallic Compounds. XXI. Organolead Radicals and Derivatives

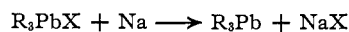
BY HENRY GILMAN AND JAMES C. BAILIE

Introduction

The general procedures for the preparation¹ of organolead radicals may be classified roughly as reductions and direct alkylations. The best illustrations of reduction are the preparation of triethyllead by electrolysis of triethyllead hydroxide, and by the recently reported² reaction of sodium in liquid ammonia on triethyllead bromide. Direct alkylations have been effected by interaction of sodium-lead alloys and alkyl halides, and by reaction of lead chloride with the Grignard reagent or organolithium compounds. The Grignard method has been the best procedure used hitherto for the synthesis of triaryllead compounds.³ It is quite probable that R_3Pb compounds are formed as intermediates⁴ in the prepa-

ration of R_4Pb compounds by the Grignard reaction. However, tricyclohexyllead and no tetracyclohexyllead is formed from cyclohexylmagnesium bromide and lead chloride.⁵

In connection with studies on relative reactivities, organolead hydrides and dissociable triaryl-triarylmethyllead compounds, we have prepared seven additional triaryllead compounds, each substituted in the nucleus with so-called positive groups. These compounds were prepared by the conventional Grignard procedure. In addition, some of them were synthesized by the sodium in liquid ammonia reduction method which is so effective with triethyllead.²



Although this method of preparation involves more steps than the Grignard procedure, it is a method of choice for some thermally unstable R_3Pb types and offers access to unsymmetrical organolead radicals: $R_2R'PbX + Na \longrightarrow R_2R'Pb + NaX$. The general sodium-liquid ammonia

(1) For excellent accounts of organolead compounds, see (a) Krause and von Grosse, "Die Chemie der metall-organischen Verbindungen," Borntraeger, Berlin, 1937; (b) Calingaert, *Chem. Rev.*, **2**, 43 (1925).

(2) Calingaert and Soroos, *J. Org. Chem.*, **2**, 535 (1938).

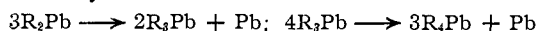
(3) Krause and co-workers, *Ber.*, **52**, 2165 (1919); **54**, 2060 (1921); **55**, 888 (1922); Goddard, *J. Chem. Soc.*, **123**, 1161 (1923); Austin, *This Journal*, **53**, 1548 (1931).

(4) See p. 409 of Ref. 1a.

(5) Krause, *Ber.*, **54**, 2060 (1921).

reaction has been used with organotin and organo-germanium compounds, particularly by Charles A. Kraus and co-workers.

Pyrolysis.—One of the outstanding characteristics of most organolead radicals is thermal instability.



In general, the alkylmetallic compounds are more thermally unstable than the arylmetallic compounds, and the order of thermal stability varies somewhat regularly with the rates of cleavage of unsymmetrical organometallic compounds, particularly by hydrogen chloride.⁶

The examination now reported of the pyrolysis of R_3Pb compounds shows that the general order of decreasing thermal stabilities of such symmetrical compounds is as follows: mesityl, cyclohexyl, α -naphthyl > *o*-ethoxyphenyl, *o*-methoxyphenyl, *o*-tolyl > *p*-ethoxyphenyl, *p*-methoxyphenyl, *p*-tolyl > *m*-tolyl, phenyl > ethyl, methyl.

This order shows a moderate correlation with the several series based on the cleavage of unsymmetrical organometallic compounds. It appears, however, that steric factors may play a significant role in the order of thermal stabilities. For example, tricyclohexyllead is uncommonly stable and accordingly is grouped with the types having distinctly aromatic radicals. Also some of the ortho-substituted radicals are higher in the series than one generally finds them on the basis of cleavage reactions. Incidentally, steric factors may account in part for the low yields of trimesityl- and tri- α -naphthyl-lead obtained by the Grignard procedure.

Sodium Triaryllead Compounds.—Sodium adds readily in liquid ammonia to triaryllead compounds to give sodium triaryllead types some of which are highly colored in liquid ammonia. These compounds also can be prepared in liquid ammonia by the addition of two equivalents of sodium to a triaryllead halide: $R_3PbX + 2Na \longrightarrow R_3PbNa + NaX$. They react smoothly with various reagents, and particularly with the benzyl halide types to give triarylbenzyllead and related compounds.

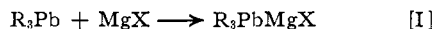
Melting Points.—Not only is tri-*m*-tolyllead less thermally stable than the corresponding para and ortho compounds, but it has a much lower melting point than the *p*- and *o*-isomers. The

(6) General accounts of thermal instability and cleavage of organometallic compounds are to be found in (a) Chap. IV of Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938. and in (b) Ref. 1a.

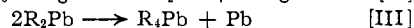
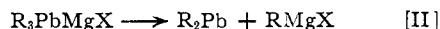
order of melting points of the symmetrical tri-tolyllead compounds accordingly follows that of the symmetrical tetra-tolyllead compounds, as well as that of the symmetrical tolyl derivatives of mercury, germanium, tin, antimony and bismuth, for in all of these the meta-tolyl derivative has the lowest melting point.^{1a}

Free Radicals in Pyrolysis.—There is little doubt that the pyrolysis of most organometallic compounds involves the intermediate formation of free radicals. It seemed of interest to determine whether unsymmetrical organolead radicals might be formed by the pyrolysis of an equimolar mixture of two R_3Pb compounds of the same general stability. It was found that the products of pyrolysis of a mixture of tri-*p*-tolyllead and tri-*p*-methoxyphenyllead were tetra-*p*-tolyllead and tetra-*p*-methoxyphenyllead. These essentially negative results do not of course preclude the intermediate formation of $R_2R'Pb$ types, although they do indicate that the free radicals are formed stepwise.

Possible Intermediate Formation of R_3PbMgX Types.—The binary system of Gomberg and Bachmann⁷ behaves as though magnesious halide was present: $Mg + MgBr_2 \rightleftharpoons 2MgBr$. In many of its reactions the as yet non-isolated magnesious halide has the characteristics of univalent metals. For example, addition takes place smoothly with triphenylmethyl to give triphenylmethylmagnesium bromide or iodide.⁸ The addition of sodium to R_3Pb compounds suggested that a related reaction might take place with the binary system to give lead analogs of Grignard reagents



We have now shown that a reaction does take place at room temperature in an ether-benzene medium and a true Grignard reagent results. The formation of R_4Pb compound and free lead, in addition to the $RMgX$ compound, indicates that the following reactions may have occurred.



Reaction III is known to take place through the intermediary formation of R_3Pb : $3R_2Pb \longrightarrow Pb + 2R_3Pb$; $4R_3Pb \longrightarrow 3R_4Pb + Pb$.

However, there are other mechanisms which may account for the products isolated. One of

(7) Gomberg and Bachmann, *THIS JOURNAL*, **49**, 236, 2584 (1927).

(8) Gilman and Fothergill, *ibid.*, **51**, 3149 (1929); Gomberg and Bachmann, *ibid.*, **52**, 2455 (1930).

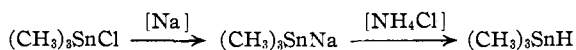
these involves the intermediate formation of R_3PbX compounds. For example, R_3Pb compounds react with magnesium iodide to give R_3PbI compounds. The other component (magnesium) of the binary system might then react with the R_3PbX to give the R_3PbMgX intermediate: $R_3PbX + Mg \rightarrow R_3PbMgX$

Actually, we have observed that triethyllead bromide and magnesium react in ether solution to give ethylmagnesium bromide, tetraethyllead and lead: $2(C_2H_5)_3PbBr + 2Mg \rightarrow 2C_2H_5MgBr + (C_2H_5)_4Pb + Pb$. Inasmuch as these products are similar to those designated in Reactions II and III it may be that triethylleadmagnesium bromide, $(C_2H_5)_3PbMgBr$, is formed as an intermediate. Whatever the mechanism, it is improbable that the organomagnesium compound came from the R_4Pb compound, for under corresponding conditions tetraethyllead reacted neither with magnesium nor with the binary system.

As additional supporting evidence for the possible intermediary action of magnesium halide are the facts that under conditions where magnesium reacted with triethyllead bromide no reaction was observed with triethyllead chloride or triethyltin chloride. Magnesium and magnesium chloride do not give magnesium chloride.⁸ It seems reasonable to expect that relatively stable compounds of the type $R_3MMgBr(I)$, where M is silicon, germanium and tin, may be formed because of the closer similarity of these elements [M] to carbon.

Finally, it should be stated that there are occasional differences in properties of R_3Pb compounds. Those R_3Pb compounds having ortho-substituted or otherwise sterically hindered radicals not only pyrolyze with uncommon difficulty, but also react differently with the binary system. The predominant reaction of such trivalent organolead compounds and the binary system is the formation of the corresponding R_3PbI types: tricyclohexyllead, for example, giving a 42% yield of tricyclohexyllead iodide.

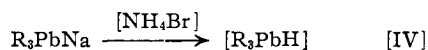
Possible Intermediate Formation of Organolead Hydrides.—The first report of a true organometallic hydride was that of Kraus and Greer⁹ who prepared trimethyltin hydride by the following reactions in liquid ammonia.



Subsequently, Kraus and colleagues extended the

study to include most of the work done on organotin hydrides¹⁰ and organogermanium hydrides.¹¹

The availability of R_3PbNa compounds offered an approach to the synthesis of the as yet unknown organolead hydrides. The following reactions was carried out in liquid ammonia with a number of R_3PbNa compounds.



However, no organolead hydride was isolated. Instead the products were trivalent organolead compounds, lead bromide and RH compound.

The instability of organolead hydrides, if formed, is to be expected. In the following series of related compounds, it is known that the instability of the hydrides increases with descent of the Group IV elements: $(C_6H_5)_3C-H$, $(C_6H_5)_3Si-H$, $(C_6H_5)_3Ge-H$, $(C_6H_5)_3Sn-H$. The same general order follows with inorganic hydrides, which may formally be considered as the first members of homologous series of the corresponding organometallic compounds. Thus, silicon hydride is stable in the absence of oxidizing agents up to 500°, whereas lead hydride is unstable at ordinary temperatures.¹²

It would be interesting to determine whether a compound like diphenyllead dihydride decomposes to lead and benzene or to diphenyllead and hydrogen. Diphenylgermanium dihydride and diphenyltin dihydride are transformed spontaneously to hydrogen, and to diphenylgermanium and diphenyltin, respectively.

Experimental Part

Customary procedures, with occasional amendments, were used for the preparations of $RMgX$, R_3Pb , R_4Pb and R_3PbX compounds. The color test^{13a} for organometallic compounds was used to follow the course of reaction, and the organolead compounds were analyzed for lead by the gravimetric procedure^{13b} used in earlier studies.

Tri- α -naphthyllead.—In a first reaction between α -naphthylmagnesium bromide and lead chloride, the mixture became quite dark on standing overnight, but only a small quantity of dark precipitate had formed. Despite

(10) Kraus and Sessions, *ibid.*, **47**, 2361 (1925); Kraus and Neal, *ibid.*, **47**, 2568 (1925), and **52**, 695 (1930); Chambers and Scherer, *ibid.*, **48**, 1054 (1926).

(11) Kraus and Foster, *ibid.*, **49**, 457 (1927); Kraus and Brown, *ibid.*, **52**, 4031 (1930); Kraus and Flood, *ibid.*, **54**, 1635 (1932); Foster and Hooper, *ibid.*, **57**, 76 (1935); Goldschmidt and Nagel, *Ber.*, **64**, 1745 (1931).

(12) Paneth, *ibid.*, **53**, 1710 (1920); see, also, Kraus, *J. Chem. Ed.*, **6**, 1478 (1929).

(13) (a) Gilman and Schulze, *THIS JOURNAL*, **47**, 2002 (1925); (b) Gilman and Robinson, *ibid.*, **50**, 1714 (1928).

(9) Kraus and Greer, *THIS JOURNAL*, **44**, 2629 (1922).

TABLE I
 PREPARATION OF R_3Pb COMPOUNDS FROM $RMgX + PbCl_2$

R_3Pb	Crystallizing solvent	M. p., °C.	Yield, %	Analysis, % Pb Found	
				Calcd.	
$(C_6H_5)_3Pb^a$	$CHCl_3-C_2H_5OH$	224-225			
$(p-CH_3C_6H_4)_3Pb^b$	C_6H_6 then C_2H_5OH	244-245	44		
$(o-CH_3C_6H_4)_3Pb^c$	$CHCl_3-C_2H_5OH$	248-250	54.9		
$(m-CH_3C_6H_4)_3Pb^d$	C_2H_5OH	109		43.12	43.40, 43.56
$[2,4,6-(CH_3)_3C_6H_2]_3Pb^e$	$CHCl_3-C_2H_5OH$	>325	12.3	36.73	35.63, 35.77
$(p-CH_3OC_6H_4)_3Pb^f$	$CHCl_3-C_2H_5OH$	198-200 (dec.)	57.1	39.23	39.27, 39.42
$(o-CH_3OC_6H_4)_3Pb^g$	$CHCl_3-C_2H_5OH$	198-201 (dec.)	59	39.23	39.52, 39.28
$(p-C_2H_5OC_6H_4)_3Pb$	$CHCl_3-C_2H_5OH$	178-179 (dec.)	58.4	36.34	35.97, 36.53
$(o-C_2H_5OC_6H_4)_3Pb^h$	$CHCl_3-C_2H_5OH$	170-171 (dec.)	23.4	36.34	35.96

^a The triphenyllead first darkened at 160° and then melted at 224-225° (the melting point of tetraphenyllead). The yields ranged from 21 to 25%. ^b The tri-*p*-tolyllead was recrystallized by dissolving in benzene and then adding an equal volume of alcohol. When viewed under a microscope, the deposition of lead took place at 195° and was accompanied by a change in crystal form from plates to needles. ^c Darkening, associated with a deposition of lead, took place at 238-242°. ^d The preparation of tri-*m*-tolyllead by means of the Grignard reagent gave a mixture of tri- with tetra-*m*-tolyllead. It was found more convenient to prepare the tri-compound in liquid ammonia (see below). The compound melted at 109° and decomposed to a dark liquid at 116-117°. ^e Subsequent to hydrolysis, the sludge was dried and extracted first with chloroform and then with boiling xylene. The compound melted above 325°. ^f The tri-*p*-methoxyphenyllead was first prepared by Mr. E. B. Towne. From the preparation starting with 0.5 mole of *p*-methoxyphenylmagnesium bromide and 0.191 mole of lead chloride there was also isolated 4.6 g. of tetra-*p*-methoxyphenyllead, m. p. 138-140°. ^g The tri-*o*-methoxyphenyllead darkened at 198° and melted to a black liquid at 201°. ^h One of the products of hydrolysis was a 47.5% yield of phenetole. This indicates an incomplete reaction. Undoubtedly the yield of tri-*o*-ethoxyphenyllead can be increased by carrying out the reaction at an elevated temperature and for a longer time, inasmuch as subsequent experiments showed that the tri-compound is relatively thermally resistant to conversion to tetra-*o*-ethoxyphenyllead.

the fact that there was no color test, the recovery of 78% of naphthalene subsequent to hydrolysis showed that the Grignard reagent was tied up in the form of some complex. The yield of tri- α -naphthyllead was 6%.

In a second experiment, the mixture was carbonated prior to hydrolysis. The products this time were 5.8% of tri- α -naphthyllead, 11% of α -naphthoic acid and 46.5% of naphthalene. These results indicate that the Grignard reagent is bound up in some form which is loose enough to react partially with carbon dioxide after having reacted partially with lead chloride. Complexes with α -naphthylmagnesium bromide have also been observed with other inorganic halides, particularly those of the Group VIII metals, and these will be reported later.

In a third preparation, the more reactive α -naphthyllithium was used in place of α -naphthylmagnesium bromide. Here the products of reaction were only traces of acid, an 18.7% yield of naphthalene and a 10% yield of yellow tri- α -naphthyllead which melted at 268-269° after darkening at 255°. Crystallization was effected from a mixture of chloroform and alcohol.

Anal. Calcd. for $C_{30}H_{21}Pb$: Pb, 35.21. Found: Pb, 34.72.

Preparation of R_3Pb Compounds from R_3PbX and Sodium.—To a suspension of 2.24 g. (0.004 mole) of triphenyllead iodide in 100 cc. of liquid ammonia was added 0.093 g. (0.004 g. atom) of sodium cut in small pieces. The residue remaining after evaporation of the ammonia was extracted with hot chloroform. From the concentrated chloroform solution there was obtained, after the addition of alcohol, a 94% yield of triphenyllead. By a similar procedure, there was obtained from tri-*m*-tolyllead bromide a 70% yield of tri-*m*-tolyllead.

Triethyllead.—Details were not provided by Calingaert and Soroos² for the procedure used by them for the preparation of triethyllead. To a well-stirred suspension of 16.35 g. (0.05 mole) of triethyllead chloride in 250 cc. of liquid ammonia was added 1.15 g. (0.05 g. atom) of sodium in small pieces and at a rate to avoid vigorous boiling of the ammonia. The yellowish-green solution containing a viscous black solid was stirred until about one half of the ammonia had evaporated. Then 150 cc. of dry ether was added slowly, and the remaining ammonia allowed to evaporate. The deep yellow ether solution was filtered through a sintered glass plate into a distilling flask, operations being carried out in an atmosphere of dry nitrogen. The ether was distilled, leaving a yellow oil containing a small quantity of suspended white solid which was removed by filtration through a sintered glass plate. The liquid was then heated on a boiling water-bath for fifteen minutes at a pressure of 3 mm. to remove tetraethyllead. The residual liquid was again filtered through a glass plate and sealed in a glass container. The yield was 10.2 g. or 69%. Triethyllead is a clear yellow liquid which decomposes even in sealed containers after standing a few days. Reaction with oxygen occurs readily to form a pale yellow solid.

Reaction of R_3PbNa Compounds with Benzyl Chloride.—As a general procedure, one equivalent of sodium was added to 0.005 mole of R_3Pb compound in 150 cc. of liquid ammonia. To the often deeply colored solution was added the benzyl chloride in ether. The ammonia was then evaporated and the residue worked up in the usual way. Triphenylbenzyllead, however, was prepared by first treating triphenyllead bromide in liquid ammonia with two equivalents of sodium and then adding benzyl chloride. The

TABLE II
 $R_3PbCH_2C_6H_5$ COMPOUNDS FROM R_3PbNa AND $C_6H_5CH_2Cl$

R_3Pb	Product	M. p., °C.	Yield, %	Analyses, % Pb	
				Calcd.	Found
$(p\text{-CH}_3C_6H_4)_3Pb^a$	$(p\text{-CH}_3C_6H_4)_3PbCH_2C_6H_5$	81-82	53	36.25	36.02
$(p\text{-C}_2H_5OC_6H_4)_3Pb^b$	$(p\text{-C}_2H_5OC_6H_4)_3PbCH_2C_6H_5$	76-77	82	31.34	31.32
$(o\text{-CH}_3OC_6H_4)_3Pb^c$	$(o\text{-CH}_3OC_6H_4)_3PbCH_2C_6H_5$	80-81	40	33.40	33.25
$(C_6H_{11})_3Pb^d$	$(C_6H_{11})_3PbCH_2C_6H_5$	228 (dec.)	39	37.84	38.19

^a The R_3PbNa compound was deep red colored in liquid ammonia, and the tri-*p*-tolylbenzyllead was crystallized from alcohol. ^b The R_3PbNa compound was cherry-red in color, and the tri-*p*-ethoxyphenylbenzyllead crystallized in needles from alcohol. ^c The tri-*o*-methoxyphenyllead crystallized in needles from alcohol. ^d The R_3PbNa compound was deep red in liquid ammonia. The tricyclohexylbenzyllead crystallized as yellow needles from a mixture of alcohol and chloroform, and decomposed without melting at 228°. Tricyclohexyllead was prepared in 64% yield by the Grignard method and after crystallization from xylene was found to darken slightly at 187° and then decompose at 196°. Because this R_3Pb compound decomposes slightly in the presence of light, it should be kept in a brown bottle in the dark. The R_3PbNa compounds react with suitably substituted RX compounds which permit the introduction of water-solubilizing groups, and these reactions will be presented later.

yield of triphenylbenzyllead was 60% and the identity of the compound was established by comparison with an authentic specimen.¹⁴ The other data on the benzyllead compounds are given in Table II.

Triphenylbenzohydrillead.—This compound was first prepared in a slightly impure state by Mr. D. M. Pontz by interaction of triphenyllead chloride and benzohydril-magnesium chloride. The impurity was largely *sym*-tetraphenylethane.

To sodium triphenyllead, prepared in liquid ammonia from 3.5 g. of triphenyllead chloride and two equivalents of sodium, was added dropwise an ether solution of benzohydril chloride.¹⁵ The residue remaining after evaporation of the ammonia was extracted with 100 cc. of hot ether. The product obtained from the ether extract was crystallized three times from ethanol and once from methanol to give 2.1 g. (54%) of triphenylbenzohydrillead, melting at 122° and turning dark at 130°. Yields were appreciably lower when larger quantities of reactants were used.

Anal. Calcd. for $C_{31}H_{28}Pb$: Pb, 34.21. Found: Pb, 33.86 and 34.02.

The cleavage and dissociation of triphenylbenzohydrillead and triphenyltriphenylmethyllead (m. p. 196-197°) will be reported later.

Triphenyllead Iodide.—The preparation by Polis¹⁶ of diphenyllead diiodide by the addition of iodine to a chloroform suspension of tetraphenyllead until the iodine color persisted suggested that triphenyllead iodide might be prepared analogously by adding the calculated quantity of iodine.

A suspension of 23 g. (0.045 mole) of tetraphenyllead in 200 cc. of chloroform was stirred vigorously during the addition of 11.43 g. (0.045 mole) of iodine in 150 cc. of chloroform. The yield of triphenyllead iodide, obtained as yellow needles from alcohol, was 88%, and the melting point was 138-139°. Identification was completed by comparison with an authentic specimen.¹⁷

Tri-*m*-tolyllead Bromide.—Five and two-tenths grams (0.009 mole) of tetra-*m*-tolyllead was dissolved in 100 cc.

of dry, freshly distilled pyridine, and to this was added powdered carbon dioxide to a mushy consistency. A solution of 1.7 g. (0.01 mole) of bromine in 50 cc. of pyridine was cooled in the same manner with solid carbon dioxide and then added to the first solution. The mixture was stirred and then allowed to warm up to room temperature. The pyridine was removed by distillation, and the residue washed with 5% hydrobromic acid and then with a little cold alcohol. Crystallization from alcohol gave a 78% yield of compound melting at 146-147°.

Anal. Calcd. for $C_{21}H_{21}PbBr$: Br, 14.28. Found: Br, 14.34.

Pyrolysis of R_3Pb Compounds.—The several R_3Pb compounds were heated in dry xylene and the times noted for deposition of lead.¹⁸ The resulting R_4Pb compounds were worked up by customary procedures.

Tricyclohexyllead.—Only a slight turbidity developed after refluxing a solution of 3 g. of tricyclohexyllead in 100 cc. of xylene for six hours, and 2.7 g. was recovered. When 2.28 g. in 50 cc. of xylene was heated in a sealed tube at 190° for three hours, free lead deposited. However, the only product isolated was 1.4 g. of the original compound.

Trimesityllead.—After heating 1.4 g. of trimesityllead in 40 cc. of xylene in a sealed tube for three hours at 190° free lead was deposited. However, the brown viscous oily product has not yet yielded an identifiable compound. Similar results were obtained when the temperature was kept at 150-160° for five hours.

Mixture of Tri-*p*-tolyllead and Tri-*p*-methoxyphenyllead.—A solution of 2.4 g. (0.005 mole) of tri-*p*-tolyllead and 2.65 g. (0.005 mole) of tri-*p*-methoxyphenyllead in 100 cc. of xylene was refluxed for four hours. After working up the reaction products there was obtained a 65% yield of tetra-*p*-tolyllead and a 57% yield of tetra-*p*-methoxyphenyllead.

Reactions with Binary System.—In Table IV, the yields of RCOOH compounds refer to the acids obtained by carbonating the Grignard reagents formed as products of the reactions.

(14) Gilman, Towne and Jones, *THIS JOURNAL*, **55**, 4689 (1933).

(15) Gilman and Kirby, *ibid.*, **48**, 1733 (1926).

(16) Polis, *Ber.*, **20**, 716 (1887); see also, p. 378 of Ref. 1a.

(17) Grüttner, *ibid.*, **51**, 1301 (1918).

(18) See footnotes to Table III. Triethyllead decomposed at about 100°; and the tricyclohexyl-, trimesityl-, and tri- α -naphthyllead compounds did not deposit lead after refluxing for six hours in xylene.

TABLE III
 PYROLYSIS OF R₃Pb COMPOUNDS

R ₃ Pb	R ₄ Pb	M. p., °C.	Yield, %	Calcd.	Analyses, % Pb Found
(C ₆ H ₅) ₃ Pb ^a	(C ₆ H ₅) ₄ Pb	224-225	93		
(<i>p</i> -CH ₃ C ₆ H ₄) ₃ Pb ^b	(<i>p</i> -CH ₃ C ₆ H ₄) ₄ Pb	238-240	90		
(<i>m</i> -CH ₃ C ₆ H ₄) ₃ Pb ^c	(<i>m</i> -CH ₃ C ₆ H ₄) ₄ Pb	122-123	90	36.28	36.23, 36.22
(<i>o</i> -CH ₃ C ₆ H ₄) ₃ Pb ^d	(<i>o</i> -CH ₃ C ₆ H ₄) ₄ Pb	198-200	37		
(<i>p</i> -CH ₃ OC ₆ H ₄) ₃ Pb ^e	(<i>p</i> -CH ₃ OC ₆ H ₄) ₄ Pb	145-146	82	32.62	32.08
(<i>o</i> -CH ₃ OC ₆ H ₄) ₃ Pb ^f	(<i>o</i> -CH ₃ OC ₆ H ₄) ₄ Pb	148-149	53	32.62	32.24, 32.35
(<i>p</i> -C ₂ H ₅ OC ₆ H ₄) ₃ Pb ^g	(<i>p</i> -C ₂ H ₅ OC ₆ H ₄) ₄ Pb	110	91	29.97	30.10, 29.90
(<i>o</i> -C ₂ H ₅ OC ₆ H ₄) ₃ Pb ^h	(<i>o</i> -C ₂ H ₅ OC ₆ H ₄) ₄ Pb	219-220	63	29.97	29.66, 29.95

^a Krause and Reissaus, *Ber.*, **55**, 888 (1922); **54**, 2060 (1921), observed that decomposition to tetraphenyllead took place slowly when a benzene solution was heated in a sealed tube at 100°, and at 60-65° in pyridine solution. There was an immediate deposit of lead in boiling xylene. ^b Tri-*p*-tolyllead decomposes in the solid state at 193° to give tetra-*p*-tolyllead and lead.²⁸ Austin, *THIS JOURNAL*, **53**, 3514 (1931), effected the pyrolysis by refluxing in toluene for five hours and obtained a yield of 89%. Lead deposited in three to five minutes in boiling xylene. ^c The tetra-*m*-tolyllead was crystallized from alcohol in needle form. There was an immediate deposit of lead in boiling xylene. ^d Austin, *THIS JOURNAL*, **53**, 1548 (1931), found that tri-*o*-tolyllead was slowly decomposed by refluxing in xylene solution, but decomposition was not complete at the end of forty-three hours. Our period of heating was twelve hours, and a black precipitate appeared after forty-five minutes. ^e The tetra-*p*-methoxyphenyllead crystallized in needle form from alcohol. Lead deposited in three to five minutes in boiling xylene. ^f After refluxing a toluene solution of tri-*o*-methoxyphenyllead for six hours, only a very slight turbidity developed and the original compound was recovered. When heated in xylene, the pale yellow color deepened to orange, and at the end of one hour a black deposit of lead started to appear. Refluxing was continued for 15 hours, and the tetra-*o*-methoxyphenyllead crystallized in the form of small plates from alcohol. ^g The total period of refluxing was one-half hour, and the tetra-*p*-ethoxyphenyllead was crystallized from alcohol. Lead deposited in one to three minutes. ^h Except for a slight turbidity, there was no appreciable change when tri-*o*-methoxyphenyllead was refluxed in toluene for six hours. Lead deposited in about seventeen minutes in boiling xylene.

 TABLE IV
 REACTION OF R₃Pb COMPOUNDS WITH THE BINARY SYSTEM [Mg + MgI₂]

R ₃ Pb	R ₄ Pb	Products and yields RCOOH	R ₃ PbI
(C ₆ H ₅) ₃ Pb	(C ₆ H ₅) ₄ Pb, 56%	C ₆ H ₅ COOH, 41%	
(<i>p</i> -CH ₃ C ₆ H ₄) ₃ Pb ^a	(<i>p</i> -CH ₃ C ₆ H ₄) ₄ Pb, 49%	<i>p</i> -CH ₃ C ₆ H ₄ COOH, 80%	
(<i>p</i> -CH ₃ OC ₆ H ₄) ₃ Pb ^b	(<i>p</i> -CH ₃ OC ₆ H ₄) ₄ Pb, 58%	<i>p</i> -CH ₃ OC ₆ H ₄ COOH, 90%	
(<i>p</i> -C ₂ H ₅ OC ₆ H ₄) ₃ Pb ^c	(<i>p</i> -C ₂ H ₅ OC ₆ H ₄) ₄ Pb, 56.7%	<i>p</i> -C ₂ H ₅ OC ₆ H ₄ COOH, 82.4%	
(<i>o</i> -CH ₃ OC ₆ H ₄) ₃ Pb ^d			(<i>o</i> -CH ₃ OC ₆ H ₄) ₃ PbI, 39.7%
(C ₆ H ₁₁) ₃ Pb ^e			(C ₆ H ₁₁) ₃ PbI, 42%
[2,4,6-(CH ₃) ₃ C ₆ H ₂] ₃ Pb ^f			[2,4,6-(CH ₃) ₃ C ₆ H ₂] ₃ PbI, 26%

^a After stirring for a few minutes, a small amount of bright yellow solid separated on the sides of the flask. Heat was applied for a short time until the solvent started to reflux, and then the source of heat was removed. In about one hour the yellow precipitate disappeared and the solution became dark. After an additional three-hour period, a color test was positive. ^b After a few minutes of gentle heating, the initial yellow color disappeared and the solution became quite dark. A color test was positive. Stirring was continued for five hours at room temperature, prior to carbonation. ^c The yellow coloration which developed after mixing the reactants, gradually disappeared leaving a greenish solution. A color test was positive after stirring for two hours. The mixture was carbonated after an additional six hours. ^d There was a negative color test after stirring the reactants for three days. The products were 0.55 g. of tri-*o*-methoxyphenyllead and a 39.7% yield of tri-*o*-methoxyphenyllead iodide which after crystallization from alcohol melted at 122-123° and deposited lead iodide at 160°. *Anal.* Calcd. for C₂₁H₂₁O₃PbI: I, 17.86. Found: I, 18.04. ^e The color test was negative after refluxing for twenty hours. The tricyclohexyllead iodide was identified by comparison with a sample prepared by the method of Krause, *Ber.*, **54**, 2064 (1921). A small amount of lead iodide was demonstrated qualitatively. ^f A negative color test was obtained after refluxing for 18 hours. The trimesityllead iodide crystallized from alcohol as pale yellow leaflets, softening at 195°, melting at 200-201° and depositing lead iodide at 210°. *Anal.* Calcd. for C₂₇H₃₃PbI: I, 18.35. Found: I, 18.18.

Triethyllead and the Binary System.—To the binary mixture, prepared from 2.5 g. of magnesium and 4 g. of iodine in 75 cc. of ether, was added 4.7 g. of triethyllead in 50 cc. of benzene. The reaction was allowed to proceed for four days before a color test was positive. The clear solution, siphoned from the insoluble material, was treated

with α -naphthyl isocyanate¹⁹ to give 0.6 g. of propio- α -naphthalide. This established the presence of ethylmagnesium halide. The mother liquors gave a small quantity of tetraethyllead.

(19) Gilman and Furry, *THIS JOURNAL*, **50**, 1214 (1928).

Tetraphenyllead and Tetra-*p*-methoxyphenyllead with the Binary System.—These R_4Pb compounds were recovered unchanged after refluxing with the binary system in a benzene-ether solution for twelve hours.

Triethyllead Bromide and Magnesium. (By EDMUND B. TOWNE.)—A solution of 16.2 g. (0.0433 mole) of triethyllead bromide in 425 cc. of ether was treated with 0.177 g. atom of magnesium or the magnesium-copper alloy.²⁰ Reaction set in at once, and the mixture was stirred for three hours at room temperature and then allowed to stand for eight days, a positive color test being noted in five days. A small amount of black residue and some white crystals separated on the walls of the flask at the surface of the ether. The transparent green solution was treated with phenyl isocyanate²¹ to yield 2.6 g. of propioanilide which is a 17% yield of ethylmagnesium bromide based on the total number of ethyl groups in the triethyllead bromide. From a corresponding experiment the yield of tetraethyllead was 40%.

Under related conditions no color test was obtained when tetraethyllead was treated either with magnesium or with the binary system.

Preparation of Triethyllead Bromide.—Instead of the low temperature reaction with bromine,²² the triethyllead bromide was obtained in satisfactory yields by the action of hydrogen bromide on tetraethyllead. Dry hydrogen bromide was bubbled slowly and for one hour through a solution of 24.25 g. (0.075 mole) of pure tetraethyllead in 320 cc. of dry ether cooled by an ice-salt mixture. A small quantity of white flocculent precipitate appeared toward the end of the treatment, together with some granular diethyllead dibromide. The solution was filtered, and removal of ether from the filtrate gave a residue of triethyllead bromide melting at 105° and weighing 19.2 g. which is a 68.6% yield.

In a related preparation using petroleum ether (b. p. 40–60°), the triethyllead bromide precipitated immediately. The passage of hydrogen bromide was continued for twenty minutes. After filtering the triethyllead bromide, the filtrate was again treated with hydrogen bromide. The total yield was 23.7 g. or 84.4% of a product melting at 101–104°. A third treatment of the filtrate with hydrogen bromide gave 4 g. of a non-melting product, probably diethyllead dibromide contaminated with lead bromide.

Reaction of R_3Pb Compounds with Magnesium Iodide.—A mixture of triphenyllead and magnesium iodide (prepared in ether and benzene) was stirred at room temperature for eighteen hours. After hydrolysis by ammonium chloride solution there was obtained a small quantity of lead iodide and 57% of triphenyllead iodide.

From a related experiment with tri-*p*-tolyllead in which the mixture was heated for six hours at 50° there was obtained a small quantity of lead iodide and a 70% yield of tri-*p*-tolyllead iodide.

Reaction of R_3Pb Compounds with Iodine.²³—A solution of 2.64 g. (0.005 mole) of tri-*p*-methoxyphenyllead in 150

cc. of chloroform was cooled by means of an ice-salt bath, and 0.64 g. (0.0025 mole) of iodine in 75 cc. of chloroform was added dropwise. The yellow precipitate of lead iodide (0.90 g.) was filtered, and from the filtrate was obtained 50.6% of tetra-*p*-methoxyphenyllead, and 7.1% of di-*p*-methoxyphenyllead diiodide which crystallized from petroleum ether (b. p. 60–68°) as thick, orange colored needles softening at 116° and melting at 122–123°.

Anal. Calcd. for $C_{14}H_{14}O_2PbI_2$: I, 37.63. Found: I, 37.52.

From tri-*o*-methoxyphenyllead (0.01 mole) and iodine, in a related experiment, was isolated 1.92 g. of lead iodide and 41.2% of tri-*o*-methoxyphenyllead iodide (mixed m. p.).

To a solution of 3.42 g. (0.006 mole) of tri-*p*-ethoxyphenyllead in 50 cc. of dry pyridine was added slowly 0.762 g. (0.003 mole) of iodine in 50 cc. of pyridine. The solvent was removed under reduced pressure, and crystallization of the residue gave 45.5% of tri-*p*-ethoxyphenyllead iodide which melted at 99–100° and deposited lead iodide at 152°.

Anal. Calcd. for $C_{24}H_{27}O_3PbI$: I, 18.18. Found: I, 18.39.

Reaction of R_3Pb Compounds with Hydrogen Chloride.²⁴—A solution of 2 g. (0.0046 mole) of triphenyllead in 200 cc. of chloroform was cooled to 0°, and a slow stream of hydrogen chloride admitted. A white solid started to precipitate immediately, and after three minutes the stream of hydrogen chloride was interrupted and the solution filtered. From the white solid was obtained 82.6% of lead chloride and 16.5% of diphenyllead dichloride.

Attempted Preparation of Organolead Hydrides.—An outline of a typical reaction follows. The deep red solution of sodium tri-*p*-methoxyphenyllead was prepared by adding one equivalent of sodium to 10.56 g. (0.02 mole) of tri-*p*-methoxyphenyllead suspended in 200 cc. of liquid ammonia. Ammonolysis by ammonium bromide resulted in a greenish-gray solution. When about one-half of the ammonia had evaporated, 200 cc. of ether was added. The ether solution became deep orange in color, and gradually faded to pale yellow. Air was excluded by a stream of ammonia. No hydrogen was collected in a buret attached to the system. From the ether layer there was obtained 1.76 g. (81%) of anisole (b. p. 154°), identified as the 2,4-dinitro derivative.²⁵ The ether insoluble material yielded 2.78 g. of tri-*p*-methoxyphenyllead and 0.38 g. of tetra-*p*-methoxyphenyllead.

From an experiment starting with 0.006 mole of sodium tri-*p*-tolyllead, the products isolated were 0.5 g. (90%) of toluene (identified as the dinitro derivative²⁶) and 0.91 g. of tri-*p*-tolyllead.

The products from an experiment with 0.0125 mole of sodium tri-*o*-tolyllead were 1.05 g. (91%) of toluene, and 2.4 g. of tri-*o*-tolyllead.

From 0.005 mole of sodium tri-*p*-ethoxyphenyllead, the products isolated were 0.48 g. (79%) of phenetole and 0.96 g. of tri-*p*-ethoxyphenyllead.

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

(21) Schwartz and Johnson, *THIS JOURNAL*, **53**, 1063 (1931).

(22) Grüttner and Krause, *Ber.*, **49**, 1415 (1916).

(23) For earlier studies on the reaction of halogens with R_3Pb compounds see Krause and Reissaus, *ibid.*, **55**, 888 (1922), and Austin, *THIS JOURNAL*, **53**, 1548 (1931).

(24) For earlier studies of the reaction of aqueous hydrochloric and hydrobromic acids with triaryllead compounds see Austin, *ibid.*, **53**, 1548, 3514 (1931).

(25) Meldola, Woolcott and Wray, *J. Chem. Soc.*, **69**, 1330 (1896).

(26) Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1935.

An experiment with 0.0144 mole of sodium triphenyllead (which is practically colorless) gave 2.1 g. of triphenyllead.

In an experiment with 0.0365 mole of sodium triethyllead the usual color changes were noted. The oil remaining after removing ether was distilled under reduced pressure to yield 4 g. of colorless fluid, b. p. 80° at 10 mm. The remaining material in the distilling flask decomposed at a bath temperature of 130° with the deposition of lead, an indication that triethyllead was present. The distillate was shown to be tetraethyllead, confirmation being made by conversion to triethyllead chloride by treating an ether solution with hydrogen chloride. The gas evolved, after removing ammonia, was shown by combustion to be ethane.

In connection with the acid cleavage of sodium triphenyllead by ammonium bromide, the following experiments were carried out in liquid ammonia. (1) Sodium triphenyllead and ethyl bromide gave triphenylethyllead (90%), triphenyllead (2.3%) and lead bromide (2.7%). (2) Five minutes after adding a 2% excess of ammonium bromide, the addition of ethyl bromide gave triphenylethyllead (10.7%), triphenyllead (45.7%) and lead bromide (30%). (3) With a two hour interval, but other conditions as in (2), the products isolated were triphenyllead (48%), lead bromide (38%), and less than 1% of triphenylethyllead. (4a) After adding a 2% excess of ammonium bromide (but no ethyl bromide), the products isolated were triphenyllead (43%) and lead oxide (PbO) (40%). (4b) The same products, in about the same yields, were obtained when ammonium bromide was not added, and the sodium triphenyllead was allowed to decompose in the air. (4c) Decomposition of sodium triphenyllead by water gave benzene, lead oxide (86%) and very small amounts of triphenyllead. (5) With 9 equivalents of ammonium bromide, and other conditions like (4a), the products isolated were triphenyllead (9.2%) and lead bromide (76.5%). (6) With conditions like (5), excepting for the addition of ether after one-half of the ammonia evaporated, the products isolated were triphenyllead (13.7%) and lead bromide (68%). Benzene undoubtedly was formed in the preceding experiments as was shown in (4c) and it was also isolated in this experiment. (7) To sodium triphenyllead, after removing ammonia under reduced pressure, was added an excess of *n*-butyl alcohol. The products isolated were benzene, a trace of triphenyllead, and lead hydroxide. The $\text{Pb}(\text{OH})_2$

gave lead analyses of 86.03 and 86.07%; calcd., 85.91%. (8) Ammonium bromide in liquid ammonia has no significant effect on powdered lead, tetraphenyllead and triphenyllead. Additional experiments are necessary to establish the possible intermediate formation of triphenyllead hydride from sodium or ammonium triphenyllead or their complexes with ammonia.

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Summary

A number of new R_3Pb compounds have been prepared, both by the Grignard method and by treating the R_3PbX types in liquid ammonia with one equivalent of sodium. The rate of thermal conversion of R_3Pb to $\text{R}_4\text{Pb} + \text{Pb}$ is influenced significantly by steric factors of the radicals attached to lead.

Non-sterically hindered R_3Pb compounds react with the binary system ($\text{Mg} + \text{MgI}_2$) to give R_4Pb compound, lead and the Grignard reagent. The reactions appear to take the following course $\text{R}_3\text{Pb} + [\text{MgI}] \rightarrow [\text{R}_3\text{PbMgI}] \rightarrow \text{RMgI} + \text{R}_2\text{Pb} \rightarrow \text{R}_4\text{Pb} + \text{Pb}$. Triethyllead bromide and magnesium react in an analogous manner $(\text{C}_2\text{H}_5)_3\text{PbBr} + \text{Mg} \rightarrow [(\text{C}_2\text{H}_5)_3\text{PbMgBr}] \rightarrow \text{C}_2\text{H}_5\text{MgBr} + (\text{C}_2\text{H}_5)_2\text{Pb} \rightarrow (\text{C}_2\text{H}_5)_4\text{Pb} + \text{Pb}$. The sterically hindered R_3Pb compounds examined ($\text{R} = o\text{-CH}_3\text{-OC}_6\text{H}_5\text{-}$, 2,4,6- $(\text{CH}_3)_3\text{C}_6\text{H}_2\text{-}$ and $\text{C}_6\text{H}_{11}\text{-}$) react with the binary system to give R_3PbI compounds.

R_3PbNa compounds have been prepared in liquid ammonia by the action of sodium on R_3Pb and on R_3PbX compounds. Ammonolysis of the R_3PbNa compounds gives products which do not provide a decisive answer to the intermediate formation of the as yet unknown organolead hydrides, R_3PbH .

AMES, IOWA

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